Study of Protection of Some Metals and Alloys from Corrosion Using Nanoparticals

By

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Study framework

The current study was protection of corrosion by using nanomaterial Silicon dioxide ($SiO_{٢}$) was used to coat specimens of aluminum, carbon steel, galvanized steel, and stainless steel. the coated specimens subjected to nanoscopic inspections; i.e. Atomic Force Microscope (AFM),Scanning Electron Microscope(SEM), Energy dispersive x-ray(EDX) ,and x-ray photoelectronic spectroscopy(XPS), and finally the corrosion protection efficiency inspection of each specimen in artificial sea water (٣,٥٪NaCl) at R.T.(~٢٥ºC) using potentiostatic techniques with three electrodes cell.

Aim of the study

In this research a new fast growing field of using nanomaterial has been chosen, that is coating metal and alloy surfaces with such smart material to enhance corrosion protection capability.

Abstract

The exclusive properties of nanomaterials, bring on to create different advanced applications incepting from small domestic to advanced electronics devices.

Protective Coatings

Protective coatings are the most widely used corrosion control technique. Essentially, protective coatings are a means for separating the surfaces that are susceptible to corrosion from the factors in the environment which cause corrosion to occur.

There are several methods used for surface modifications of materials. The following techniques are few used for applying coatings on metals:

a. ***Electroplating**:* metals and alloys can be plated on a conducted substrate that acts as a cathode. Ceramics and plastics need to be treated before they can be electroplated. The metal cations are suspended in solution and reduced by an external current passing through the electrolyte. The cation concentration, both temperature and current density determine the deposition rate [٥].

b. ***Electroless plating:*** the process of deposition of metal ions from electrolyte solution onto the substrate, when no electric current is involved and the plating is a result of chemical reactions occurring on the surface of the substrate [٦].

c. ***Hot dipping**:* designates the coating application process of immersing a metal substrate in a molten metal bath, which is usually aluminum, zinc, tin, or lead. Since the applied coating consists of a molten metal, the melting temperature of the metal coating should be relatively low [٧].

d. ***Physical Vapor Deposition (PVD)**:* the process involving vaporization of the coating material in vacuum, transportation of the vapor to the substrate and condensation of the vapor on the substrate surface [٣٢]. The process proceeds atomistic ally and mostly involves no chemical reactions. The thickness of the deposits can vary from angstroms to millimeters [٨].

e. ***Chemical Vapor Deposition (CVD):*** The process, in which the coating is formed on the hot substrate surface placed in an atmosphere of a mixture of gases, as a result of chemical reaction or decomposition of the gases on the substrate material [٦].

f. ***Thermal spraying***: Deposition of the atomized metal at high temperature and delivered to the substrate surface in a high velocity gas stream [٦].

g. ***Electrophoretic Deposition:*** (EPD) is a simple method for the formation of a coating on an electrode using a stable suspension in a direct current (d.c.) field [٩, ١٠]. EPD is a two-step process: (١) charged particles suspended in a liquid migrate toward an electrode under the influence of an electric field (electrophoresis) and (٢) the particles deposit on the electrode, forming a relative dense and even film [١١]. EPD methodology is one of a choice in application of this work and will be discussed in more details(١,٦)

h. ***Sol Gel:*** The sol gel process is a wet-chemical technique for the fabrication of materials (typically metal oxide) starting either from solution or colloidal particles to produce an integrated network (gel) [١٢]. Sol-Gel methods are the wide range of accessible shapes, which include fine powders, fibers, thin films, xerogels, and aerogels [١٣]. This process will be discussed in details (١,٧).

Silicon dioxide ($SiO_{٢}$), was used to coat specimens of aluminum, carbon steel, galvanized steel, and stainless steel. the coated specimens subjected to nanoscopic inspections; i.e. Atomic Force Microscope (AFM),Scanning Electron Microscope(SEM), Energy dispersive x-ray(EDX) ,and x-ray photoelectronic spectroscopy(XPS), and finally the corrosion protection efficiency inspection of each specimen in artificial sea water (٣,٥٪NaCl) at R.T.(~٢٥ºC) using potentiostatic techniques with three electrodes cell.

AFM,SEM,EDX, and XPS inspections revealed a useful data on particle size ,shape, and surface elemental composition, Applying $SiO_{٢}$ applied by sol-gel controlled hydrolysis of teterethoxyortosilane (TEOS) ,produces a layer of particles in the range of ٤٤nm , The evaluation of established tafel plots revealed quantitative data on corrosion potential, corrosion current density, corrosion rate, weight loss, and penetration rate . The protection efficiencies (PE) were estimated from the available data for all coating types as listed below:

Aluminum:

SiO٢ sol-gel	> uncoated
٥٦,١٣٪	٠٪

Carbon steel:

SiO٢ sol-gel	> uncoated
٥٠,٤٢٪	٠٪

Galvanized steel:

SiO٢ sol-gel	> uncoated
٧٨,٤٧٪	٠٪

Stainless steel:

SiO٢ sol-gel	> uncoated
٣٤,٥٢٪	٠٪

It is clear that coatings applied enhanced corrosion protection, and the layers appled by the sol gel approach (method) give always excellent protection.

Introduction and Literature Survey

١,١. Corrosion Concepts

The word **Corrosion** stands for material or metal deterioration or surface damage by chemical or biological agents. Corrosion is a chemical or electrochemical oxidation process, in which the metal transfers electrons to the environment and undergoes a valence change from zero to a positive value. The environment may be a liquid, gas or hybrid soil-liquid. These environments are called electrolytes since they have their own conductivity for electron transfer [١, ٢].

Corrosion of metallic materials can be divided into two main groups.

a. Wet corrosion, where the corrosive environment is water with dissolved species. The liquid is an electrolyte and the process is typically electrochemical.
b. Dry corrosion, where the corrosive environment is a dry gas. Dry corrosion is also frequently called chemical corrosion [٣].

Electrochemical corrosion is the dissolution of a metal through the oxidation process. Oxidation and reduction chemical reactions occur simultaneously and are interdependent. Corrosion only occurs at the site of the oxidation reaction. Oxidation involves the loss of electrons; reduction involves the gain of electrons. The electron transfer between oxidation and reduction reaction sit establishes the electrical current required for electrochemical corrosion [٤].

١,٢. Concepts of Sol-Gel Process

A SOL: is defined as colloidal suspension in a liquid of solid particles, which dimensions, in the range of ١ to ١٠٠ nm, are small enough to ignore the gravity force. In this way the interaction between the particles are dominated by short – range forces (i.e. Vander Waals and superficial charges) [١٤].

A GEL: is a colloidal or polymeric solid containing a fluid component which has an internal network structure is highly dispersed [١٥].

Alcogel: is a wet monolithic gel, its pore liquid is primarily alcohol-based.

Xerogel: is a gel (or alcogel) dried by evaporation of its pore liquid under normal conditions (ambient pressure), shrinkage during drying is often occurring.

Aerogel: is a product of the supercritical (or hypercritical) drying, where the wet gel is placed in an autoclave and dried under supercritical conditions, there is no interface between liquid and vapor, so there is no capillary pressure and relatively little shrinkage [١٦].

Sol gel divided into

a. Aqueous sol gel process: It is an economical and ecological process. Agglomeration is a major drawback
b. Non aqueous sol gel process: It is expensive with limited ecological and agglomeration properties [١٧].

Sol gel coatings are thin, ranging from nano meter to several micro meters. Sol-Gel derived films can be deposited on metals to improve their resistance to oxidation and corrosion, abrasion and scratch resistance and to modify their surface properties [١٨]. The properties of sol–gel-derived coatings can be engineered at the molecular level for optimum physical and chemical properties such as better adhesion, improved hydrophobicity, low permeability, as well as texture, morphology, optical properties, and other characteristics. These materials can also be easily processed in the form of a coating using inexpensive, environmentally-friendly, and technologically-compatible methods [١٩, ٢٠].

A large number of factors have to be considered in proceeding with sol–gel processing to fabricate an aimed material.

a. The composition of the starting solution which represents for the type (alkoxide type, pH, water/alkoxide ratio , solvent nature and stabilizers) [٢١].
b. The condition of the sol–gel reaction such as temperature, time and atmosphere and the condition of heat treatment such as heating rate and temperature [٢١].
c. The rate of solvent evaporation [١٧].
d. Concentration of components, additives and catalyst [٢١].
e. Sequence of addition [٢٢].

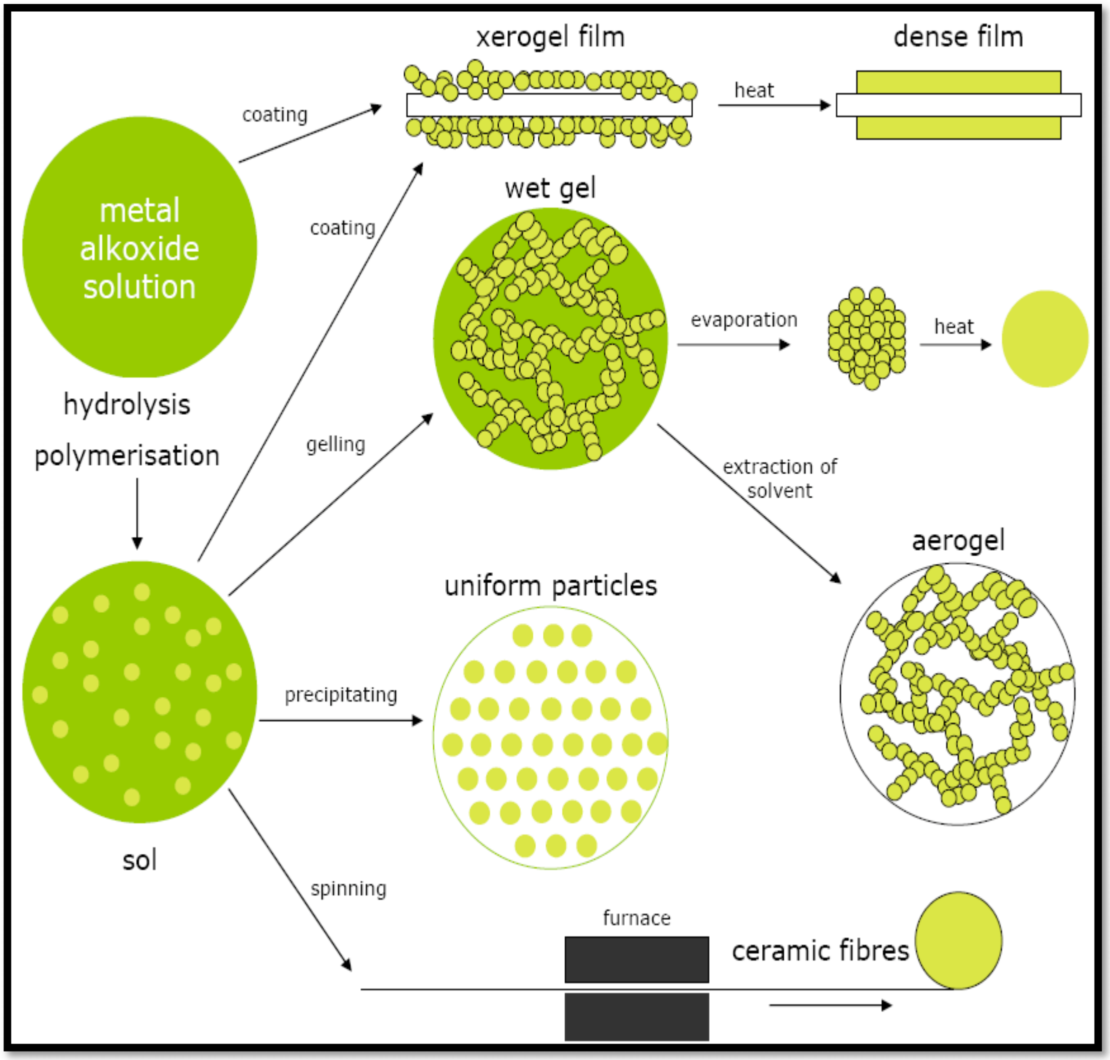


Figure (1.1) The sol-gel process proceeds through several chemical and physical processes [16].

Results and Discussions

In this chapter the following results will be presented and discussed in details:

١. The surface morphologies and compositions of coating type $SiO_٢$ appliedon carbon steel specimens, as representative of all four metals (aluminum, carbon steel, galvanized steel , and stainless steel),using different analyzing techniques; atomic force microscope (AFM), scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX), and X-ray photoelectron spectra (XPS).

٢. The corrosion protectiveness of the above mentioned layers applied on metal specimens of (aluminum, carbon steel, galvanized steel, and stainless steel) in artificial sea water (٣,٥٪ NaCl) at R.t. (~ ٢٥ºC), in comparison with the same uncoated specimens by Tafel extrapolation method using advanced potentiostat with three electrodes standard cell.

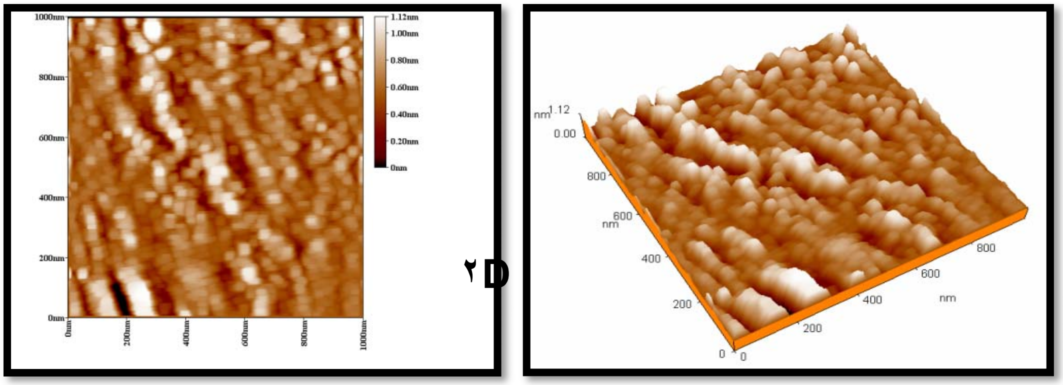
٣,١. The Surface Morphology and Composition of the Coated Layer:

The surface morphology of a protective coated layer plays a great role in enhancing the corrosion protection efficiency. More uniform grains may lead to more inhibition results, ٢D and ٣D views. AFM images for all applied layer were estimated in addition to the statically determining the particles size distribution. SEM images gave additionally more clear shape of the clustering and particles laid on metals surfaces some less accurate particle size measures conducted using image processing software (WCIF Imager J).

The coverage integrity of the coated metals surfaces were established by the elemental analysis using (EDX/SEM), while the surface chemical composition of the bulk films was determined by (XPS).

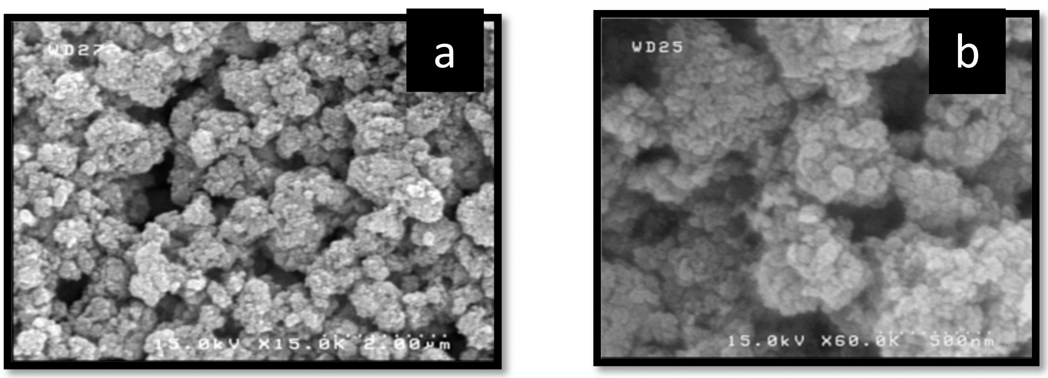
٣,١,١. The Surface Morphology Analysis by AFM & SEM

Figure (٣,١) show the topographic structures in ٢D and ٣D views for the layers; sol-gel $SiO_٢$, the types seem to be very smooth surfaces and high homogenized and sizes around (٤٢nm). The particles size distribution reports conducted via AFM analysis are tablated in appendix A .



Figure(3.1) 2D and 3D views of AFM image of sol-gel-SiO_2 nanoparticles applied on carbon steel.

The SEM images(x١٥,٠٠٠ and x٦٠,٠٠٠) for the sol- gel -$SiO_{٢}$ layers showed a similar morphology to AFM images but clustering shape like observed led to the formation of highly agglomerated nanoparticles (cluster mass is made up of small particles) which are coherent together. The size of smallest cluster was around ٣٠ nm (two particles).



x ١٥,٠٠٠ **x ٦٠,٠٠٠**

Figure.(3.2) SEM image of Sol - Gel-SiO_2 nanoparticles applied on carbon steel a)x15,000,and b)x60,000.

Table (3.1) Chemical elements of the SOL-GEL SiO_2/carbon steel.

Element	Intensity	Weight%	Atomic%
C	٠,٢٩٦٩	٣,١٥	٥,٦٥
O	١,٠٥٣٩	٥١,٠٩	٦٨,٨٧
Na	٠,٤٢٣٠	٠,٣٩	٠,٣٧
Si	٠,٦٩٦٥	١٩,٧١	١٥,١٤
S	٠,٧٠٣١	٠,٠٦	٠,٠٤
Cl	٠,٦٧٦٢	٠,١١	٠,٠٧
Ca	٠,٩٨١٣	٠,١١	٠,٠٦
Fe	٠,٨٦٥٧	٢٥,٣٨	٩,٨٠
Totals		١٠٠,٠٠	

More evidence for the existence of a continuous layer of SiO٢ was revealed also by the XPS spectrum as shown in figure (٣،٣).

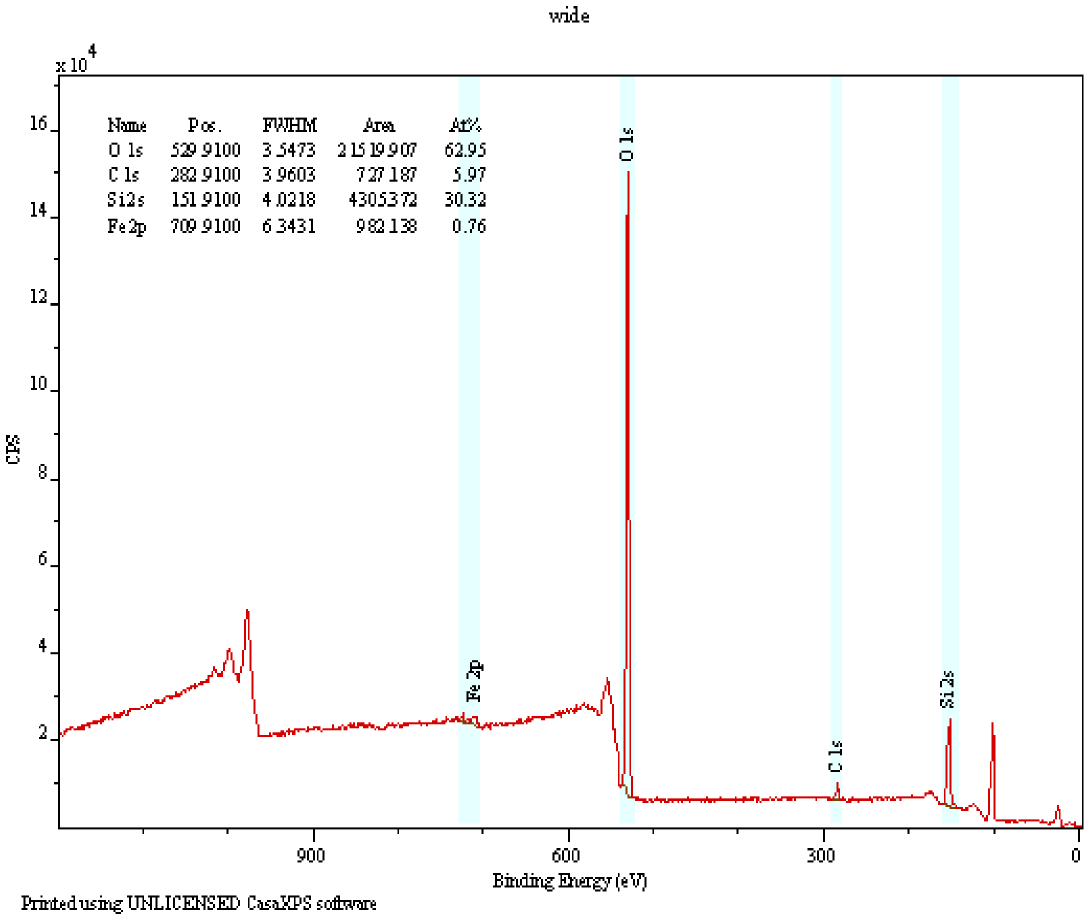


Figure (3.3) XPS spectrum of the SiO_2 applied on carbon steel.

The XPS spectrum of prepared $SiO_{٢}$ containing layers indicates that the elements of Si, O and Fe were the major detectable elements. The Si and O elements result from the silicon dioxide and $H_{٢}O$, and the Fe comes from the metal base. The binding energies of the Si ٢s, O ١s, C ١s and Fe ٢p were observed approximately (١٥١ ev, ٥٣٠ ev, ٢٨٢ ev, and ٧٠٩ ev) respectively ,appendix B١.

٣,٢. Corrosion Protectiveness Study:

The corrosion protection properties of all applied nanostructured layers on four types of specimens; Aluminum, Carbon Steel, Galvanized Steel, and Stainless Steel, in artificial sea water (٣,٥٪NaCl) at R.t. (~ ٢٥ºC). They were established using electrochemical method via Tafel polarization curves.
The layers of; $SiO_{٢}$, were applied sol-gel.

The measurements of each metal or alloy which will be presented in the following section will includes; corrosion potentials (E_{corr}), corrosion current densities (I_{corr}), corrosion rates (CR), and penetrations rates (PR).

Protection efficiencies (PE) of all types of coating estimated by comparison with the measurements of the uncoated surface of each type of specimens using equation (١,١٩):

$$PE = \frac{(I_{cor})_{uncouted} - (I_{cor})_{coated}}{(I_{cor})_{uncouted}} \times ١٠٠$$

٣,٢,١. Corrosion Protectiveness of Aluminum Specimens.

The applied nanostructured coating mentioned above on aluminum samples showed different degrees of protection capabilities in comparisons with the uncoated aluminum specimens in the saline environment used (٣,٥٪NaCl).

The corrosion potentials seemed to be little affected by the type of coating, they ranged between -٦٧٣ and -٧١٣ mv, silica applied by the sol-gel procedure showed more than ٥٠٪ PE with a results similar to a previous work on self-assembled nano-phase silane-based particle coating prepared through sol-gel technique [٢٧]. Table (٣,٢) shows all measurements and calculations conducted from Tafel curves, appendix C١. Figure (٣,٤) shows the polarization curves of aluminum coated with SiO٢ nanomaterials.

No.	State	E_{corr} (mv)	I_{corr} (μA/cm٢)	P%	W.l. (g/m٢ d)	Pent. (mm/a)
١	Uncoated	-٦٧٣,٧	٢٠,٦٣	-	١,٦٦	٠,٢٢٤
٨	SiO٢ sol-gel	-٦٣٩,٣	٩,٠٥	٥٦,١٣	٠,٧٢٨	٠,٠٩٨٤

Table (3.2) Corrosion protection efficiency (PE), corrosion potentials $E_{corr.}$, corrosion current density I_{corr} , weight loss and penetration loss of different aluminum coated specimens in 3.5%NaCl at R.T.

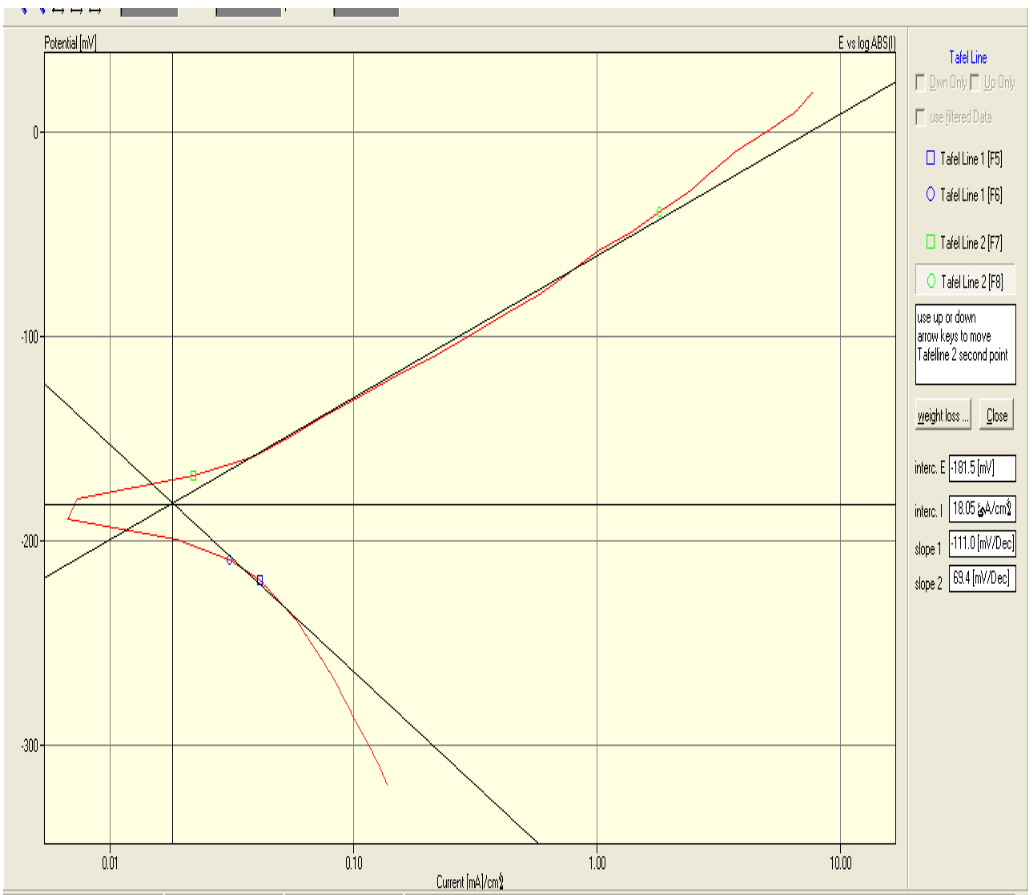


Figure (3.4) Polarization curve of aluminum coated with different nanomaterials in 3.5%NaCl.

٣,٢,٢. Corrosion Protectiveness of Carbon Steel Specimens

Protection capabilities of the nanomaterial coatings on carbon steel specimens in the brine environment (٣,٥٪NaCl) correlated to the type of coating applied.

Again the corrosion potentials seem to be little affected by the type of coating they ranged between -٤٩٤ and -٦٣٥ mv. Silica applied by the sol-gel procedure showed more than ٥٠٪ PE. A previous work on silica sol gel thin film applied on mild steel by spin coating showed that the protective barrier against wet corrosion is excellent [٢٨].

Table (٣,٣) show all measurements and calculations conducted from Tafel curves, appendix C٢. Figure (٣,٥) shows the polarization curves of carbon steel coated with different nanomaterials.

Table (3.3) The values of $E_{corr.}$, I_{corr} , W.l.and pent.l. of the carbon steel coated with different nanomaterials and different method.

No.	States	E_{corr} (mv)	I_{corr} (µA/cm٢)	P%	W.l. (g/m٢ d)	Pent. (mm/a)
١	**Uncoating**	-٤٩٤,٢	٤٢,١٦	—	٣,٣٩	٠,٤٥٩
٨	**SiO٢ sol-gel**	-٥٦٧,٨	٢٠,٩٠	٥٠,٤٢	٥,٢٣	٠,٢٤٣

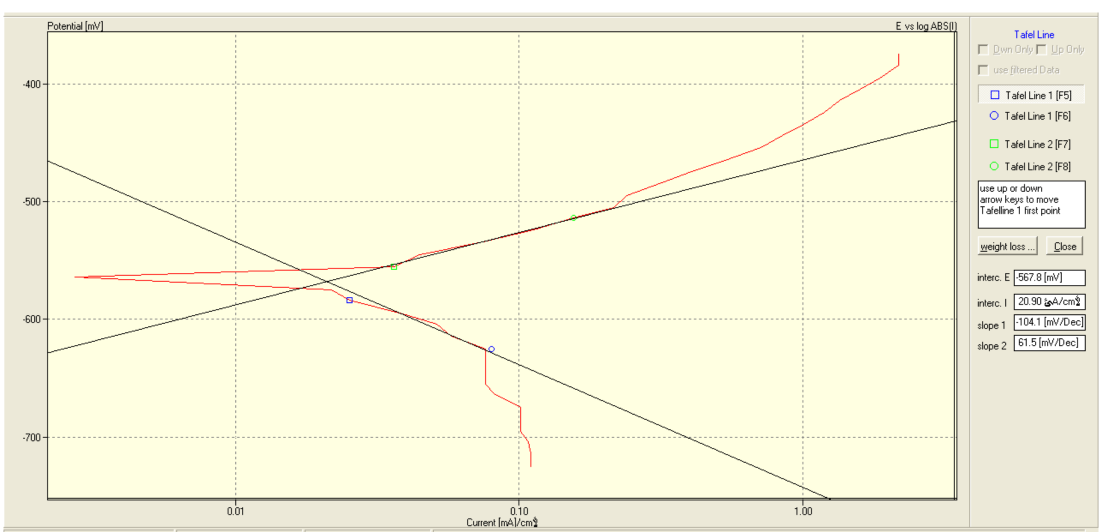


Figure (3.5) Polarization curve of carbon steel coated with different nanomaterials in 3.5% NaCl.

٣,٢,٣. Corrosion Protectiveness of Galvanized Steel Specimens

The enhancement of PE of the galvanized steel plays important roles in industries because the well known sacrificial acts of Zn [٧].

The corrosion potentials reveal to more affects by the type of coating. They ranged between -٨٥٠ and -١١٠٨,٤ mv, silica applied by the sol-gel procedure showed more than ٧٨٪ PE this may make TEOS have four -OR groups, which allow Si atom to form three dimensional SiO٢ network in the polycondensation reaction. Results similar to a previous work on organic-inorganic hybrid materials have been prepared from the hydrolysis of tetraethylorthosilicate and silanol-terminated polidymetilmetoxysilane using a sol-gel process [٢٩].

Table (٣,٤) shows all measurements and calculations conducted from Tafel curves. Figure (٣,٦) shows the polarization curve of galvanized steel coated with different nanomaterials.

Table (3.4) The values of $E_{corr.}$, I_{corr} , W. l. and pent.l of the galvanized steel coated with different nanomaterials and method.

No.	States	E_{corr} (mv)	I_{corr} (µA/cm٢)	P%	W.l. (g/m٢ d)	Pent. (mm/a)
١	Uncoating	-٩٤٦,٤	٤٩,٩٨	__	١٤,٦	٠,٧٤٩
٨	SiO٢ sol-gel	-١٠٢٩,١	١٠,٧٦	٧٨,٤٧	٣,١٥	٠,١٦١

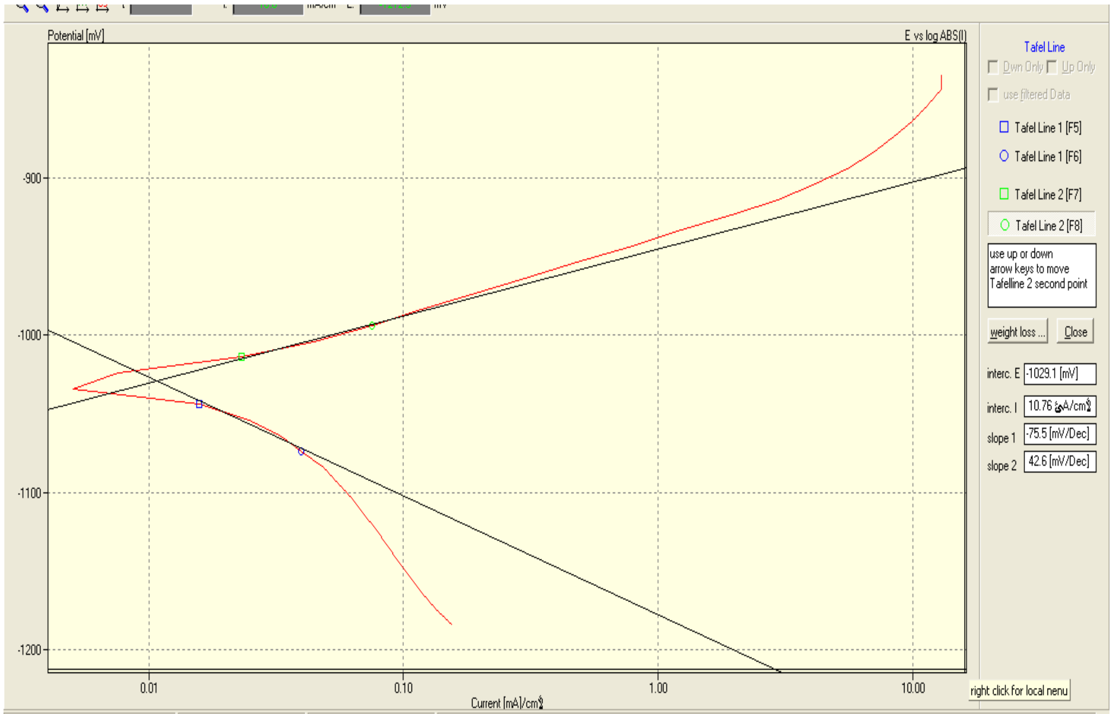


Figure (3.6) Polarization curve of galvanized steel coated with different nanomaterials in 3.5%NaCl.

٣,٢,٤. Corrosion Protectiveness of Stainless Steel Specimens

Coated stainless steel specimens showed protection capabilities in comparisons with the uncoated stainless steel specimens in the salt water environment used (٣,٥٪NaCl).

While SiO٢ sol gel showed lower protection efficiency (٣٤٪). This may make lower adhesion to the metal surface

Silica based ceramic oxides coating was developed using tetraethoxyorthosilane (TEOS) prepared by acid catalyzed hydrolysis using sol-gel process which were deposited onto ٣١٦ stainless steel substrate by dip-coating technique [٣٠].

Sol-gel-derived coatings were made from tetraethylorthosilicate (TEOS) and ٣-methacryloxypropyltrimethoxysilane (MPS) enhanced corrosion protection by forming a physical barrier [٣١].

The corrosion potentials ranged between -١٤١ and -٢٤٣mv vs SCE. Silica applied by the air atomizer showed more than ٥٧٪ PE. This may due to completely cover the stainless steel.

SiO٢ sol gel> uncoated

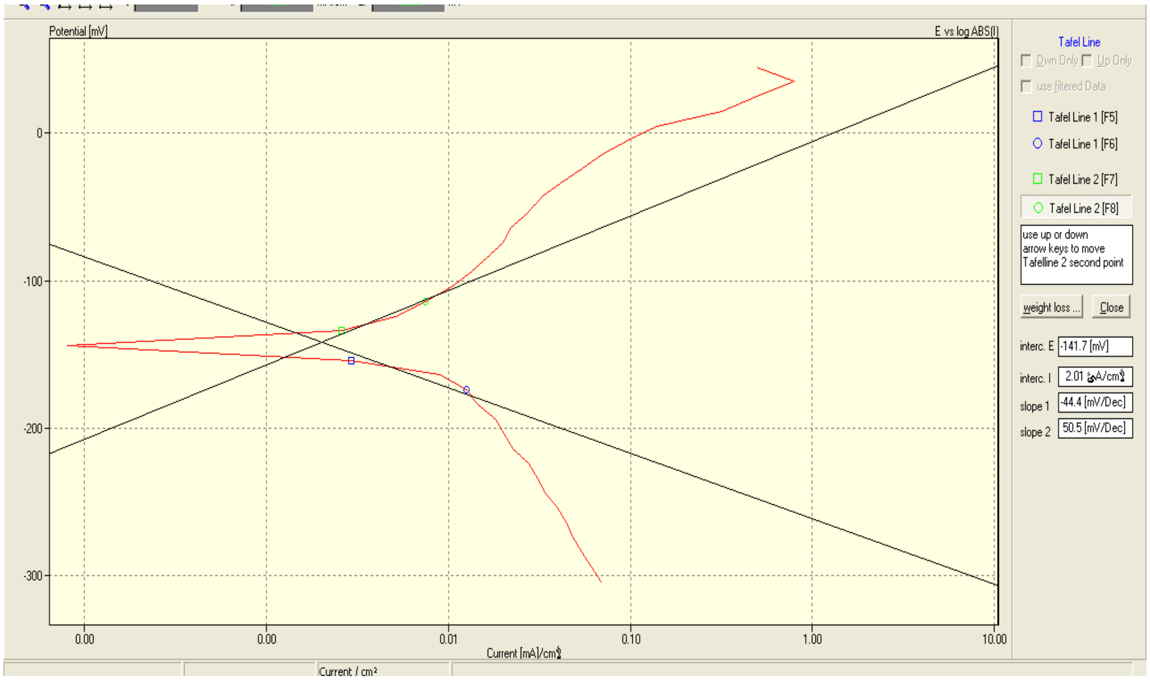


Figure (3.18) Polarization curve of stainless steel coated with nanomaterials in 3.5%NaCl.

Table (3.5) The values of $E_{corr.}$, I_{corr}, W. l. and penet. L. of the stainless steel coated with nanomaterials .

No.	States	E_{corr} (mv)	I_{corr} (μA/cm^{٢})	P%	W.l. (g/m^{٢} d)	Pent. (mm/a)
١	Uncoating	-٢٤٣,٢	٣,٠٧		٠,٧٦٩	٠,٠٣٤٢
٨	SiO$_{٢}$ sol-gel	-١٤١,٧	٢,٠١	٣٤,٥٢	٠,٥٠٥	٠,٠٢٢٥

The established results of the coated metals showed difference degree of corrosion protection.

Corrosion protection enhancement in all causes but as comparative studies the more benefits was achieved for the carbon steel (٤٢,١٦μA/cm^{٢} – ٨,٥٣ μA/cm^{٢}) and galvanized steel (٤٩,٩٨ μA/cm^{٢} – ٩,٣٥ μA/cm^{٢}).

Aluminum showed less important (٢٠,٦٣ μA/cm^{٢} – ٢,٦٩ μA/cm^{٢}) and it is not sure that pitting process diminished which well know as an expected damage in Cl environment.

Also stainless steel revealed minimum benefits (٣,٠٧ μA/cm^{٢} – ٠,٦١٦ μA/cm^{٢}) and need to be subjecting to pitting corrosion evalution.

٤- Conclusions

The exclusive properties of nanomaterials, bring on to create different advanced applications incepting from small domestic to advanced electronics devices.

Silicon dioxide ($SiO_{٢}$), was used to coat specimens of aluminum, carbon steel, galvanized steel, and stainless steel. the coated specimens subjected to nanoscopic inspections; i.e. Atomic Force Microscope (AFM),Scanning Electron Microscope(SEM), Energy dispersive x-ray(EDX) ,and x-ray photoelectronic spectroscopy(XPS), and finally the corrosion protection efficiency inspection of each specimen in artificial sea water (٣,٥٪NaCl) at R.T.(~٢٥ºC) using potentiostatic techniques with three electrodes cell.

AFM,SEM,EDX, and XPS inspections revealed a useful data on particle size ,shape, and surface elemental composition, Applying $SiO_{٢}$ applied by sol-gel controlled hydrolysis of teterethoxyortosilane (TEOS) ,produces a layer of particles in the range of ٤٤nm ,

The evaluation of established tafel plots revealed quantitative data on corrosion potential, corrosion current density, corrosion rate, weight loss, and penetration rate . The protection efficiencies (PE) were estimated from the available data for all coating types as listed below:

Aluminum:

$SiO_{٢}$ sol-gel > uncoated
٥٦,١٣٪ ٠٪

Carbon steel:

$SiO_{٢}$ sol-gel > uncoated
٥٠,٤٢٪ ٠٪

Galvanized steel:

$SiO_{٢}$ sol-gel > uncoated
٧٨,٤٧٪ ٠٪

Stainless steel:

$SiO_{٢}$ sol-gel > uncoated
٣٤,٥٢٪ ٠٪

It is clear that coatings applied enhanced corrosion protection, and the layers appled by the sol gel approach (method) give always excellent protection.

٥- Recommendation:

١. Investigation of influence thin film sol gel titania of the anti corrosion coatings on metals.

٢. Studying the corrosion protection of metals by using different alkoxysilanes such as tetramethoxysilane (TMOS), vinyltrimethoxysilane (VTrMOS), and ٣-aminopropyltriethoxysilane (APTrEOS) via sol gel method.

٣. Studying the electrophoretis deposition (EPD) of nano-particulate ($SiO_٢$ and $TiO_٢$) hybrid coatings for corrosion protection. Or studying the electrophoretis deposition (EPD) of nano-particulate ($Al_٢O_٣$) coatings for corrosion protection.

٤. Studying the corrosion resistance of the same coatings on the metals in different temperature.

٥. Establishing the enhancing the pitting preventation of aluminum and stainless steel in saline water by Nanoparticles coating.

٦. Studying the condition effect on deposition layer by using EPD such as time of deposition, temperature of emulsion, current density, voltage, solvent type, and emulsion concentration.

٧. Studying the effect of gas type for atomized method such as type of gas and the pressure.

٨. Evaluate the adhesion force of various coatings.

Experimental Part

٢,١. Introduction

The experimental section of the research can be divided into two parts; the first part includes functions of:

١. Performing corrosion tests for (Aluminum, Carbon Steel, Galvanized Steel, and Stainless Steel ٣١٦) specimens without coating the surfaces, by using sea water solutions prepared in the laboratory to determine the corrosion rate.
٢. Performing electrochemical tests using open circuit potential and Tafel extrapolation.

The second part includes functions of:

١. Coating processes of the specimens with $SiO_٢$, nanoparticle by using: Sol-Gel.
٢. Testing of coated layers due to corrosion to determine the corrosion resistance rate in the sea water solution.
٣. Structure studies by atomic force microscopy, energy dispersive x-ray, scanning electron microscopy, and x-ray photoelectron spectroscopy.

٢,٢. Sample Preparation

The investigated materials were (Aluminum, Carbon Steel, Galvanized Steel, and Stainless Steel). The materials were fabricated in circular samples with dimensions of ٢,٥ cm in diameter .The experimental procedure which was based on the standard reference method for making potentiostatic polarization measurement, which was under the jurisdiction of ASTM committee G١ on corrosion of metals and involved the following steps.

١. The specimen (Carbon Steel) was further cleaned just, prior to immersion in HCl solution (١٠-١٥) % for (١٠) min.

٢. The specimens (Aluminum, Galvanized Steel, Stainless Steel) were degreased with acetone and washed distilled water, and finally with ethanol. Therefore, the specimens were put inside desiccators for protecting and preventing them from oxidation.

٢,٣. Testing Techniques

٢,٣,١. Preparation of Corrosion Cell

The electrochemical system consists of potentio state device, corrosion cell, and electrodes.

a. Corrosion cell made of Pyrex with (١L) capacity consists of two vessels, internal and external. Chiller device was used to make the temperature of water which flows through the external vessel constant at ٢٥ C. Figure (٢,١) shows the corrosion cell and the three electrodes.

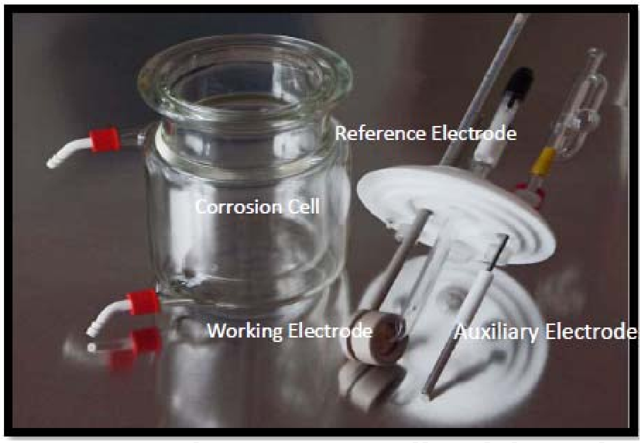


Figure (2.1) Set up the corrosion cell and three electrodes.

b. Sea water solution (٣,٥٪ salt) was used as corrosive media. The solution was prepared by adding ٣٥g of NaCl to ١ L of distilled water. The solution was added to the corrosion cell with stirring until the salt resolved.
c. Three electrodes and thermostat replaced in the internal vessel.

The three electrodes can be explained as follows:

١. Reference Electrodes is used to determine the working electrode potential according to the potential of reference electrode. The potential of reference electrode is well known and accurate, and it is combined of two tubes; the inner tube contains AgCl, Ag, KCl. The outer tube filled with the prepared sea water solution (٣,٥٪ NaCl). The reference electrode replaced at the distance ٢ mm from working electrode.

٢. The Auxiliary Electrode consists of high purity platinum metal; its length is (١٠ cm) .

٣. The Working Electrode is the studying and testing subject which potential will be measured; this electrode is formed from ٢٠ cm length metallic wire and connected to the mounted specimen.

٤. The unmounted subjected in the holder in which the diameter of the exposed surface to the sea water solution is (١ cm^{٢}). Figures (٢،٢), (٢،٣) show the complete system set up of polarization measurement.

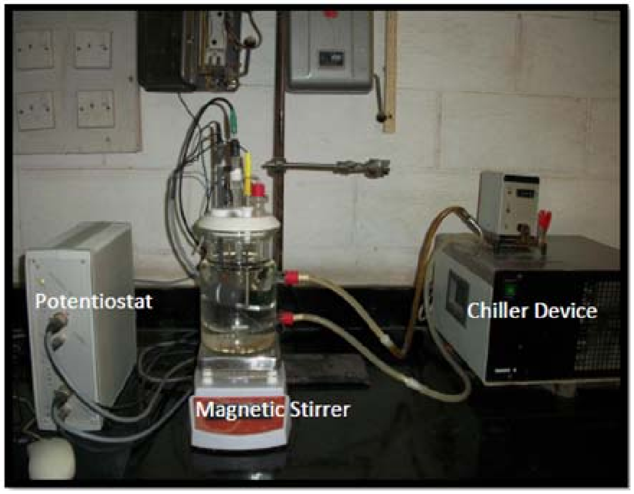


Figure (2.2) Complete system set up for polarization measurements.

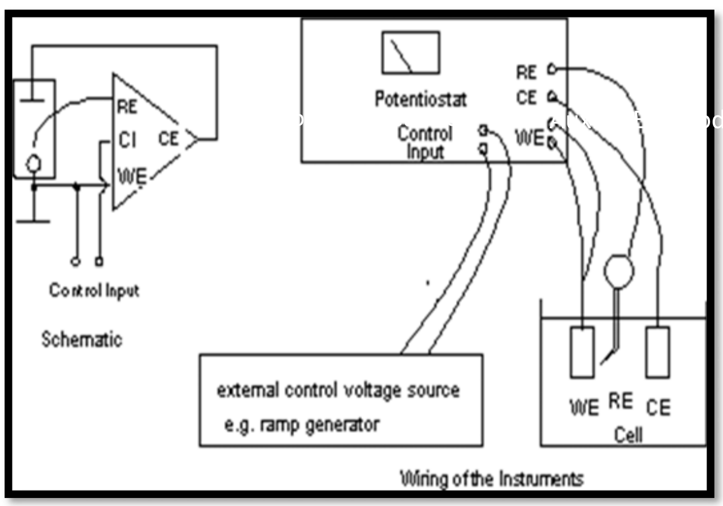


Figure (2.3) Schematic of the potentiostatic control loop. RE Reference electrode, WE working electrode, CE counter electrode, CI control input.

٢،٣،٢. *Open Circuit Potential*

To determine the open circuit potential of the specimens, the specimens have been immersed in the sea water solution prepared in the laboratory to reach the steady state between the specimen's material and electrolytic solution. The change in potential according to the current were determined during (١٥min), and time step equal to ٦٠ seconds for each specimens. After reaching the steady state condition, the determined potential is known as corrosion potential or free potential or open circuit potential.

٢،٣،٣. Tafel Extrapolation

The theorem of mixed potential is considered as the base of the tafel extrapolation to determine the corrosion rate. In this method, the determined values of potential from cathodic and anodic polarization. After determining the open circuit potential, low current from cathodic current will be pass through the specimens by reducing magnitude of variable resistance gradually. Then the working electrode potential will be measured against the current which measured by potentiostate device to measure the value of current density, this will be done by analyzing value of (current-potential) data using potentiostate device soft ware.

٢،٤. Molar Ratio Calculations

In order to measure the required volumes of the chemical materials to obtain the $SiO_{٢}$ sol which transferred to $SiO_{٢}$ gel, we used the basic following equations:

a. To calculate the weight and number of moles of the chemical materials, the following equation was used:

$$n' = \frac{W}{Mwt} \text{ .... (٢،١)}$$

where:

n´: number of moles (mol).

W: weight of the material (g).

Mwt: molecular weight of the material (g/mol).

b. The corresponding volumes of these weights were calculated from the equation (٢،٢).

$$V = \frac{W}{\rho} ....(2.2)$$

Where:

ρ: Density of the material (g/cm٣).

V: the required volume (ml).

٢,٥. Nanomaterials Coating Procedures:

This section describes procedures applied during the early stages of the research. The reliable procedure to prepare the sol gel, and the application to the specimens are as follows:

٢,٥,١. *Preparation of SiO٢ Sol Gel*

The sol gel process of the sample is described as follows:

A two step hydrolysis method was adopted for the sample:

١. The precursors were first mixed with water and isopropanol to initiate the reaction with tetraethoxyorthosilicate (TEOS):H٢O:isopropanol(C٣H٧OH) =١:١:١(molar ratio) using an HCl as catalyst HCl/H٢O=٢x١٠-٤ (molar ratio), these solution was put into the jacket cell which consists of two vessels, internal and external. Chiller device was used to make the temperature of water which flows through the external vessel constant at ٥ C.

٢. The solution and the thermometer replaced in the internal vessel. Figure (٢,٤) shows the sol-gel set up system.

٣. After well stirring for ٩٠ min and keeping at room temperature for two days, the iso propanol was evaporated at ٥٠ C, the second hydrolysis was conducted by adding H٢O into the solution with the molar ratio of H٢O/TEOS =٠,٥:٠,١ at ٧٠-٨٠ C°. Figure (٢,٥) shows the preparation process of sol-gel.

٤. The sol gel was applied to coat the specimens using air atomizer coating technique [٢٣]. Figure (٢,٦) shows the SiO٢ sol gel.

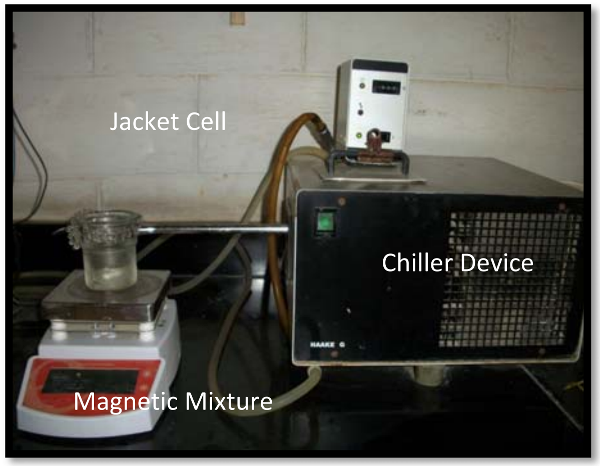


Figure (2.4) The sol gel set up system.

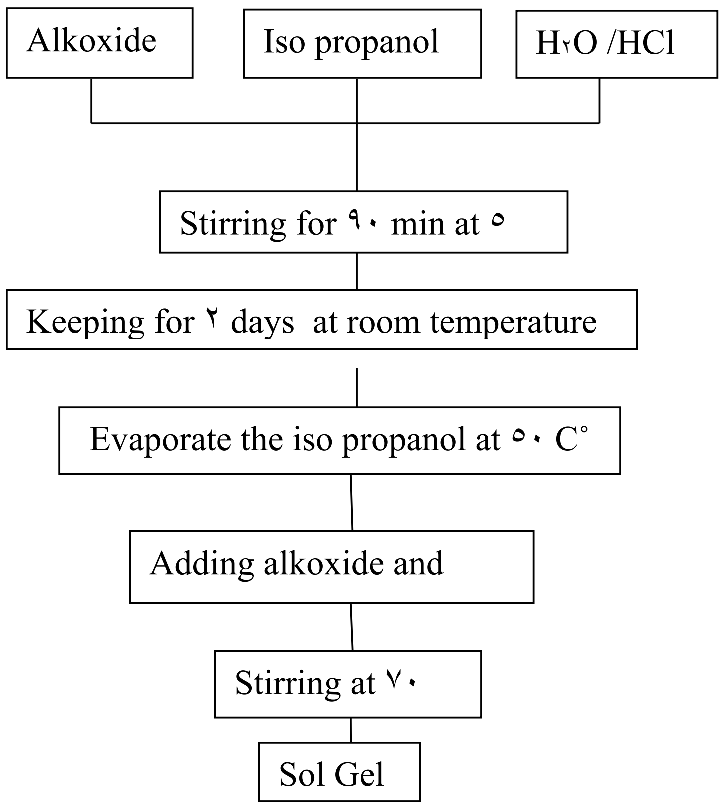


Figure (2.5) Preparation Process of Sol Gel.

Figure (2.6) The Sol Gel.

٢,٦. Air Atomizer Coating Technique:

Air atomizer was used as spraying technique which composed of the following components:

١. Electrical heater was used to heat the specimen to about ١٠٠-١٥٠ C.
٢. Temperature measurement device as thermocouple was used to measure the specimen temperature.
٣. Air compressor was used to compress air into the atomizer.
٤. Air atomizer unit, which contains solution container, valve used to control the solution flow and a nozel with small orifice used to spray the solution using the compressed air. The nozel was directed onto the specimen surface.

The nozel of the air atomizer unit must be placed about (١٠ cm) above the specimen which heating of the specimens will help to improve the adhesion between the coating layer and the metal surface. Figure (٢,٧) shows the air atomizer set up system, and figure (٢,٨) shows the unmounted specimens coated by air atomizer technique.

Figure (2.7) The air atomizer set up system.

Figure (2.8) The unmounted specimens coated by using air atomizer technique.

٢,٧. Surface Structure & Topography Testing

Table (2.1) Surface sensitive analytical techniques, principles and applications

Analytical technique	Principle	Target information
Surface structure techniques		
Atomic force microscopy (AFM)	Microscopic force sensor (cantilever) is used to sense the force between a sharp tip and the sample surface	Imaging of insulated surface structure at atomic resolution [٢٤].

	as the sample is scanned to generate an image.	
Energy dispersive X-ray spectroscopy (EDX)	Used for the elemental analysis or chemical characterization of a sample.	Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing x-rays that are characteristic of an element's atomic structure to be identified uniquely from each other [٢٥].
Scanning electron microscopy (SEM)	Incident electron beam generates a secondary electron emission that is used to generate the surface image.	Microscopic imaging of the surface structure [٢٤].
Chemical identity and composition techniques		
X- ray photoelectron microscopy (XPS).	Based upon the photoelectric effect.	Each atom in the surface has core electron with the characteristic binding energy that is conceptually, not strictly, equal to the ionizing energy of that elecyton [٢٦].

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ملخص البحث

الخواص الاستثنائية للمواد النانوية ادت الى ابتكار مختلف التطبيقات بدءا من الاجهزة المنزلية الى الالكترونية المتقدمة. في هذا البحث تم اختيار مجال متناهي حديث لاستخدام المواد النانوية وهو اكساء سطوح المعادن والسبائك بمثل هذه المواد الناشطة (الذكية) لتقدير قابلية الحماية من التاكل وتم اخضاع العينات الى فحوصات مجهرية نانوية مثل مجهر القوة الذرية(AFM) و المجهر الماسح الضوئي (SEM) و حيود طاقة الاشعة السينية (EDX) ومجهر الطيف الالكتروني الضوئي للاشعة السينية (XPS) واخيرا فحص كفاءة حماية التاكل لكل عينة في ماء البحر (الماء المالح)[NaCl٣,٥٪] في درجة حرارة الغرفة باستخدام تقنية المجهاد الساكن ذو خلية ثلاثية الاقطاب. تم استخدام تقنية المحلول الهلامي. وقد اظهرت فحوصات AFM و SEM و EDX و XPS معلومات مفيدة حول حجم الجسيمات والاشكال والتركيب العضوي, $SiO_٢$ بواسطة التحكم بالتحليل المائي للمحلول الهلامي لـ (TEOS) انتج طبقة من الجسيمات بحدود ٤٤nm وقد اظهرت الحسابات معلومات كمية حول التاكل والجهد وكثافة تيار التاكل ومعدلات التاكل وفقدان الوزن ومعدل التغلغل , كما تم حساب كفاءة الحماية من هذه البيانات لجميع انواع التغطية والترتيبات المتحققة والتي تتلخص بما يلي

Aluminum:

$SiO_٢$ sol-gel > uncoated
٥٦,١٣٪ ٠٪

Carbon steel:

$SiO_٢$ sol-gel > uncoated
٥٠,٤٢٪ ٠٪

Galvanized steel:

$SiO_٢$ sol-gel > uncoated
٧٨,٤٧٪ ٠٪

Stainless steel:

$SiO_٢$ sol-gel > uncoated
٣٤,٥٢٪ ٠٪

ومن الواضح ان التغطية المستخدمة عززت حماية التاكل. بطريقة اعطت حماية ممتازة دائما

وزارة التخطيط
الجهاز المركزي للتقييس والسيطرة النوعية
دائرة السيطرة النوعية
قسم تقويم المطابقة للسلع المستوردة

دراسة في حماية بعض اسطح المعادن والسبائك من التاكل باستخدام الجسيمات النانوية

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سنة اعداد الدراسة :٢٠٢٤