University Mohamed Khider - Biskra
Faculty of Exact Sciences and Sciences of Nature and Life
Department of Matter Sciences

Dissertation of Master

Domain: Matter Sciences
Field: Physics
Speciality: Materials Physics

Réf. : .....

Presented by :

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On: Saturday, April 26th 2019

Optimization of Ti/TiO_2 multilayers deposition parameters for corrosion applications

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Jury :

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College year : 2018 - 2019

ملخص

قمنا في هذا العمل، بترسيب شرائح رقيقة من التيتانيوم و أكسيد التيتانيوم Ti و TiO_2 على مساند من الفولاذ و ذلك باستخدام تقنية الترسيب الكهروكيميائي و تقنية Sol-Gel على التوالي بغرض الحصول على شرائح متناوبة Ti / TiO_2 متعددة الطبقات مع تغيير عدد الطبقات. قمنا بدراسة خصائص السطح و التركيب الكيميائي بواسطة مجهر المسح المجهري الإلكتروني (SEM) و الأشعة السينية الطيفية التشتت (EDX). كما تمت دراسة سلوك الشرائح متعددة الطبقات ضد التآكل في محلول حمض الهيدروكلوريك 10 ٪ من الوزن. أظهرت النتائج أن الظروف المثلى للترسيب الكهروكيميائي للتياتانيوم Ti هي 15 فولت، 5 دقائق و درجة حرارة المحيط. اما بالنسبة لترسيب أكسيد التيتانيوم فإن الشرائح الجيدة المتحصل عليها كانت تحت الشروط التالية: 0.5 مول / لتر، 5000 دورة في الدقيقة و 45 ثانية. بعد اختبارات الاستقطاب وقياسات كثافة تيار التآكل، أظهرت النتائج أن مقاومة التآكل في الشرائح متعددة الطبقات أعلى من مقاومة الشرائح الأحادية. يمكن أن تعزى هذه النتيجة إلى حقيقة أن زيادة عدد الطبقات يزيد من الحماية ضد التآكل.

Abstract

In this work, Ti and TiO_2 thin films deposited onto stainless steel using Electrodeposition and sol gel spin coating processes respectively in order to realize the Ti/TiO_2 multilayer coatings with different number of films. Surface morphology and chemical composition were characterized by scanning electron microscopy (SEM) and x ray electron dispersive spectrometer (EDX) methods. Their corrosion behavior was tested in 10wt% hydrochloric (HCl) acid. The results showed that the optimal conditions for Ti electroplating are 15 V, 5 min and room temperature and the parameters which gave the best spin-coated TiO_2 thin films are 0.5 mol/L, 5000 rpm and 45 seconds. After polarization tests and corrosion densities measurements, the results showed a higher multilayer corrosion resistance than that of single layers. This result can be attributed to the increase in number of layers which could enhance and improve the protection against corrosion.

Keywords: Ti/TiO_2, multilayer, electrochemical corrosion, optimization, electroplating.

Résumé

Dans ce travail, des couches minces de Ti et TiO_2 sont déposées sur acier en utilisant l'électrodéposition et la technique sol-gel respectivement dans le but de réaliser des revêtements multicouches Ti/TiO_2 en variant le nombre de couches. La morphologie de la surface et la composition chimique ont été caractérisées par microscopie électronique à balayage (MEB) et spectroscopie dispersive des rayons X (EDX). Leur comportement face à la corrosion a été étudié dans l'acide hydrochlorique (HCl) à 10 % wt. Les résultats ont montré que les conditions optimales pour l'électrodéposition de Ti sont 15 V, 5 min et température ambiante. Les paramètres qui donnent les bons films par spin-coating sont 0.5 mol/L, 5000 rpm et 45 secondes. Après les tests de polarisation et les mesures de densités de corrosion, les résultats ont montré que la résistance à la corrosion des multicouches est plus haute que celle d'une monocouche. Ce résultat peut être attribué au fait que l'augmentation du nombre de couches augmente la protection contre la corrosion.

Mots clés: Ti/TiO_2, multicouches, corrosion électrochimique, optimisation, électrodéposition.

Introduction:

In this chapter, we will give a description of the tests which will make it possible to highlight the objectives of this work and to better situate it with the work realized by other researchers, on the same subject.

At first, we have identified all the experimental parameters, which allow a good reproducibility of the results. Then, we adopted an experimental approach that is to say a protocol of investigations allowing an easy comparison of the performances obtained for each sample

In this study we will describe the experimental Electrodeposition device and the spin coating technique, the experimental procedure (preparation of surfaces, composition of the bath and solution used, experimental conditions, etc.) as well as the different characterization techniques used to study the different coatings Produced. These techniques are complementary, each of them allowing the production of coatings that the others do not provide.

We will also talk about the characterization methods and finally describe the corrosion tests procedure. This work has been realized in the laboratory of physics of thin films and Applications (LPCMA)-University of Biskra.

II.1 Description of the used material:

II.1.1 The substrate:

In our study, we used stainless steel type X70 provided by COSIDER with specimens' area (4*4) cm^2 and thickness 12.95 mm. the latter is the pipe line stainless steel.

II.1.2 Chemical composition:

The chemical composition of the stainless X70 is given in the following table:

Table II.1 The X70 stainless steel composition (mass %)

Element	C	S	P	Al	Nb	V	Ti	Ni	Cu	Cr	Si	Mn	Mo	B	Fe
Standard $\%x10^{-3}$	78	3	11	44	55	83	1	24	24	61	351	1542	2	0.2	Balance

II.1.3 Sample preparation:

Samples were prepared according to the following steps:

II.1.3.1 samples cutting:

At the first step we cut the samples in the mechanical lobby to obtain specimens with area of (3x3) cm^2. Our samples after cutting are given in the following picture (Fig. II1):

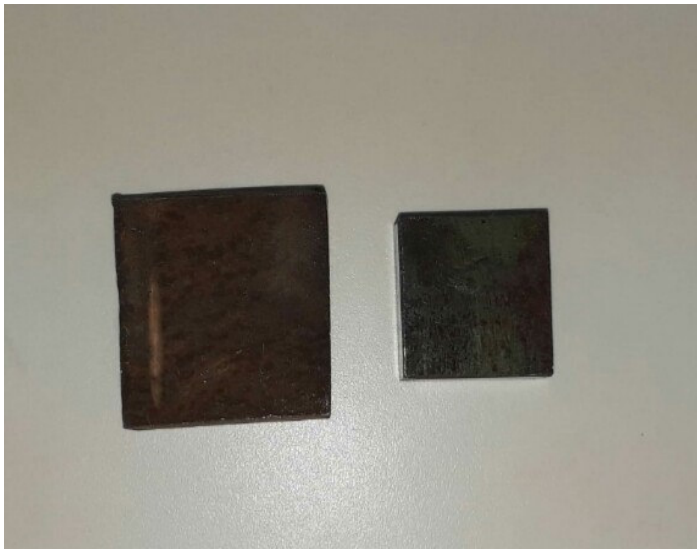


Fig. II.1 Stainless steel X70 after cutting

II.1.3.2. Polishing:

Polishing of the substrate is necessary to obtain clean surface. It is done at using sic abrasive papers of grades 180, 240, 400 and 800 then we used abrasive paper of 1200 just for one sample and after we treated this sample by chemical attack “Nital” in order to show the metallographic observation (Fig. II.2).

This preliminary surface treatment leads a roughness of the sample surface.

As already mentioned in order to reduce the surface roughness by mechanical sand paper polishing and finishing is done with diamond paste to obtain a mirror surface and characterize it by XRD and SEM.

Fig. II.2 Samples after polishing

II.1.3.3 cleaning the samples:

Cleaning could be defined as the reduction of contaminations at the level of acceptable. This contaminations result most often from:

- The reaction with the ambient atmosphere.
- The traces of the previous process (oils, fingerprints…)
- The dust particles.

Before deposit all must be cleaned to a minimum impurities on the surface and don't pollute the enclosure to deposit.

In our work, we have cleaned the substrate by the following procedure:

- We rinsed the substrate in acetone for 5 min.
- Then we put it in ethanol and finally we stored in pure alcohol before deposit.

Between each of these steps the simples are rinsed in distilled water.

II.2. Preparation of TiO_2 solution and Ti electrolyte (bath):

II.2.1. Preparation of TiO_2 solution:

In order to prepare the spinning solution, the following components were used:

- Titanium isopropoxide (Ti $(C_3H_5O_{12})_4$) TTIP as a precursor.
- Isopropanol as a solvent.
- Acetic acid as a catalyst member.

Methodology: In the first step of solution preparation, we mixed 10 ml of ethanol with 0.612 ml of acetic acid then we added 0.605 ml of TTIP in order to obtain a solution with concentration of 0.2 mol/L. After that we stirred the solution using a magnetic stirrer for 30min. After this time the solution was combined and left for stirring for 3 hours with temperature 50 °C until a clear mixture was obtained and finally we obtained a viscous and transparent solution [13].

The solution composition and the conditions process are shown in the following table:

Table II.2 Solution composition and conditions for a spinning TiO_2 [13]

Solution composition and conditions process	Concentrations
Titan isopropoxide	0.6 ml
Ethanol	10 ml
Acetic acid	0.1 ml
Temperature	50 °C
Drying temperature	100 °C
Time of drying	10 min
Deposit time	30 s
Annealing temperature	300 °C
Annealing time	30 min

II.2.2. Ti bath:

In order to prepare a Ti bath, we used a highly pure titanium chloride ($TiCl_3$) (99.99 %) as a precursor, Ethanol as a solvent and drops from hydrochloric acid (HCl). Then we added drops of hydrogen peroxide H_2O_2 in order to pre-oxidize Ti^{+3} to Ti^{+4} ions and finally we mixed this bath with a magnetic stirrer just for a few minutes to obtain an homogeneous solution [12].

The highly pure titanium and stainless steel plates were used in Electrodeposition as anode and cathode respectively. The distance between them was 2cm. The cathode was placed parallel to the cell bottom to ensure the laminar flow of the electrolyte. All coatings were electrodeposited from the watts bath.

The composition of the bath and operating parameters are given in this Table II.3:

Table II.3 Operating parameters and bath composition for Ti Electrodeposition.

Composition and parameters	Values
$TiCl_3$	2 ml
Ethanol	100 ml
Voltage	10 V
pH	0.59
Bath temperature	Room temperature (23 °C)
Time of deposition	10 min

II.3. Elaboration of thin layers:

II.3.1. Deposition techniques details:

II.3.1.1. Electroplating:

Electrolysis is used to deposit one or more metal layers on a metal surface. The principle of producing an electrolytic deposit is simple: the part to be covered is placed in electrolysis thank to act as a cathode on which metal ions are deposited. The electrolyte is chosen according to the desired deposit. The layer obtained obviously has precise characteristics, which depend on the various parameters of the electrolytic mechanism and this, as well with regard to its structure as its properties [48].

Titanium electrodeposition:

Titanium electro-deposition is similar to other Electrodeposition processes using soluble metal anodes. This process requires the passage of the current between two electrodes which are emerge in an aqueous conductive solution of titanium salts. The flow of current causes the dissolution of one of the electrodes (the anode) and the covering of the other electrode (cathode) with the titanium. Titanium in solution is present in the form of positively charged divalent ions (Ti^{+3}). When the current flows, the positive ions react with three electrons and are converted into metallic titanium on the surface of the cathode. The opposite occurs in the anode where the titanium is dissolved to form positively divalent charged ions that penetrate the solution.

Most commercial solutions of titanium are based on the watt bath including titanium chloride as a main source of titanium ions. The latter that corrodes the anode increases the diffusion of titanium ions [49].

In our research we used Titanium trichloride as a source of titanium. The stainless steel was used as the substrate of cathode and plate of Titanium was used as the anode. Electrodeposition was carried out by applying constant voltage of 10 V for 10 min under room temperature and pH =0.59. The figure II.3 show the Electrodeposition device used in our work.

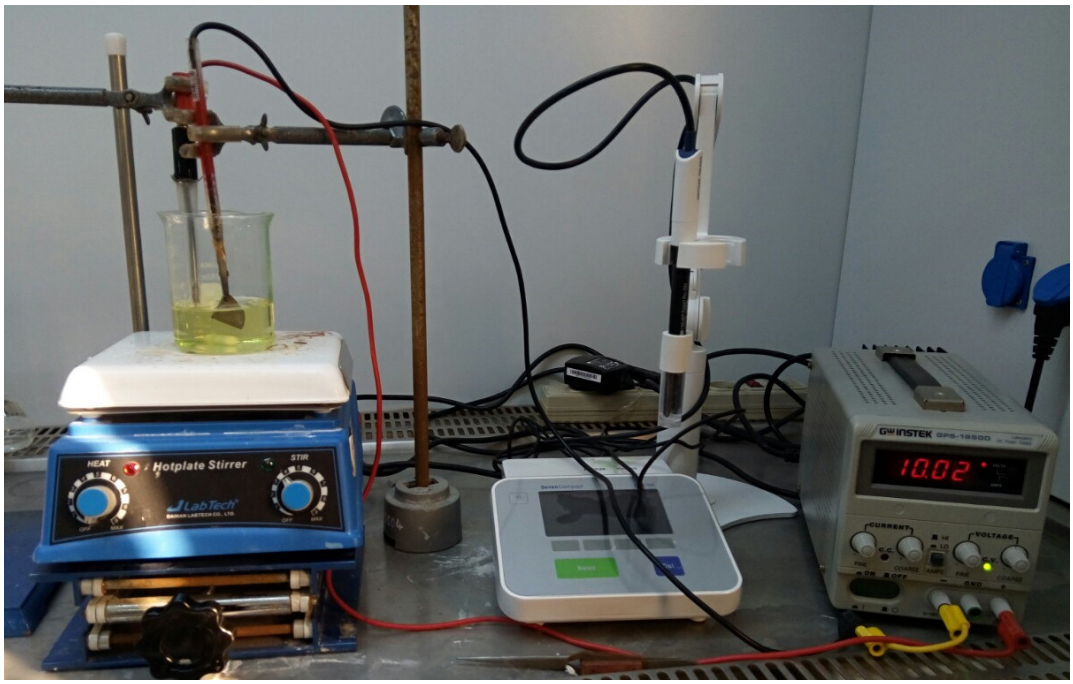


Fig. II.3 The Electrodeposition process

II.3.1.2 Sol-gel method:

The sol-gel pathway is a process that makes possible to develop a solid from a solution using a sol or gel in the intermediate step. The sol-gel process is described in three main stages:

• The physicochemical stage, where the chemical parameters predominate, is in fact the stage of the preparation of the deposit solution.

• The deposition step of the thin layers or the physicochemical parameters play an important role. It is at this stage that the thin layer of gel is formed.

• The drying step or the temperature plays the fundamental role. At this stage, the amorphous xerogel thin layer is formed [50].

II.3.1.2.1 Spin coating process:

This technique has the advantage of being easily implemented, for moderate investments. It gives excellent results on flat substrates of small surfaces (a few cm^2).

In our work the machine used for this operation is called spinner or spin coater HOLMARC (figure II.4) to deposit titanium dioxide.

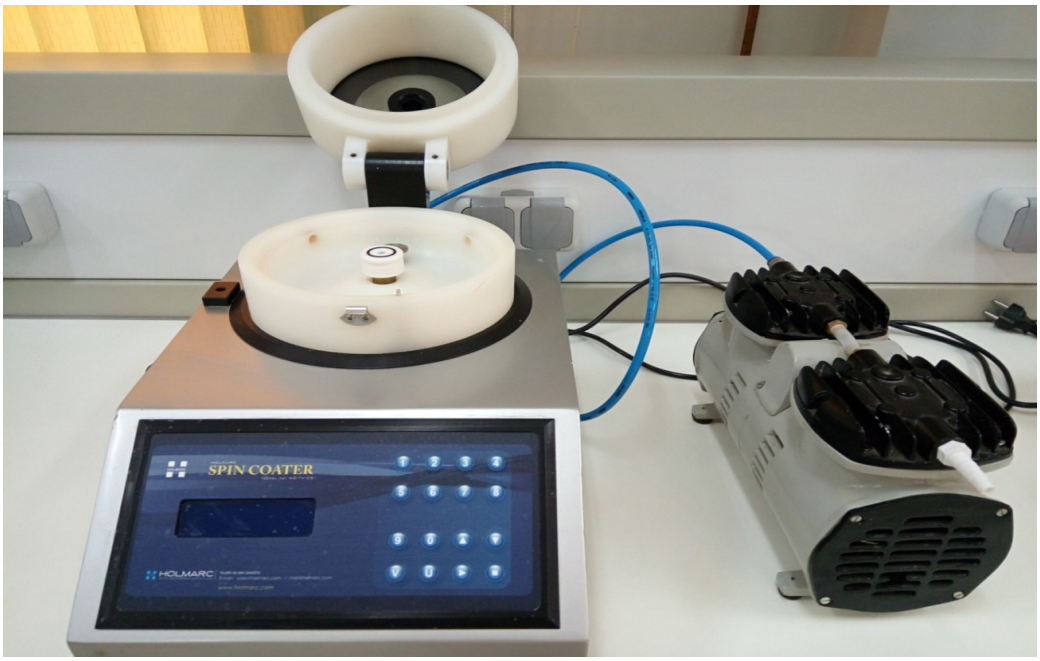


Fig. II.4 Spin coater HOLMARC device

The substrate is placed and held by vacuum on a turntable at high constant speed which is 4000 rpm and acceleration of 400 rpm and the substrate has been rotated for 30 s, in order to spread the deposited material depends on two factors:

• Factor related to the spinner: angular velocity, acceleration, time of the operation.

• Factor related to the deposited compound: deposited quantity, molar mass, viscosity, etc.

The preparation of a layer passes as follows:

• The first step of this technique is to deposit a few drops of the solution on the surface of the sample.

• The second corresponds to the application of a rotation thus causing the liquid to flow outwards.

• Then comes the third step, where the rotation is constant, it consists in ejecting the excess of liquid and decreasing the thickness of the layer.

• The last step is to evaporate the most volatile solvents on the heating plate, which accentuates the decrease in the thickness of the layers [50].

II.3.1.2.2 drying the films

Drying of the deposited layer is a very important step in the realization of quality materials. Once deposited, the thin layers have been dried at 100 °C for 10 minutes, to evaporate residual solvents and gel the layer with repeating 5 times to obtain a film.

II.3.1.2.3 Annealing

Annealing has two main functions: elimination of organic species present in the starting Solution and the densification of the material. Only after this annealing that the desired material can be obtained. After drying, the organic groups of Alkyl type (-OR-) are always present in the deposited film, only annealing eliminates. In our study annealing is carried out at temperatures between 400 °C and 600 °C for 2 hours in air. The annealing is carried out in a resistance ordinary furnace [13].

II.4 Characterization methods:

In order to analyze and study different properties of the thin elaborated layers, several characterization techniques are used such as structural, morphological characterizations. We summarize in the following basic principles:

II.4.1. Adherence:

The adherence test used before doing any characterization on the films is Thermal shock, that we heated up our specimens in certain temperature and rapidly we rinsed it in ice water to know if the film is adherent on substrate or not.

II.4.2. Morphological and structural characterizations:

II.4.2.1. X-ray diffraction (XRD):

X-ray diffraction (XRD) is the essential technique used in the crystallographic study of solids with ordered structures (crystals) causing a discontinuous phenomenon (unlike gases, liquids and continuous diffusion) by returning the incident X beam only certain privileged ones**.** The direction of the diffracted beam is given by Bragg's law:

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

λ: wavelength of the beam of X-rays

d: distance of two reticular planes.

θ: the angle of incidence of X-rays.

n: the diffraction order

The Bragg relation has three parameters: d (hkl), Θ and λ. The term d (hkl) is determined by the nature of the material, to realize the diffraction conditions on a family of planes (hkl), only one of the two others necessarily fixed the other being necessarily variable [49].

In our study, we characterized our samples by X-Ray diffraction "Rigaku Mini Flex 600" apparatus in the laboratory of physics of thin films and Applications LPCMA University of Biskra Showing in (Figure II. 4).

Fig. II.4 X Ray diffraction

II.4.2.2. Scanning Electron Microscopy (SEM):

The general principle of SEM is to send an electron beam that interacts with the sample. In response, the sample returns several specific rays that are detected and analyzed according to the chosen technique. I n scanning electron microscopy (SEM) we work under a primary vacuum of the order of 1.3 Pa with all kinds of samples without special preparation. An electron beam is produced at the top of the apparatus using an electron gun. This gun is placed in a column kept under vacuum and the electrons are obtained by heating a tungsten filament. The primary electron beam thus formed follows a vertical path in the microscope column. It is then focused on the sample using electromagnetic lenses and deflection coils. When the beam interacts with the sample, the detectors placed for this purpose collect the secondary electrons and the signal obtained is then analyzed and transformed into a visual signal. Scanning electron microscopy is currently the most widely used method for

observing the morphology of thin films (in normal or transverse section obtained after cleavage of the substrate) and for measuring their thickness. These observations also provide additional information on how the layers grow. Surface images can be observed practically for all materials with a large depth of field (Fig. II.5) [51]. The SEM used in our work is Tescan-Vega 3 in the laboratory of physics of thin films and applications (LPCMA) University of Biskra.

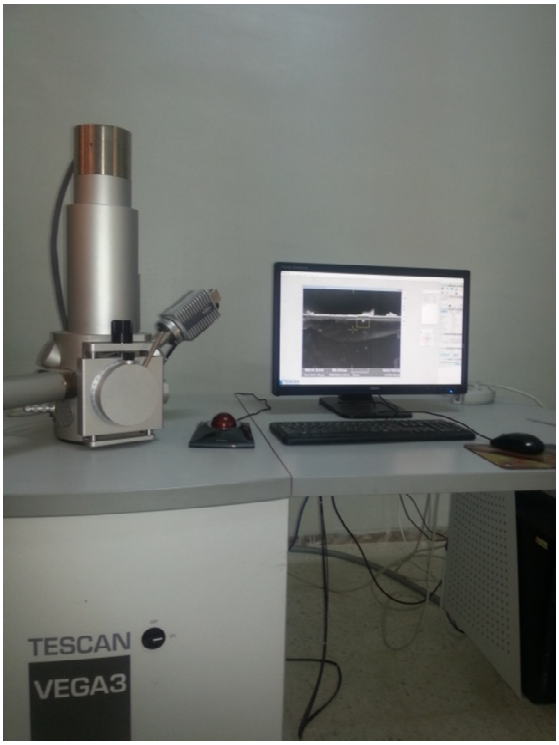


Fig.II. 5 The scanning electron microscopy

II.4.2.3 Energy dispersive X-ray spectroscopy (EDX):

The X-ray spectroscopy emitted by an electron beam bombardment sample can be analyzed using the technique Energy Dispersive Spectroscopy (EDX), coupled with the SEM, the EDX detector makes possible to perform surface chemical, qualitative and quantitative analyzes with a penetration of about few micrometers, depending on the energy of the incident electron beam and the studied material [51].

II.5 Corrosion test:

To study the anticorrosive properties of the elaborated films, we propose to use the potentiostat-galvanostat technique.

II.5.1 Polarization test

Potentiodynamic polarization measurements were performed in a glass cell with three electrodes: working electrode, platinum counter electrode and saturated calomel (SCE) reference electrode. This cell, shown in Figure II.6, is designed to maintain a fixed distance between the three electrodes. The passage of the current in the cells made through the counter electrode [48]. The electrochemical measurements were carried out using a Voltalab PGZ Model 301 Potentiostat/Galvanostat. The polarization curves were carried out using the volt master 4 software.

For the determination of the polarization curve, potentials are applied between the working electrode (room to be studied) and the reference electrode, using a potentiostat, and then the stationary current which is established after some time the electrical circuit between the working electrode and a control electrode (platinum)

The potentiostat is connected to a computer and with the aid of software the curves I=f (E) (current according to potential) are traced. The used device is shown in Fig. II.6

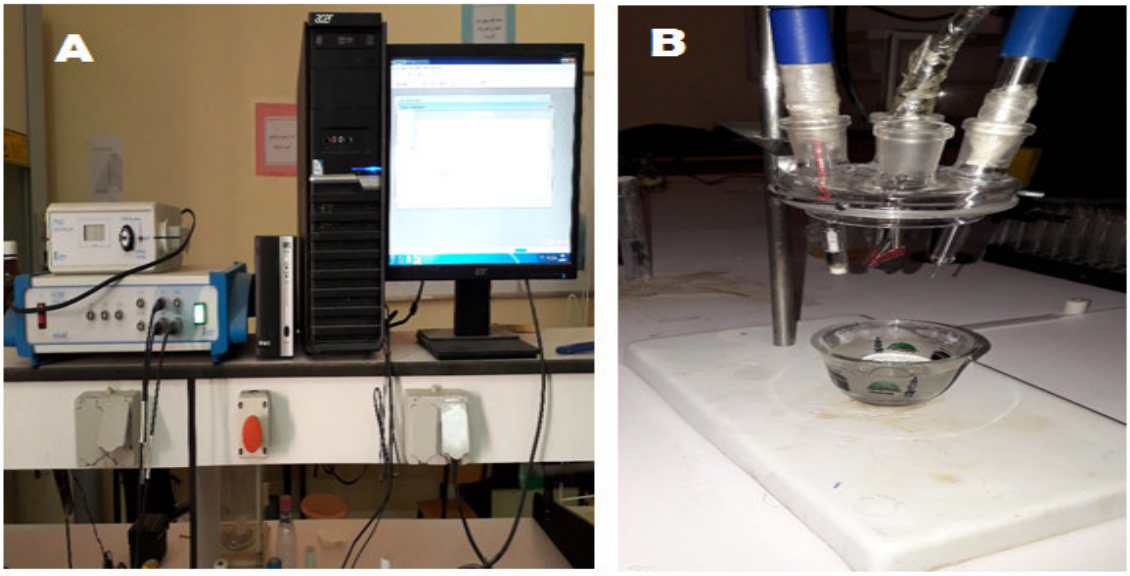


Fig. II.6: Polarization cell

Conclusion:

In this chapter we reviewed all the details of experimental and laboratory work and described the equipment used in the process of elaboration and characterization and also the solutions and conditions used in the production of thin films.

Introduction:

In this chapter we will determine the optimal parameters of deposit of Ti and TiO_2thin films elaborated by Electrodeposition and sol gel spin coating methods and we will realize the Ti / TiO_2 multilayer coatings on stainless steel substrate with different number of films.

The characterization techniques used in this chapter are X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX).

III.1. Optimization of Ti electroplating process:

A watts plating bath was chosen for deposition of Ti thin films. The bath had the following components (composition): Titanium trichloride $TiCl_3$, Ethanol and H_2O_2 ($TiCl_3$+H_2O_2+Ethanol). The solution was mixed at constant room temperature 23 °C for 10 min. The pH of all these baths was 0.59.

The preparatory conditions are summarized in Table III.1 below:

Table III.1. Preparatory conditions and bath composition

Parameters	Values
Volume of $TiCl_3$ (ml)	2
Volume of the solution (ml)	100
pH	0.59
Deposition time (min)	10
Voltage (V)	10
Volume of H_2O_2 (ml)	2
Bath temperature (°C)	Room temperature (23 °C)

In this part, we have optimized the Ti parameters elaborated on stainless steel substrate using Electrodeposition method. We have changed the voltage, the bath temperature and the deposition time conditions.

III.1.1. Morphological characterization of Ti thin films:

III.1.1.1. Voltage / current density:

We fixed all parameters and we changed the voltage values (10, 15 and 18 V). Figure III.1 represents the SEM analyses of Ti thin films in different voltage values.

When we applied the voltage equals to 10 V, we didn't have Ti film at all. Probably this value is not enough to form the film and it is known that the Ti demands a big voltage or current density to extirpate the Ti atoms and deposited on steel substrate.

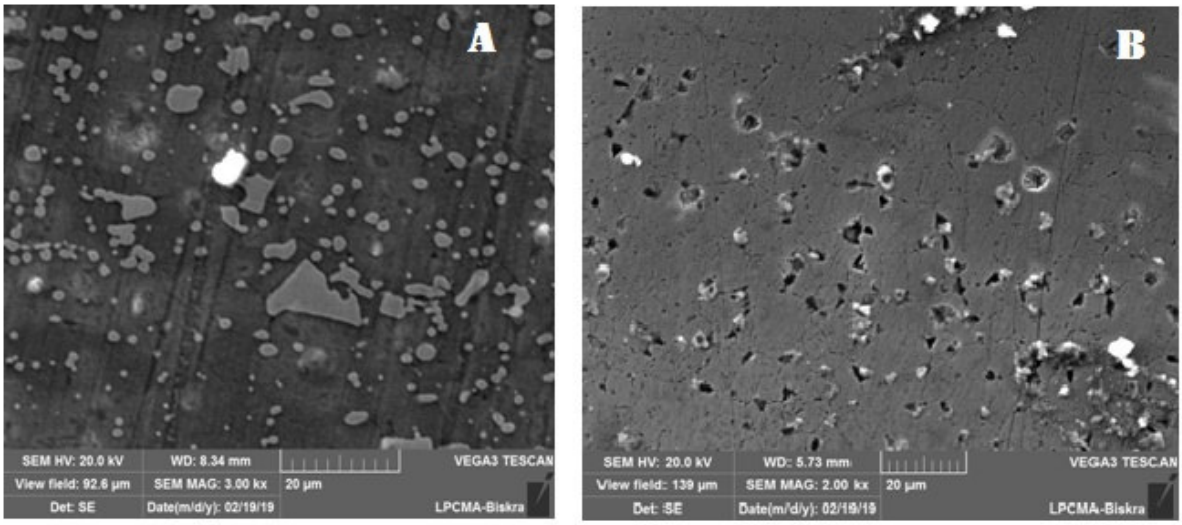


Fig. III.1. SEM images for Ti thin film applied by (A) 15 V and (B) 18 V.

Figure III.1.A presents SEM image for Ti thin film applied by 15 V. We can observe that the film exists and cover all steel surfaces.

It can be seen that the Ti electroplating presents a good adhesion with the substrate in agreement with a thermal choc test. Thus, the Ti thin film was obtained with different colors may be due to the difference in thickness or orientations.

We noted that the surface showed a smooth morphology with some grey spots probably because of the increase of Ti concentration.

This voltage value provides more reactive circumstance and consequently more activation energy for deposition. This is more beneficial for deposition of the species dominantly controlled kinetically than that controlled by diffusion [52].

When we increased the voltage to18 V, we observed that the Ti thin film exists but with no adhesion and homogeneity, perhaps because the deposition time is very big and the voltage is so high (See Fig. III.1. B).

According to the SEM results, we can deduce that the voltage value which must be applied in order to find a Ti thin film with a good adhesion and morphology is 15 V.

III.1.1.2. Deposition time:

In this experience, we changed the deposition time (4, 5, 8 and 10) min and we fixed all other parameters.

Figure III.2 (A) revealed the SEM image of Ti deposition for 4 min. it can be seen that the deposited Ti had bad adhesion with the substrate. Besides, the film was not distributed on all surfaces.

For Ti electroplating for 5 min (Fig. III.2 (B)), we observed that the Ti thin film was adherent with substrate according to the thermal choc test.

The surface morphology was homogeneous with some spots which had a globular forms and the film covered all steel surfaces.

We tried to rise the deposition time to 8 min in order to electroplate Ti thin film. Figure III.2. (C) showed the surface morphology; we can observe that the film clearly presented with defects on the Ti surface morphology it means cracking structure. The film was distributed on all surfaces with great homogeneity.

However, when the deposition time was increased up to 8 min (10 min), the film was disappeared at all, may be due to the influence of the long time in Ti deposition.

It is worth to be paid attention that the Ti electroplating thin film gave good results deposited for 5 min.

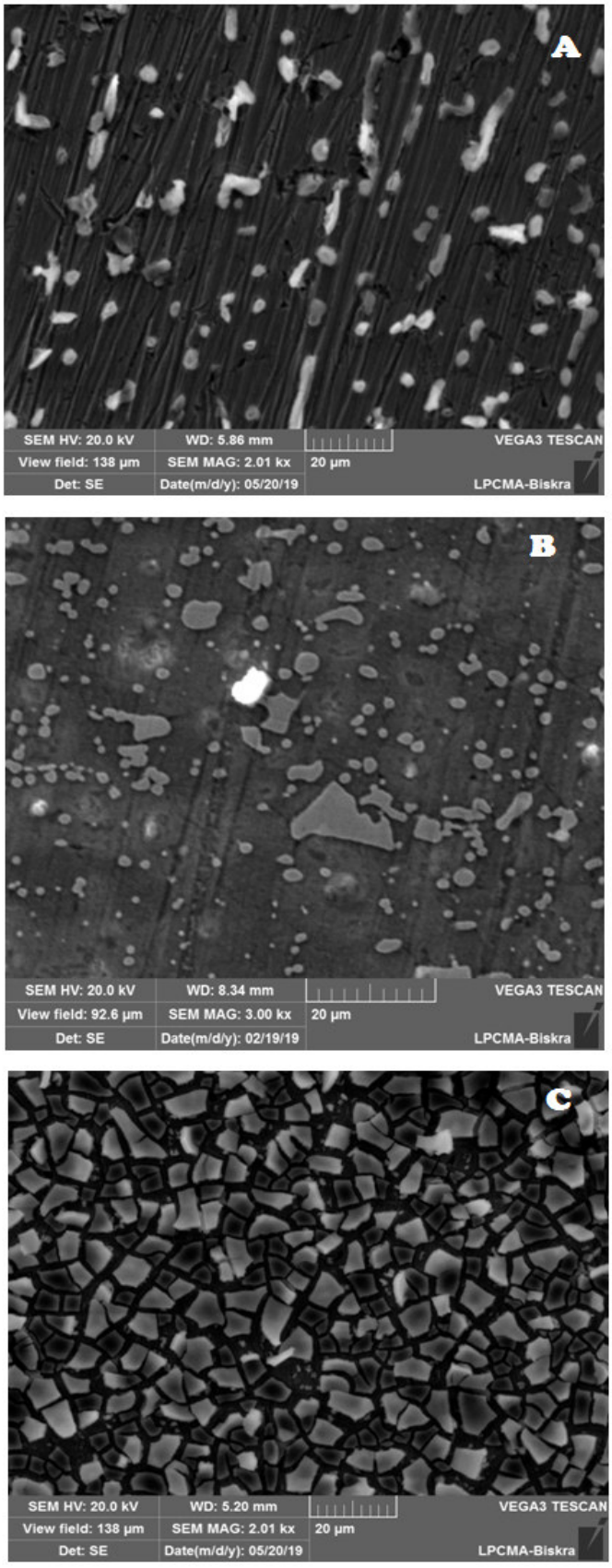


Fig. III.2 SEM results of Ti thin film deposited at 15 V for 4 min (A), 5 min (B) and 8 min (C) respectively.

III.1.1.3. Effect of bath temperature:

Another point can affect the Ti electroplating is the increase in temperature. In this part we changed this parameter from room temperature 23 °C to 30, 50 and 80 °C.

It is known that the temperature is a parameter which favorite the sedimentation of thin films generally but in our case we will see if the increase in temperature value enhance the morphology proprieties of Ti thin films or not.

Figure III.3 shows the SEM investigations of Ti thin film deposited under 20, 30 and 50 °C.

The Ti thin film morphology deposited at constant room temperature (23 °C) is shown in Fig. III.3 (A). The surface morphology was observed with a good adhesion and homogeneity. However, the increase in temperature rate changed the Ti morphology. It can be seen that a fibrous structure was appeared at 30 °C, probably due to the high speed of Ti^{+2} ions in bath solution and consequently the random deposition of Ti atoms on stainless steel substrate (See Fig. III.3 (B)).

In other hand, the SEM picture of Ti thin film deposited under 50 °C is shown in Fig. III.3. (C). We can note that a bad Ti film was obtained, and also we can see that the oxidation reaction of stainless steel was started.
It can be indicated that the increase of temperature bath up to 50 °C (80 °C in our experience) leads to the complete oxidation of the steel, which appears completely black after the end of the process. We can say that the steel was burned.

According to the previous discussions, we can deduce that the optimal parameters for Ti electroplating on stainless steel substrate are 15 V, 5 min and room temperature. The following table summarizes the optimal conditions for Ti deposition by Electrodeposition process. (Table III.2).

Remarque:

Based on our experience, when we deposit the Ti thin film using Electrodeposition process and we applied a high voltage we have to decrease the deposition time in order to obtain Ti thin film with a good adhesion and morphology. The same condition with a temperature

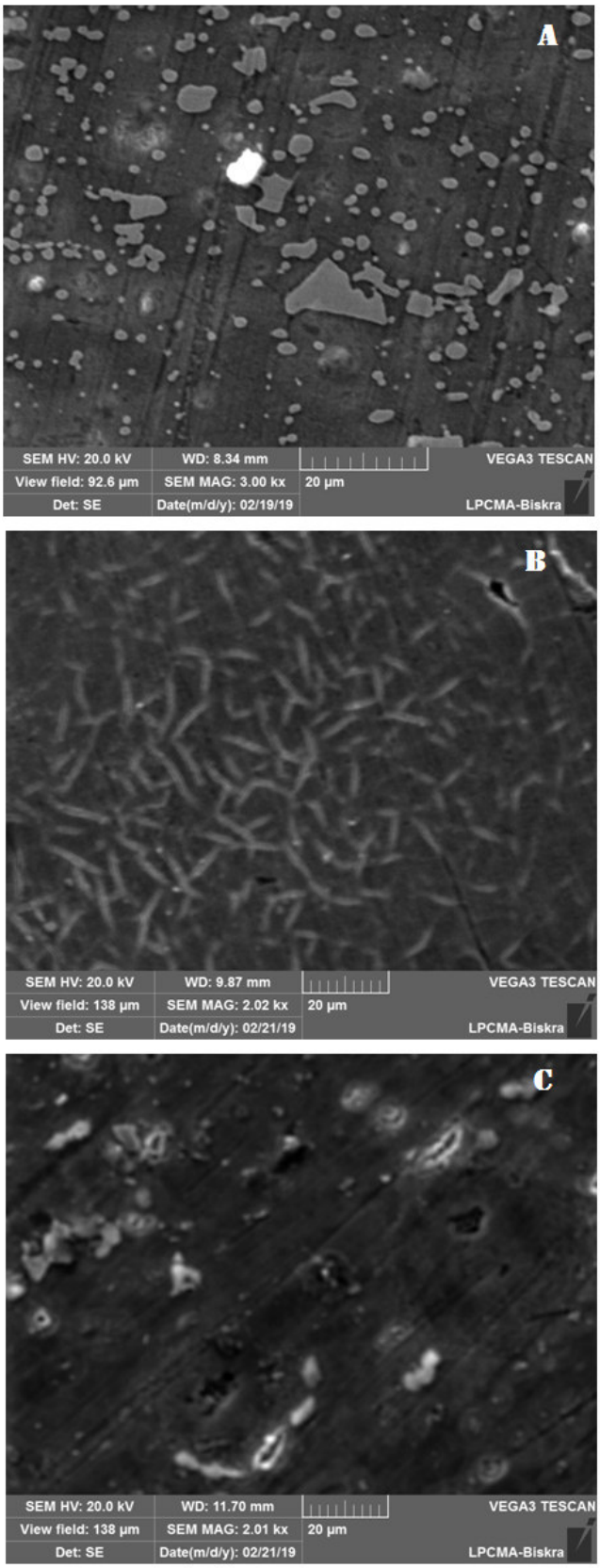


Fig. III.3 SEM images of Ti electroplating deposited under (A) room temperature, (B) 30 °C and (C) 50 °C.

Table III.2 Optimal conditions of Ti electroplating

Parameters	Values
Volume of $TiCl_3$ (ml)	2
Volume of the solution (ml)	100
pH	0.76
Deposition time (min)	5
Voltage (V)	15
Volume of H_2O_2 (ml)	1
Bath temperature (°C)	Room temperature (23 °C)

III.1.2. Structural characterization of Ti electroplating:

Figure III.4 illustrates the XRD patterns of the Ti thin films obtained by Electrodeposition method. The XRD results indicate that the Ti thin film has a crystallite structure. The peaks at 44° and 63° are related to the steel substrate. However, diffraction peaks at 35 and 39.5° were observed. These peaks indicate clearly the presence of Ti (crystalline) thin film. Other peak was appeared at 2Θ= 42° showed the existence of the rutile TiO_2 phase. This result is logic because the Ti film is very reactive metal and the oxygen is existing in solution (H_2O) or in air.

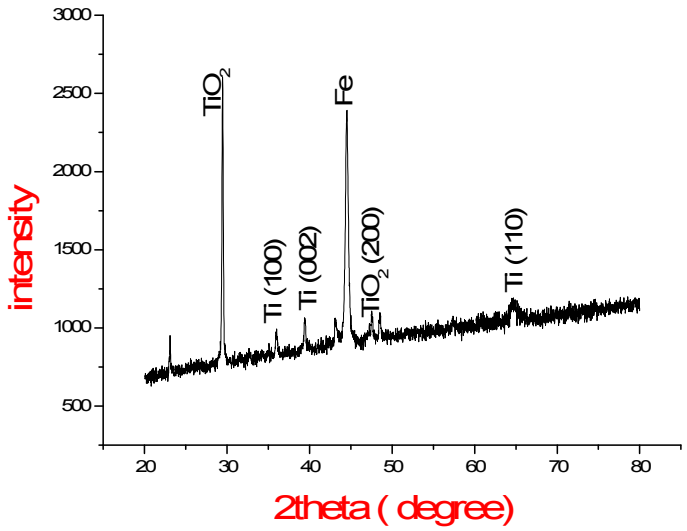


Fig. III.4 XRD patterns of Ti electroplating thin films.

III.2. Optimization of TiO_2 thin films parameters deposited by spin coating:

Layers of TiO_2 are obtained from a solution formed by a mixture of titanium isopropoxide, isopropanol and some drops of acetic acid. Table III.3 shows the TiO_2 components and the preparatory conditions.

Table III.3: Preparatory conditions

Parameters	Values
Molarity (mol/L)	0.2
Volume of the solution (ml)	10
Rotation speed (rot/min)	4000
Acceleration (r/min^2)	400
Deposition time (s)	30
Drying temperature (°C)	100
Drying time (min)	10
Number of repetition (spin + drying)	5 times

The deposition was performed by spin coating sol gel technique. The procedure requires to applying 5 layers for each sample. The gel films grown on the stainless steel substrate contain residual of solvent and probably water from the condensation reaction, the spin coated stainless steel substrate was therefore left to dry at ambient temperature followed by heating at 100 °C for 10 min between two deposition on a hot plate. The TiO_2 coatings are obtained after 5 spinning and various parameters.

In this study, we are only focusing on how these different parameters affect the surface morphology and structural proprieties.

The porosity, the surface roughness, the film thickness and the microstructure, although the influence of all these parameters is still a matter of debate [52].

So it is important to optimize the preparation process to obtain TiO_2 film with appropriate phase composition.

III.2.1. Analysis of structure, morphology and chemical composition:

III.2.1.1. Deposition time:

The titanium dioxide TiO_2 layers were deposited on stainless steel substrate under the same conditions as previously described pH = 3.05, rotation speed = 4000 rpm, acceleration = 400 rpm/s.

In this part we have changed the deposition times (30 s, 45 s and 60 s).

Figure.III.5 (A), (B) and (C), (A'), (B') and (C') shows SEM/EDX images of TiO_2 thin films deposited for 30, 45 and 60 s on steel substrate using spin coater process.

The morphological characteristic of TiO_2 has been studied using scanning electron microscopy (SEM) and the energy dispersive X-ray spectroscopy (EDX).

The Figure III.3.(A), (B) and (C) shows respectively the surface morphology of TiO_2 films prepared for 30 s, 45 s and 60 s.

For the film obtained at 30 s, the SEM image showed a good adhesion at the interface between the stainless steel substrate and the TiO_2 film, in agreement with the thermal shock test.

The film is presenting but not dense and does not cover the surface sufficiently to cast the substrate as well as the sedimentary layer is not homogeneous .

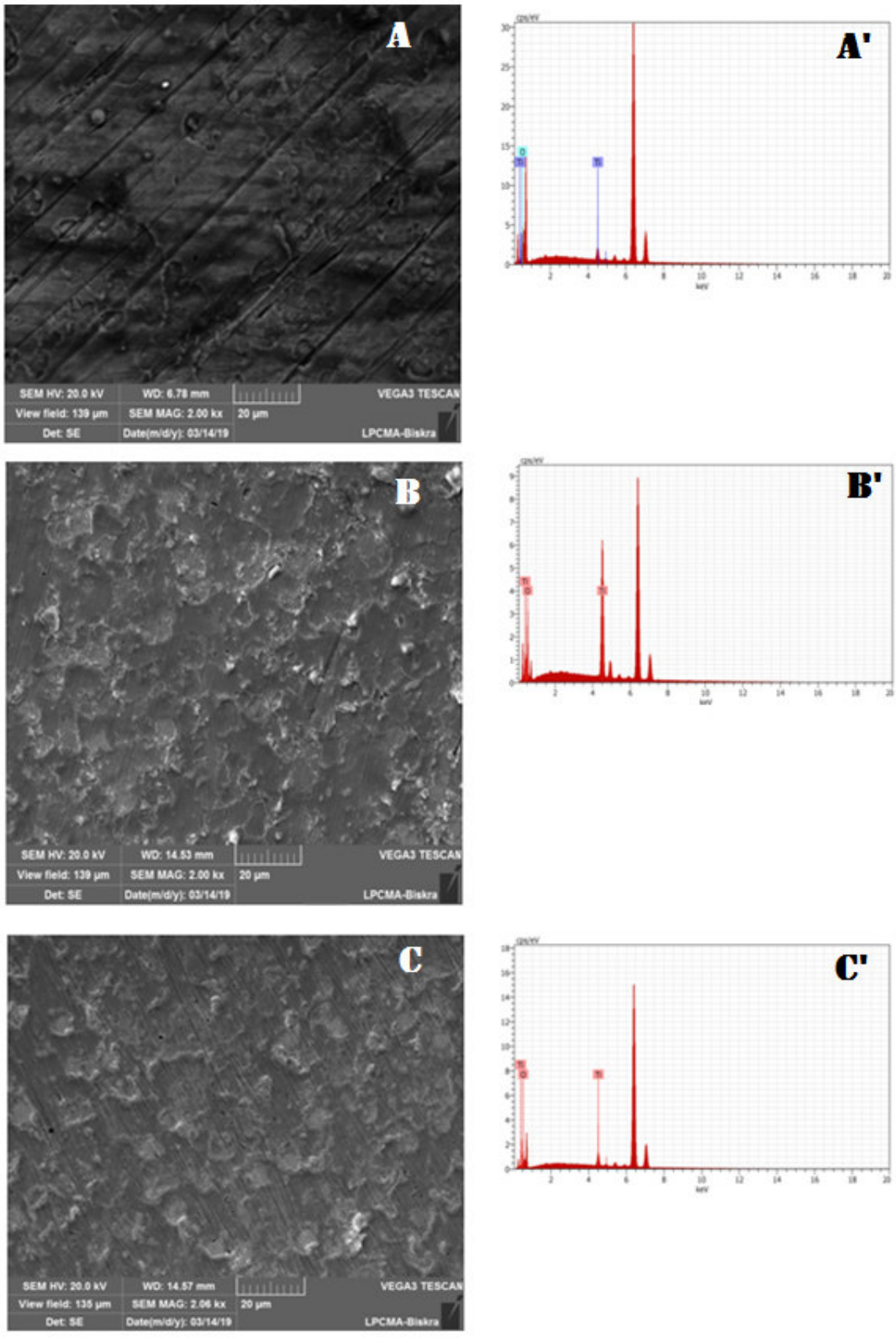


Fig. III.5. (A), (B) and (C)/(A'), (B') and (C') SEM/EDX image of TiO_2 thin films deposit in 4000 rpm for 30, 45 and 60 seconds on stainless steel substrate using spin coater method respectively

The EDX results confirmed the presence of titanium in small quantities in the entire surface (20.34 %) . Table III.4 shows the EDX results of TiO_2 films deposited for 30 s.

Table III.4: EDX results of TiO_2 films deposited for 30 s.

Element	AN	unn [wt %]	C $_{norm}$ [wt%]	C $_{Atom}$ [at%]
O	8	4.94	79.66	92.14
Ti	22	1.26	20.34	7.86

Another characteristic of metal substrate is surface roughness on the microscale. This roughness is often wanted,helping the adhesion of the coating to the substrate but in same time can be a limitation when investigating physical properties such us viewing the nanoscaled grains [53].

In Figure III.5 (B) the film is deposited for 45 seconds. The SEM analyzes showed a great adhesion between TiO_2 film and substrate, the film is very dense, the layer has a homogeneous stucture without cracks and damage. All surfaces are covering by TiO_2 film. It can be seen that the structure is found to be strongly enriched in titanuim dioxide.

The EDX results (Table III.5) determined the chemical composition of the TiO_2 thin films, the obtained EDX spectrum from the areas presented in (Fig. III.5 B') showed that the layers obtained from a previous solution corresponded to the chemical and stoichiometric composition of the TiO_2 compound this is demonstrated by oxygen (57 %) and titanium (43 %) composition with a very large amount compared to the previous film, and the increase is due to an increase in concentration of TiO_2 and improvement in crystalline quality; while the remaining elements are derived from the substrate material on which the coatings applied.

Table III.5: EDX Results of TiO_2 films deposited for 45 s.

Element	AN	unn [wt%]	C $_{norm}$ [wt%]	C $_{Atom}$ [at%]
O	8	17.75	57.00	79.87
Ti	22	13.39	43.00	20.13

The Figure III.5 (C) shows the coating deposited for 60 seconds. The SEM characterization showed that the TiO_2 film exists with homogenous and dense structure but it was full of pores because the surface is not filled with TiO_2 layer.

The EDX results (Fig. III.5 (C')) confirmed that the titanium element exists but with a small quantities (29.5 %) (Table III.6).

Table III.6: EDX Results of TiO_2 films deposited for 60 s.

Element	AN	unn [wt%]	C_{norm} [wt%]	C_{Atom} [at%]
O	8	4.43	70.49	87.73
Ti	22	1.85	29.5	12.27

Taking into account above discussion, we can conclude that the best film of TiO_2 is obtained by spinning process for 45 seconds.

III.2.1.2. Rotation speed:

In this study, we changed the rotation speed (2000, 4000, and 5000) rpm and we fixed the other previous parameters.

Figure III.6 (A), (B) and (C) shows respectively the surface morphology of TiO_2 films Spinning at 2000, 4000 and 5000 rpm for 45 seconds.

The SEM image shows the surface morphology of TiO_2 obtained with a speed rotation equals to 2000 rpm in (Fig.III.6 A), the results demonstrated that the film exists in some place on the substrate with some TiO_2 particles, the polishing scratches are visible on the surface and this means that the film is not evenly distributed on the substrate, perhaps due to the low velocity that was not sufficient to precipitate the TiO_2 in a homogeneous manner. The EDX (Fig. III.6 A') showed the chemical compositions of the sedimentation layer and it confirmed the existence of oxygen and titanium by observes elements but with a decrease in Ti quantities compared to the precedent film (35.59 %) (Table III.7).

Table III.7: EDX results of TiO_2 films obtained for 2000 rpm, 45 s

Element	AN	Unn [wt%]	$C._{Norm}$ [wt%]	$C._{Atom}$ [at%]
O	8	12.63	64.41	84.41
Ti	22	6.98	35.59	15.59

Figure III.6 (B) shows the SEM morphology of TiO_2 indicated that a porous and fine structure with a great homogeneity, density and adhesion for the layer elaborated with 4000 rpm (speed rotation).the TiO_2 particles were disappearing probably is due to the coalesce of these particles to form an homogeneous and smooth surface morphology.

Figure III.6 (C) shows the morphological surface of the sediment layer by spin coating and a speed of 5000 rpm for 45 seconds

The SEM image shows the morphological proprieties of TiO_2 film. The speed increases, the surface morphological changes were observed then we can note the well separated particles are getting larger and starting to agglomerate and coalesce and then forming clusters which prevent the aggregation during heating. The surface morphology is composed of clusters of varying size with irregular shapes.

The irregular shape of the particles is caused by the low temperature and the kinetic energy is not enough to induce the recombining of grains [55].

The film is dense, homogeneous and covers the entire substrate surface. The surface of the film is not uniform due to the aggregations.

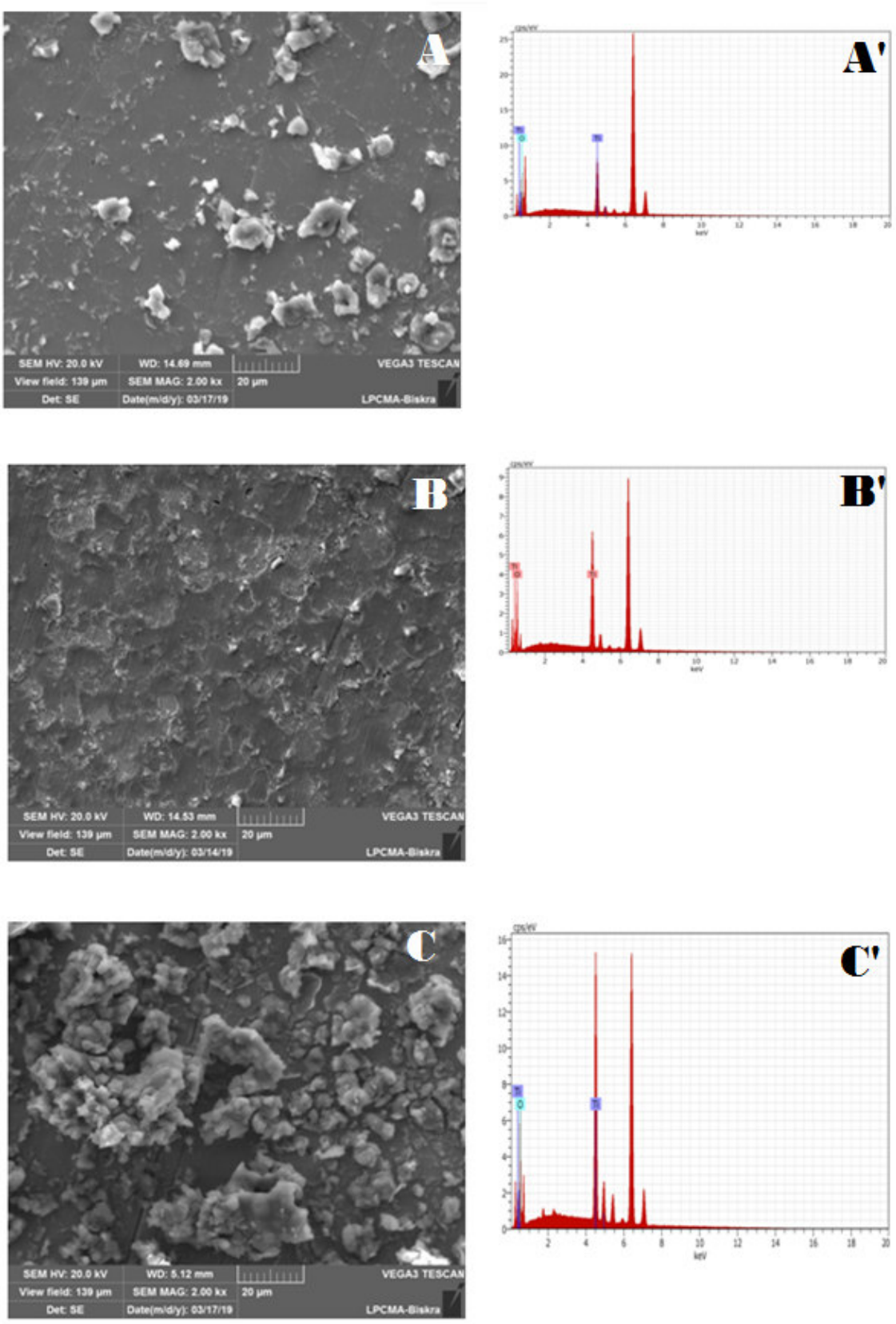


Fig. III.6 (A), (B) and (C)/(A'), (B') and (C') SEM/EDX image of TiO_2 thin film deposit in 2000, 4000 and 5000 rpm for 45 seconds on stainless steel substrate using spin coater method respectively

The EDX results confirmed the existence of high amount of titanium dioxide (% O 71.47, % Ti 28.53) in all surface. The Table III.8 shows the EDX composition.

Table III.8: EDX results of TiO_2 films obtained for 4000 rpm, 45 s.

Element	AN	Unn [wt%]	C.Norm [wt%]	C Atom [at%]
O	8	6.54	71.47	88.23
Ti	22	2.61	28.53	11.77

The chemical composition of the TiO_2 deposited on steel is investigated by EDX. Photoelectron peaks for Ti and O are recorded on the coatings and with a large quantity of Ti especially in aggregate, this confirm that the particles or grains are coalescing and agglomerating to get a dense structure with a big concentration of Ti (43.64 %) (Table III.9).

Table III.9: EDX results of TiO_2 films obtained for 5000 rpm, 45 s.

Element	AN	unn [wt%]	C norm [wt%]	C Atom [at%]
O	8	21.60	56.36	79.44
Ti	22	16.72	43.64	20.56

According to the previous discussion, we can deduce that the high velocity, which is 5000 rpm in our experience, gives good results in sedimentation of TiO_2 thin films on a stainless steel substrate.

III.2.1.3. Bath concentration:

In this part we tried to know the influence of concentration on TiO_2 morphology films, we prepared three TiO_2 solutions with different concentration of titanium isopropoxide (0.5, 0.6 and 0.8) mol/l.

The morphology of TiO_2 sol-gel coatings applied to the stainless steel substrate was analyzed by means of scanning electron microscopy (SEM). Figure III.7 (A, B and C) shows the surface morphology of the thin oxide layers observed with the use of SEM and

(A', B' and C') represent the chemical composition of TiO_2 thin oxide layer obtained by EDX.

From the recorded images (Fig.III.7 (A)), it is observed that the layer deposited with 0.5mol/L concentration has a large part of the crystallites relatively regular shape. As it can be seen, this sample consists of particles with a very large distribution of shape. It can be even observed of smaller and regular particles. A detailed SEM examination of the particle surfaces shows that the grains are constituted by agglomerate of very small TiO_2 particles. However, TiO_2 thin film consists very homogeneous and dense structure without any cracks or pores.

The formation of separated particles is probably due to the low concentration of (Ti). A similar result was reported by I. N. Kuznetsova and all [56]. The isolated particles can also be due to the agent (acetic acid) in initial solution, which prevents the aggregation during heating [56].

Fig .III.7 (B) shows the micrograph obtained for TiO_2 with 0.6 mol/L concentration. The SEM characterization demonstrated that the TiO_2 morphology changed compared to a previous film, it can be seen that the well separated particles are getting larger and starting to agglomerate and coalesce and then forming clusters which prevent the aggregation during heating. The surface morphology is composed of clusters of varying size with irregular shapes. The film exists with a great density and adhesion.

Figure III.7 (C) shows the surface morphology of TiO_2 films obtained with 0.8 mol/L. The surface indicates poor concentration of Ti with a decrease in TiO_2 particles and grains but it is homogeneous and covers all surface of substrate. Also we observed that in some regions the Ti presents a large concentration.

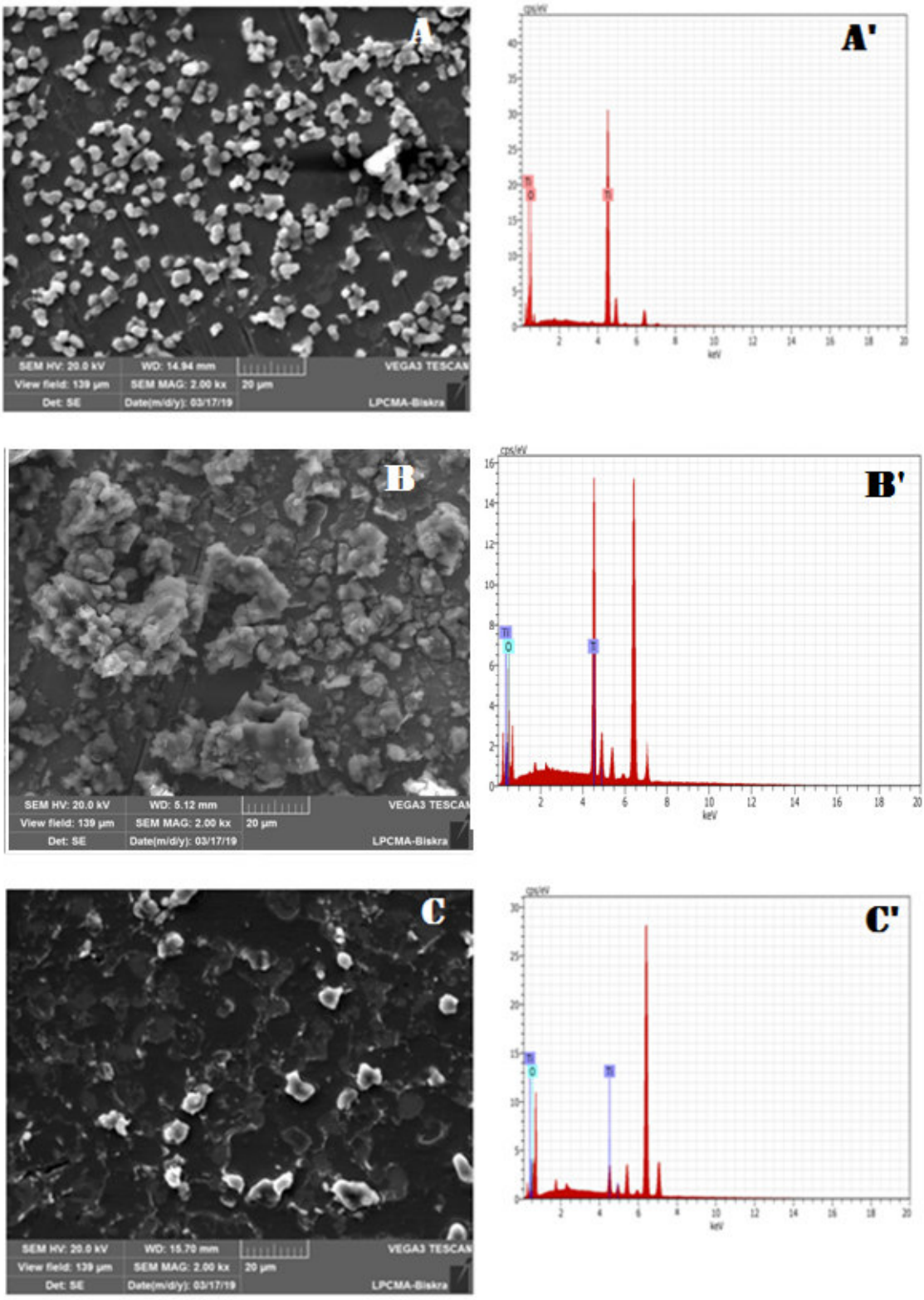


Fig. III.7 (A), (B) and (C)/(A'), (B') and (C') SEM/EDX image of TiO_2 thin film deposit with 0.5, 0.6 and 0.8 mol/L at 5000 rpm for 45 seconds on stainless steel substrate using spin coater method respectively.

EDX analysis of the 0.5 mol/L sample showed that the oxygen and titanium elements always are presented with a very big and large amount; the practical absence of signals attributable to stainless steel confirms that the film covers, to a large extent, the substrate. Table III.10 shows the EDX composition (Fig. III.7.A').

Table III.10: EDX results of TiO_2 films obtained for 0.5 Mol/L, 5000 rpm, 45 s.

Element	AN	unn [wt%]	C $_{norm}$ [wt%]	C $_{Atom}$ [at%]
O	8	51.17	54.62	78.27
Ti	22	42.51	45.38	21.73

The EDX analysis determined the existence of Ti and O with a great amount (56.36 % for O and 43.64 % for Ti). The presence of elements is remaining to substrate. Table III.11 summaries the EDX results. (See Fig. III.7.B').

Table III.11: EDX results of TiO_2 films obtained for 0.6 Mol/L, 5000 rpm, 45 s.

Element	AN	unn [wt%]	C $_{norm}$ [wt%]	C $_{Atom}$ [at%]
O	8	21.60	56.36	79.44
Ti	22	16.72	43.64	20.56

In order to find the chemical composition of different regions on the TiO_2 surface, we used the EDX spectrum. The results showed that the grey region contains the important quantity of Ti (34.41%) while the black one consists of less amount of Ti (21.21 %) (Table III.12). (See Fig. III.7.C').

Table III.12 EDX results of TiO_2 films obtained for 0.8 Mol/L, 5000 rpm, 45 s.

Element	AN	[wt%] unn	C $_{norm}$ [wt%]	C $_{Atom}$ [at%]
O	8	3.34	78.79	91.75
Ti	22	0.90	21.21	8.25

Proceeding to the debate, we can conclude that the best results in TiO_2 morphology are obtained with 0.5 mol/L concentration.

Finally, in this study we have successfully elaborated TiO_2 thin films on stainless steel substrate by sol gel spin coating method. The desired morphological proprieties were examined by SEM and chemical composition.

We have optimized the preparatory conditions in order to obtain TiO_2 thin films with great morphological proprieties and we got these results after many experiences: the optimal parameters to deposit TiO_2 by spin coating process are:

0.5 mol/L in concentration, 5000 rpm in rotation speed and 45 seconds for the deposition time.

The Table below summaries the optimal conditions to deposit TiO_2 thin films on stainless steel substrate:

Table III.13: Optimal conditions for TiO_2 thin films

Parameters	Values
Molarity (mol/L)	0.5
Volume of the solution (ml)	10
Rotation speed (r/min)	5000
Acceleration (r/min^2)	500
Deposition time (s)	45
Drying temperature (°C)	100
Drying time (min)	10
Number of repetition (spin + drying)	5 times

III.2.4. Structural Characterization by XRD:

Figure III.8 presents the X-ray diffraction spectra of the samples with and without annealing under 300 °C for 30 min.

We made the structural characterization by the X-ray diffraction for our samples with a mini-Flex (Miniaturk) difractometer (Rigaku thin layers-Biskra). The device is equipped with a copper anode having a beam of Wavelength XRD of K (Cu) = 1, 5405 (Å) and the conditions of excitation are U = 40 kV, I = 15 mA. The angular domains canned is between 10 and 80 with a counting step of 0,01 s.

The X-ray diffraction makes possible to determine the nature of the material (crystalline or amorphous) and the nature of the phases in the presence of the planes (hkl).

In our case, it can be seen that no TiO_2 peak is appeared in all samples and this result is logical because the TiO_2 thin film without annealing or calcinations has an amorphous structure and this is similar of T. Tanski and all [11].

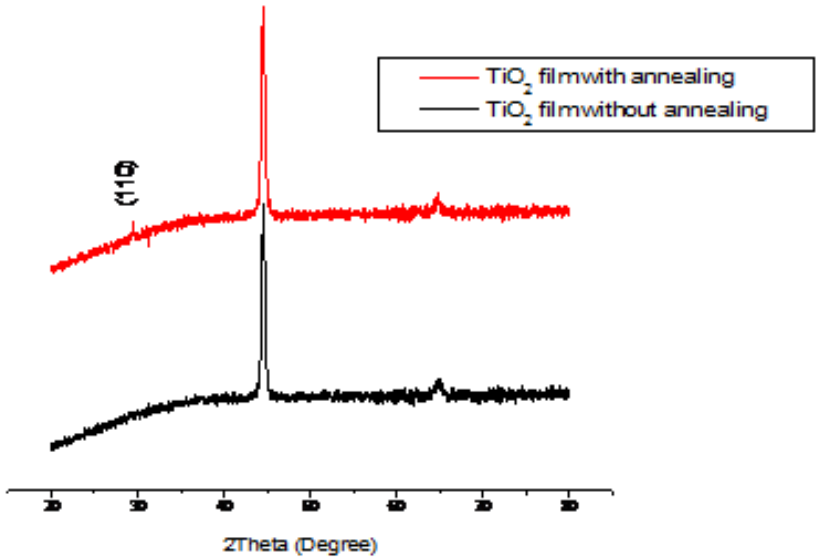


Fig. III.8. X-ray Diffractogrammes of TiO_2 monolayer deposited on stainless steel with and without annealing

In other hand, we annealed one sample of TiO_2 thin film at 300 °C for 30min then we analyzed it by XRD, we have observed that a pronounced (110) peak of TiO_2 at 2Θ=27,7° was observed indicating the presence of the rutile polymorphic phase. Other characterization diffraction peaks from rutile TiO_2 was observed at 2Θ range between 60° and 70°. This result means that TiO_2 thin film was crystallized after annealing less than 300 °C for 30 min. This is consistent with what found by T. Tanski and all [11].

The iron phase peaks are originated from the stainless steel substrate due to the thin oxide film deposited. Some X rays peaks from the substrate were detected in 2Θ=45 and 63°.

The morphology of TiO_2 film before and after annealing is shown in Fig. III.9. We can see that the annealing favorite the agglomeration of TiO_2 particles and the structure become crystalline. Also we can note that the grain size of the TiO_2 increased with annealing

temperature, so the surface morphology of TiO_2 could be affected by annealing temperature and this reported by M. K. Ahmad and all [57].

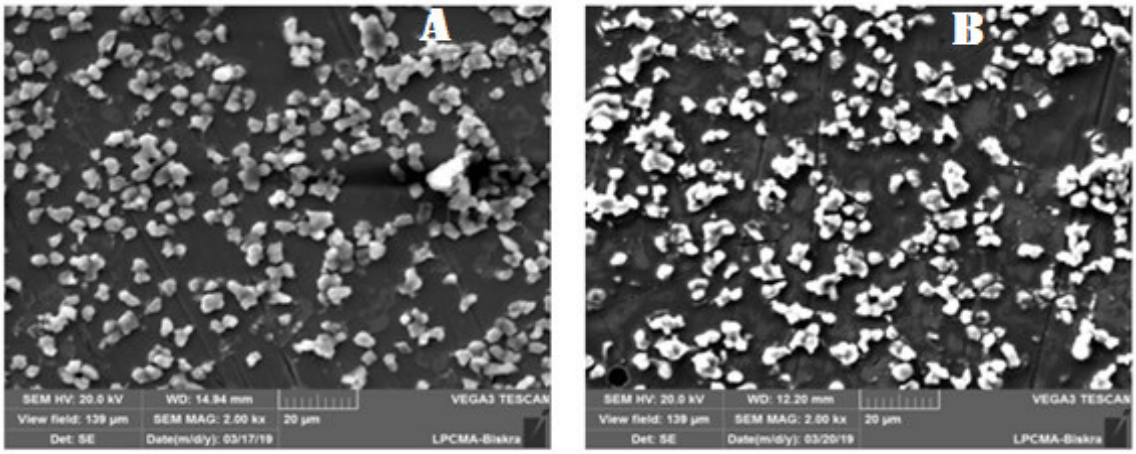


Fig. III.9 SEM micrograph of the titania spin coating films with and without annealing: (A) TiO_2 without annealing and (B) with annealing at 300 °C for 30 min

Remarque:

In our case, probably the crystallization of TiO_2 coating is not as good those for the sintered ceramics because of the corrosion application [37].

Conclusion:

To summarize, we have successfully prepared TiO_2 thin films on stainless steel substrates using titanium isopropoxide as precursor by employing a simple and inexpensive sol-gel spin-coating technique. XRD and SEM analysis of TiO_2 thin films show that films exhibited a good adherence, morphology and structure after annealing in the optimal conditions which are 5000 rpm, 45 s and 0.5 mol/L of solution concentration.

III.3 Multilayer coatings:

We have already deposited the titanium Ti and titanium dioxide TiO_2 thin films on stainless steel substrate by Electrodeposition and sol gel spin coating methods respectively. We have found the optimum conditions for the sedimentation layers as follows: for Ti coatings the optimum parameters are 15 V, 5 min, and 23 °C and for TiO_2 are 5000 rpm, 45 seconds and 0.5 mol/L concentration.

This part reported on the realization of Ti/TiO_2 multilayers periodically on stainless steel substrate using Electrodeposition and sol gel spin coating methods respectively with different number of layers (2, 4, 6 and 8) layers.

The aim of this experience is to find the effect of the number of layers on composition, surface morphology, and corrosion resistance.

Results and discussions:

III.3.1. Characterization of coatings:

The morphology of the multilayer coatings was investigated by scanning electron microscopy (SEM).

The relative amounts of Ti and O in the deposited coatings were obtained based on the EDX analysis coupled with SEM.

III.3.1.1. Coating with 2 layers:

Figure III.10 shows the surface morphology of the multilayer coatings with 2 layers.

The multilayer with 2 films exhibited relatively smooth morphology with formation of clusters with different geometric forms and homogeneously distributed on the surface.

We noticed also a great adhesion between substrate and Ti/TiO_2 multilayer based on the thermal shock test.

The covered surface represents 40 % and the rest represents a very thick film with a small percentage of Ti confirmed by EDX analysis.

We can see that the surface morphology seems as an “islands” with a linear extent. These later begin to coalesce so that a meanding Ti network is established and this is similar of what is found by P. C. Lansaker and all [58].

It seems that the morphology consists of three different regions with various colors (grey, white and black). The white region probably contains TiO_2 with crystallite structure; the grey region may be containing an amorphous TiO_2 and the black one the substrate covers with a small amount of Ti (Fig.III.10 (B), (C) and (D)).

Indeed the surface EDX result shows that the Ti/TiO_2 multilayer ratio is different in three regions, it can be seen that the Ti and O amounts in white region are higher than the others (25.15 %).

The EDX results of the chemical composition of the selected layers are presented in Tables III.14, III.15 and III.16.

Table III.14: EDX results of grey region

Element	AN	[wt.%] unn	C $_{norm}$ [wt.%]	C $_{Atom}$ [at.%]
O	8	13.49	76.96	90.91
Ti	22	4.04	23.04	9.09

Table III.15: EDX results of white region

Element	AN	[wt.%] unn	C_{norm} [wt.%]	C_{Atom}[at.%]
O	8	17.64	74.85	89.91
Ti	22	5.93	25.15	10.09

Table III.16: EDX results of black region

Element	AN	[wt%] unn	C $_{norm}$ [wt%]	C $_{Atom}$ [at%]
O	8	11.56	76.26	90.58
Ti	22	3.60	23.74	9.42

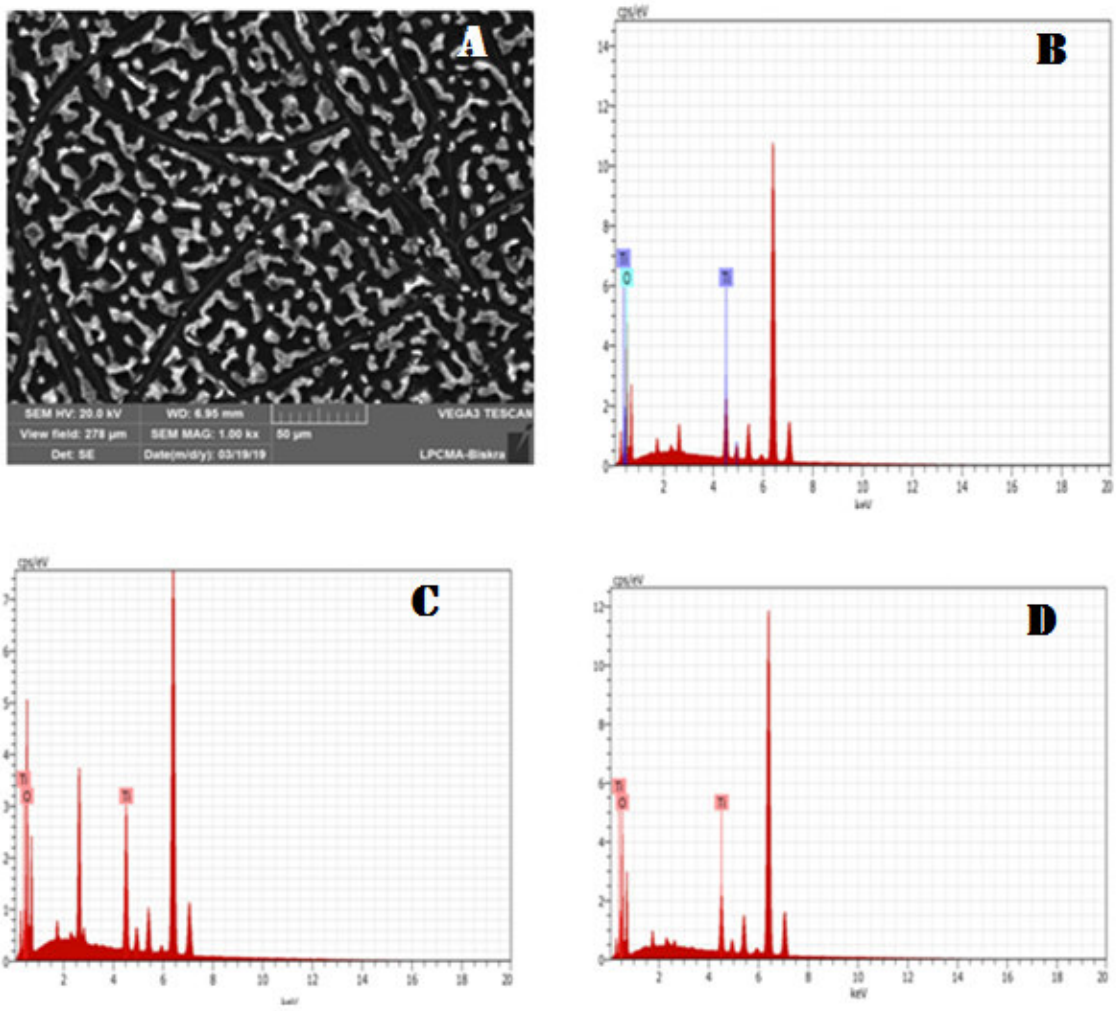


Fig. III.10 SEM/EDX images for Ti/TiO_2 multilayer with 2 films: (A): SEM image of the Ti/TiO_2 multilayer with 2 films, (B) EDX spectrometer of the black region, (C) EDX spectrometer of the white region, (D)EDX spectrometer of the grey region

III.3.1.2. Coating with 4 layers:

The multilayer with 4 films is shown in Fig. III.11, we observed a different surface morphology compared to the multilayer with 2 layers, the covered area by the film increased to 80 %.

The agglomerations of the particles increased with the increase of number of layers significance of the aggregation of Ti and TiO_2 particles together and overlapping to form a cracked structure. As we have seen previously the cracks comes from the spinning TiO_2 thin films probably due to the constraints or the effect of drying.

The structure showed great homogeneity as seen from the decrease of white particles compared with the previous specimen.

The EDX results confirmed that the Ti concentration is increased in all regions to form aggregates due to the sedimentation of TiO_2 thin film on Ti and the particles are gathered and the surface is full of Ti particles (Fig.III.11).

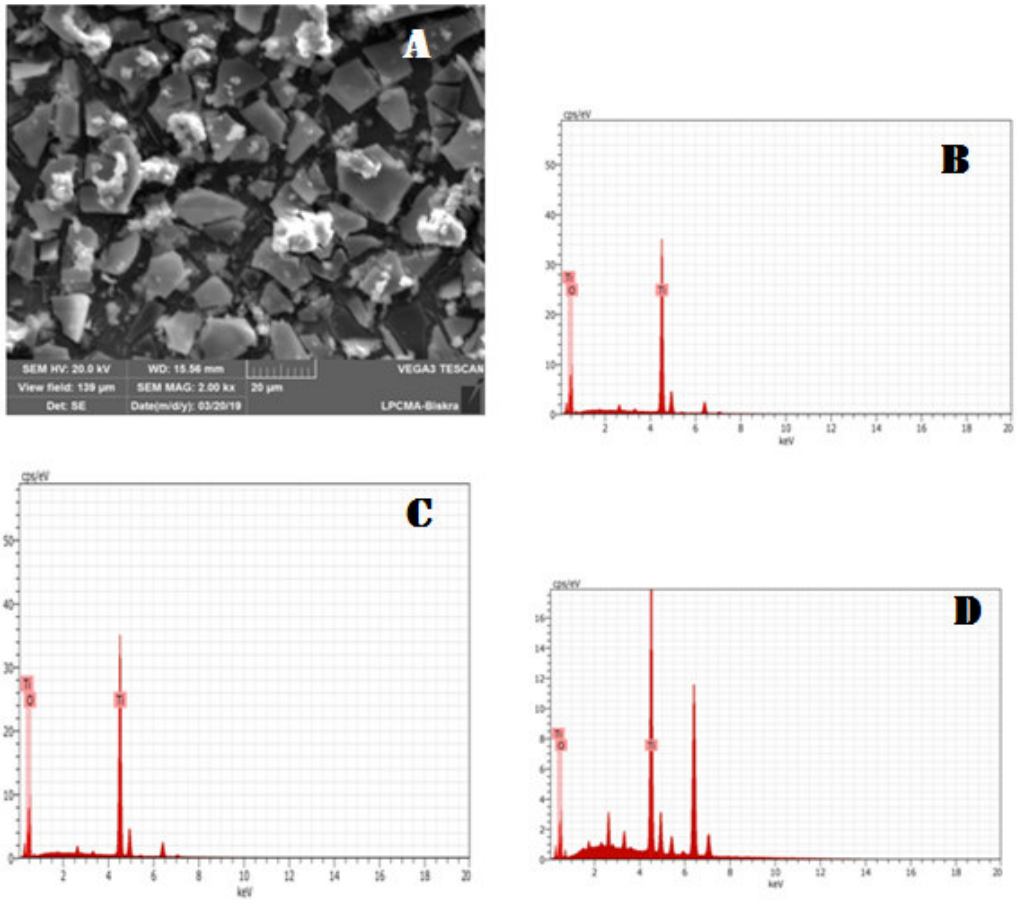


Fig.III.11: SEM/EDX images of Ti/TiO_2 multilayer with 4 films deposited on stainless steel: (A) SEM image of the Ti/TiO_2 multilayer with 4 films, (B) EDX spectrometer of the grey region, (C) EDX spectrometer of the global surface and (D) EDX spectrometer of the black region.

The EDX results for the global surface and the different regions are summerized in tables III.17, III.18 and III.19.

Table III.17: EDX results of global surface

Element	AN	[wt%] unn	C $_{norm}$ [wt%]	C $_{Atom}$ [at%]
O	8	25.13	60.36	82.01
Ti	22	16.50	39.64	17.99

Table III.18: EDX results of grey region

Element	AN	[wt%] unn	C norm [wt%]	C Atom [at%]
O	8	50.67	52.82	27.22
Ti	22	45.26	47.18	72.78

Table III.19: EDX results of black region

Element	AN	[wt.%] unn	C norm [wt.%]	C Atom [at.%]
O	8	25.50	62.20	35.47
Ti	22	15.50	37.80	64.53

III.3.1.3. Coating with 6 layers:

The Ti/TiO_2 multilayer with 6 layers is represented in Fig. III.12 (A). The SEM shows Roaster structure, fine surface morphology with a great adhesion between the substrate and layers.

The film is homogenous, dense and also it can be seen the decrease of cracks with increase of number of layers. This indicates that the new layer covers the layer before it and fills the existing spaces and thus reduces cracking and defects.

The film covers the surface almost completely compared to the samples with 2 and 4 layers.

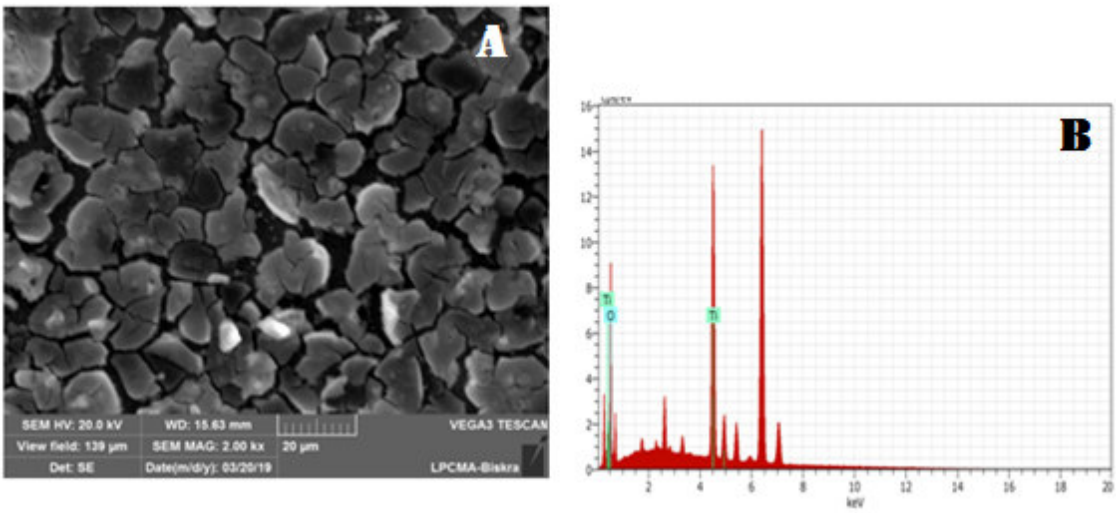


Fig.III.12. SEM/EDX images for Ti/TiO_2 multilayer with 6 films deposited on stainless steel.

The EDX results show that the Ti and O elements exist with large quantities (61.96 % for O and 38.04 for Ti). This confirms that the Ti/TiO_2 multilayer exists (Table.III.20).

Table III.20 represents the chemical composition of Ti/TiO_2 multilayer of the global surface.

Table III.20: EDX results of Ti/TiO_2 6 layers

Element	AN	unn[wt.%]	C $_{norm}$ [wt%]	C $_{Atom}$ [at%]
O	8	22.83	61.96	82.98
Ti	22	14.01	38.04	17.02

III.3.1.4. Coating with 8 layers:

The multilayer coating with 8 films is shown in Fig. III.13. (B), the SEM image shows a dense structure with cracks, less homogeneity. It seems that the Ti concentration increased with the increase of number of layers to 8 films. However, it can be observed that the structure contains many cracks.

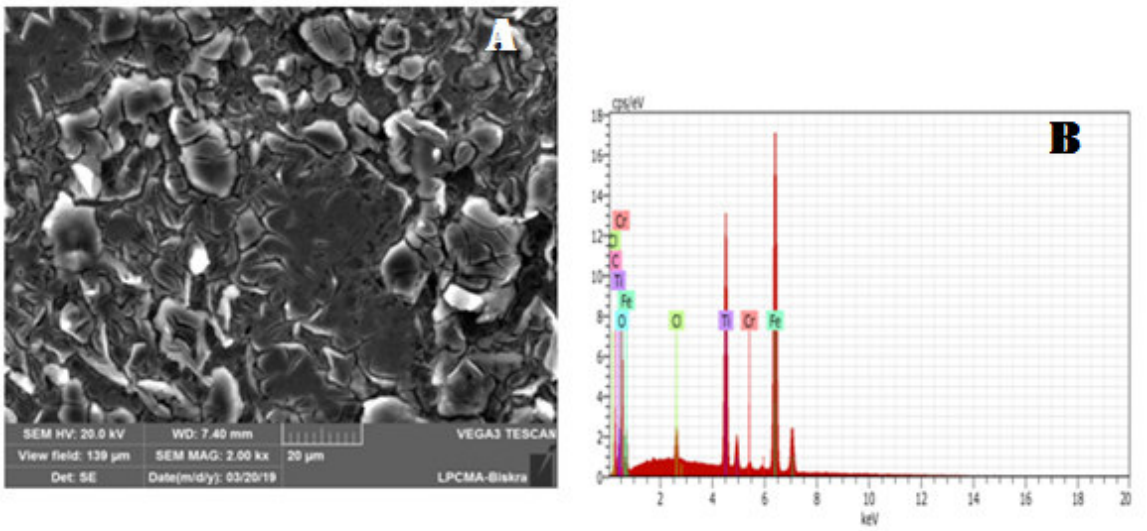


Fig. III.13 SEM/EDX images for Ti/TiO_2 multilayer with 8 films deposited on stainless steel.

The EDX confirms that always Ti and O exist and with a big amounts. Because of the increase of number of layers and consequently, the increase in Ti concentration (Table III. 21).

Table III.21: EDX results of Ti/TiO_2 with 8 layers

Element	AN	[wt%] unn	C $_{norm}$ [wt%]	C $_{Atom}$ [at%]
O	8	20.56	43.00	36.99
Ti	22	17.08	57.45	10.27

III.3.2. Cross section of the Ti/TiO_2 multilayer:

According to Fig. III.14 displays the SEM morphology of the cross-section of the film deposited on stainless steel substrate; the images show that multilayer with 4 (A) and 6 films (B) structures were characterized as having more roughness, good adhesion at the interface between the substrate and the Ti/TiO_2 multilayer in agreement with a thermal choc test. Furthermore, the Ti/TiO_2 multilayer coatings thickness was increased with the increase of number of layers compared to the monolayer thin films samples. It was around 12 µm and 25 µm respectively were controlled by the precursor solution, viscosity and the rotating speed [59].

The structure showed the heterogeneity and it is not so dense that the layers appear on top of each other in an almost overlapping manner in a multi-layered form with spaces.

It is thought that the interuption of the film growth by alternating depositon of Ti and TiO_2 is producting an increase in the roughness.

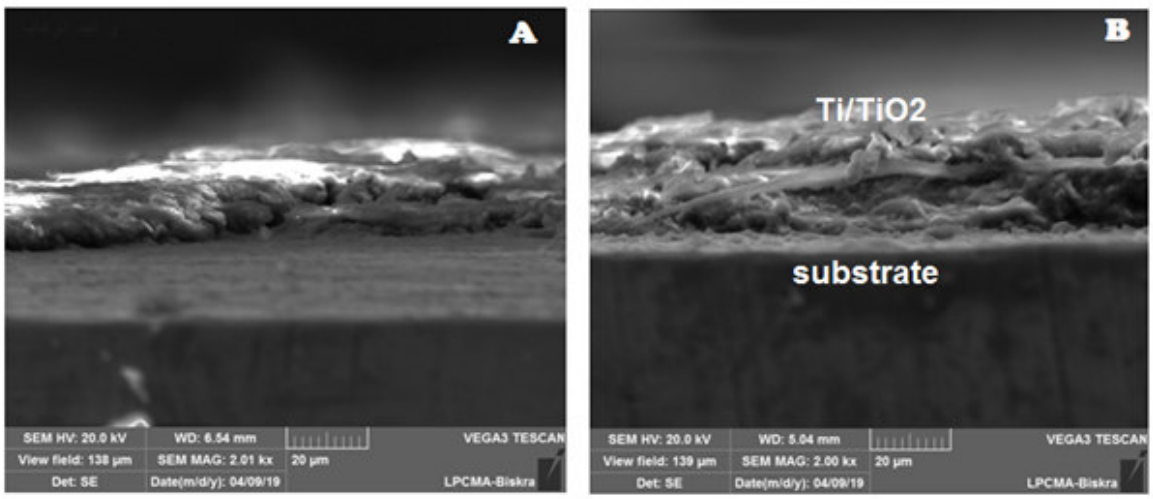


Fig. III.14 Cross-section SEM images for Ti/TiO_2 multilayer with 4 and 6 films (A):4 layers and (B):6 layers

III.3.3 Structural characterization of Ti/TiO_2 multilayer coatings:

We characterized non-annealed multilayer specimens (2, 4, 6 and8) by XRD in the same conditions; we have observed that no peak was appeared because the TiO_2 structure is amorphous. Always some peaks of substrate (iron) were detected in 2Θ=45 and 63° (Fig. III.15).

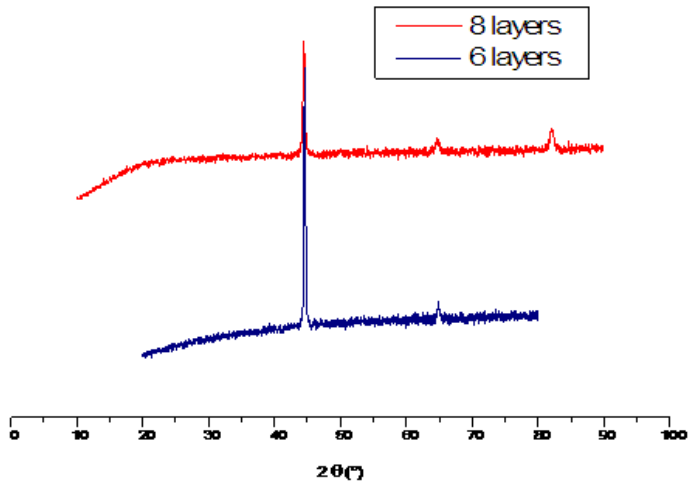


Fig.III.15. X ray Diffractogrammes of Ti/TiO_2 multilayer coatings with 6 and 8 layers.

According to the results obtained from this experience, we can conclude that Ti/TiO_2 multilayer coatings with 6 films gave excellent results in morphological proprieties compared to the multilayer with 2, 4 and 8 films.

Conclusion:

Ti/TiO_2 multilayer coatings were prepared with deferent number of films (2, 4, 6 and 8) on stainless steel substrate by Electrodeposition and sol gel spin coating methods respectively. The SEM and XRD characterization show good results in Ti/TiO_2 multilayer with 6 films compared to others.

It is known that the properties of the coatings are affected not only by the chemical composition and the microstructures, but also by the surface morphology of the films.

Introduction:

In this chapter, we have studied the effect of number of layers on the rate of corrosion of Ti/TiO_2 coatings on stainless steel in acidic environment 10 wt. % (HCl). The multilayers studied are 2, 4, 6 and 8 films.

The corrosion tests are carried out by the Voltalab potentiostat in the laboratory of Valorization Technologies of Saharan Resources, University of Eloued. The potentiodynamic anodic polarization method was used to determine the results of the corrosion resistance.

IV.1. Electrochemical tests:

Corrosion resistance was evaluated by electrochemical measurements using Voltalab PGZ 301 potentiostat. The potentiodynamic anodic polarization test was performed in a three-electrode cell where the specimen was connected to a working electrode; auxiliary and reference electrodes were platinum and saturated calomel (SCE), respectively. Scans were conducted from -100 to 100 mV with a 1 mV/min potential sweep after 10min of immersion in 0.1 M HCl electrolyte. Corrosion potential (E_{corr}) and corrosion current (I_{corr}) were obtained by means of Tafel's extrapolation, using Volta master 4 software.

The plots of polarization curves made from the most commonly used techniques in electrochemistry to determine the polarization resistance and the rate of corrosion. Tafel plots allow us direct access to the values of current densities.

IV.2. Potentiodynamic polarization measurement of monolayer coatings:

Fig. IV.1 shows Tafel plots obtained for a stainless steel substrate (a), Ti (b) and TiO_2 (c) monolayer coatings in 0.1M HCl solution. Table IV.1 summarizes electrochemical parameters and corrosion rates.

It is known that the stainless steel metal presented the most noble than the titanium and titanium dioxide monolayer. Therefore, it is logical to find lower corrosion current density for the substrate than the other monolayer films.

We can see that the titanium dioxide thin film have better corrosion resistance (0.1380 mA/cm^2) than the titanium deposit (0.4 mA/cm^2) because the titanium is an extremely oxidizable metal, in the series of standard electrochemical potentials. It is therefore not a noble metal, and it is formidable in corrosion resistance due to its reactivity i.e. it is able to form the passive layer (TiO_2) on the surface having a dance microstructure (see chapter I).

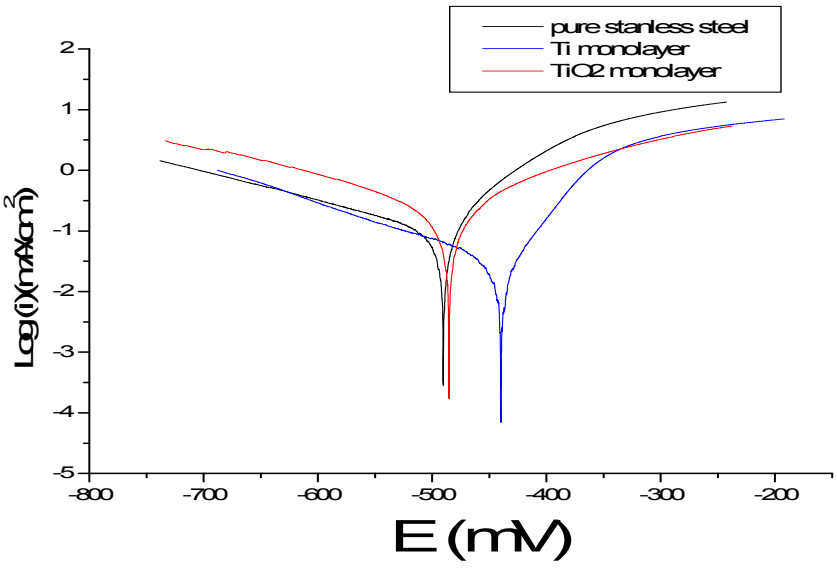


Fig. IV.1 Potentiodynamic polarization behavior of stainless steel, Ti and TiO_2 monolayer in HCl solution

Table IV.1. Potentiodynamic polarization data of SS substrate, Ti and TiO_2 coatings.

Specimens	E_{corr}(mV)	I_{corr}(mA/cm^2)	R_p (Ohm.cm^2)	CR (mm/year)
Pure SS	-490.3	0.1023	232.02	1.196
Ti monolayer	-455	0.4	42.38	1.842
TiO_2 monolayer	-474.4	0.1380	212.9	1.614

IV.3. Corrosion resistance of Ti/TiO_2 multilayer coatings:

The electrochemical performance of coated stainless steel was investigated using potentiodynamic polarization measurements in acidic environment. Figure IV.2 shows the curves of logarithmic polarization for the coating specimens tested in 10 wt% HCl and the curve of uncoated stainless steel is also shown for comparison. The obtained values of corrosion potential E_{corr} and current density I_{corr} of all coated samples by Ti/TiO_2 multilayer are listed in Table IV.2

For the potentiodynamic polarization, I_{corr} is the critical parameter for evaluating the corrosion resistance of materials [37].

Corresponding corrosion rates are reported in Table IV.2 from the corrosion data, it may be noted that the corrosion rates of Ti/TiO_2 multilayer coatings decreases with increase in number of layers. In other words, multilayer coating tends to become dense without any

pores. Hence, it may be concluded that corrosion rate of multilayer coatings can be decreased with the increase of layers, and then decreased due to the interlayer diffusion [58].

Current density I_{corr} and absolute corrosion potential E_{corr} values are lower than those of coated specimens and uncoated stainless steel. Although the corrosion values are much higher than those relating to Ti/TiO_2 multilayers.

The bilayer Ti/TiO_2 specimen (Fig. IV.2.(b)) exhibited relatively the highest corrosion current density (0.1576 mA/cm^2) in 10 wt% due to the TiO_2 top layer and the porosity of the surface.

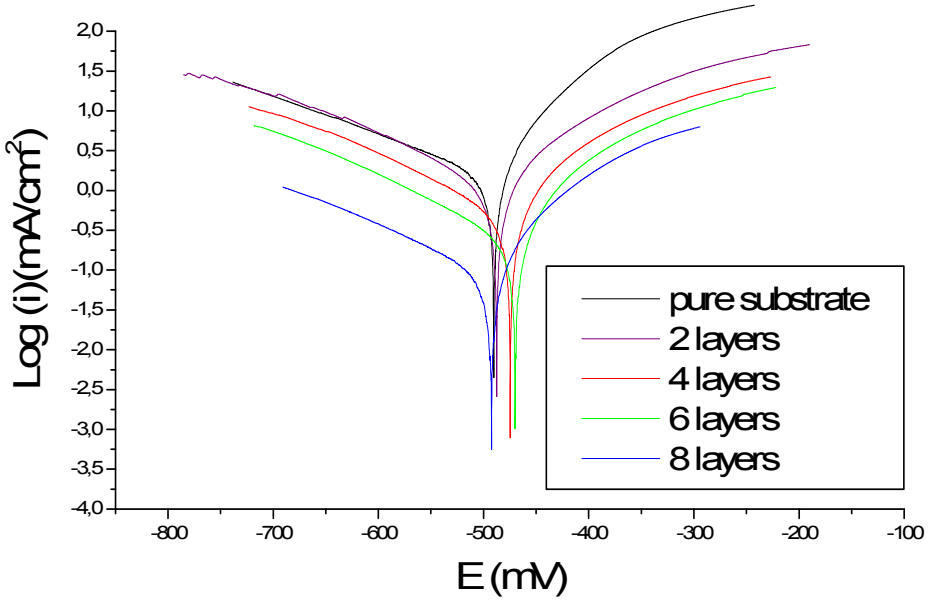


Fig. IV.2. Polarization curves of Ti/TiO_2 multilayer coatings with 2, 4, 6 and 8 films

The multilayer coatings with 4 films Fig. IV.2.(c) presented lower current density and more positive corrosion potential compared to the previous sample and also the corrosion rate decreased (from 1.842 mm/year for 2 layers to 1.614 mm/year for 4 layers). Corrosion potential and current density decreased for each thickness evaluated by the lower number of interfaces, thereby increasing their efficiency as a barrier. This was related to the shorter diffusion path, slowing corrosive medium diffusion toward the coating/substrate subsequent stainless steel substrate passivation interface. [15]

Corrosion rates of Ti/TiO_2 multilayer coatings with 6 films Fig. IV.2.(d) were found to be decreased, due to interlayer diffusion.

It may be inferred that multilayer Ti/TiO_2 coating, having 8 layers Fig. IV.2. (e) is the most corrosion resistant. It can be seen that this sample presented the lowest current density and the corrosion rate compared to the previous samples.

The multilayer Ti/TiO_2 coating succeffully protected stainless steel in a highly harsh environment tested in 10 wt% concentrated HCl solution. The reasons are:

The multilayer structure with a uniform thickness for each sub layer reduces the large stress in coating. (See chapter III).

The interfaces should block the propagation paths of the cracks. The multilayer coating has a combined enhancement effects from the toughness of TiO_2 sub layer. Thus, promising as the protective coating for stainless [37].

As the number of interfaces increased, more micro-pores and microcracks were blocked due to continuous re-nucleation [15].

Values compared to the substrate. Such a pattern was due to the formation of a dense and compact structure reducing the number of defects such as cracks, pinholes and pores within the coatings, thereby further restricting corrosive electrolyte diffusion.

The multilayer coating with 8 films corrosion resistance was better than others (see Table IV.2 for details of these coatings).

Table IV.2. Corrosion data of Ti/TiO_2 multilayer coatings

Specimens	E_{corr} (mV)	I_{corr} (mA/cm^2)	R_p (Ohm.cm^2)	CR (mm/year)
Pure SS	-490.3	0.1023	232.02	1.196
2 layers	-487.7	0.1576	42.38	1.842
4 layers	-474.4	0.1380	212.9	1.614
6 layers	-469.8	0.1216	58.97	1.422
8 Layers	-493	0.1052	67.72	1.320

Figure IV.3 presents the variation of E_{corr} as function as the nature of the films. We can see clearly that the film with 8 layers is the better one (more positive value). The pure substrate has absolute corrosion potential more than the films 2, 4 and 6 layers which confirm the nobility of the stainless steel than titanium or titanium oxide monolayer. We can also see that 2 layers is better than 4 and 6 layers thanks to the good morphology (absence of cracks).

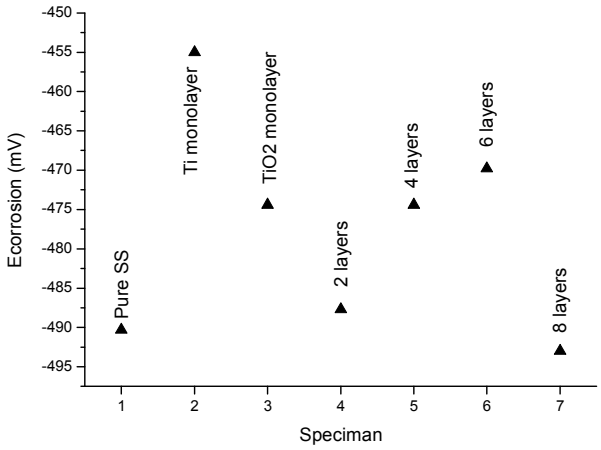


Fig. IV.3. corrosion potential as function as the number of layers.

Figure IV.4 represents the corrosion current density in terms of number of layers. We can observe that always the pure stainless steel has the lowest corrosion current density. Then, the film with 8 layers affords the best protection of metallic substrate against corrosion than the mono and multilayer with 2, 4 and 6. It can be seen clearly that Titanium monolayer presents higher current density, which confirm that, the increase in number of layer decrease the current density. These results show the effectiveness of the multilayer coatings in corrosion resistance.

In other side, according to the results we can show that the type of coatings in our work is the anodic protection.

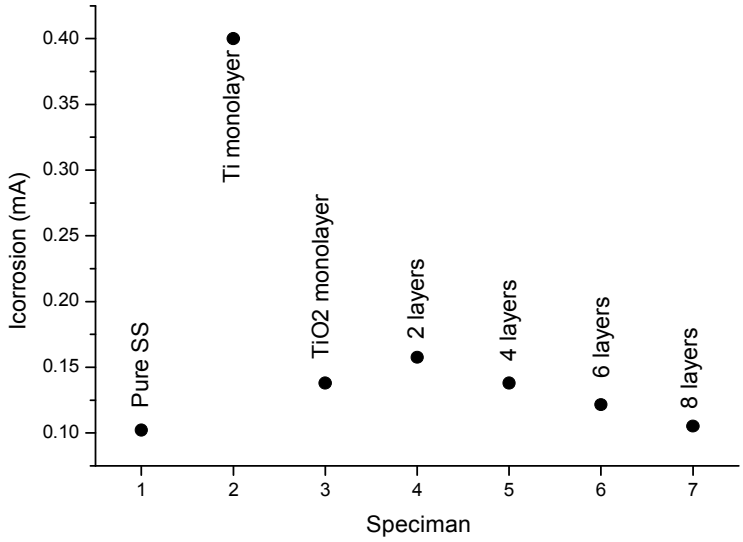


Fig.IV.4. Corrosion current density in terms of number of layers

In figure IV.5, we expressed the corrosion rate always in terms of nature of layers. We observe that the corrosion rate significantly decrease when we increase number of layers. The pure substrate recognizes the lowest corrosion rate due to its nobility. Thus, the Ti/TiO_2 coatings present smaller corrosion rate than others, which confirm that the multilayer coatings enhance and improve the corrosion performance and behavior as we have seen previously.

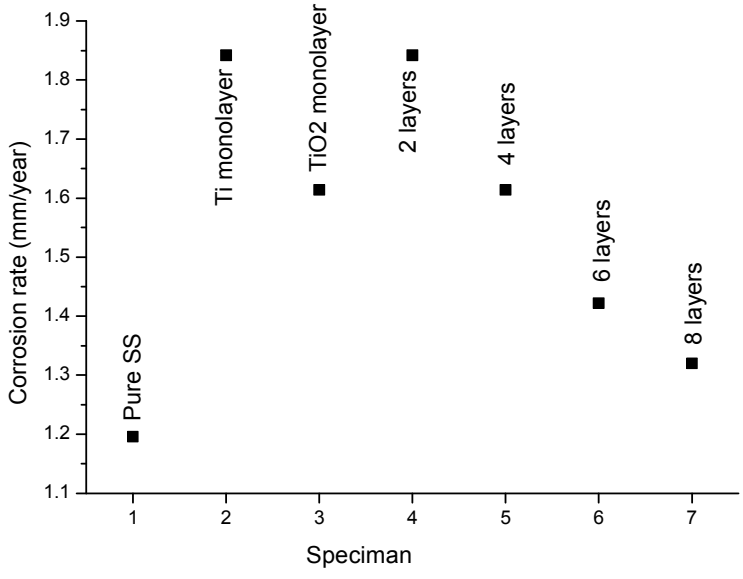


Fig. IV.5 Corrosion rate in terms of nature of specimens

IV.3. Mechanism of corrosion:

The efficacy of corrosion protection of the stainless steel substrate by multilayer coatings in contrast to homogeneous and dense coatings is attributed to the selective dissolution of several layers with alternatively varying composition [58]. When the layered coating is exposed to the corrosion medium, the top layer is exposed directly and is corroded first. The layers present beneath are safe until the breakdown of the topmost layer occurs. As the corrosive agent penetrates the lower layers, the corrosion product spreads laterally at the interface. Once that layer breaks down, the lower layer is exposed to the corrosive medium and this process repeats layer after layer. Hence, this process blocks or extends the path of the corrosive agent. Thus, if the number of layers (interfaces) are more, the corrosive agent takes a longer time to penetrate through the layers and then into the substrate.

IV.4. SEM study of Ti/TiO_2 mono and multilayer coatings:

Generally, structured multilayer coatings exhibit special improved properties due to the increased effect of surface/interface arising from the exceptional thickness of the layers [58].
Fig. IV.6. present the SEM images of Ti, TiO_2 monolayer and stainless steel after corrosion test.
SEM picture (Fig. IV.6. (A)) presenting uncoated stainless steel revealed that there are a few holes on the sample surface due to the corrosion resistance as we indicated in the previous discussion.

Fig.IV.6.(B) shows the Titanium monolayer thin film. We can see that the Ti morphology contained a lot of pores and pinholes on its entire surface. It has the lowest corrosion protection, may be because of its easily oxidation and reactivity.

The SEM results of TiO_2 monolayer thin film were investigated in Fig. IV.6. (C). It can be seen that the film exhibited the best corrosion resistance compared to the Ti thin film because it concluded relatively less pores and holes confirm the polarization result.

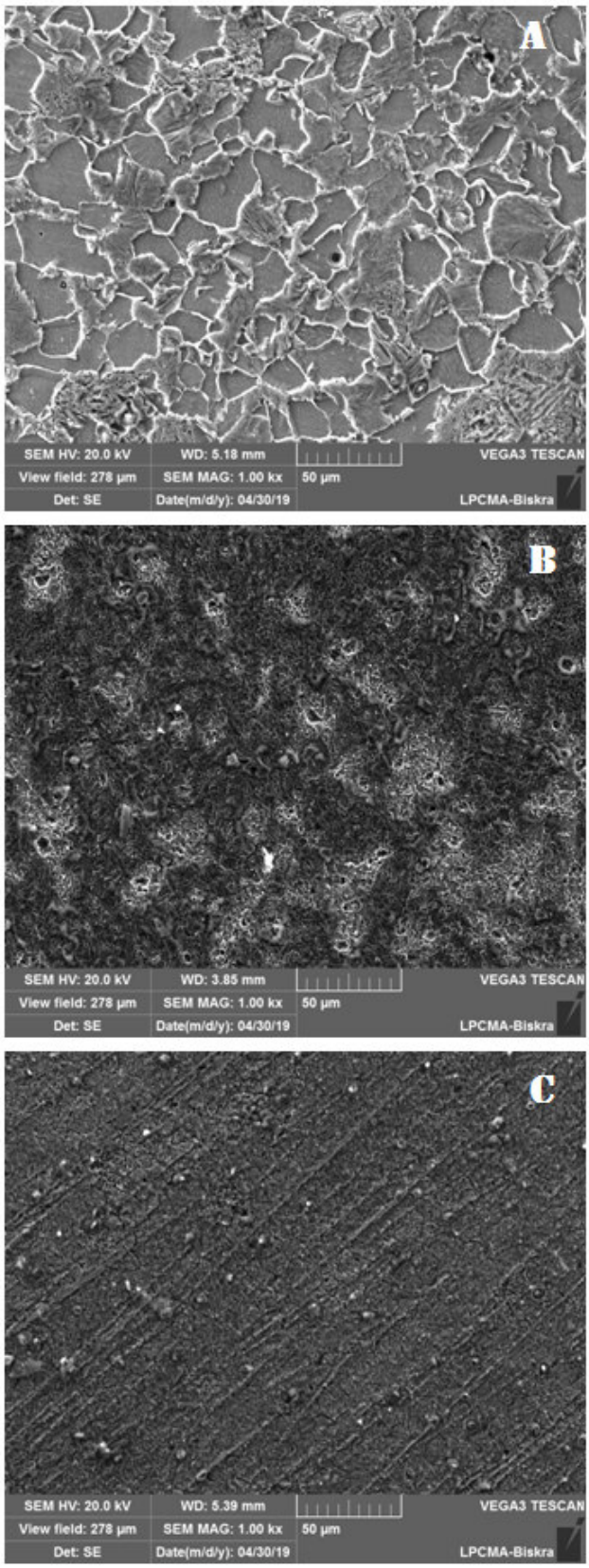


Fig. IV.6. SEM characterization of Ti, TiO_2 monolayer and stainless steel after corrosion test in 10 wt% HCl solution

Fig. IV.7. represents the SEM results of Ti/TiO_2 multilayer coatings after corrosion test in 10 wt% HCl solution.

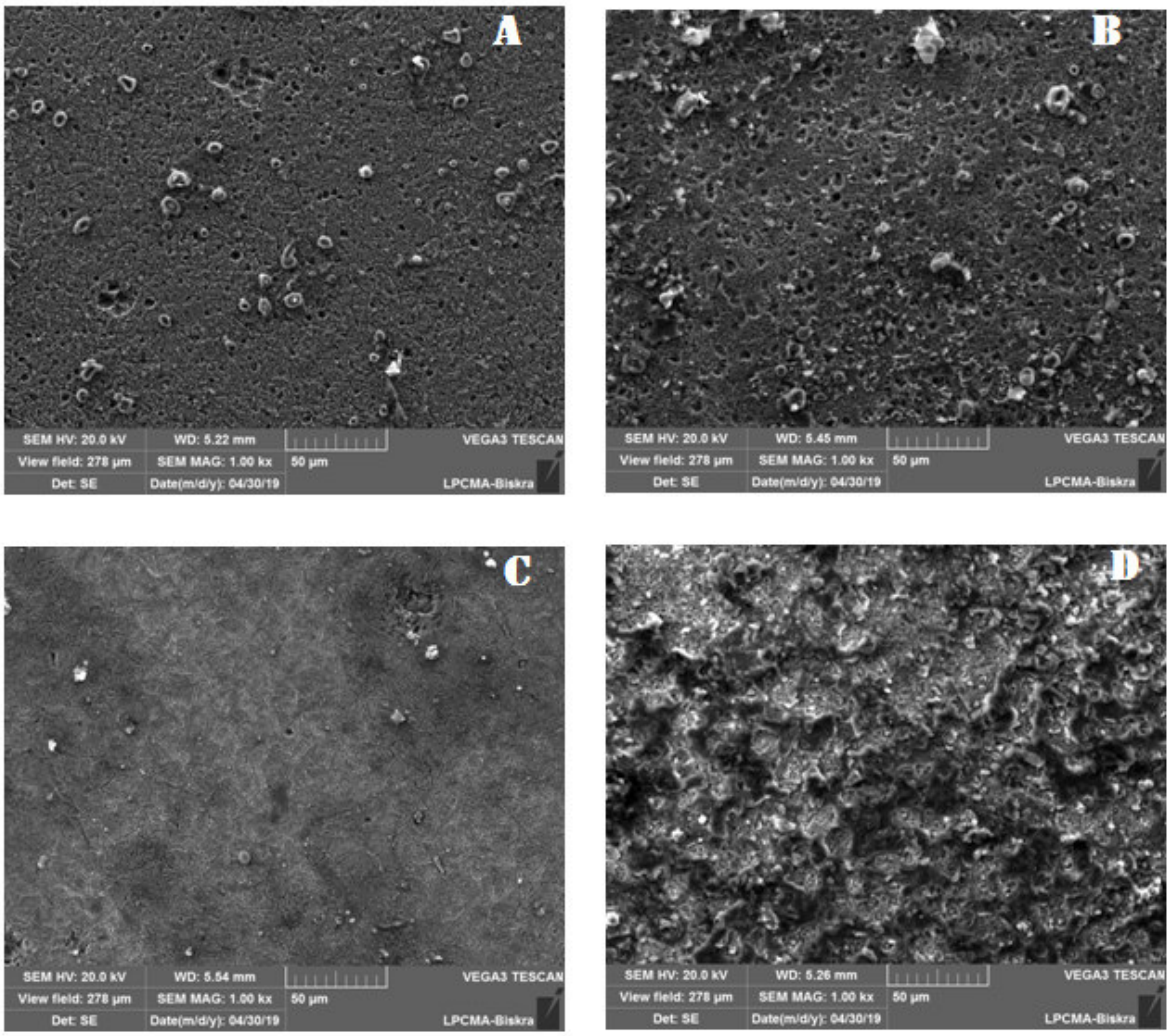


Fig. IV.7. SEM images for Ti/TiO_2 multilayer coatings with (A) 2layers, (B) 4 layers, (C) 6 layers and (D) 8 layers after corrosion test.

Figure IV.7. (A) showed the SEM results of Ti/TiO_2 multilayer with 2 films. We can note that the coating have been damaged by HCl solution. Few holes and micro pores were appeared after corrosion test. Then, we can say that the multilayer with 2 films had bad corrosion protection. This result can be related to structural defects (pores, pinholes and droplets) which favorite the pitting corrosion and eventually accelerate local corrosion of the coating.

Ti/TiO_2 multilayer coatings with 4 films were characterized by having the largest amount of micro-pores and pinholes compared to the previous film as it's shown in Fig. IV.7 (B). This corroded morphology probably is due to the corrosion process i.e. some pits of corrosion products were appeared or produced on the sub layer TiO_2 surface. These later were a source,

which led to cracks formation. Whereafter, the cracks can penetrate the oxide film and propagate into the beneath layer.

Ti/TiO_2 multilayer coatings having 6 films presented lower superficial damage, most of the area being preserved without visible corrosion products. It can be seen that the surface morphology was improved by increasing number of layers or interfaces, probably due to the less surface defects as cracks showed in this film and the decrease of the surface roughness can reduce the corrosion damage, Fig. IV.7 (C).

Fig. IV.7 (D) showed the SEM photo of Ti/TiO_2 multilayer having 8 films. We observed that this coating presented the most corrosion resistant. Pores and pinholes were relatively disappeared. The surface morphology and corrosion resistance were enhanced may be due to the large concentration of Ti, dense and compact structure (low cracks) which prevent leaking solution and HCl ions to the entire surface.

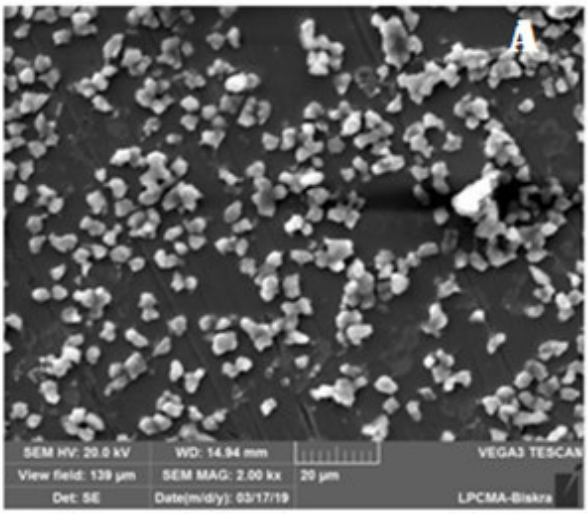
Roughness increased for this coatings suggesting that the outmost layer was probably dissolved during the corrosion test.

According to the debate above, we can conclude that the Ti/TiO_2 multilayer coatings having 8 films showed the greatest enhancement for corrosion protection. This result was confirmed by the polarization curves and SEM characterization.

CONCLUSION:

What we can retain in this chapter can be summarized in these points:

1- The stainless steel has better corrosion resistance compared to the titanium coated stainless steel due to its higher nobility.
2- The titanium dioxide monolayer thin film exhibited a great corrosion protection than titanium film.
3- The increase of layers number improves the corrosion resistance than the monolayer films.
4- This study confirms many researches that the multilayer coatings enhance the corrosion performance.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WD: 14.94 mm
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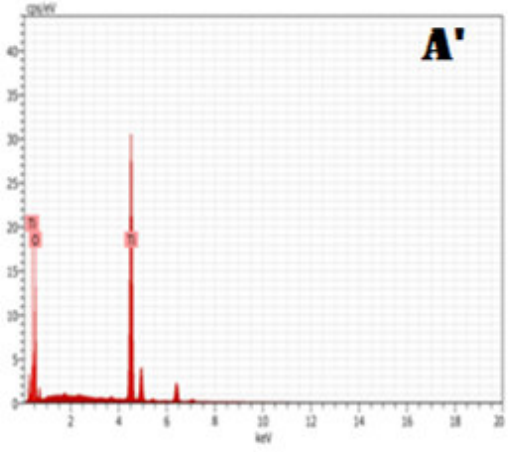
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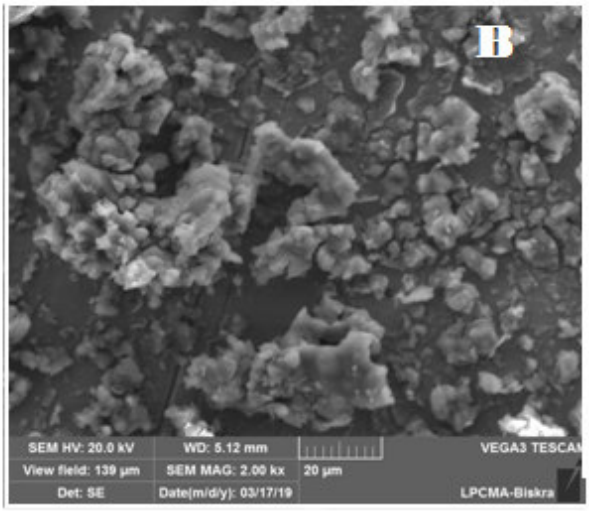
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SEM HV: 20.0 kV
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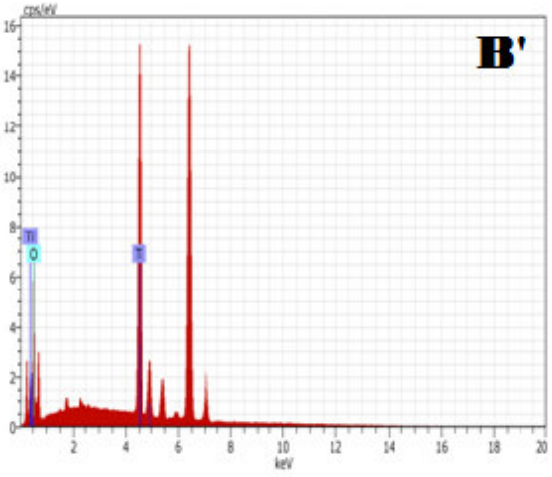
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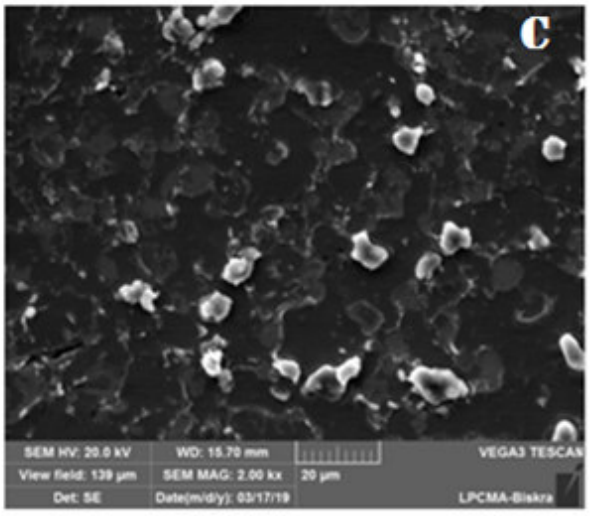
C
SEM HV: 20.0 kV
WD: 15.70 mm
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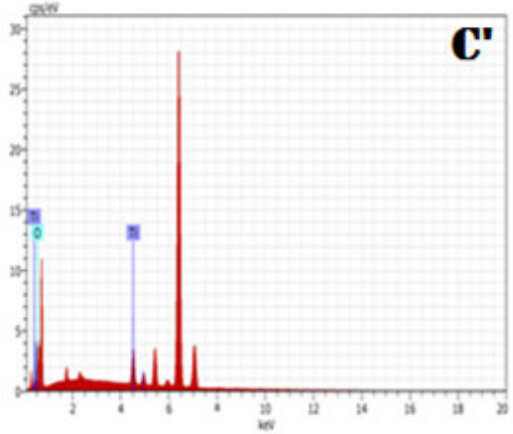
C'
cps/eV
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Contents

Chapter II

Experimental methods

Chapter III

Optimization of deposit parameters

Chapter IV

Results and discussions: corrosion behavior

Dedications

I dedicate this work to:

My parents and my family

To my grandmother: Haja Khoukha

To my teachers one even by his name

To whom did I know how to find them and taught me not to waste them. My friends

Raouia

I modestly dedicate this work to:

My father and mother who are very dear

My brothers: Rabie and Hatem

My sisters: Hanin, Amani and Loudjain

The whole family, as well as all my daughters, uncles, cousins,

All my teachers Specifically Pr. Dr. Chala Abdelouahad and all those who participated from near and far in order to carry out this scientific research, as well as all my friends.

Kheloud

General conclusion

The theme of this research is the optimization of Ti/TiO_2 multilayer deposition parameters for anti-corrosion applications. The problem in question is to study the effectiveness of these coatings in the protection against corrosion. We expect to have multilayers that have a high resistance against corrosion. The main purpose of this study is to see the possibility of the use of multilayer deposits for corrosion protection purposes and especially in the industry that suffers from the phenomenon of corrosion**.**

In our work we used two deposition techniques: spin-coating gel sol to deposit titanium dioxide TiO2 and electroplating to deposit titanium Ti both on steel substrates. The deposit parameters by the two techniques were optimized. These are: spin speed, deposition time for spin coating; and the concentration of the bath, the deposition time, the temperature and voltage for electroplating. The structural characterization was made by X-ray diffraction (XRD), while the morphology and chemical composition were defined by scanning electron microscopy (SEM) and dispersive energy spectrometer (EDX).

2, 4, 6, and 8 layers of metal /oxide layer coatings Ti / TiO_2 type were also realized to see the performance on corrosion protection. For this, corrosion tests were carried out on mono and multilayers coatings in a 0.1M HCl solution by electrochemical polarization.

The main results obtained in our study show that:

- All the deposit coatings presented a very good adherence with substrate.
- XRD and SEM analysis of TiO_2 thin films show that films exhibited a good, morphology and amorphous structure in the optimal conditions which are 5000 rpm, 45 s and 0.5 Mol/L of solution concentration.
- SEM and XRD investigations confirmed that the obtained Ti thin films gave best results in morphology and chemical composition at room temperature, 15 V and 5 minutes.
- SEM and XRD characterization show great results in Ti/TiO_2 multilayer with 6 films compared to others in morphology properties.
- Ti/TiO_2 multilayer coatings exhibited better corrosion resistance than Ti and TiO_2 monolayer thin films.
- The polarization curves and Tafel's plots confirmed that the corrosion resistance has been improved or enhanced by Ti/TiO_2 multilayer coatings; the Ti/TiO_2 multilayer with 8

films exhibited the best corrosion protection because of the increased number of interfaces or layers and the decrease of cracks and stresses so The corrosion current density I_{corr} was decreased with the increase of number of layers.

Perspectives:

- Study of the interfaces phenomena and its influence on corrosion resistance.
- Using more sophisticated techniques such as XPS, SIMS for the determination of layers composition and corrosion products.
- Possibility to increase the number of multilayers in order to study their corrosion behavior.
- Use of PVD methods to elaborate multilayer films.

General introduction

Corrosion is a naturally occurring phenomenon commonly defined as the deterioration of a material (usually a metal) that results from a chemical or electrochemical reaction with its environment. Corrosion can cause dangerous and expensive damages to everything from vehicles, home appliances and wastewater systems to pipelines, bridges and public buildings, unlike weather related disasters. These phenomena will happen with a metal: uniform thickness loss, pits, cracks, and blistering….etc. We have to keep in mind that many corrosion phenomena influence such important functions of metallic equipment as mechanical and electrical properties. However, there are time-proven methods to prevent and control corrosion that can reduce or eliminate its impact on public safety, the economy and the environment. One of these methods occurred for protection against corrosion is thin films. Thin films are very important because they offer the potential for low cost processing with minimal material usage while fulfilling application requirements. Coatings are a field of the utmost importance in today's materials science, electrical engineering, applied solid-state physics and industrial applications in microelectronic, computer, manufacturing and physical devices. Thin films have different forms such as: composites, multilayer films, ceramics, graphite…etc. Among of various systems we are going to study multilayer coatings, which present a new technology of thin films in last twenty years.

In our work, we will optimize Ti/TiO_2 multilayer films deposition parameters and their corrosion behaviour. We will also use these films deposited by sol gel-spin coating and electrodeposited methods to protect the stainless steel X70M psl2 substrates. The aim of this study is to show the possibility of using the Ti/TiO_2 multilayer films for protective purposes especially in industry that suffer from the corrosion phenomena. This topic poses a big issue: Does these coatings have a great effectiveness in the protection against corrosion? Then we expect to get multilayer films that have high corrosion resistance.

This research will contain four chapters in addition to an introduction and general conclusion.

Chapter 1 will contain bibliographic synthesis in relating of multilayer coatings and the results obtained from many researchers in this field.

Chapter 2 is reserved to the description of experimental methods used in the elaboration and characterization of our samples.

In chapter three, we present the optimization of coatings parameters of Ti and TiO_2 monolayer and the realization of Ti/ TiO_2 multilayer coatings.

Finally, Chapter 4 studies the corrosion behaviour of Ti/TiO_2 multilayers by potentiodynamic methods.

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