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A study of properties of ZnO thin films deposited by spray pyrolysis technique on steel

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Dedication

From the bottom of my heart, I dedicate this work to all those who are dear to me,

To my father and my mother

Your patience, encouragement and advice to me and the great effort you have made for me

I ask God to protect you for me and to witness other successes for your little daughter

To my brothers : Daoud and Ayoub

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To my friends : Fedoua and Nedjma

To all those I love from near and far. And to all those who have supported me who have participated and supported the realization of this work



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Dedication

From the bottom of my heart, I dedicate this work to all those who are dear to me,

To my father

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To my mother's pure soul

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To my sister : Amani

To my partner : Roumaïssa

To my friends : Roumaïssa and Selma

To all those I love from near and far. And to all those who have supported me who have participated and supported the realization of this work



Berima Kaouthar 2021



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General Introduction

Nowadays it is necessary to pay more attention to corrosion due to the increased use of metals in all areas of technology and the increase in air and water pollution there resulting in a more corrosive environment.

Corrosion is a major problem in many industries. It causes massive waste of mineral materials, which leads to huge economic losses all over the world. In the United States, financial losses from erosion amounted to 451.3 billion US dollars and 140.1 billion US dollars in the Arab world annually; This is what makes us pay attention to it, and to address any problem we must first recognize and define, corrosion is the deterioration or destructive attack of metals due to their environments. Most of the scientific and engineering aspects of corrosion focus on figuring out how to mitigate the effect of corrosion.

Among the available methods of corrosion prevention, the use of inhibitors is one of the most promising, especially for closed systems. Due to its ease of application and cost-effectiveness, it has attracted great interest from corrosion scientists and engineers all over the world. Among the many types of known inhibitors we will focus in our work on.... In recent years, transparent conductive oxides (TCO'S) play an increasingly important role in the field of nanotechnology. Among these materials, zinc oxide (ZnO) is currently one of the most studied oxides in the literature thanks to the great availability of the raw material in nature, its non-toxicity in the environment, its great thermal stability, and its very low prices for zinc. Chemical steam, spraying, colloidal solution gel, magnetron spraying and spray pyrolysis. However, the physical, chemical and structural properties of these layers are largely related to production processes and conditions. It is in this context that our research is carried out. It is a matter of developing thin layers of zinc oxide with a spray pyrolysis technique. In the next step, we will use a number of techniques to study the properties of these layers.

Therefore, our manuscript is structured in four chapters:

- The first chapter is devoted to a bibliographic study of steel and corrosion, and in this chapter we will present some concepts about steel, its classifications, types, and then move on to corrosion. We will start by defining it, its types, causes and how to treat it

in preparation for the next point in our chapter which is inhibitors, one of the methods of treating corrosion.

- The second chapter will also be a bibliographic study on ZnO 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 devoted the third chapter to include all the stages of preparing the thin layers of ZnO with the specified and mentioned parameters using spray pyrolysis technique and at the end of the chapter we will test the corrosion in two different ways: Gravimetric study and electrochemical measurements we will define both methods and mention their basics.
- Finally, we collected all the results in the fourth chapter, accompanied by an analysis and interpretation of them (structural and optical characterization of the thin films and finally the results of the corrosion test of the two methods.).
- The general conclusion on the whole of this work, will come close our study.

PART I: BIBLIOGRAPHIC STUDY

- ✓ **Chapter I: corrosion of metals and inhibitors**
- ✓ **Chapter II: ZnO thin films deposition and characterization**

Chapter I

Corrosion of metals and inhibitors



Introduction

Steel is an important material in the economy of the modern world, and due to its importance and its many uses, this led to the emergence of many obstacles, including corrosion. To avoid this obstacle, many techniques and methods appeared with the development of science to address this obstacle, including inhibitors. In this order in this chapter, we will go over concepts and definitions of steel, corrosion and inhibitors.

I Steels

I.1 History of steels

Extremely old steel is probably the earliest form of use of ferrous metals. It is indeed around 1000 years BC that the discovery of these steels seems to go back thanks to the technique of cementation and the art of quenching, which were found by chance, the iron-absorbing carbon in contact with materials. Organic was used to heat it to hammer it [1]. Its versatile range of physical properties and chemical resistance make it the main structural and engineering material today, and an indispensable component in the manufacture of cars, trucks, ships, oil and gas installations and pipelines, electrical and mechanical machinery environmental control equipment, household appliances buildings, factories, roads and bridges Steel- has a positive environmental profile in many respects, particularly with regard to its recyclability (around 300 million tonnes of used steel are processed and issued annually)[2].

I.2 Definition of steel

Steel is an iron alloy containing less than 2% carbon. It can be classified according to this carbon content which sets its maximum hardness level in the quenched state. High carbon steel will be used for its high hardness while lower-grade steel is softer and more malleable. It usually contains small amounts of other elements besides iron and carbon, incorporated, intentionally or not, during its preparation. You can also add larger amounts of alloying elements [3].

I.3 Classification of steels

Steels can be classified according to:

- ✓ The composition, such as carbon, low alloyed, or stainless steels...
- ✓ Manufacturing methods, such as Thomas furnace, basic oxygen process, or electric furnace methods.
- ✓ The finishing method, such as hot rolling or cold rolling.
- ✓ The product shape, such as bar, plate, sheet, strip, tubing, or structural shape.
- ✓ The use of deoxidizers, such as calmed, semi-calmed, covered, or edged steel.
- ✓ The microstructure, such as ferrite, pearlitic, and martensitic...
- ✓ The required level of strength, as specified in ASTM standards.
- ✓ Heat treatment, such as annealing, and thermomechanical treatment.

Of the classification systems mentioned above, chemical composition is the most widely used internationally and will be underlined as follows.

The more carbon you have, the harder the steel. Steel was therefore initially classified into categories [4]:

- General purpose carbon steels.
- Heat treatment steels, alloyed or not.
- Tool steels.
- Stainless steels [3].

I.3.1 Ordinary steels or carbon steels

Ordinary steels are standard steels in general use which are sometimes incorrectly called carbon steels. They are used as they are, without further processing, and constitute about 80% of the production of steels (Table 1). In addition to carbon, these steels contain additional elements and impurities, the presence of which results from their mode of production: manganese (1.2%), silicon (0.6%), sulfur (0.06%), phosphorus (0.06%). These percentages show the limited contents of these elements in these steels.

Table (I.1): Ordinary steels or unalloyed carbon steels.

Shade	Percentage of carbon (C)	Resistance R_m (MPa) annealed condition	Jobs
extra soft	$C < 0,15$	330-420	sheet metal for bodywork, straps, hardware, forge pieces
Soft	$0,15 < C < 0,20$	370-460	metal framework, profiles, construction ordinary mechanics, bolts, ordinary wires
semi-sweet	$0,20 < C < 0,30$	480-550	machine parts for applications mechanical parts, molded parts or frames, parts forged
half hard	$0,30 < C < 0,40$	550-650	small tools, parts of agricultural machinery,
			transmission components
Hard	$0,40 < C < 0,60$	650-750	tooling, armament, slides, rails and
			tires, springs, cutlery, castings and
			Processed
extra hard	$0,60 < C$	>750	machining and cutting tools, cables, springs

Although they can be obtained with various mechanical properties, ordinary steels do not meet all the requirements for use. The main properties of carbon steels that can be improved are:

- Mechanical resistance in the standardized state or in the annealed state.
- hardenability.
- weldability.
- heat resistance.
- Resistance to wear and corrosion [3].

I.3.2 Heat treatment steels

Heat treatment steels are defined in relation to their chemical composition because it makes it possible to determine the treatments that can be applied to them according to the desired properties. Heat treatment steels are either carbon steels with no additional elements other than standard elements Mn and Si, or alloy steels containing in varying proportions of one or more additional elements (Cr, Ni, V, etc) [3].

I.3.3 Tool steels

Tool steels are of paramount technological importance, no manufacturing step, and whatever process is used can do without a tool. World production of this kind of steel is only a small percentage ~ 0.1%, but in America, for example, it has more than 75 grades. Each of these shades is intended for a very specific function [5].

I.3.4 Stainless steels

Today, we are experiencing an extraordinary development of stainless steel; this is due in large part to the availability of metallic elements used in their composition, (chromium, nickel, molybdenum, and manganese...). A metal is said to be stainless if it resists well to the action of the atmosphere at varying degrees of humidity and salinity, to chemical attacks (acids, bases, salts, any other corrosion agent). In many applications that have become increasingly severe in terms of corrosion, it has been necessary to substitute special and alloy steels for ordinary steel. The high operating temperature also requires good mechanical strength when hot, in particular, good resistance to creep. Most of these refractory steels are stainless steels whose properties are improved by additions of molybdenum, titanium, niobium, etc.

Stainless steels include a set of families of metal alloys which all contain iron and chromium: it is essentially chromium that gives steels good resistance to corrosion by formation on the extreme surface of a very thin layer of non-porous chromium oxide. Depending on their chromium content, the threshold of which minimum is 13%, and the metallurgical treatments they have undergone, they exhibit a wide range of properties. Among others [5], we distinguish :

I.3.4.1 Martensitic

- ✓ Chromium steels can be hardened by heat.
- ✓ Characteristics: great load and shock strength, low corrosion resistance.
- ✓ Some uses: knives, blades, mill parts, nuts, bolts.
- ✓ Typical member: Type 410 [6].

I.3.4.2 Ferritic

- ✓ Chromium steels having larger amounts of chromium than the martensitic; not appreciably hardened by heat.
- ✓ Some uses: trim, molding, counters, exteriors.
- ✓ Typical member: Type 430 [6].

I.3.4.3 Austenitic

- ✓ Chromium nickel alloys; not hardenable by heat.
- ✓ Characteristics: high degree of corrosion resistance.
- ✓ Some uses: suitable for product contacts, such as milk processing and handling equipment.
- ✓ Typical member: 300 series stainless steels[6].

I.3.4.4 Precipitation-hardenable stainless steels

- ✓ Of the different alloys in this group, the chromium nickel-copper type probably has widest application in food processing; hardenable by heat.
- ✓ Characteristics : the copper is not extractable by food products or sanitizers (unlike "white metals"), and would not be a potential cause of oxidized flavor; it has good corrosion resistance and great strength, and is not subject to preferential corrosion in contact with 300 series, 18-8 type steels.
- ✓ Some uses: shafts, pistons, bearings, bolts, and nuts.
- ✓ Typical member: 17-4-PH (Armco Steel Corporation designation) [6].

II Corrosion

The considerable importance of corrosion in everyday life (domestic or industrial) no longer needs to be demonstrated. Indeed, this phenomenon affects practically all the achievements of the engineer, from the largest to the smallest: energy production, construction, transport, medical sector, electronics, etc. Corrosion is a big worldwide problem affecting all sectors out of all in the petroleum industry, in this chapter we can present some main notions about corrosion, its types, its forms and the factors which due to this problem [7].

II.1 History

The full history of corrosion has yet to be written. But it is certain that it goes hand in hand with the discoveries of materials. By referring to the first ages of man on earth, we realize that the first materials used were those which were found in nature or which required only a simple transformation. Gold, silver and bronze have been used since the earliest times, while meteoric iron was used early in the Bronze Age.

However, it must have corroded very quickly, as bronze was used almost exclusively thereafter. Corrosion has therefore been known for a long time, but its scientific study had to await the tests of Delarive, at the University of Grenoble, and those of Faraday on electricity and the current stack in 1830. These researchers then discovered that the Corrosion of metals was an electrochemical phenomenon. However, this explanation does not apply to all forms of corrosion, dry corrosion involves the chemical reaction of the external environment directly on the material, it is typical of gas corrosion and occurs at high temperature.

The economic importance of corrosion in our daily life, domestic or industrial, is well established. The damage caused by this phenomenon causes losses in the world that amount to billions of dollars every year and without methods of prevention and protection these numbers can be higher. As a result, the development of safer, more economical and environmentally friendly protection technologies represents a new challenge for the engineer who will need to have in-depth scientific knowledge in the fields of electrochemistry and corrosion of metals. Should become familiar with modern experimental methods as well as new materials [8].

II.2 Definition

There are a number of proposed definitions of corrosion; the term "erosion" from the Latin for erosion, meaning to nibble, to attack [9]. Defined in a simple way, corrosion is the process of deterioration or failure of a material resulting from a chemical reaction between the material and its surrounding environment. It is an indispensable area of research in materials science and engineering, because wear resistance characterizes the stability or durability of a material, and is one of the most important elements of material performance in application [10].

There are several definitions of corrosion and according to the International Standards Union of Pure and Applied Chemistry (IUPAC) "Corrosion is an irreversible interaction of a substance (metal, ceramic, polymer) with its environment which results in the consumption of the substance or its dissolution in a component of the environment. Often, But not necessarily, corrosion leads to adverse effects with the use of the materials considered. Physical or mechanical processes such as melting, evaporation, abrasion or mechanical fracture are not included in the term corrosion" [11].

II.3 Classification

Corrosion has been classified into different methods. They are :

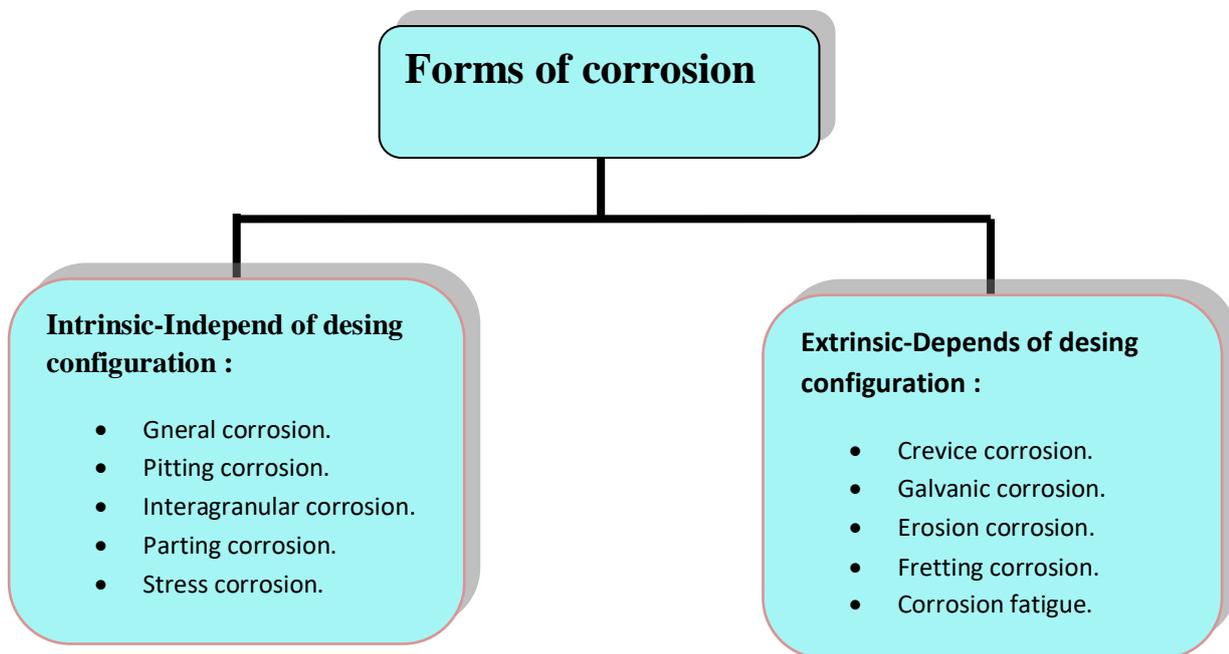
- Low temperature corrosion and high temperature corrosion (or)
- Electrochemical corrosion and chemical corrosion (or)
- Wet and Dry corrosion.

Wet corrosion occurs when the metal is in contact with an electrolytic conducting liquid or when two dissimilar metals or alloys are either immersed or dipped partially in the electrolytic conducting solutions. This is always associated with low temperature conditions.

Dry corrosion takes place mainly through the direct chemical action of atmospheric gases and vapors present in the environment [12]. This is most often associated with high temperature [12].

II.4 Forms of corrosion

Corrosion can manifest itself in many forms such as uniform corrosion or general corrosion, galvanic corrosion, crevice corrosion, pitting corrosion, intergranular corrosion, selective leaching, erosion corrosion, stress corrosion, corrosion fatigue and fretting corrosion. In order to improve the understanding between corrosion and design engineers it is classified into two broad categories. They are expressed in flow chart (figure 1) [12].



Figure(I.1): Forms of corrosion.

II.4.1 General corrosion

Is a most common form of corrosion that can be seen almost everywhere. It is also known as uniform or atmospheric corrosion. It is normally characterized by a chemical or electrochemical reaction which proceeds uniformly over the entire exposed surface or over a large area [12].

II.4.2 Galvanic corrosion

It is also known as bimetallic corrosion. It occurs when a potential difference exists between two dissimilar metals immersed in a corrosive solution. This potential difference produces a flow of electrons between the metals. Several investigations have shown that, galvanic corrosion is directly proportional to the area of the cathodic to the anodic metal [13] (Figure 2).



Figure (I.2): Schematic representation of galvanic corrosion.

II.4.3 Crevice corrosion or deposit corrosion

Crevice corrosion usually occurs in crevices, splits, and gaps or cracks present in metal structures. It is also a widely occurring form of corrosion (Figure 3) [14].



Figure (I.3): Schematic representation of crevice corrosion.

II.4.4 Pitting corrosion or localized corrosion

Pitting is a well known form of corrosion that causes a lot of pits on metal surfaces. The pits are primarily very small in size but they become bigger with time. Generally, the pits become deeper and wider, as the corrosion process continues. The growing rate of pitting depends upon the corrosivity of the surrounding environment(Figure 4) [14].

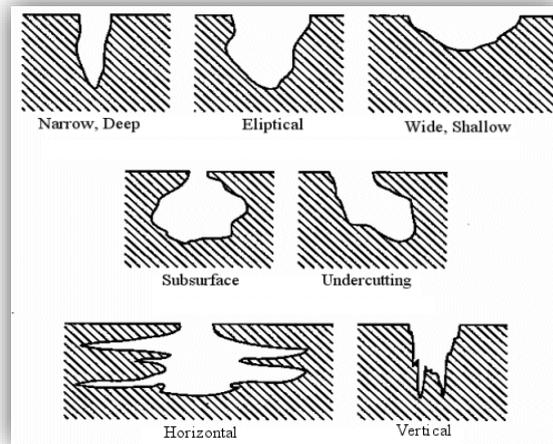


Figure (I.4): Schematic representation of pitting corrosion.

II.4.5 Intergranular corrosion (IGC)

Most of the metals and alloys are susceptible to intergranular corrosion, when exposed to specific corrosion environment which is shown in the Figure 5. Grain boundaries are usually more reactive than grain matrix. Hence localized attack occurs at and adjacent to grain boundaries with relatively little corrosion of the matrix. This type of attack is usually rapid and penetrates deep into the metal [12].



Figure (I.5): Schematic representation of intergranular corrosion.

II.4.6 Selective leaching corrosion

Selective leaching is the removal of an element from an alloy by corrosion. Selective removal of zinc from brass is a prime example of this form of attack. A similar attack has been observed with other alloys in which iron, aluminum, cobalt and chromium are removed. This type corrosion is undesirable as it yields a porous metal with poor mechanical properties (Figure 6) [12].



Figure (I.6): Schematic representation of selective leaching corrosion.

II.4.7 Erosion corrosion

It is the increase of attack of a metal because of relative movement between a corrosive medium and the metal surface. This type of erosion corrosion is usually associated with systems where high velocities of corrosive fluids or gases are encountered.

This corrosion can be observed in piping system such as bends, elbows, pumps and condensers, etc. A Schematic representation of erosion corrosion is shown in Figure 7.

Factors affecting erosion corrosion are nature of surface film, corrosion environment and presence of air bubbles with its size, chemical composition, suspended solids, corrosion resistance and metallurgical properties of metals and alloys [12].

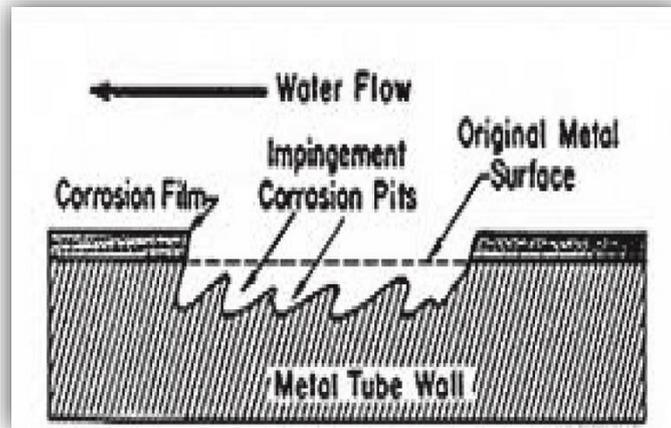


Figure (I.7): Schematic representation of erosion corrosion.

II.4.8 Stress corrosion

The cracking of metal or alloy by the combined action of a tensile stress and a corrodent (Figure 8) is known as stress corrosion cracking. The susceptibility to stress corrosion cracking is due to certain metallurgical factors such as:

- Chemical composition.
- Preferential orientation of grains.
- Composition and distribution of precipitates.
- Dislocation structure and environmental factors and structure of metal [12].

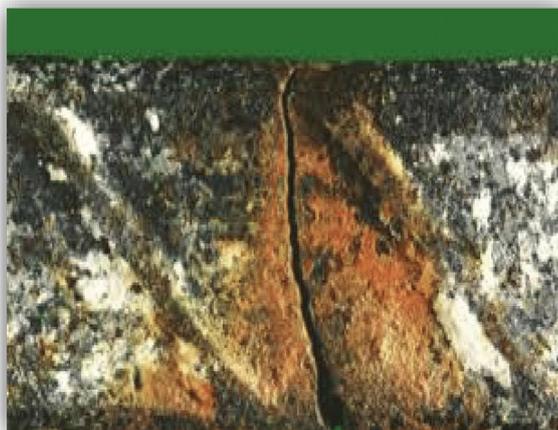


Figure (I.8): Schematic representation of stress corrosion.

II.4.9 Corrosion fatigue

It is defined as, “the reduction of the fatigue strength due to the presence of corrosive environment”. Corrosion fatigue occurs due to the combined action of tensile and compressive stress alternatively. Fatigue occurs at lower stress in corrosive environment (Figure 9) [12].



Figure (I.9): Schematic representation of Corrosion fatigue.

II.4.10 Fretting corrosion

Fretting is a wear phenomenon enhanced by corrosion. It involves wear of a metal or alloy when in contact with another solid material in dry or humid air.

Fretting is the result of abrasive wear surface oxide films, which form a contacting surfaces under load in atmospheric air which is shown in (Figure 10). The factors which affect fretting corrosion are:

- Magnitude of relative motion.
- Temperature.
- Environment.
- Metallurgical factors.

Due to slight motion such as vibration, surface oxide and underlying metal, gets spoiled. The metal particles as a result of wear get oxidized to hard oxides which act as an additional abrasive medium. Further, the motion grinds the oxides particles thus causing wear (Figure 10) [12].



Figure (I.10): Schematic representation of Fretting corrosion.

II.4.11 Cavitations corrosion

It is a special type of erosion corrosion which is caused due to the formation of vapor bubbles in a corrosive environment near a metal surface and when the bubbles collapse, attack arises for example, hydraulic turbulence, ship propellers, etc. It is similar to pitting corrosion but the surface is rough and has many close spaced pits (Figure 11) [12].



Figure (I.11): Schematic representation of Cavitations corrosion.

II.5 Factors influencing corrosion

Corrosion phenomena depend on a large number of factors and they can be classified into four main groups (Table 2) [15, 16].

Table (I.2): The main corrosion factors.

Corrosive environmental factors	Metallurgical factors	Factors defining conditions of employment	Time dependent factors
<ul style="list-style-type: none"> - Reagent concentration - Oxygen content - pH of the medium - Temperature - pressure 	<ul style="list-style-type: none"> - Composition of the alloy - Development processes - Impurities - Heat treatment - Mechanical treatment 	<ul style="list-style-type: none"> - Surface condition - Shape of parts - Use of inhibitor - Assembly processes 	<ul style="list-style-type: none"> - Aging - Mechanical tensions - Modification of protective coatings

II.6 Corrosion assessment methods

II.6.1 Gravimetry

This method has the advantage of being easy to implement, of not requiring significant equipment, but does not allow the approach of the mechanisms involved during corrosion[17]. Its principle is based on the measurement of the loss of mass undergone by a sample of surface S, during the time t of immersion in a corrosive solution maintained at constant temperature.

The corrosion rate, by the mass loss method, is determined by the following formula:

$$\Delta m = m_i - m_f$$

m_i (mg) : the mass of the sample before the test.

m_f (mg) : the mass of the sample after the test.

Δm (mg) : the mass loss (corrosion rate) of the sample.

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

$$V = \frac{\Delta m}{S t}$$

Δm :mass loss in mg.

S : the exposed surface in cm^2 .

t : the exposure time in the solution in hours.

The inhibitory efficiency (E%) of the compounds studied is calculated using the following relationship :

$$E\% = \frac{V - V_{inh}}{V} (100)$$

V and V_{inh} represent respectively the values of the corrosion rate in the absence and in the presence of the inhibitor [18].

II.6.2 Electrochemical methods

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

- Stationary methods.
- Transitional methods[18].

II.6.3 Stationary method: polarization curves

The polarization curve of the metal-solution interface is a fundamental characteristic of electrochemical kinetics, but only accounts for the slower stage of the overall process at the electrochemical interface.

To determine a potentiostatic polarization curve, different potentials are applied using a potentiostat between the working electrode and a reference electrode. We measure the stationary

current which is established after a certain time in the electrical circuit between this working electrode and a counter-electrode (Figure 12).

This method makes it possible to precisely determine the electrochemical parameters of a metal in contact with an electrolyte, namely: the instantaneous corrosion rate (I_{corr}), the corrosion potential (E_{corr}), the Tafel slopes, the resistance polarization (R_p), the diffusion limit currents.

It gives quick measurements and its implementation is relatively simple.

The determination of the corrosion rate from the polarization curves is closely related to the kinetics governing the electrochemical process. There are three main types of kinetics:

- Pure activation kinetics.
- Mixed kinetics (activation + diffusion).
- Pure diffusion kinetics.

The detailed description of the mode of determination of I_{corr} and E_{corr} has been carried out previously [17]. In order to experimentally determine these electrochemical parameters, a logarithmic presentation of the current density is generally preferable, as it highlights the linear relationship between the logarithm of the current density and the potential (Figure 13).

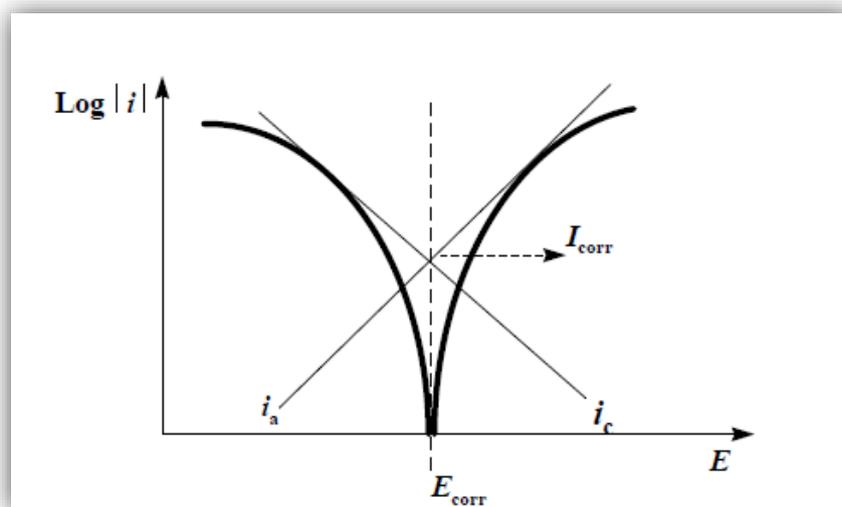


Figure (I.12): Determination of electrochemical parameters from Tafel lines.

The device used for plotting the curves (Figure: 12) consists of a conventional assembly with three electrodes, composed of a potentiostat, a generator programming the evolution of the potential as a function of time and a recorder. The potential is measured using a high impedance millivoltmeter with respect to the reference electrode[18].

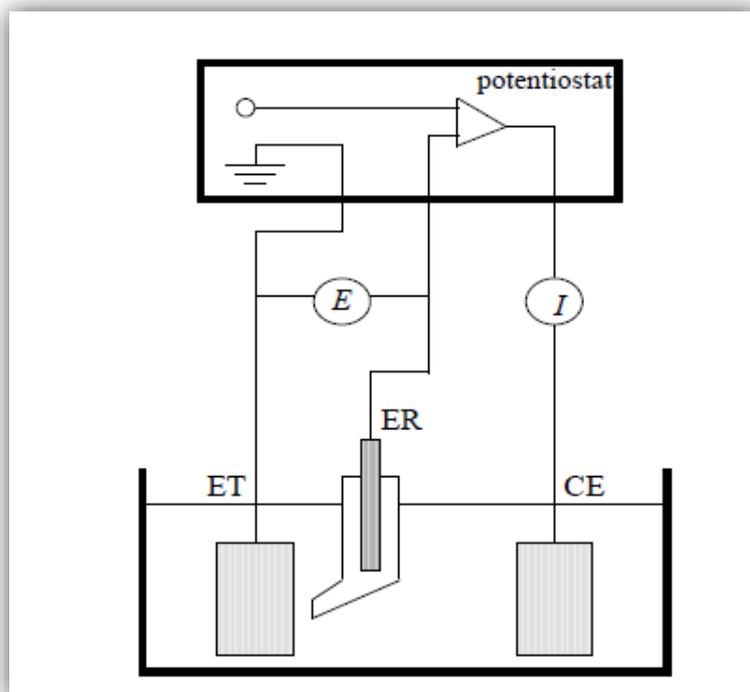


Figure (I.13): Device for measuring a potentiostatic polarization curve. ET: working electrode, ER: reference electrode, CE: counter electrode.

II.6.4 Transient method: electrochemical impedance spectroscopy

The non-stationary methods can be classified into two categories, namely: the large amplitude disturbance methods (cyclic voltammetry) and the low amplitude method (electrochemical impedance spectroscopy). Previous work has shown that electrochemical impedance spectroscopy (S.L.E.) can identify the elementary steps involved in the overall process taking place at the metal / solution interface, in the form of various time constants. The S.L.E. is employed today in following fields:

- Photoelectrochemistry.
- the semiconductor / electrolyte interface.
- organic electrochemistry and the study of adsorption phenomena.
- Bioelectrochemistry.
- corrosion and its inhibition [18].

III Corrosion inhibitor

The fact that corrosion needs to be controlled cannot be overemphasized in view of the colossal amount of money that is expended on it annually. Materials are protected from corrosion through a wide variety of methods. In most cases, the occurrence of corrosion is prevented or suppressed by the modification of the environment, modification of the materials properties, application of protective coatings and, cathodic and anodic protection [13].

III.1 Definition of inhibitor

There are a number of definitions proposed for inhibitors but International Standard Organization defines it as "A chemical substance which retards the corrosion when added to an environment in small concentration without significantly changing the concentration of any other corrosive agent." In view of this definition, a chemical added to an environment to neutralize the acidic constituent or oxygen scavengers added in water to remove oxygen from the electrolytes can not be classified as the inhibitors although they help in bringing down the corrosion rate. The prerequisite that needs to be satisfied for a corrosion controlling chemical to be termed as the corrosion inhibitor is that the chemical should be adsorbed at the corroding interface either in the form of molecule or as ions (anions or cations)[19].

In order to avoid or reduce the corrosion of metallic materials, inhibitors used in cooling system must satisfy the following criteria:

- It must give good corrosion protection at a very low concentration of inhibitor.
- It must protect all exposed materials from the attack of corrosion.
- It must remain efficient in extreme operating conditions (higher temperature and velocity).

- In case of an under or over dosage of inhibitor, corrosion rate should not increase drastically.
- The inhibitor or reaction products of the inhibitor should not form any deposits on the metal.
- It should suppress both uniform and localized corrosion.
- It should have long range effectiveness.
- It should not cause toxicity and pollution problems [12].

III.2 Classification of Inhibitors

Inhibitors are briefly classified (Figure 14) as follows [12].

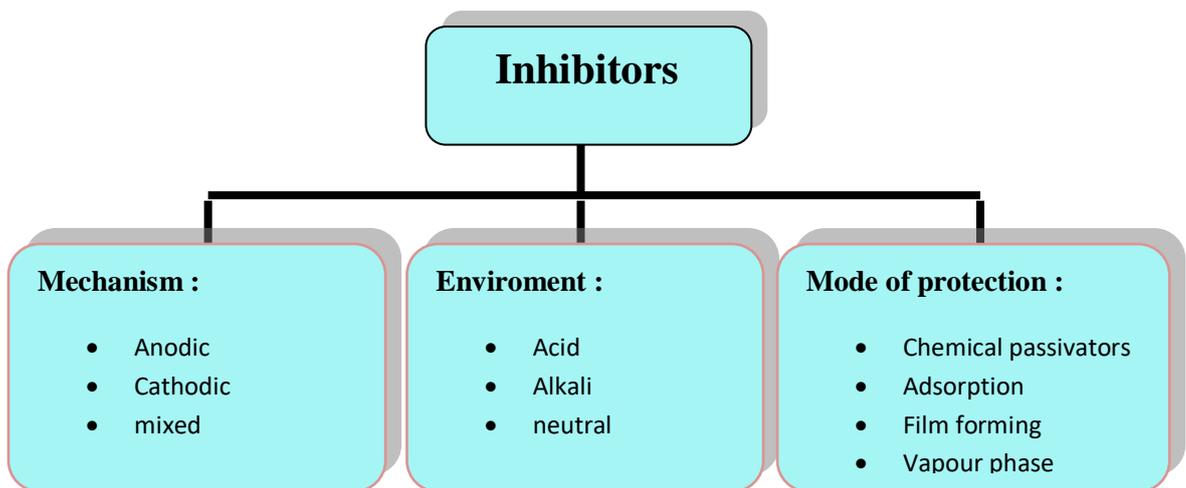


Figure (I.14): Classification of corrosion inhibitors.

III.2.1 Based on electrode process

III.2.1.1 Anodic inhibitors

They are passivating inhibitors which raise the corrosion potential of the material to a value where there is passive film formation. These inhibitors are chemical compounds such, CrO_2^- , $\text{C}_6\text{H}_5\text{COONa}$, which by reaction with the ions of the corroded metal or other ions contained.

In the water, are capable of forming a protective passive deposit on the anode surfaces of heating systems corrosion[9]. Even though anode inhibitors are widely used, a few of them have undesirable properties. If such inhibitors are used in very low concentrations, they cause stimulation of corrosion such as pitting and for this reason anodic inhibitors are qualified as dangerous.

- The oxidizing anions such as chromates, nitrites and nitrates that can passivate steel in the absence of oxygen.
- The non-oxidizing ions such as phosphates, tungstates and molybdates that require the presence of oxygen to passivate steel.

In general, passivation inhibitors can actually cause pitting and accelerate corrosion when concentrations fall below minimum limits. For this reason, it is essential to monitor the inhibitor concentration [12].

III.2.1.2 Cathodic inhibitors

Cathodic inhibitors reduce corrosion by slowing the reduction reaction rate of the electrochemical corrosion cell. This is done by blocking the cathodic sites by precipitation. Cathodic inhibitors are effective when they slow down the cathodic reaction. Elements As, Bi and Sb are referred to as cathodic poisons which reduce the hydrogen reduction reaction rate and lower the overall corrosion rate. Removal of oxygen from the corrosive environment will significantly decrease the corrosion rate. This can be done through :

- The use of oxygen scavengers such as sodium sulfite and hydrazine which react with the oxygen and remove it from the solution.
- Vacuum deaeration or.
- Boiling to lower the dissolved oxygen concentrations.

Cathodic inhibitors shift the corrosion potential to the anodic direction [12].

Here the cations migrate towards the cathode surfaces where they are precipitated chemically or electrochemically and thus block these surfaces. The inhibiting action of cathodic inhibitors takes place by three mechanisms:

- **Cathodic poisons:** The cathodic reduction process is suppressed by impeding the hydrogen recombination and mode of protection discharge but increase the tendency of the metal to be susceptible to hydrogen induced cracking [12].
- **Oxygen scavengers :** The substance which inhibit the corrosion by removing dissolved oxygen are called oxygen scavengers e.g. hydrazine and sodium sulphite[20].
- **Cathodic precipitates:** Compounds such as calcium, magnesium will precipitate as oxides to form a protective layer which acts as a barrier on the metal surface [12].

III.2.1.3 Mixed inhibitors

Mixed inhibitors act at the same time on anode and cathode surfaces where they decrease the rate of the two partial reactions by adsorption, but modify little the corrosion potential. These are organic products such as: Dicyclohexylamine nitrite ; Benzotriazole (BTA) ; Sodium benzoate[9].

III.2.2 Based on environment

III.2.2.1 Acidic environment inhibitors

III.2.2.1.1 Inorganic inhibitors

Mineral inhibitors are used in neutral / alkaline medium but rarely in medium acid. It is often their dissociation products (anion or cation) that are effective as corrosion inhibitors. Among the inhibitory anions are chromates, phosphates, molybdates, nitrates, nitrites, silicates, etc.... and among, Inhibitory cations are found mainly ions Ca^{2+} and Zn^{2+} . Inhibitors minerals are used less and less because of their toxicity. Their use is limited to certain closed-circuit systems [18].

III.2.2.1.2 Organic inhibitors

Organic compound containing oxygen, nitrogen, sulfur with multiple bonds have been reported as good corrosion inhibitors. Many organic inhibitors such as amines, aldehydes, alkaloids, nitro and nitroso compounds have been studied and tried as corrosion inhibitors. Organic inhibitors can be anodic, cathodic and mixed type based on its reaction at the

metal surface and potential. These are effective depending upon its size, carbon chain length, aromaticity, conjugation and nature of bonding atoms [12].

III.2.2.1.3 Alkaline inhibitors

Metals, which form amphoteric oxides, are prone to corrosion in alkaline solutions. Many organic compounds are often used as inhibitors for metals in basic solutions. Compounds such as thiourea, substituted phenols, naphthol, β -diketone, etc., have been used as effective inhibitors in basic solutions due to the formation of metal complexes [12].

III.2.2.1.4 Neutral inhibitors

Inhibitors which are effective in acidic solutions do not function effectively in neutral solutions, since the mechanism is different in the two solutions. In neutral solutions, the interaction of inhibitors with oxide covered metal surface and prevention of oxygen reduction reaction at the cathodic sites takes place. Such inhibitors protect the surface layers from aggressiveness. Some surface active chelating inhibitors have been found to be efficient inhibitors in near-neutral solutions [12].

III.2.3 Based on mode of protection

III.2.3.1 Chemical passivators

Substances which usually have a sufficiently high equilibrium potential (redox or electrode potential) and sufficiently low over potential decrease corrosion rate on attainment of passivity and are called chemical passivators [12].

III.2.3.2 Adsorption inhibitors

These represent the most widely used class of inhibitors. In general, they are organic compounds which get adsorbed on the metal surface and provide a blanketing effect over the entire surface, that is, both in cathodic and anodic cases.

Generally they effect both cathodic and anodic reactions equally, but in many cases the effect may not be equal. These are commonly used in the acid pickling of hot rolled products in order to remove the black mill scale and are thus known as pickling inhibitors [12].

III.2.3.3 Film forming inhibitors

In contrast to the adsorption inhibitors which form the straight forward adsorbed film of the inhibiting species, many substances called film forming inhibitors, appear to stop corrosion by forming a blocking or a barrier film of a material other than the actual inhibiting species itself. Such materials tend to be specific either to the cathode or to the anode. Zinc and calcium salts are the most common examples of cathodic film forming inhibitors. Benzoate is the common example of anodic film forming inhibitors, which inhibit corrosion during voyages[21].

III.2.4 Vapor phase inhibitors

Atmospheric corrosion of metals in closed spaces as in parcels during storage and shipment can be prevented by the use of certain substances called vapor phase inhibitors also called as volatile inhibitors. These are substances of low but significant vapor pressure. The vapor comes in contact with the surface of the metal and the adsorption of the inhibitor takes place. The moisture then hydrolyses it and releases protective ions which have corrosion inhibiting properties. Figure 15 shows the representation vapor phase inhibitors [12].

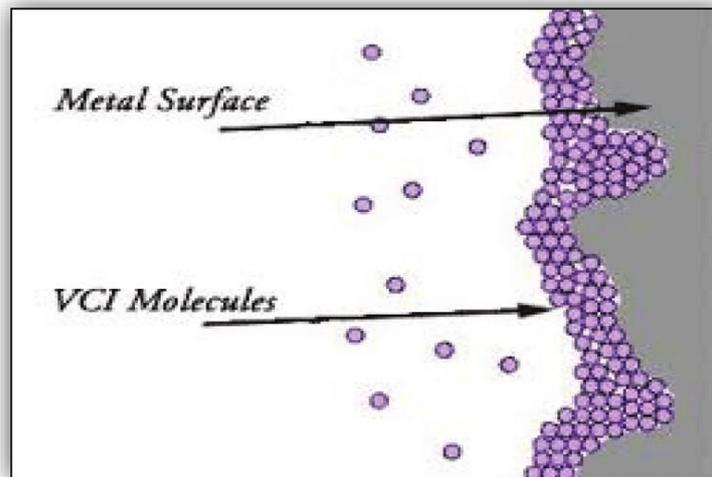
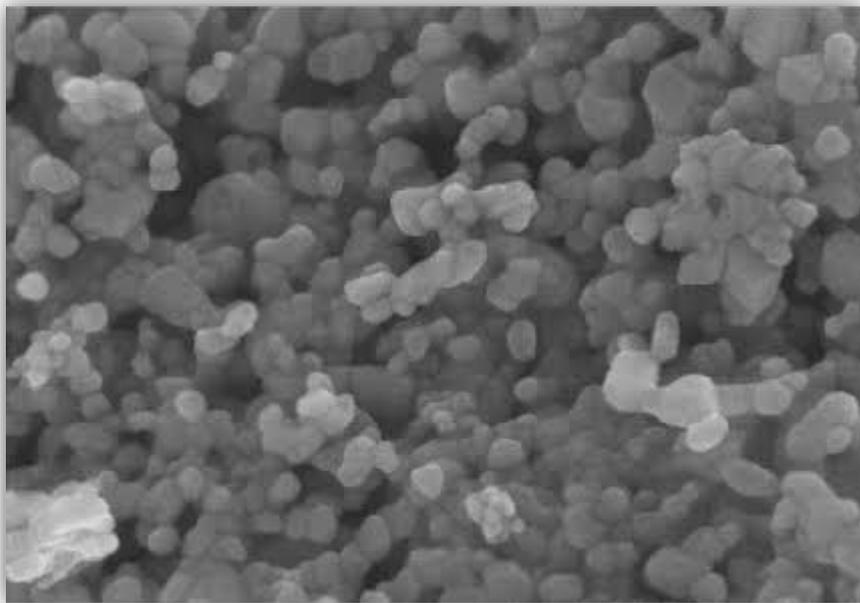


Figure (I.15): Schematic representation of vapor phase inhibitor.

Chapter II

ZnO thin films deposition and characterization



Introduction

This bibliographic chapter is devoted to start from the general to the special, and in this chapter we mention the main of transparent conductive oxides, especially those of zinc oxide, and we describe the main characteristics of them and present the criteria for choosing the method of spray pyrolysis to produce films or thinning films. The objective of this chapter is to reveal the study of the properties of ZnO and how to make thin films using the spray pyrolysis method.

I Transparent and conductive oxides

TCO's are promising materials, since the discovery at the beginning of the century of the electrical conductivity and transparency in the visible range, research has really intensified since the 80s. The advent of new technologies with the democratization of flat screens or solar panels has contributed to this emergence. One of the factors illustrating the activity linked to a specific research is the number of publications published per year on these materials. The evolution of publications concerning zinc oxide, indium oxide and tin oxide from the 1970s to 2009. These three metal oxides are the most studied because they have demonstrated the best properties [22].

II Zinc oxide

In recent years, zinc oxide has become an interesting research topic and this is due to the interesting characteristics of ZnO (Table 1) [23].

Table (II.1): Different characteristics of ZnO.

characteristics	Paramètres
Structure cristalline	Wurtzite
Group d'espace	P6 _{3mc}
Paramètre de maille à 300 K	a=3.249 Å c=5.2042 Å
Densité volumique à 300K	5.675 g /cm ³
Gap optique à 300K	3.37 eV
Energie de liaison d'exciton	60 meV
Indice de réfraction	2.008

II.1 Definition

Zinc oxide, known as zincite in its natural state, ZnO is an n-type semiconductor with a wide band gap, around 3.3eV, and has an excitonic binding energy of the order of 60meV, which makes it a good candidate for emissive devices. Other areas of interest for ZnO have developed in recent years in application areas such as piezoelectric transducers, optical waveguides, gas detectors and transparent electrodes [22]. It is a II-VI semiconductor with a wide direct band gap whose color varies according to the impurities it contains (its red color, for example, is due to the presence of manganese in the material; pure, it is transparent) and according to its deviation from the stoichiometry [24].

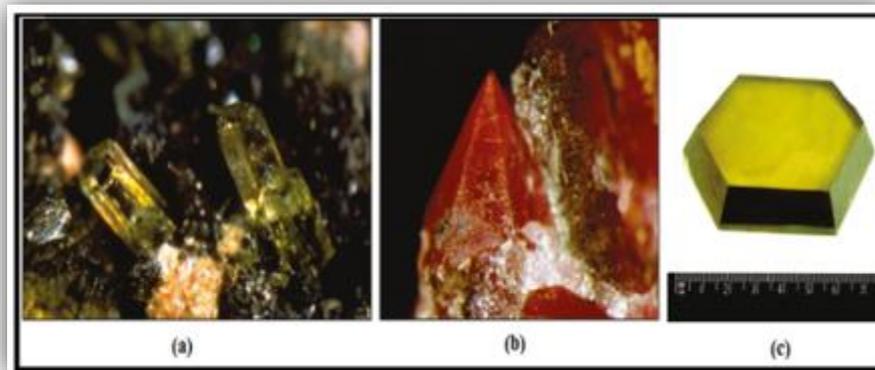


Figure (II.1): Solid ZnO in its natural form (a) and (b) and from synthesis.

II.2 The ZnO selection

The main advantage of ZnO is that its components are non-toxic (unlike, for example, indium in ITO), and very abundant on Earth. This is an undeniable advantage, as it reduces production costs. In addition, ZnO [25], when exposed to hydrogen plasma, it is much more stable than SnO₂ and ITO, whose optical transmission is degraded by this plasma. As the silicon layers are, in many cases, deposited on the TCOs layer, this one is thus necessarily exposed to this kind of plasma.[22] Zinc oxide has a range of physical properties that can be used in electronics and optoelectronics. Applications in the field of electronics and optoelectronics. The implementation of technologies for the manufacture of ZnO thin films has led to numerous applications in a wide range of fields [22].

II.3 Properties of zinc oxide ZnO

II.3.1 Crystallographic properties

From the crystallographic point of view, zinc oxide crystallizes under three different conditions, in three different types of structures: hexagonal Wurtzite (B4), Zinc blende (B3) and the NaCl structure (B1). Under ordinary conditions of temperature and pressure zinc oxide films are mainly known as the Wurtzite structure (Figure 2. (a)) This structure is a thermodynamically stable structure at room temperature; the Blende (cubic) structure is observed when ZnO is deposited on certain substrates with cubic symmetry (Figure 2. (b)), and the Rocksalt (NaCl) structure is obtained when a hydrostatic pressure (10-15 GPa) is applied to the Wurtzite structure (Figure 2. (c)). the latter is a metastable phase that can persist at atmospheric pressure.⁷

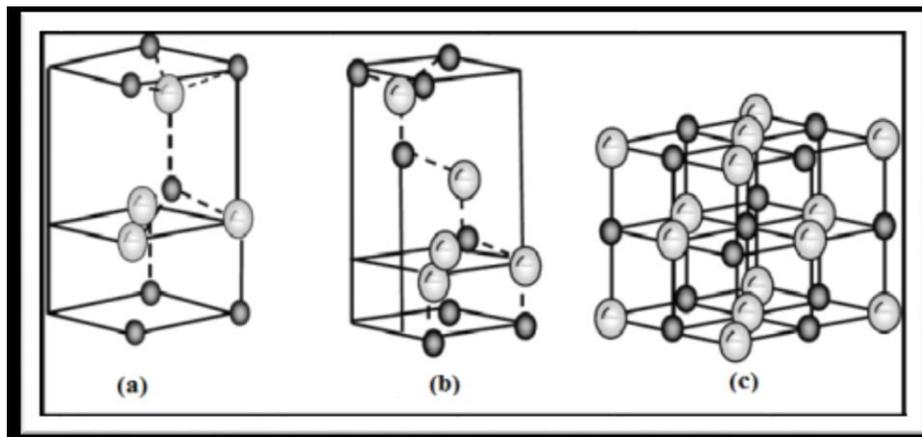


Figure (II.2): Representation of crystal structures of ZnO: (a) hexagonal wurtzite, (b) zinc blende, (c) cubic rocksalt. The large gray spheres represent zinc atoms and the small black spheres represent oxygen atoms [24].

According to [25], the simplest way to see the unit cell is to look at the tetrahedron, shown in Figure 4, whose base and vertices are made up of four oxygen atoms. In fact, the zinc atom is not exactly in the center of the tetrahedron but displaced by 0.11 \AA in a direction parallel to the c -axis. The oxide molecules thus maintain their individuality to some extent, contrary to what one would expect from a purely ionic crystal. This phenomenon is due to the homopolarity of the Zn - O bonds.

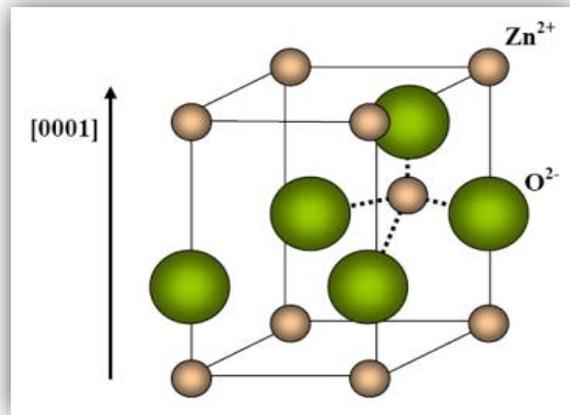


Figure (II.3): crystal structure of zinc oxide.

As mentioned earlier, ZnO has many important properties that make it a deserving candidate for primacy in the semiconductor industry. Some of its properties are wide band gap, large exciton-binding energy and high resistance to radiation damage, among others. ZnO has a melting point of 1975°C and is insoluble in water and alcohol, but can be dissolved in dilute acids. Some of the other properties of ZnO are given in Table 2.

Table (II.2): Properties of ZnO [26].

Properties	Specifications	Comments
Structure	Wurtzite	Same as hexagonal
Bandgap	3.3 eV	Wide bandgap semi-conducteur
Exciton-binding energy	60 meV	Higher than GaN (21–25 meV)
Piezoelectricity	1.2 cm-2	Highest among all semi-conducteurs
Hardness	*5 X	For single Crystal
Toxicity	Very low	Same as other compound semiconductors

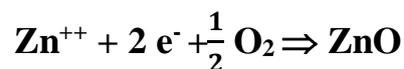
II.3.2 Electrical properties

In general ZnO is a semi conductor of type n, the high conductivity of the pure oxide layers is due to the high concentration of carriers (electrons), since the mobility in these that the mobility in these layers is considerably lower than that in the volume of the corresponding material. The high concentration of electrons is attributed to the deviation from to the stoichiometry (or defects in the structure).

Zinc oxide (ZnO) is a direct gap material. There is a certain anomaly in the literature concerning the gap energy; Srikant and Clarke[27] claim that the energy gap energy gap at room temperature of ZnO is 3.3 eV, while a valence band at the donor level transition at 3.15 eV explains the fact that a smaller value (typically 3.2 eV) is often reported. Thus, the room temperature gap of ZnO can be placed in the range 3.2 to 3.3 eV.

The high conductivity ($> 5000 \Omega^{-1} \text{ cm}^{-1}$) is possible in n-type ZnO due to intrinsic defects, dopants (Al, In, Ga, B, F) or in combination. The mobilities reported of electrons in ZnO thin films are typically on the order of ~ 20 to $30 \text{ cm}^2/\text{V.s}$; in contrast, the maximum mobility obtained in single crystals of ZnO is $\sim 200 \text{ cm}^2/\text{V.s}$.

The deviation from stoichiometry can be due to anion vacancies or to an excess of cations in interstitial position. The exact nature of the structural defects in most cases is still uncertain. The stoichiometric ZnO formation reaction [28]:



II.3.3 Optical Properties

The optical properties of ZnO thin films depend on the preparation conditions and the method of elaboration. Table 3 shows the transmission and gap energy of ZnO thin films obtained by different deposition techniques. ZnO has a high optical transparency in the visible and near-infrared range, which is due to the wide band gap. In addition to the possibility of emitting in the near UV (375 nm), ZnO attracts the interest of the scientific community because it has very robust excitons whose emission persists beyond room temperature (binding energy of 60 meV). The refractive index of zinc oxide in the bulk form is equal to 2.0. Usually zinc oxide is used in the form of thin layers and has a refractive index that varies between 1.7 and 2.20 depending on the preparation conditions.

Table (II.3): Optical properties of ZnO[23].

Méthode de dépôt	Température du substrat	L'épaisseur (nm)	Transmittance %	E _g (eV)
Spray	500	-	80	3.27
	420	210	98	3.31
	350	-	85	3.32
CVD	500	-	100	3.44
	320	460	85	3.28
	140	-	93	3.44
PLD	400	-	99.8	3.17

The fundamental absorption threshold of ZnO is in the ultraviolet. The shape of the intrinsic absorption spectrum can be observed only on thin films because of their large absorption coefficient. We observe an abrupt rise in the absorption coefficient around $\lambda = 385$ nm ($E_g = 3.3$ eV), as seen in Figure 4 below:

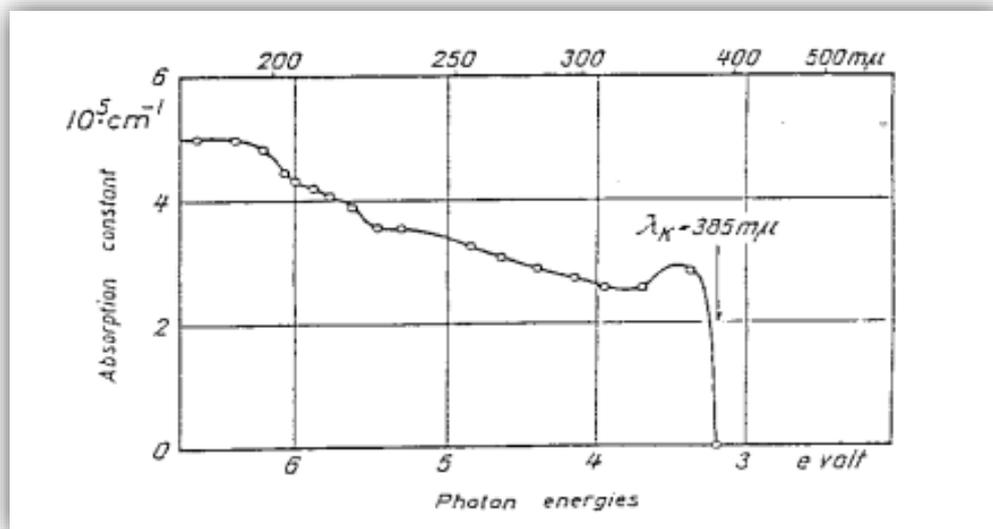


Figure (II.4): the absorption spectrum at room temperature, after annealing [28].

II.3.4 Chemical Properties

The reactivity of zinc oxide depends on its method of preparation than on a modification of the crystal lattice. Three temperature ranges correspond to different chemical properties:

- Above 1000°C the lattice defects can diffuse from the surface to the interior of the crystal. Thus the different chemical reactions can reach their thermodynamic equilibrium.
- From 600°C to 1000°C, the defects remain localized at the surface and only the surface reactions are reversible.
- Below 600°C, the chemical activity of zinc oxide is frozen.

Zinc oxide is soluble in most mineral acids and also dissolves in bases to give zincates ions $Zn(OH)_4^{2-}$. It remains insoluble in liquid ammonia and in liquid sulfur dioxide [29].

II.3.5 Catalytic properties

Semiconductors in general are excellent catalysts for oxidation, dehydrogenation and desulfurization reactions. Zinc oxide is a photochemical catalyst in many reactions. It is used as a trap and chemical scavenger of certain gases such as H_2S , CO_2 , H_2 and. Suspended in water, it can act as a photochemical catalyst in the oxidation of oxygen to ozone, the oxidation of ammonia to nitrate, the reduction of methylene blue, the synthesis of hydrogen peroxide, and the oxidation of phenols. ZnO thin films have also been used to catalyze the copper deposition reaction [29].

II.4 Bienfaits of ZnO

The main bienfaits of ZnO are:

- High thermal conductivity of 0.54 Wcm⁻¹K⁻¹ (compared to 0.5 for GaAs).
- The highest exciting binding energy of semiconductors 60meV.
- Détecteurs UV avec une réponse spectrale maximale à 350nm.
- Non-toxic.
- Very abundant on Earth.[30]
- Very large shear modulus ~ 45.5 Gpa (indicates crystal stability), e.g. for example: 18.35 for ZnSe, 32.60 for GaAs, 51.37 for silicon [24].

III Thin films

III.1 General concept of thin films

In principle, a thin layer of a given material is an element of this material whose one of the dimensions called the thickness has been greatly reduced so that this small distance between the two boundary surfaces remains of the order of nm [31].

The essential difference between the material in the solid state and in the state of thin layers is indeed related to the fact that in the solid state one generally neglects with reason the role of the limits (the surfaces) in the properties, while in a thin layer it is on the contrary the effects related to the limit surfaces which are preponderant. It is quite obvious that the smaller the thickness, the more pronounced this two-dimensional effect will be, and that conversely, when the thickness of a thin layer exceeds a certain threshold, the thickness effect will become minimal and the material will regain the well-known properties of the bulk material.

The second essential characteristic of a thin film is that whatever the procedure used for its manufacture, a thin film is always procedure used for its manufacture, a thin film is always attached to a support on which it is built (even if, sometimes, it happens that the thin film is separated from the support). Consequently it will be imperative to take into account this major fact in the design, namely that the support influences very strongly the structural properties of the layer deposited on it. Thus a thin layer of the same material, of the same thickness may have significantly different physical properties depending on whether it is deposited on an amorphous insulating substrate such as glass or a monocrystalline substrate of silicon for example.

The consequence of these two essential characteristics of a thin film is the following : a thin film is anisotropic by construction.

III.2 Principle of thin film deposition

To form a thin layer on a solid surface (substrate) the particles of the coating material must pass through a coating material must pass through a conductive medium to intimate contact with the substrate.

On arrival from the substrate, a fraction of the coating particle adheres (thanks to Van der Waals forces) or chemically reacts with the substrate. The particles can be atoms, molecules, ions or ionized fragments of molecules. The transport medium can be solid, liquid, gas, or vacuum.

- A. Solid:** in this situation the substrate is in contact with the solid, only the particles that diffuse from the solid to the substrate form a layer.
- B. Liquid medium:** it is easier to use than the first case, because the material is more versatile in this state (Epitaxy in liquid phase, and electrochemical, sol gel).
- C. Gas or vacuum:** CVD deposition the difference between the gaseous medium and the vacuum is the mean free path of the particles.

There is no standard method of thin film deposition that can be used in different situations. Substrate preparation is often a very important step for thin film deposition in order to achieve good adhesion. To characterize the different deposition processes the following parameters have to be specified:

- ✓ The transport medium (solid, liquid, gas or vacuum).
- ✓ The nature of the coating particles (atoms, molecules, ions).
- ✓ The method of introducing the coating material into the medium (mixing, dissolution, evaporation, reaction on one of the electrodes).
- ✓ The nature of the reaction on the substrate surface (condensation, chemical reaction, and implantation)[30].

The growth process of a thin film can be summarized in three main steps:

1. Production of ionic, molecular or atomic species of the material to be deposited on a substrate.
2. Transport of species in a gaseous or inert environment.
3. Condensation of species to form a solid deposit[29].

Depending on the type of material used as a source (solid, gas, liquid) to deposit a thin film and according to the process of transport towards the substrate, one distinguishes two categories of methods of elaboration of thin layers:

- a.** When the deposited material is solid, its transport to the substrate is done by vaporization. This deposition can be achieved by thermal evaporation, electron gun, laser ablation or by positive ions (sputtering). All these methods are classified under the name of Physical Vapor Deposition (PVD).
- b.** Processes that use the base material in the form of evaporated gases or chemically evaporated solids are known as Chemical Vapor Deposition (CVD), and Atomic Layer Epitaxy (ALE), while spray-pyrolysis, sol-gel, spin-coating and dip-coating methods use solutions as precursors.

The diagram below shows, some chemical and physical methods, for the elaboration of the elaboration of ZnO thin films.

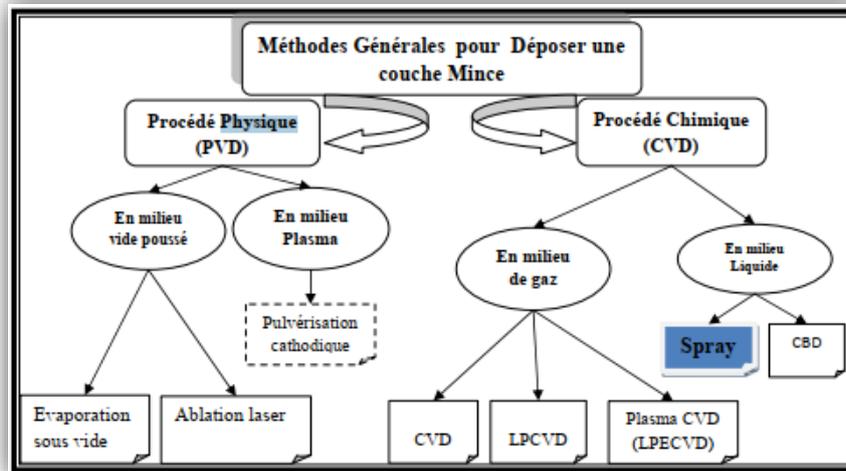


Figure (II.5): Different methods of film processing[24].

III.3 Selection of a thin film deposition technique

The realization of thin ZnO layers requires the mastery and the control of their development. The selection of a deposition method involves several criteria:

- ✓ The nature of the material to be deposited.
- ✓ The deposition rate.
- ✓ the thickness of the desired layer
- ✓ The constraints imposed by the substrate (vacuum degassing, maximum temperature...).
- ✓ The desired stoichiometry, the crystalline quality and density of the layers, the adhesion of the deposit on the substrate.
- ✓ Finally, the reproducibility and the cost of the realization.

Until today, the elaboration of ZnO layers used as TCOs for solar cells have been mainly deposited by sputtering methods from a solid target or by gas discharge, which requires huge material resources. For this reason, the method of deposition by pyrolysis spray or air is spraying or reactive chemical spraying in liquid phase, of precursor dissolved in methanol is presented as an alternative with the following advantages:

- ✓ Relatively simple and feasible development in Algeria
- ✓ Non-bulky, non-hazardous and above all low-cost drop-off bench.
- ✓ Gives satisfactory results.

IV Spray pyrolysis

Several research teams have focused in recent years on the preparation of thin films of metal oxides by simple methods (evaporation, sol-gel, chemical sputtering ...). These methods have the bienfaits of being less expensive, easy to handle and allowing depositing thin films of large surface[30].

IV.1 Definition

The term "spray pyrolysis" is composed of two words:

"Spray" is the English word that expresses the jet of a liquid (perfume, deodorant, insecticide, etc.) projected by fine droplets by spraying. "Pyrolysis" that expresses the chemical decomposition of the liquid jet on the heated substrate.

The spray-pyrolysis method is a widely used technique to prepare materials in various forms: thin, thick, dense, porous and powder. Even multilayer deposits and ceramic coatings can be prepared using this technique[24].

IV.2 Principle of the technique

The spray or reactive chemical spraying is a technique based on the principle of thermal decomposition of an aerosol. It consists in spraying an atomized solution, on a substrate previously heated to a given temperature. These systems make it possible to transform the solution into a jet of very fine droplets of a few tens of microns in diameter. The spray arrives on the surface of the heated substrates at a sufficient temperature to allow the decomposition of the products dissolved in the solution and to activate the reactions likely to produce the TCO's. At these temperatures, some of the reaction products will be immediately eliminated (volatile elements); only the compound to be deposited on the substrate remains[23].

Generally the thickness of the layer deposited by this method depends on the concentration of the precursor, the volume of the solution to be sprayed and the deposition time. Among the bienfaits of this method we can mention:

- Possibility to form a wide variety of multi-elemental compounds and to obtain a uniform chemical composition.
- Well suited for obtaining thin layers.
- High deposition speed.

- Very low energy consumption.
- Very simple, inexpensive and profitable equipment [24].

IV.3 Installation description

The description of the film formation by the spray-pyrolysis method can be divided into three main steps:

- **Aerosol generation:** Finer droplets are generated by the atomizer at the nozzle outlet.
- **Transport of the aerosol:** the transport of the sprayed species to the substrate is carried out by a compressed gas (compressed air), electrostatic field.
- Decomposition of the precursor solution on the substrate surface by pyrolysis reaction[24].

A typical pyrolysis spray system typically contains a sprayer, a precursor solution, a heating system and a thermocouple for temperature sensing (Figure 6).

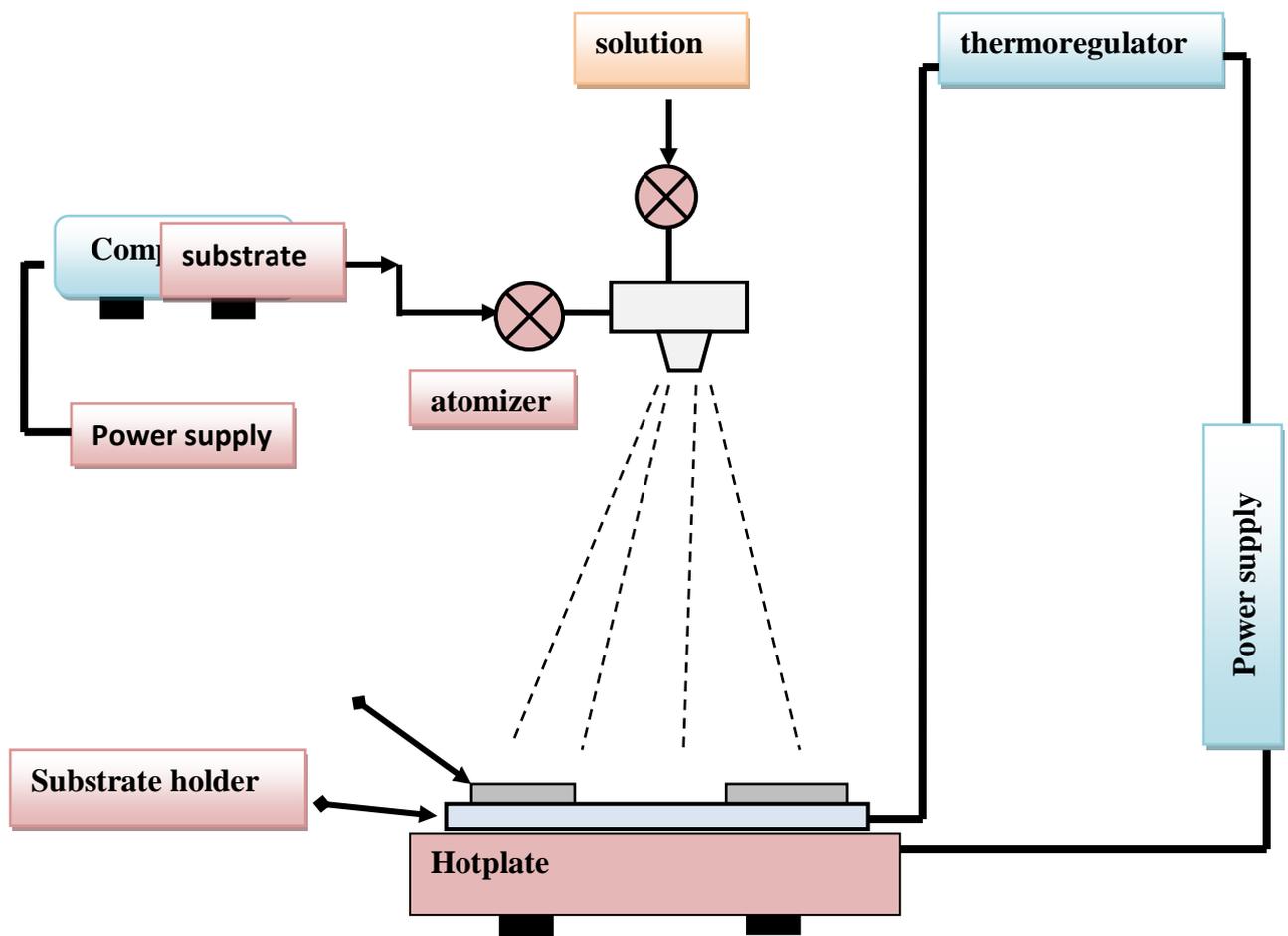


Figure (II.6): Schematic diagram of a pyrolysis spray deposition equipment.

1. **Solution vial:** It can contain 30ml of precursor solution. It is gravity fed with a low flow mist.
2. **A substrate heater and holder:** it is an electrical resistance, topped by a ceramic plate, heated by joule effect whose temperature is regulated by means of a digital temperature controller which is connected to a thermocouple
3. **An atomizer and flow solution controller:** The location in which we can control the flow of precursor solution and turn it into an atomizer by small droplets by compressed air. On the basis of the level of flow, the thickness and characteristics of the layer will vary, as the spray side affects the formation of the layer and its properties.
4. **An atomizer holder:** The atomizer holds, based on which we can control the distance between the substrate and the atomizer.
5. **Air compressor:** it is reservoir type electrical air compressor. A rotary pump in this section mode draws atmospheric air and keeps it reserved in a large capacity air tank. At the outlet of the tank a pressure gauge is attached which records the pressure of air at the time of supplying it from the tank. There is a bypass control valve which can keep the output pressure constant. Where compressed air is transferred to the atomizer through a non-expandable tube [32].

IV.4 Spray deposition process

Several processes occur simultaneously during the elaboration of a thin layer by the spray technique: the spraying of the starting solution, the transport and evaporation of the evaporation of the solvents, diffusion and decomposition of the precursor on the substrate. The understanding of these processes allows improving the quality of the layer. Thus the formation can be divided into three steps: aerosol generation, aerosol transport and aerosol transport and precursor decomposition.

IV.4.1 Aerosol generation

The atomization of the solution is done by one of the methods described above. This process occurs at the lower end of the nozzle (spout) when the solution flow contacts the with the air pressure. It is important to know which type of atomizer is most suitable for which it is important to know which type of atomizer is most suitable for a given application and how the

performance of the atomizer is affected by variations in the properties of the liquid and the operating conditions.

IV.4.2 Transport of the aerosol

The transport of the generated spray is the second important step of the Spray process. The transport of the aerosol is a step that can be subject to many phenomena and many influencing variables, among them: the forces that are exerted on the solid or liquid particles of an aerosol such as gravitational, electrostatic or thermophoretic forces. These forces tend to influence the trajectory of the particles, but also their evaporation sites.

During the deposition, the sputtered species can be transported under the pressure of a gas. This mode of conduction has two advantages, on the one hand, the flow can be controlled with great sensitivity, and on the other hand, gases can also be used as reactive elements entering in the composition of the material to be deposited, generally argon and nitrogen are the most used inert gases, while compressed air is generally used to deposit oxides. Indeed, during the transport of the aerosol, some droplets remain in the air and the others evaporate transforming into powder forming the thin layer to deposit (Figure 7).

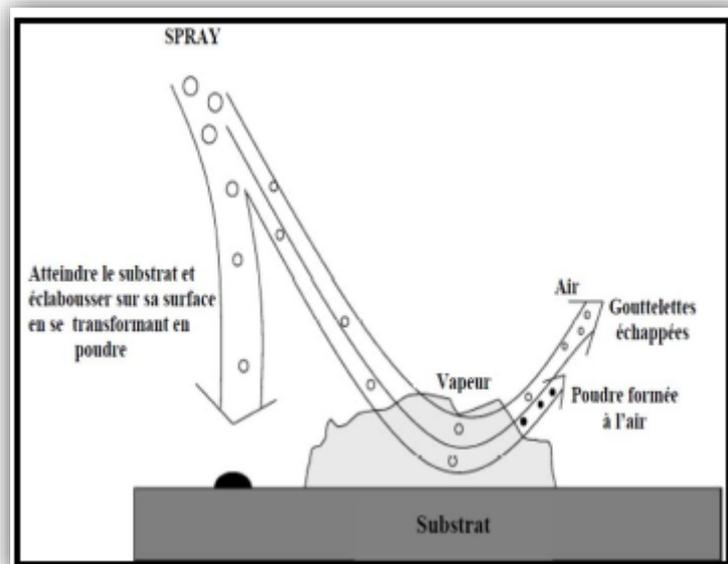


Figure (II.7): Aérosol transport.

IV.4.3 Chemical decomposition

When the droplets reach the surface of the substrate heated to appropriate temperatures, several several processes take place simultaneously: evaporation of the residual solvent diffusion of the droplet, and salt decomposition. Indeed, the temperature of the substrate is the most influential parameter on the elaboration process. While the concentration of the solution of the precursor has a weak influence on the morphology of the film. The authors, Viguie and Spitz proposed the processes described in Figure 8, which occur with The authors, Viguie and Spitz proposed the processes described in Figure 8, which occur with the increase of the temperature of the substrate.

➤ **In the low temperature regime (process I):**

The aerosol droplets are projected directly onto the surface of the substrate and decompose. In this temperature range the aerosol reaches the substrate surface in a liquid in this temperature range the aerosol reaches the substrate surface in a liquid state, which causes a spreading of the droplet along the surface. This is due to evaporation too late in the process. This process promises layers that can be thick and therefore occur where high porosities, roughness or non-adherence and cracks may appear. And cracks can appear.

➤ **At higher temperatures (process II):**

In this case the evaporation of the solvent and/or the precursors is located at the right time during the flight of the droplet and before hitting the substrate surface. This results in dry precipitates that decompose and undergo the necessary chemical reactions to form the to form the desired material layer. This process promises layers that can be dense and excellent adhesion to substrates.

➤ **At even higher temperatures (process III):**

Solvent evaporation occurs before contact with the substrate surface the precursor passes into the gas phase without decomposition. The vapor produced during this process adsorbs and diffuses to the surface, then undergoes chemical reactions to form the layer. This process results in dense films with excellent adhesion.

➤ **At very high temperatures (process IV):**

In this case the evaporation of the precursor occurs before reaching the substrate, and therefore fine therefore fine solid particles of product are unrolled in the vapor phase. The resulting deposit obtained has a high porosity and has a low adhesion to the substrate.

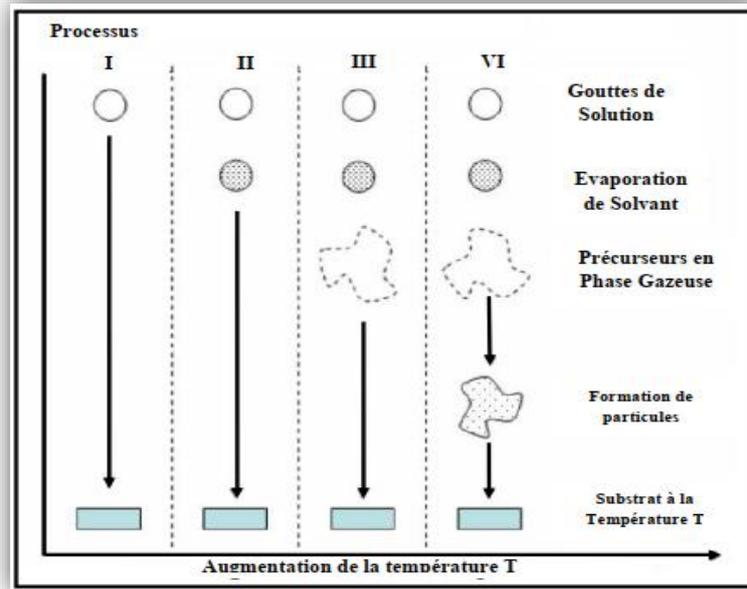


Figure (II.8): Description of deposition processes with increasing substrate temperature [24].

IV.5 Advantages of spray pyrolysis technique:

In our work chemical spray pyrolysis technique has been chosen for preparation of ZnO nanostructure layers because has a number of advantages:

1. Spray pyrolysis is a simple and low cost technique for the preparation of semi-conductor thin films.
2. It has capability to produce large area, high quality adherent films of uniform thickness.
3. Spray pyrolysis technique does not require high quality targets or substrates nor does it require vacuum at any stage, which is a great advantage if the technique is to be scaled up for industrial applications.
4. The deposition rate and the thickness of the films can be easily controlled over a wide range by changing the spray parameters.

5. A major advantage of this method is operating at moderate temperature (200-600 °C) and can produce films on less robust materials.
6. Not like high-powered strategies like frequency electron tube sputtering (RFMS), it doesn't cause native heating that may be prejudicial for materials to be deposited. There are nearly no restrictions on substrate material, dimension or its surface profile.
7. By dynamic composition of the spray solution throughout the spray method, it is often used to create bedded films and films having composition gradients throughout the thickness.

It's believed that reliable elementary kinetic information are additional seemingly to be obtained on significantly well characterized film surfaces, provided the films area unit quiet compact, uniform which no aspect effects from the substrate occur. Spray pyrolysis technique offers such a chance [32].

IV.6 Influence of the some main 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 on properties of the deposited films.

IV.6.1 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. 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.

IV.6.2 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 changing the composition of the precursor solution. Such as film thickness, morphology precursor solution. Thus, many properties of the deposited film can be changed by gy, chemical structure, and

electrical and optical properties. N. Lehraki et al. they deposited thin films of zinc oxide (ZnO) by pyrolysis technique using different liquids. Three starting solutions salts namely: zinc acetate, zinc chloride and zinc nitrate were used. The properties of these solutions and their influence upon ZnO films growth rate are investigated. The obtained results indicate that the dissociation energy of the starting solution plays an important role on films growth rate. A linear relationship between the solution dissociation energy and the growth rate activation energy was found. However, the surface tension of the used solution controls the drop-let shape impact. Both solution surface tension and dissociation enthalpy alter the microstructure of the formed film. Films deposited with zinc acetate are characterized by a smooth surface, dense network and high transparency, while films deposited with zinc chloride have a better crystallinity and low optical transmittance [32].

V Methods of thin film characterization

The different characterization techniques used in this work are described below:

V.1 X-ray Diffraction (XRD)

X-ray diffraction (XRD) is a technique used to determine the structure and crystallographic orientations of materials. In this method, the sample is irradiated with a monochromatic beam of X-rays at an angle to the sample surface (incident angle). The incident X-ray radiation excites the crystal atoms (electron cloud) and they relax by emitting spherical wave radiation. When the sample has a crystalline structure, diffraction can occur when the waves associated with X-rays are in phase (constructive interference (Figure9)).

This happens when the following Bragg condition is verified:

$$n\lambda = 2d \sin\theta$$

With: d (h, k, l), the distance between the reticular planes (hkl) of the crystal network.

θ , the incident angle of the x-rays with respect to the sample surface.

λ , the wavelength of the incident beam.

n , an integer representing the order of the diffraction mode.

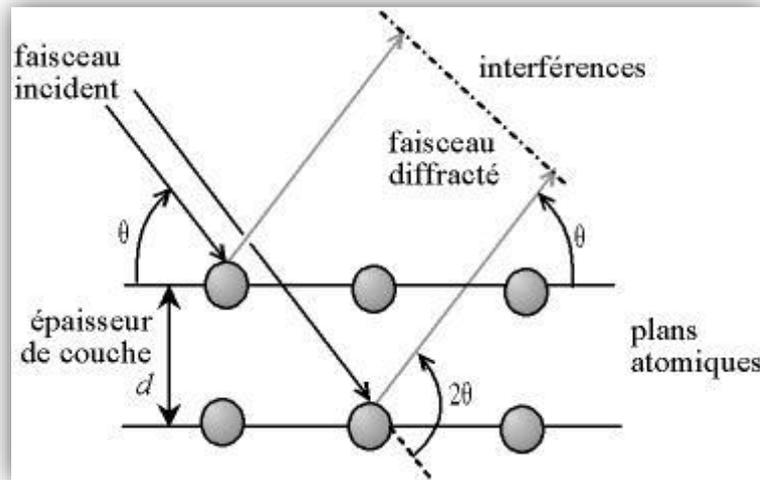


Figure (II.9): Principal of Bragg's law.

In this work, measurements were performed by a Bruckers D8 Advance diffract meter using the Bragg-Brentano geometry with a θ - 2θ configuration (Figure 9). X-rays were produced from a copper $K\alpha$ radiation source ($\lambda=0.154056$ nm), with an accelerating voltage of 40 kV and a current of 40 mA. Acquisition range between 0° and 90° with step accuracy down to 0.01° .

The principle of the θ - 2θ diffract meter is to fix the X-ray source and rotate the counter by an angle 2θ when the goniometry which carries the sample rotates by an angle θ . A scan of the angles θ is then performed. When an angle corresponding to a family of planes (h, k, l) under Bragg conditions is reached, the counter registers an increase in the reflected intensity. Thus, the position of the peaks on a diagram of the reflected intensity as a function of the angle of incidence θ is characteristic of the crystal lattice. When analyzing absorbers with a thickness of about 20 nm, the samples were also analyzed in grazing incidence mode to get better information about the surface material. According to Bragg's law, scanning in θ - 2θ allows us to measure the value of the inter-reticular distance d (hkl) of the crystal lattice. Let us take the example of the hexagonal system, which is a system observed in the ZnO compound that we have studied, the distance d (hkl) is given by:

$$d_{hkl} = \frac{1}{\sqrt{\frac{4(h^2+k^2+hk)}{3a^2} + \frac{l^2}{c^2}}}$$

Where a and c are the mesh parameters and (h, k, l) are the Miller indices of the planes[23].

The grain size of the different samples was first determined from the diffraction spectra. In order to be sure of these grain size values of our films, we used the Scherer relation

$$D = \frac{0.9\lambda}{\beta \cos \theta_{hkl}}$$

Where: D: the average crystallite size (grain size)

β : the width at half height expressed in radians (Figure 10)

Θ : the diffraction angle

λ : the wavelength of the Cu line $K\alpha_1$.

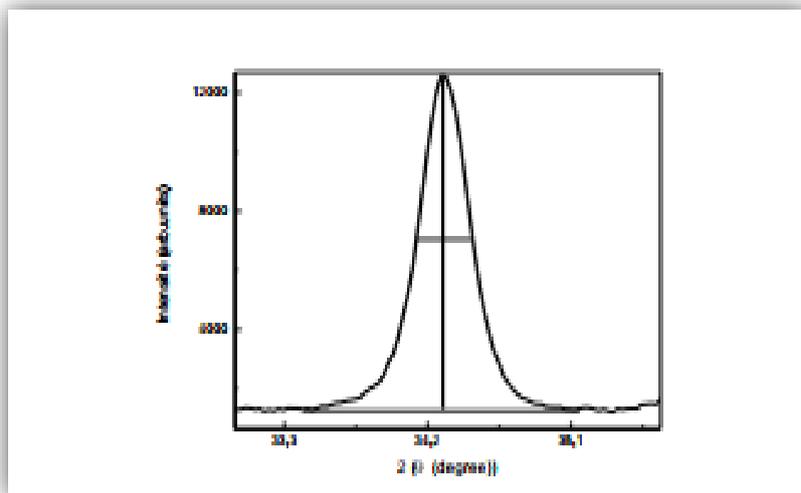


Figure (II.10): Illustration showing the definition of β from the X-ray diffraction pattern.

To determine the texturing coefficients we used the following relationship:

$$TC(hkl) = I(hkl) / \sum I^l(hkl)$$

TC (hkl): texturing coefficient according to the plane (hkl).

I (hkl): the peak intensity related to the (hkl) plane.

$\sum I^l$ (hkl): the sum of the intensities of the most intense peaks including the intensity I (hkl).

In the case of TC (002) the above relationship becomes:

$$TC (002) = I_{(002)} / [I_{(100)} + I_{(002)} + I_{(101)}] \quad (\text{II.20}) \quad [30].$$



Figure (II.11): Photo of X-ray diffraction system.

V.2 Scanning Electron Microscope (SEM)

Scanning electron microscopy (SEM) is an analytical technique capable of producing micron-scale images of the surface of a sample. This technique is based on the interaction between electrons and matter. When a sample is subjected to electron bombardment, several phenomena can occur:

- A backscattered electron: it interacts in a quasi-elastic way with the atoms of the sample and is re-emitted by the sample in a direction close to its original direction with a small loss of energy.

- A secondary electron can be re-emitted: the primary electron gives up part of its energy to an electron of the energy to an electron of the electron chain which is then ejected.

- Atoms in an excited state can de-excite by emission of an Auger electron or of a photon X (fluorescence).

Two modes of analysis are generally available on a scanning electron microscope: backscattered electron analysis or secondary electron analysis. Backscattered electrons come from a greater depth of samples (several hundred nanometers); they are sensitive to chemical contrast, while secondary electrons, of lower energies, come from a small thickness of sample (10 to 50 nanometers deep) and are sensitive to topographic contrast [23].



Figure (II.12): Photograph of the scanning electron microscope.

V.3 Optical microscope

An optical microscope, often referred to as an "optical light microscope", is a type of microscope that uses visible light and a system of lenses to magnify images of small samples. Optical microscopes are the oldest design of a microscope and were probably designed in their present composite form in the seventeenth century. Basic optical microscopes can be very simple, although there are many complex designs aimed at improving the resolution and contrast

of a sample. Historically, optical microscopes have been easy to develop and popular because they use visible light, so samples can be observed directly with the eye.

The image can be captured from a light microscope by ordinary light-sensitive cameras to generate a microscopic image. Originally, images were captured by photographic film, but recent advances in anodic, semiconductor and charge-coupled device (CCD) supplementary cameras allow digital images to be captured. Pure digital microscopes are now available that use a CCD camera to examine a sample, and the resulting image is displayed directly on a computer screen without the need for lenses [33].



Figure (II.13): Photograph of optical light microscope.

V.4 Energy Dispersive X-Ray Analysis (EDX) :

EDX does not fit under a technique for surface science, as the X-rays are generated in a region of about 2 microns in depth. By moving the electron beam across the material, an image of each element in the sample can be obtained. It generally takes long hours to acquire the images, as the intensity of the X-ray is low.

The composition or amount of nanoparticles near and at the surface can be estimated using the EDX, provided they contain some heavy metal ions. For instance, nanoparticles like silver, gold, and palladium on the surface can be easily identified using EDX. Elements of low atomic number are difficult to detect by EDX.

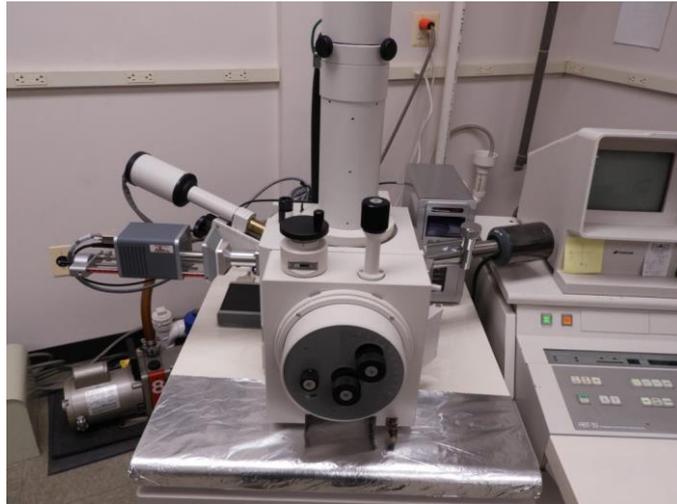


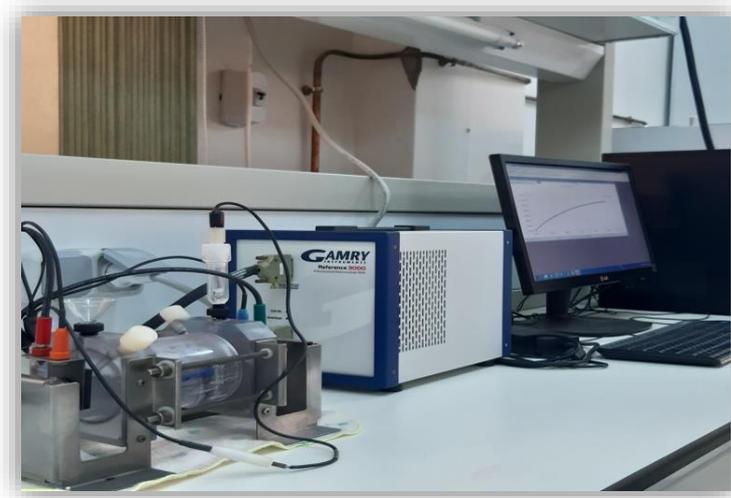
Figure (II.15): Energy Dispersive X-Ray Analysis (EDX).

PART II: EXPERIMENTAL STUDY

- ✓ **Chapter III: Materials and Methods**
- ✓ **Chapter IV: Results and discussion**

Chapter III

Methods and Materials



Introduction

We present in this chapter all the experimental steps we had to perform in order to achieve our thin layers, starting with the cleaning of the substrates and the preparation of the precursor solutions until the presentation and discussion of the results of our study. The results will focus on the identification of samples by the X-ray diffraction technique and on the different morphological characterizations by scanning electron microscopy and also the microscope.

I Experimental Procedure

We will be depositing the thinning layers of ZnO that we will be using in the course of this work Steel substrate by spray pyrolysis. This process makes it possible to obtain deposits it adheres well, transparent and has good crystal quality.

I.1 Substrate preparation

The properties of the films depend greatly on the state of the substrate's nature Prepare its surface.

Table (III.1): Chemical composition of the steel (wt. %).

C	Si	Mn	P	S	Cr	Ni	Cu
0,037	0,141	1,291	0,006	0,013	0,011	0,156	0,024
Mo	Nb	Co	Al	B	Ti	V	Fe
0,207	0,018	0,015	0,055	0,006	0,017	0,039	97,964

I.1.1 Cutting We have two types of sample.

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

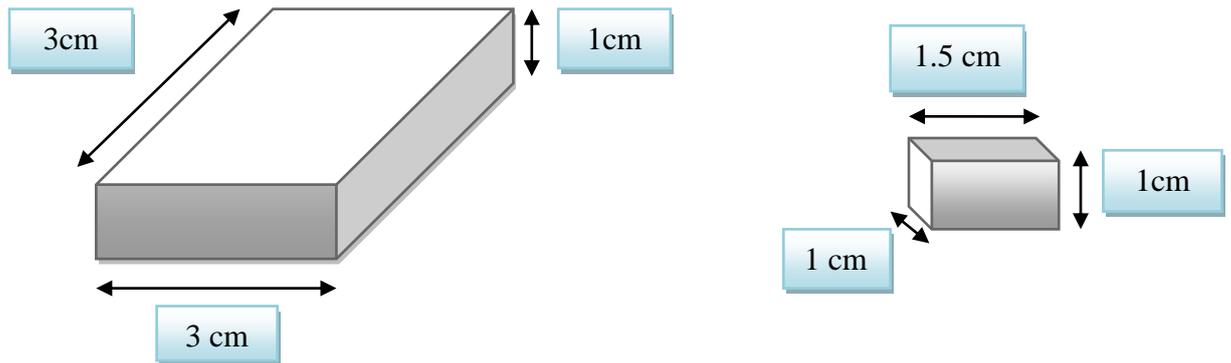


Figure (III.1): the big and small samples of steel.

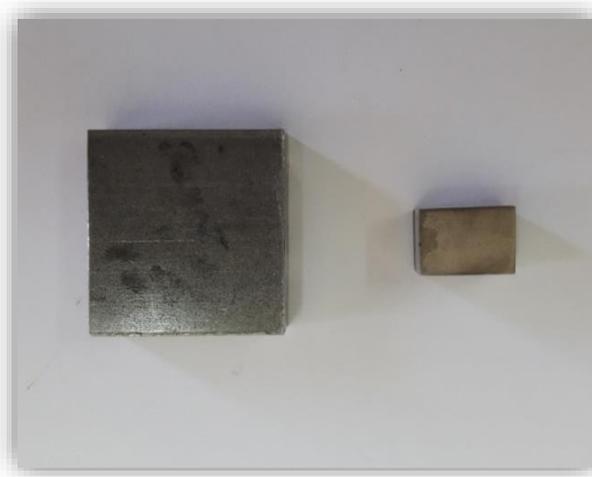


Figure (III.2): Steel sample.

I.1.2 Polishing

Polishing a material consists of making it smoother by removing any imperfections remaining on the surface. So we will prepare the sample by polishing it on a mechanical polisher with abrasive papers of different grain sizes (200,800, 1000, and 1200). Then we

rinse the part with distilled water and dried using a dryer electric to obtain a smooth surface having the appearance of a mirror.



Figure (III.3): The polishing apparatus (polisher).

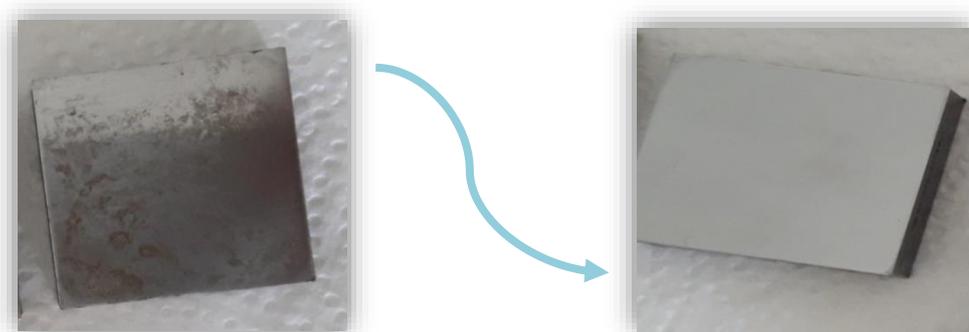


Figure (III.4): Sample before and after polishing.

I.2 The preparation of the solution of acetate of zinc

In order to obtain a specific molar concentration (0.25 mol/l) of the precursor solution, we will dissolve a known amount of zinc acetate ($M = 3.430$ g) into (50 ml ethanol + 12.5 ml water). Then the solution was stirred with a magnetic stirrer, 2ml of solution HCl .let the solution mix for 40 minutes to obtain a transparent, homogeneous, clear solution.at this point the solution becomes usable for spraying.

chapter III: Methods and Materials

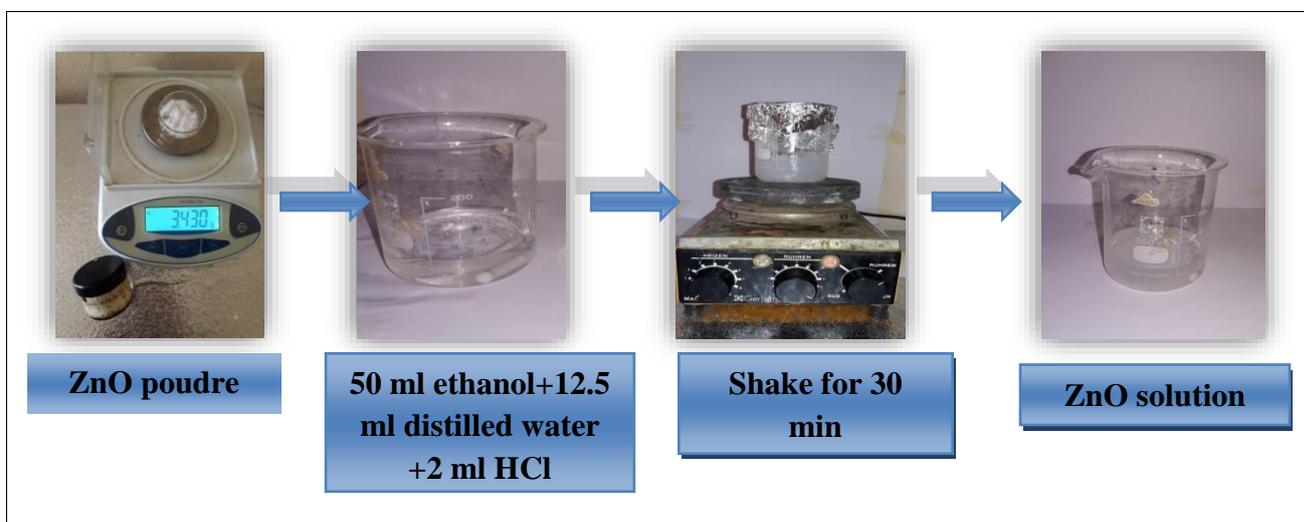


Figure (III.5): ZnO solution preparation.

Table (III.2): some physic-chemical properties of zinc acetate.

Property	Value
Physical state	Solid
Molecular formula	$Zn(C_2H_3O_2)_2$
Synonyms	Zinc salt , Zinc diacetate
Molecular weight	219.55 g/mol
Density	1.735 g/cm ³
Melting point	237 °C
Boiling point	Decomposes

I.3 Elaboration of thin ZnO films

At this stage we will include a diagram of the spray pyrolysis technique accompanied by the steps used to prepare the thin layers

I.3.1 Thin film deposition parameters

Film properties depend on a wide range of variables including the temperature of the substrate and the distance between the substrate and the atomizer and other properties that affect the parameters of the film, we will install some parameters to complete our study and Which we will mention in the male table below.

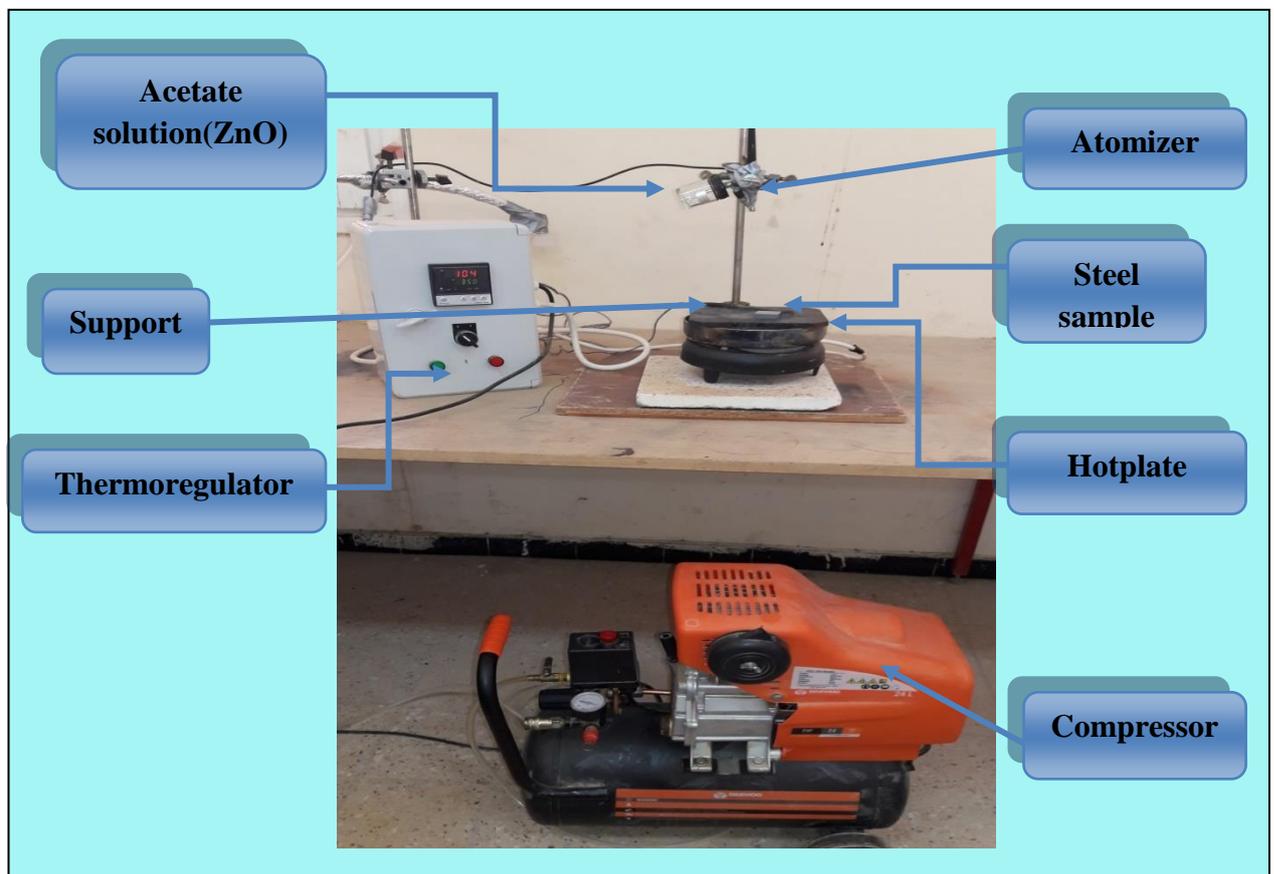


Figure (III.6): Homemade pyrolysis spray system.

Table (III.3): The values rang of ZnO thin film deposition parameters.

Parameters	Values
Air pressure	2. 5bar
Temperature	300-350°C
Distance between the atomizer and the substrate	15-20 cm
Concentration of the precursor solution	0.25 mol/l
Deposition time	7-9 min
Flow of the solution	1.5-2 ml/min

I.3.2 Layers deposition

Before proceeding to the deposits of the thin layers, we started by an adjustment of the depositing bench of the system (the temperature, the pressure and the distance between the sample and the Atomizer), and an operational test on the paper.

- ✓ After its preparation, the solution is sprayed onto a hot steel substrate 350°C on which the solvent (volatile) evaporates and only the compound ZnO forming the thin film remains.
- ✓ Repeat the spraying process several times (about 30 min for each sample) and when the temperature reaches 250°C we move the atomizer away from the substrate to allow the temperature to rise again.
- ✓ Finally, we will stop the heating and allow the substrates to cool gradually over the substrate holder to room temperature to avoid damaging the layer.



Figure (III.7): Thin layer on steel using the spray pyrolysis method.

II Experimental characterization

II.1 Optical microscope observation

The optical or electron microscope has been used to follow the evolution of the microstructure of the samples, and we used a microscope the degree of magnification of its lenses 0.40 and 0.65 micrometers available at the Mohamed Khaider University.



Figure (III.8): Optical microscope.

II.2 Scanning Electron Microscope (SEM)

This equipment makes it possible to characterize the surface and determine the chemical composition of a material under study. The scanning electron microscope (SEM) is an imaging technique used to know the morphology (shape, size, arrangement of particles, etc.), the surface topology (relief, texture, etc.), and the chemical composition (ratios relative chemical elements) and provide valuable crystallographic information (atomic structure). This technique allows the analysis of a multitude of samples of all shapes, compositions and sizes.



Figure (III.9): Scanning Electron Microscope (SEM).

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

❖ Basic principle

EDX is used in conjunction with SEM. An electron beam with energy of 10–20 keV strikes the conducting sample's surface, causing X-rays to emit from the material, and the energy of the emitted X-rays depend on the material under examination.

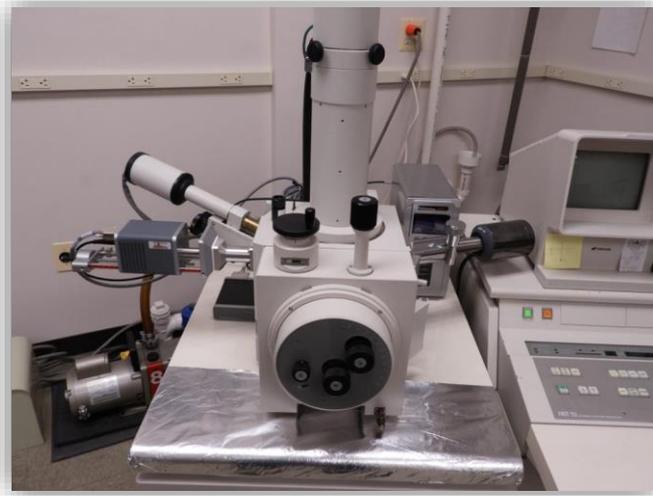


Figure (III.10): Energy Dispersive X-Ray Analysis (EDX).

II.4 X-ray diffraction studies (XRD)

It is the only laboratory technique that reveals structural information such as chemical composition, crystal structure, crystallite size, strain, preferred orientation and layer thickness. Researchers are therefore using XRD to analyze a wide range of materials, from powders and solids to thin films and nanomaterials.



Figure (III.11): X-ray diffraction studies (XRD).

III Taste of corrosion

III.1 Gravimetric study

The results of the corrosion layers tests of steel, immersed in hydrochloric acid in the absence and presence of the zinc acetate layer, were obtained by the lost mass method.

The corrosion rate is determined after 24 hours at room temperature. The corrosion rate (V) is determined by the following equation :

$$V = \frac{\Delta m}{S t} \quad (g \cdot cm^{-2} \cdot h^{-1})$$

Where $\Delta m = (m_i - m_f)$ is the mass loss, S is the exposed surface, t is the exposure time in the solution.

The inhibitory efficiency (E%) of the compounds studied is calculated using the following relationship :

$$E\% = \frac{V - V_{inh}}{V} (100)$$

V and V_{inh} represent respectively the values of the corrosion rate in the absence and in the presence of the thinitor.

III.1.1 Preparation of corrosive media

1M HCl obtained from the dilution of commercial hydrochloric acid with distilled water.

The solution were obtained as follows:

Table (III.4): Some proprieties of HCl.

M (g/mol)	D (Kg/L)	P (%)
36.46	1.18	36.5

III.1.2 Testing techniques

- For the corrosion test we need two samples, one with a layer of ZnO and the other only undergo a polishing.
- These samples are weighed (m_1) before introduced into the corrosive environment.
- The samples are immersed flat in a small beaker containing HCl (1M) using a support.
- After 24 hours, the samples are washed, dried using an electric dryer, the mass m_2 is weighed using a precision analytical balance at 0.001 g (Figure 12).

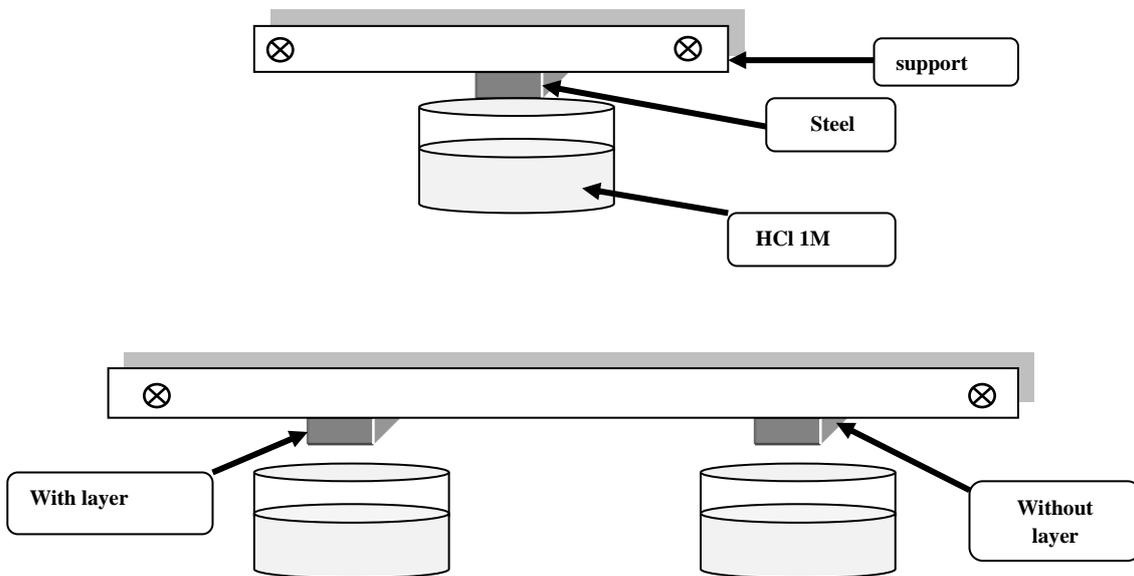


Figure (III.12): Diagram of gravimetric study.

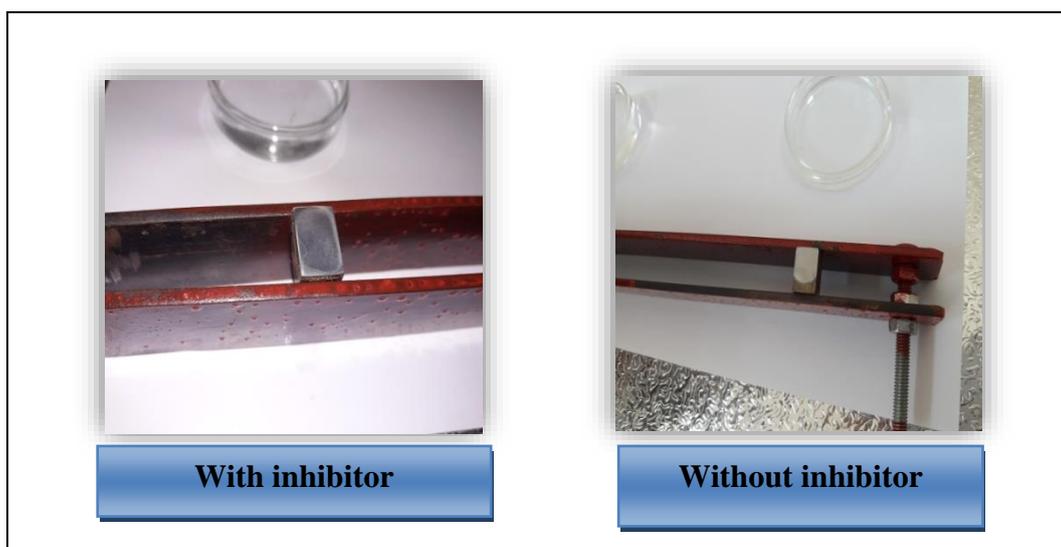


Figure (III.13): the steel after 24 hours of immersion.

III.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 cm².



Figure (III.14): Electrochemical study.

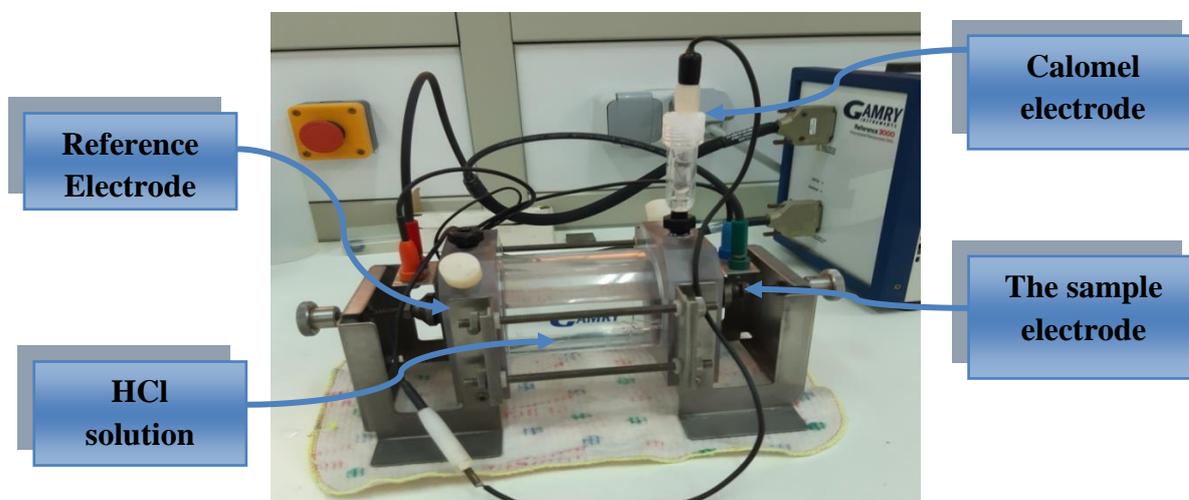
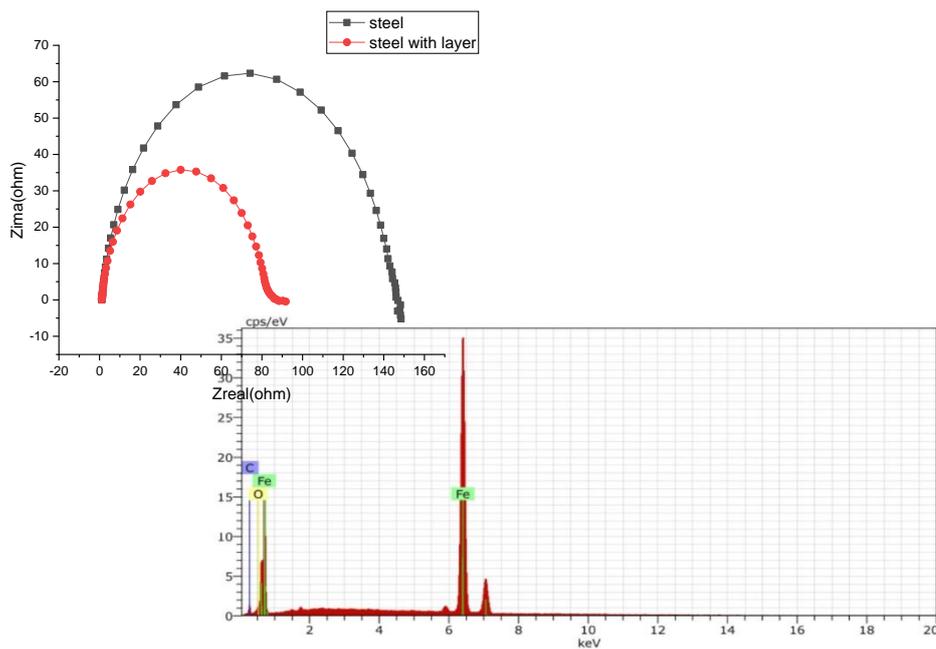


Figure (III.15): Gamry device.

Chapter IV

Results and discussions



Introduction

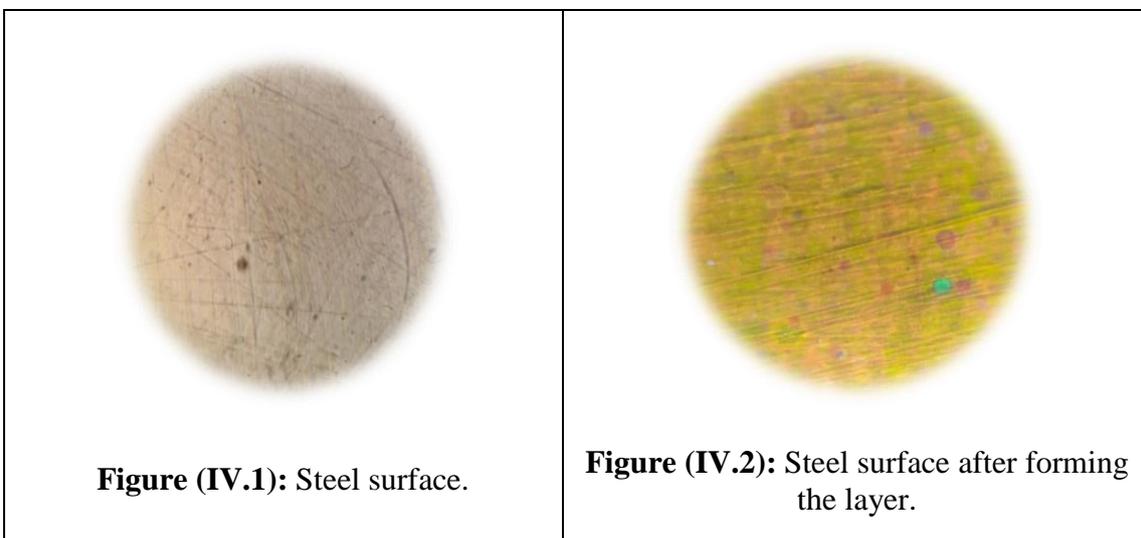
This chapter is devoted to presenting, discussing and interpreting results It was obtained from thin films of zinc oxide (ZnO) produced by the technique Pyrolysis spray. The structural characterization is done by three devices. The first is the optical microscope, the second is the X-ray diffract meter is "mass" type (XRD), the third is the Scanning Electron Microscope (SEM). Finally, we will conduct a study on erosion in two ways, and we will discuss them in detail in this chapter.

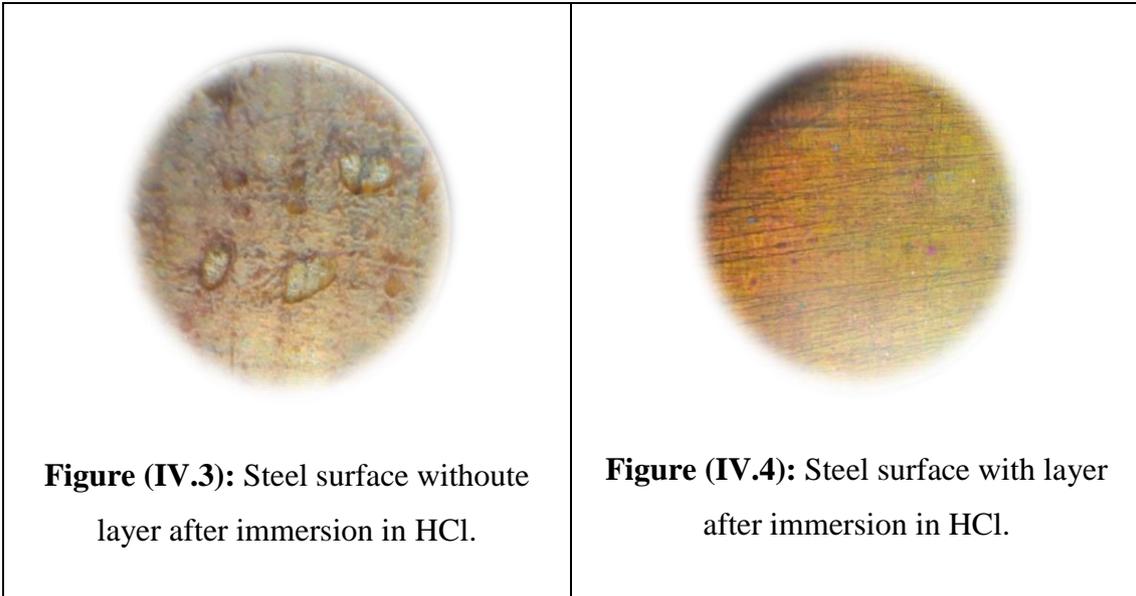
I Experimental characterization

I.1 Optical microscope observations

Depending on the microscope we will photograph the surface of the samples before and after preparing the layer of ZnO and we will notice that there is a clear difference between them, as the image of a sample before spraying its surface is free of any sediment. Any change as for the image of the sample after preparing a layer of ZnO We will notice a comprehensive and almost total spread of the solution on the surface of the sample with the presence of some drops of varying color.

The microscopic observation of sample microstructure using the degree of magnification of its lenses 0.40 and 0.65 micrometres after the test we find the following figures.





I.2 Scanning Electron Microscope (SEM) Characterization

Figure 05 shows a SEM image for a thin film of ZnO. This image indicates that the layers are of dense and uniform granular structure with very small and nanometric grains.

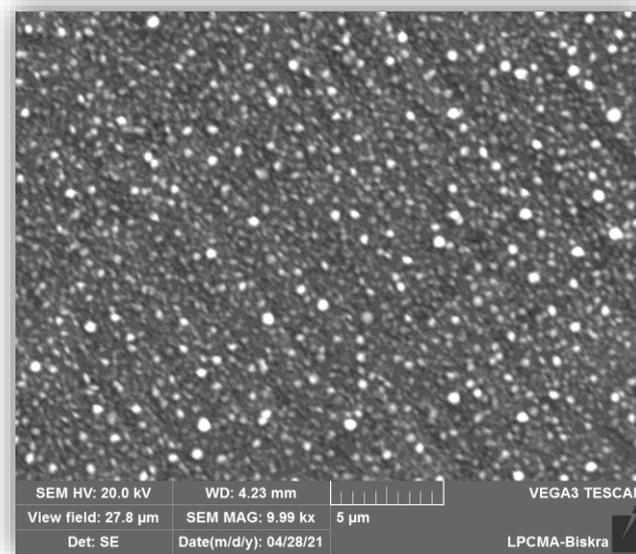


Figure (IV.5): SEM image of a ZnO thin film.

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

The corresponding curve represents an X-ray scattering energy spectrum for steel.

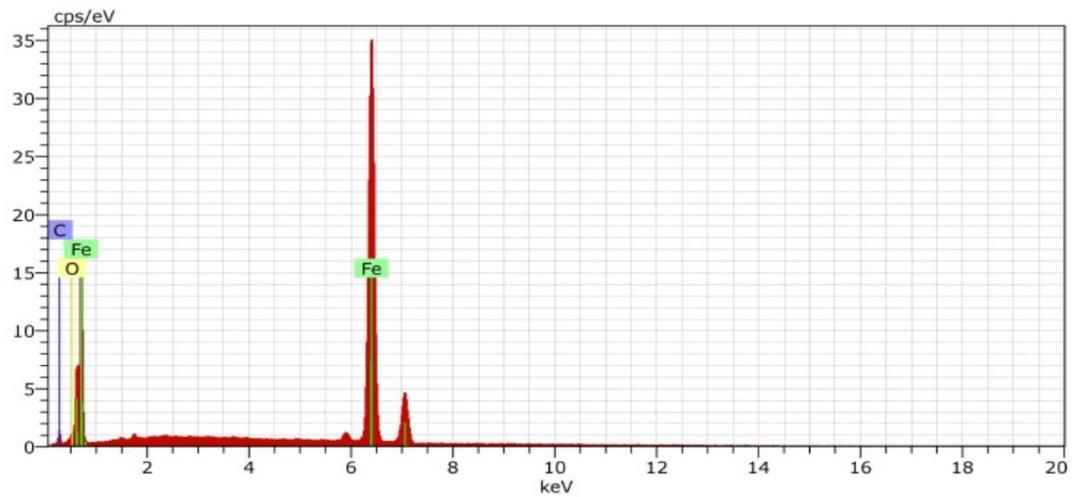
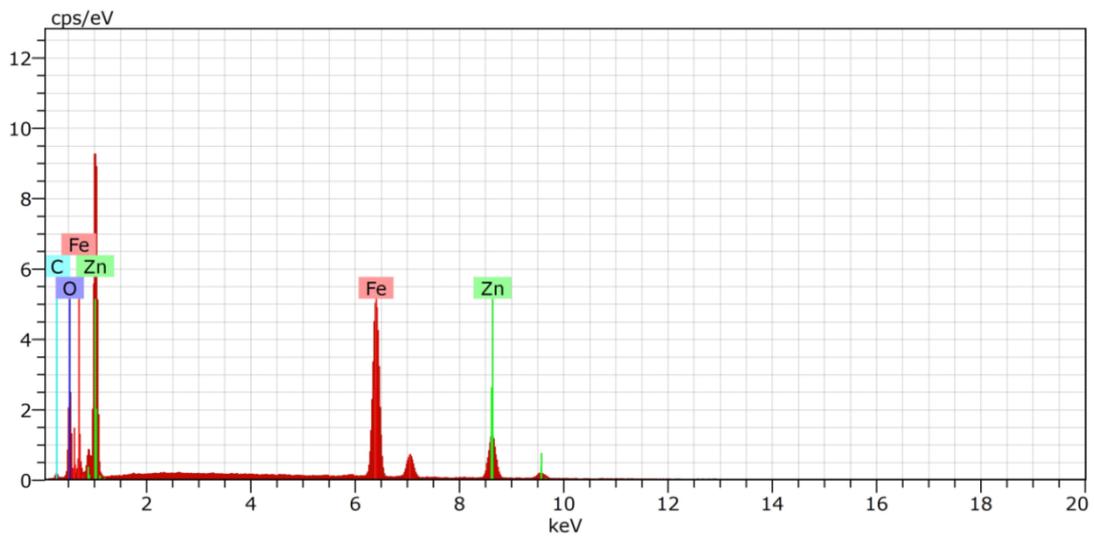


Figure (IV.6): X-ray scattering energy spectrum of X70 steel without layer.



El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]
Fe	26	K-series	49.59	54.08	38.70
Zn	30	K-series	27.17	29.63	18.11
O	8	K-series	12.18	13.28	33.18
C	6	K-series	2.76	3.01	10.01
Total:			91.71	100.00	100.00

Figure (IV.7): X-ray scattering energy spectrum of X70 steel with layer.

I.4 X-ray diffraction studies (XRD)

Deposition of the diffraction patterns of ZnO films at a temperature range of 250 ° C to 350 ° C for a specific solution concentration at C = 0.25 M, They are shown in the figure ... each detected peak is indicated by the Miller Indexes.

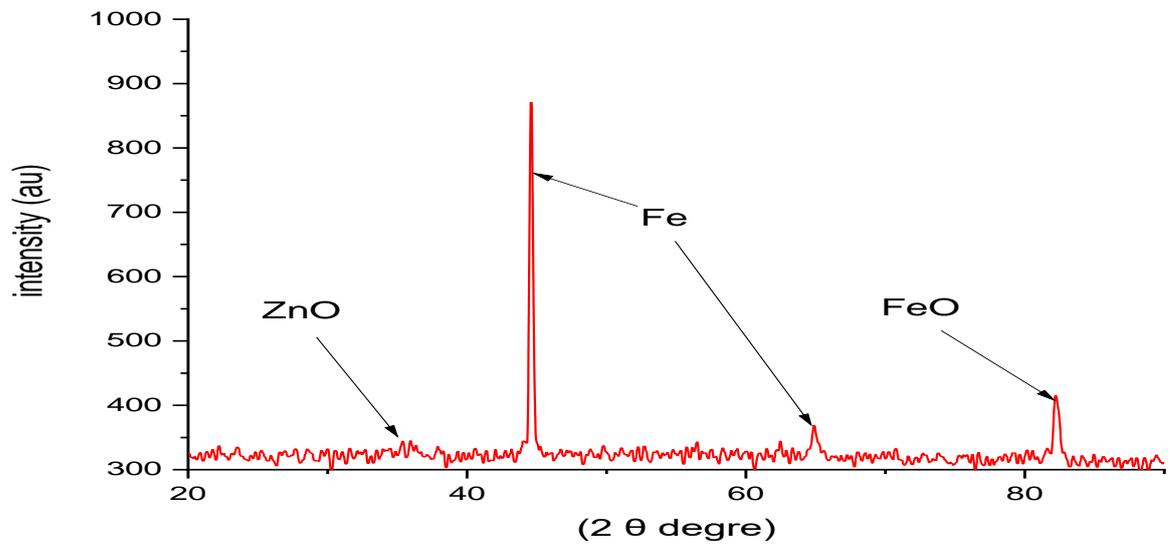


Figure (IV.8): X-ray diffraction analysis of samples.

II. Taste of corrosion

II.1 Gravimetric study

In order to determine the speed of corrosion and the inhibitory efficiency , we have developed tow samples (the first with layer of ZnO and the second layer without layer) in HCl solution (1M) for 24 hours.

The table below represents the results of obtained for mass loss and corrosion speed.

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

	m1(g)	m2(g)	Δm	V (g/h cm ²)
Without layer	8.820	8.819	0.005	$1.389 \cdot 10^{-4}$
With layer	9.040	9.045	0.009	$2.5 \cdot 10^{-4}$

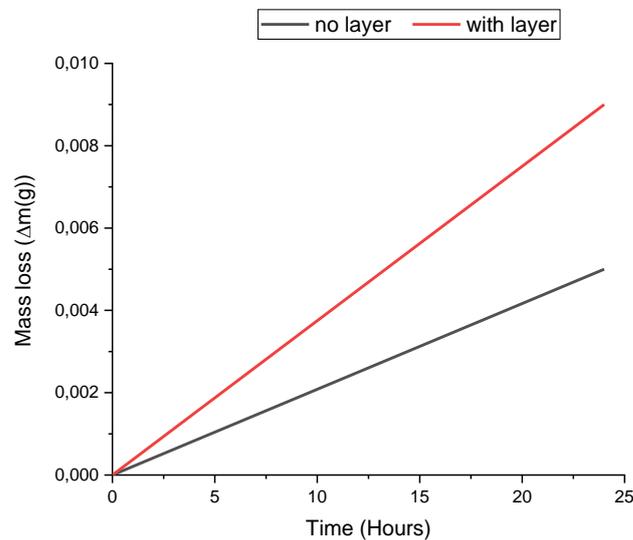


Figure (IV.9): Variations in the loss of mass curve of steel with and without a layer as a fonction of time .

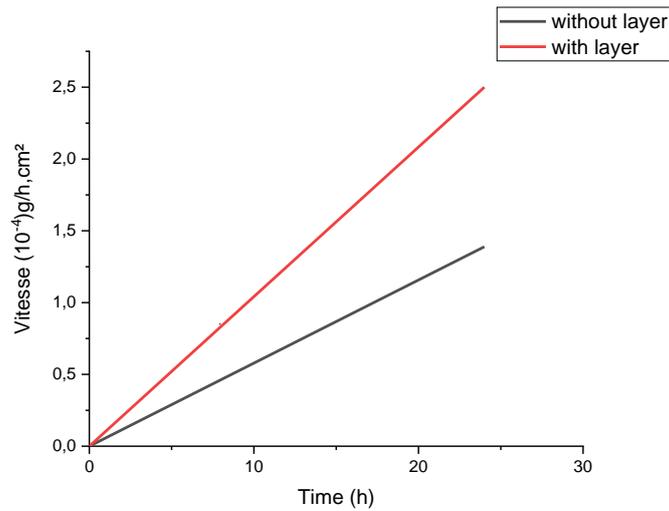


Figure (IV.10): Corrosion rate curve for steel with and without layer.

After we calculate mass loss we noticed that the sample of a layer is more upset than the sample without a layer and this is as a result The inhibitory efficiency (E %) :

$$E = \frac{(1.389 - 2.5) \cdot 10^{-4}}{1.389 \cdot 10^{-4}} = -79.98\%$$

II.2 Electrochemical measurements

EIS was used to assess the corrosion resistance of the steel substrate and the Zinc oxide coating deposited by the Spray method on a steel substrate. EIS data were obtained after immersion in 1M HCl solution for about 1 hour.

The EIS spectrum of the substrate of the cleaned steel in the plot of Nyquist containing a semicircle. For the EIS spectrum of the Nyquist plot, the diameter of the semicircle represents the load transfer resistance (Rct). We can see from the curve 1 in figure IV.11, the Rct of the cleaned steel substrate is about 150 (ohm), while for the zinc oxide coating, Rct reduced to 90 (ohm), a coating deposited from Zinc Oxide alone is not capable of providing corrosion protection to steel substrates.

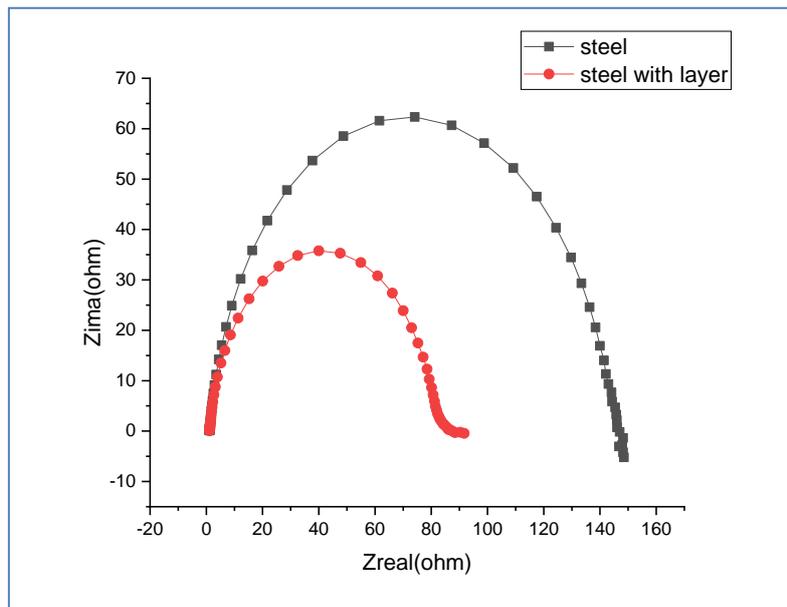


Figure (IV.11): Impedance diagram for steel in 1 M HCl and in the presence and absence of ZnO layer.

The polarization resistance obtained by the Tafel adjustment indicates negative corrosion protection of this coating.

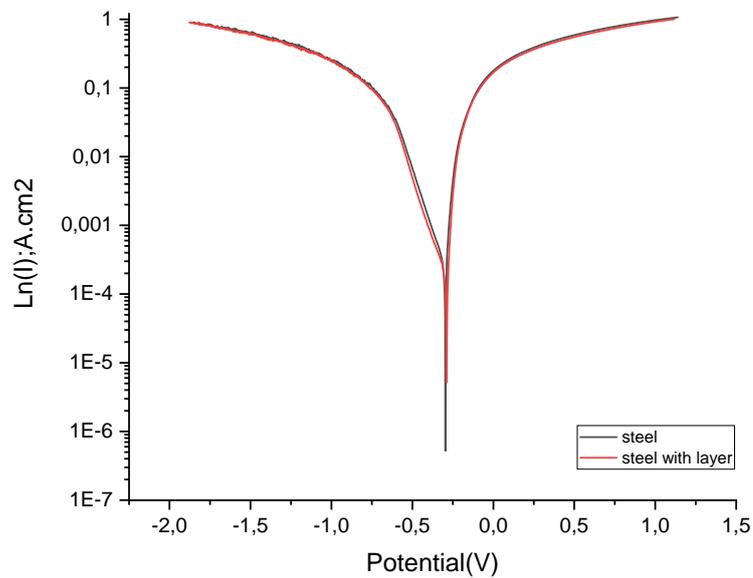


Figure (IV.12): Tafel curve for steel in 1M HCl solution in absence and presence of ZnO layer.

GENERAL CONCLUSION

General conclusion

This work focused on studying the properties of inhibitors on steel samples and observing their corrosion in a medium of hydrochloric acid (1 M). We chose to prepare layers of ZnO which we will adopt in our study as an inhibitor. And we will study its effectiveness in inhibiting the corrosion of steel.

Initially, we deposited zinc oxide (ZnO) thin layers with a spray pyrolysis technique, based on zinc acetate on steel substrates. Using various methods of characterizations we will check the positioning of the layers on the steel.

Secondly, we tested the effectiveness of the layers against corrosion in two different ways, where we immersed two samples of the first steel containing a layer of ZnO and the second without a layer in a solution of hydrochloric acid (1 M) for a period of 24 hour.

Finally, we will summarize our study with the following conclusions:

Based on methods of characterizations we concluded that layer of ZnO were formed on all surfaces of the steel sample

We observed using tow different methods for corrosion test that the average mass loss of the steel sample that contains the layer ZnO is greater than that of the steel sample that does not contain the layer in the medium of hydrochloric acid where the corrosion of the steel sample without the layer was supposed to increase , but the results were the opposite of what was assumed, as the corrosion speed for the sample with a layer ZnO was $2.5 * 10^{-4} \text{ g/h cm}^2$ As for the sample without layer $1.389 * 10^{-4} \text{ g/h cm}^2$, this is also what was confirmed by the result of The inhibitory efficiency which we calculated last was **-79.98 %**.Also, there was agreement between the results obtained using Electrochemical measurements where the curves of Tafel and Impedance diagram for steel in 1 M HCl and in the presence and absence of ZnO layer showed that the sample with a layer had more erosion than the sample without the layer.

The thin film prepared by spray pyrolysis technique using only Zinc Oxide (ZnO) has a uniform structure. It should be mentioned that the thin film prepared with only Zinc oxide was not able to protect the steel substrate from corrosion. .

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Abstract:

Corrosion is the process of deterioration or failure of a material resulting from a chemical reaction between the material and its surrounding environment. It is a phenomenon of special importance from the economic side and at the level of all human activities.

Through this work, our goal was to find a way to reduce steel corrosion by using inhibitors, specifically by using layers of ZnO located using Spray pyrolysis technique and to study its effectiveness against corrosion in hydrochloric solution.

We conducted this study using two different methods, mass loss study and electrochemical measurements, and we obtained results showing that using thin layers of ZnO alone was not able to protect the steel substrate from corrosion.

Keywords: steel, Corrosion, Inhibitors, ZnO, Spray pyrolysis , Electrochemical measurements , Gravimetric study.

Résumé :

La corrosion est le processus de détérioration ou de défaillance d'un matériau résultant d'une réaction chimique entre le matériau et son environnement. C'est un phénomène d'une importance particulière du côté économique et au niveau de toutes les activités humaines.

A travers ce travail, notre objectif était de trouver un moyen de réduire la corrosion de l'acier en utilisant des inhibiteurs, notamment en utilisant des couches de ZnO localisées en utilisant la technique de pyrolyse Spray et d'étudier son efficacité contre la corrosion en solution chlorhydrique.

Nous avons mené cette étude en utilisant deux méthodes différentes, l'étude de perte de masse et les mesures électrochimiques, et nous avons obtenu des résultats montrant que l'utilisation de couches minces de ZnO seule n'était pas en mesure de protéger le substrat en acier de la corrosion.

Mots clés : acier, Corrosion, Inhibiteurs, ZnO, Pyrolyse par pulvérisation , Mesures électrochimiques, Étude gravimétrique.

ملخص:

التآكل هو التدمير التلقائي للمعدن نتيجة التفاعل الكيميائي بين المادة والبيئة المحيطة بها. فهو ظاهرة ذات أهمية خاصة من الناحية الاقتصادية وعلى مستوى جميع الأنشطة البشرية.

من خلال هذا العمل هدفنا إلى إيجاد طريقة لتقليل تآكل الفولاذ باستخدام المثبطات، وتحديدًا باستخدام طبقات رقيقة من ZnO باستخدام تقنية الانحلال الحراري بالرش ودراسة فعاليتها ضد التآكل في محلول الهيدروكلوريك.

لقد أجرينا هذه الدراسة باستخدام طريقتين مختلفتين هما دراسة ضياع الكتلة والقياسات الكهروكيميائية وحصلنا على نتائج تبين أن استخدام طبقات رقيقة من ZnO وحدها لم يكن قادرًا على حماية الركيزة الفولاذية من التآكل.

الكلمات المفتاحية: الفولاذ ، التآكل، المثبطات، أكسيد الزنك، الانحلال الحراري بالرش، القياسات الكهروكيميائية ، دراسة ضياع الكتلة.