Characterization of Titanium-Based Films Deposited by DC Sputtering Reactive on AISI 1018 Steel

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Abstract: The coated surfaces first layer Ti and second layer TiO2 as coating Nanostructured thin films of using DC sputtering on structural steel (AISI 1018) and study characterization of coating SEM/EDS inspection shown a clearly perfect incorporation of layer by dc sputtering a granular structure of the layer with a variable hemisphere’s forms varied from 33 to 46 nm in size. X-XRD test complete for specimen indicates was found anatase phase titanium dioxide, the resulted coating layer of the target of Ti powders gives different morphology from the Ti layer alone. The Specimens roughness average of coated Ti and TiO2 with respectively was 4.831nm, 7.93 nm. Found that titanium layer will show a major part in increasing the bonding with improving the bond between the substrate steel AISI (1018) and the titanium oxide layer. The Vickers hardness increases when the coating with a layer of titanium with an oxygen content of ceramic layer is formed from 192.3 HV to 227 for Ti as well as important increase was detected in the TiO2 coating to 240 HV. In addition, Ti and TiO2 thin layer considered as a good barrier for hydrogen permeation through steel structure especially at cathode protection in pipelines.

Keywords: DC sputtering, hydrogen permeation, anatase phase, Nanostructured

I. INTRODUCTION
Titanium and its alloys are widely used for medical and industry because of the excellent biocompatibility, good mechanical properties and high corrosion resistance special in application in industry [1]. the used of long fatigue life are widely in spacecraft, motorized, dentistry and orthopedic field [2]. Once period, materials nanostructured take of countless attention as substances and other request because of their unique textural and physical features.

The Physical due to the constancy of its chemical structure, physical, visual, biocompatibility, and electrical properties. Its photo catalytic properties take stayed used in several environmental applications to eliminate contaminants from together air and water [3]. TiO2 exists in three inorganic formulas: anatase, Rutile, and Brookite [4]. Anatase type TiO2 has a crystalline structure that corresponds to the tetragonal system and is used mainly as a photo catalyst under UV radioactivity. Rutile sort TiO2 likewise has a tetragonal crystal structure).
Generally, TiO2 is favored in anatase arrangement since of its high photo catalytic action, since it has a more negative conduction band edge potential (higher potential energy of photo generated electrons), in height exact area, non-toxic, photo chemically stable and comparatively Nanotechnology is a promising technique for control and reduce corrosion rates especially in industry [5]. The nanotechnology suggested many solutions as the drilling process by using nanofluid (mixing of Nano sized atoms and drilling mud) Also, Nano materials are used as catalysts in petroleum refining reactors in petroleum downstream industry and as coating materials to the transportation pipelines and storage tanks in petroleum middle stream industry [6-7]. Many nanomaterials are used as a thin film in petroleum industry such as TiO2, SiO2, CuO, and Al2O3. Unlike coating technologies, for example chemical vapor deposition (CVD), thermal spraying, and physical vapor deposition (PVD) [8,9]. PVD coatings shaped through arc plasma machinery exhibit high strength and excellent adhesion possessions, thus empowering it to coat almost every kind of instrument. PVD coatings have been successfully used in industrial applications for their automatic properties and wear also it has good corrosion resistance [10]. Coating procedures provide defense to surface of structure that visible to corrosion surroundings in several fields then destructive, consequently careful needed aimed at specific application [11]. Thin layer otherwise coating is named a new field of materials chemistry. The structure of thin layers, similar all material, is distributed into polycrystalline structures and amorphous, dependent on the state of preparation also the composition of material. Thin layers include of two portions: the substrate and the bed rock on which the layer is riding [12]. Glow dischargers also related plasma break used in countless quantity of application fields. The taster is exposed to ionized atoms, plasma then molecules may respond by the surface exposed. Numerous properties are typically perceived counting etching, material surface alteration then sputtering [13, 14]. The (plasma) is produced in a plasma method glow discharge DC via providing a possible DC amid two electrodes. The electrodes are confidential a jar that is expatriate. Vacuum was practical in plasma starting intermediate. Usual plasma methods originally ionized a minor collection of atoms covering the cell. The communication of a intergalactic beam or photon by the molecule otherwise plasma gas atom announcements an electron. This will a plasma device for ion DC; the plasma is shaped by supplying the potential glow discharge as of two electrodes. Sputtering coating system predicts that sputtering affected via the creation of in height limited temperatures by bombing ions, which contributes to the evaporation of material target as of those native zones [15]. Dc moreover is a technique of emitting atoms from the solid surface through the act of active atoms [16]. Therefore, in this research will depend coating those surfaces with a layer of metal–ceramic to increases the chemical resistance and determine that coated by Ti and TiO2 nanoparticles as protective, as well as the titanium layer will play a major part in increasing the bonding then improving the bond between the substrate steel AISI (1018) and the titanium oxide layer. In addition, the Ti and TiO2 thin layer considered as a good barrier for hydrogen permeation through steel structure especially at cathode protection in pipelines and storage tanks sector petroleum with environments by DC sputtering technique.

2. Experimental method
2.1. Preparation of Target coating and technique

The targets used in sputtering method made of compacted titanium powder without demanding of sintering process. Titanium target consist of 20 gram of titanium powder with a grain size of (46 μm) and the process of making the target consist of pressing in cylindrical stainless-steel mould with a diameter of 50 mm and height of 5mm as shown in Figure (1). The compacting time was 10 minutes at full load with a pressure of 240 MPa. The resulting target thickness was 3 millimetres.
2.2. Substrate Preparation

Steel (AISI 1018) specimens prepared to study various surface testing by preparing a specimens with dimensions of (20×20×2) mm then grinded and polished to achieve smooth scratch-free surface with roughness of (Ra 3.01nm). The chemical composition test is using X-ray fluorescence spectrometers (XRF) as indicated in Table (1) and Table (2) contain the DC spattering parameters. After implementation sputtering process for Ti the oxidation process or called anodizing layer of TiO₂ done using low pressure argon with oxygen gas meditation of 30%. The substrate specimens attached top of target using adhesive leading tape as shown in Figure (2). After coating process figure (3) shows the form of steel specimen’s surface.

Figure 1. A- Titanium powder, B-Stainless steel mould, C- Hydraulic pressed 20 minutes at 50 MPa, D-Titanium compacted powder target.

Figure 2. the substrate before coating.

Figure 3. the substrate after coating.
2.3. Coating process

The technique DC sputtering was completed in argon discharge a low-pressure gas device involving of an evacuated chamber, the target (cathode), an anode disk of stainless steel. The cathode faced the gas discharge with electrical field by 4kV DC power supply, the anode then make available, a cathode electrodes bottommost change is endangered via an insulator disk (ceramic) then quartz tube the diameter of the top electrodes is 14.5 cm though the target electrode (effective cathode dark space area) is 7.5 cm and the distance between them is 4 cm. The gas source-flow controller system is responsible for supplying the feedstock at the wanted flow rate and gas pressure to the plasma chamber. It is contains of dual-step controllers, fittings and tubes for the Argon. Dual-stage needle valve controlled a flow pressure to the plasma hollow.

A vacuum organisation involves a pump turbo (Variant, V-1000HT) aided via a hydraulic rotary pump (60 m³/h, Blazer), The connection of confining (Edward CP25-K by supervisor 1102) then LH-Thermo vac, the plasma chamber was required to monitor the real pressure also the part pressure of the discharge gases. As shown in figure (4).

![Figure 4. Low pressure (dc-glow discharge) plasma system.](image)

| Tested result | Alloying Element | C   | Si  | Mn   | Cr   | S   | MO  | Fe   |
|---------------|-----------------|-----|-----|------|------|-----|-----|------|
| Wt.%          |                 | 0.18| 0.22| 0.76 | 0.096| 0.034| 0.01| 98.69|
Table 2. Substrate condition of low carbon steel ASTM A29 Grade 1018 coated by spattering using Titanium target.

| Layer | Time (hour) | Sputter chamber Pressure (mbar) | Voltage (V) | Current (mA) | Power (W) | Temp°C | Gas          |
|-------|-------------|---------------------------------|-------------|--------------|-----------|--------|--------------|
| Ti    | 3           | 6×10^{-2}                        | 1400        | 20           | 30.8      | 200    | Ar           |
| TiO₂  | 3           | 6×10^{-2}                        | 1400        | 20           | 30.8      | 200    | with O₂ of (30 %) at 20 sccm |

2.4. Characterization of coating layer
The morphologies of coating thin layer analysed by means of scanning electron microscope assisted with energy dispersive spectrometer detector (SEM) as well as (EDS), where the Nano-morphology of the surface obtained using atomic force microscope.

3. Results and Discussion

3.1. Microstructure of base metal and powder
A substrate material that used in this work is AISI 1018 carbon steel. Figure (5) shows the microstructure of it at 10X etched using 1% nitric acid at alcohol where it is clear that the metal is deformed by drawing with directional grains and figure 2 shows higher magnification image for the same steel with ferrite and 26% of pearlite using ImagJ® software.

![Figure 5. A The microstructure of 1018 carbon steel 10X etched using 1% nitric acid](image1)

![Figure 5. B The microstructure of A1018 carbon steel 10X etched using 1% nitric acid](image2)
3.2. Characterization of SEM Nano coating Ti

SEM/EDS examination was done aimed at coating surfaces to check the attendance of first layer Ti and second layer composite TiO₂ as coating. Coated specimen surface by titanium layer scratched by a blade gently to identify the layer as shown in Fig (4a) where the scratched by sharp blade. It can be seen that Ti coating layer very smooth taking the exact substrate morphology but the scratch at 4kx magnification cannot show evidence of coated layer. The Specimens of coated with Ti was 4.831 (nm) and TiO₂ roughness average 7.9 nm when measured by AFM.

AFM scanning for Titanium nano layer as in figure (6 – a) show a 3D topography of scanned surface layer and maximum peaks were less than 60 nm but the average values as mentioned above were less than 5 nm. The cause of this peaks belongs to prior surface topography before coating where the coated steel grinded with 1200 grid emery papers and not polished. AFM scan image gives good information about the surface topography of the film. In addition to the statically determining the particles size from the SEM images and granularity accumulation distribution as shown in Figures (8) b that represent the Ti layer takes a hemispherical shape with a vertically spaced, and similar grain size. The average grain size was in range of 30 to 50 nm. for the same sample show identical morphology of the SEM imaging as it shown in Fig 8

![Figure 6](image6.png)

**Figure 6.** A- AFM image of (Ti) by DC sputtering process and B- its distribution chart.

![Figure 7](image7.png)

**Figure 7.** AFM image of (TiO₂) by DC sputtering process and its Distribution chart.

It can be noted from the above three figures the surface topography of the coating layers highly affected by the steel specimen priory grinded where it can be seen the coating thin layer distributed on the steel surface and follow its topography.
On the other hand when the steel surface polished well can gives bad adhesion with thin layers for that resin fine grinding using 1200 grit silicon carbide emery paper gives good surface roughness to steel specimens compatible with adhesion performance, In the table(4) shown that the Vickers hardness increases when the coating with a layer of titanium with an oxygen content of ceramic layer is formed, which is titanium oxide about 30%, this indicates an improvement in the mechanical properties. Note that Substrates (As it is) for low carbon steel ASTM A29 Grade 1018 steel was 192.3 The increase is noticeable when coting, as shown in the table (4)

### Table 3. Comparison between coating layer of titanium and titanium dioxide.

| Experiment No. | Characterization of Nano thin layer | Layer Coated Ti | Layer Coated TiO2 |
|----------------|------------------------------------|-----------------|-------------------|
| 1.             | Adhesion force (Psi)                | 309             | 340               |
| 2.             | Thickness of film(nm) measurement system by pulse laser deposition | 159.8           | 192               |
| 3.             | Deposition rate nm/h                | 53.3            | 64                |
| 4.             | Vickers Hardness (Kg/mm2)           | 227             | 240               |
| 5              | roughness average of Coated with Ti (nm) | 4.831           | 7.93              |

3.3. Characterization of SEM Nano coating Ti and TiO2

Testing the resulted coating layer of the target compound of TiO2 gives different morphology from the Ti layer alone. Figure (8-a) of SEM image showing scratched surface of coating layer with clear coating layer of Ti. Figure (8-b) showing a granular structure of the layer with a variable hemisphere’s forms varied from 33 to 46 nm in size.

![Figure 8. Scanning electron micro images for a-c) titanium b-d) TiO2 Nano layers.](image-url)
In figure (8-c) more magnification for image (8-a) the scratched titanium layer is clearly shown and the layer follow the base steel topography while image (8-d) show the columnar structure for the Nano layer which is clearer shown in figure (9).

![Figure 8-c](image)

**Figure 8-c.** Image showing the scratched titanium layer with more magnification.

**Figure 9.** Columnar structure of the Nano coating layer at magnification of 300kx

### 3.4 Characterization of EDS, XRD for Ti and TiO2 Nano coating layer

Testing the surface using EDS as shown in Table (5) indicate there are no oxygen which approve that the layer is titanium thin coat on steel substrate. As it known EDS (energy dispersive spectrometer) is a probe connected to SEM devise which sense the X-ray fluorescence from incidence of high energy electron beam on the tested surface. The depth of generated X-ray resulted from electron beam of 20kv on Iron reach to 1.5 micrometres [17] in depth. This is meaning that the characteristic generated X-ray detected by EDS probe will read and substance with depth of 1.5 micrometre which include Iron and titanium and oxygen in this case. The chemical analysis for EDS spectrum of resulted Ti target sputtering on (1018) steel read 1.14% and shown in figure (10) A and B

| Elt. | Line | Int  | Error | K    | Kr   | W%   | A%   | ZAF | Ox% | Pk/Bg | Class | LConf | HConf |
|------|------|------|-------|------|------|------|------|-----|-----|-------|-------|-------|-------|
| S    | Ka   | 80.5 | 0.5996| 0.0265| 0.0262| 2.98 | 5.07 | 0.8795| 0.00| 4.22 | A     | 2.88  | 3.09  |
| Ti   | Ka   | 19.8 | 0.3081| 0.0124| 0.0123| 1.14 | 1.30 | 1.0765| 0.00| 2.82 | B     | 1.06  | 1.22  |
| Fe   | Ka   | 791.0| 0.8494| 0.9612| 0.9526| 95.88| 93.63| 0.9935| 0.00| 54.37| A     | 94.82 | 96.94 |

By matching the content according to above the titanium content calculated by multiplying by division of x-ray penetration depth of 1500 nm on the layer thickness which is here 120 nm. Then the real titanium content is reading multiplying by 12.5 therefore titanium percentage is not less than 15%. The sulphur
content may be found due contamination from Nital etching agent which compound from 1% nitric acid and alcohol.

Testing titanium coat on glass as shown in figure (11) showing of peaks titanium spectrum which indicates that the coat is a nanostructured layer. By annealing the coated glass specimen at 400°C for two hour the structure begin to be obviously with higher peaks as in figure (11) which indicate annealing process lead to change the layer to more ordered Titanium atoms which improve the layer stability.

Figure 10. A : EDS spectrum of resulted chemical analysis of Ti target spattering on (1018) steel.

B: EDS spectrum of resulted chemical analysis of Ti target spattering on (1018) steel with oxygen gas
**Figure 11.** XRD analysis of the Ti coat layer on glass sheet.

**Figure 12.** A- XRD analysis of the TiO$_2$ coat layer on glass sheet, B- standard TiO$_2$ XRD card.
TiO₂ coated layer on glass with tested in XRD-Diffraction figure (12) shows that the anatase phase is the result when comparing result spectrum with a standard card. To pumping Oxygen in low frame rate of 30 sccm (standard cubic centimetre per minutes) during sputtering process the Oxygen indicated in spectrum in a presence of Titanium, oxygen and iron. So, these elements presence indicate there are oxidation process for coat elements. But EDS mapping dose not gives a qualitative result for compounds types but just a quantity of the present’s elements in mapped area. XRD test done for the same specimen but using glass substrate instead of steel and figure (12) indicates TiO₂ titanium dioxide as it shown in tested and standard this compound card.

5- Conclusions

Some findings can be drawn from the results and discussions presented in the study, these can be summarized as follows: The (Ti and TiO₂) layers was deposited by DC sputtering is a good bonding and high adhesion. The mechanical properties of TiO₂ coatings were improved as an effect of dc sputtering. However, an improvement in properties with increasing oxygen pumping. The coating surfaces with a layer of metal-ceramic to increases the chemical resistance and determine that coated by Ti and TiO2 nanoparticles as protective. The hardness of the substrate has better from 192.3 HV to 227 for Ti and important increase was experiential in the TiO₂ layer to 240 Hv. The results of XRD, SEM, AFM examination showed good evidence of the protective layer formation and founding the anatase phase which it was found that the bonding between the Ti layer with TiO₂ ceramic coatings was mechanical and metallurgical by DC sputtering process. When using titanium target the thickness about 159.8nm but used target titanium with oxygen gas 30 % the thickness about 192nm generated. The appearance of the anatase phase which also lessening the Hydrogen permeation phenomena in applications of cathode protection

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