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Investigation Nano coating for Corrosion Protection of Petroleum Pipeline Steel Type A106 Grade B; Theoretical and Practical Study in Iraqi Petroleum Sector

Abstract- *In the present investigation, titania (TiO_2) nano-thin films were deposited on steel type A106-B, by using the Pulse Laser Deposition (PLD) technique to obtain passive layers of nano-coating. Electrochemical methods (Tafel completion) are used for study corrosion behavior of steel coating. The A106-B specimens were evaluated in 3.5 wt. % NaCl aqueous solution by using polarization technique with pH adjustment to 4.0 in order to determine the corrosion rate. The samples of TiO_2 thin films were characterized by SEM, AFM, XRD, and FTIR. The input parameters were substrate temperature (100, 200 and 300) '^{0}C', number of pulse (300, 400 and 500) and fluencies energy (800, 900 and 1000) mJ/cm^2, have been investigated to detect their impact on corrosion reduction rate using Taguchi methodology orthogonal array and Analysis of Variance (ANOVA).The ANOVA results indicates that number of shoots pulse significantly affecting the corrosion rate in PLD technique, which is highest among the contributions of the other parameters which is (58.03%) about three times of the fluencies energy (19.12%).The results show that the TiO_2 deposition on steels offers an excellent corrosion resistance about 99 times as compared with uncoated steel. The optimum conditions to minimum values corrosion rate are: temperature of 300ºC, number of laser pulses at 300, and fluencies energy equal to 1000 mJ/cm^2. Finally the optimal parameters that was used to predict the conclusions were (98.6) to the response of corrosion rate.*

Keywords- *Nano-thin film of TiO_2, low carbon steel, PLD, Taguchi design, Corrosion rate.*

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1.Introduction

In petroleum industry the pipeline damage failure caused by corrosion is one of the most common problem in petroleum sector especially transmission pipelines which were buried or sub buried in the soil or water. Thus considered as the biggest engineering problems and the economy and the most widespread in the world and is most distinguished through the significant impact of these problems on those projects [1, 2].

According to the Iraqi environment and climate variation, there are too many corrosion areas which are affected on corrosion projects include thousands of kilometers of pipeline transports natural gas, crude oil and petroleum fractions as well as other projects under the surface of the earth ground tanks prepared for storage [3, 4].

Mild steel is regarded one of the major materials used for petroleum transportation pipelines due to its physical, mechanical characteristics, and low cost. This material is highly affected by corrosion where environmental conditions play an important role especially in the external corrosion of the oil pipeline. Also, other factors such as content of the petroleum product passing through it, moist, temperature, pH and soil type affected Mild steel corrosion rate [1, 5, 6]. Nanotechnology is a promising technique for control and reduce corrosion rate especially in petroleum and gas industry [7]. The nanotechnology suggested many solutions to improve petroleum sector. It is used in the drilling process by using nanofluid (mixing of nanosized particles and drilling mud) to improve the petroleum drilling process and increase of crude oil production. Also, nanomaterials 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 [8-10].Many nanomaterials are used as a thin film in petroleum industry such as Al_2O_3, SiO_2, CuO, and TiO_2. Among all nano-coatings using titania

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TiO_2 considered to be as the most common corrosion protection thin films due to their unique chemical, electrical and optical properties. TiO2 thin films possess high dielectric constant, wide optical band gap, high refractive index, photo catalytic, low absorption and high transparency with high thermal and chemical stabilities. Because of its excellent properties, it finds applications in heterogeneous catalysis, photo catalysts, self-cleaning windows, solar cells, gas sensors, corrosion resistant coatings, optical coatings [11, 12].In nanotechnology, many processes and techniques are used to deposit nanomaterials as thin films including sol gel process, thermal evaporation technique PVD, chemical-vapor-deposition CVD, sputtering process, and pulsed-laser-deposition PLD. Among these techniques, PLD is simple and efficient technique to achieve, good adherent with high quality and good mechanical specifications thin film also working in higher pressures and possibility of growth several types of multicomponent thin films with high quality . The mechanism of PLD operation depends on the rate of ablation from target surface that promotes the constituents of the target to evaporate congruently and adhering to the film [13, 14]. The aims of the present work are to determine corrosion behavior in petroleum pipelines type A106-B that coated by TiO2 nanoparticles as protective films using PLD technique. In addition, use of Taguchi method for the design of experiments to optimize the TiO2, PLD process for the production of coatings purpose at corrosive media.

2. Experimental Setup

I.Preparation of Substrate Material

The substrate material that used in this study is ASTM A106 grade B carbon steel supplied from the Petroleum Pipeline Company/ Ministry of Oil-Iraq. Figure1 shows the area friction of ferrite to pearlite of microstructure of A106-B, and Table 1 is chemical compositions of the used carbon steel. Samples sheet of the material was cut into the size with dimensions (12 mm ×12 mm×2mm) in order to use as substrate. On the other hand, Titanium oxide was present purchachased from Fluka with mean particles size of 20 nm. Table 2 gives the general specifications of TiO_2.

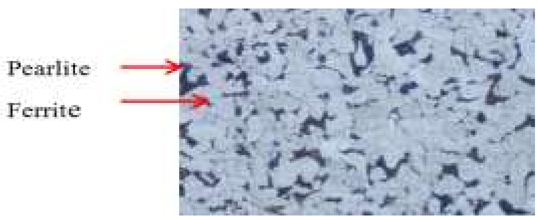


Figure 1: Microscopic structure of A106 carbon steel.

Table 1: The nominal and the analytical chemical compositions of carbon steel [7].

Chemical Composition%	Stander Values	Analytical Values
C	Max.0.30	0.13
Mn	0.29–1.06	0.6
Si	Min.0.10	0.33
P	Max.0.035	0.007
S	Max.0.035	0.009
Cr	Max.0.40	0.12
Ni	Max.0.40	0.05
Mo	Max.0.15	0.01
V	Max.0.08	0.004
Cu	Max.0.40	0.024
Fe	Remaining.	Remaining.

Table 2: Specifications of TiO_2 nanoparticle.

Property	The value	Units
Average particle diameter	20	nm
Purity	99.98	%
Bulk Density	0.46	g/cm3
True Density	4.23	kg/m3
Color	White	-

II.Thin Film Preparation Procedure with PLD

A TiO2 nanoparticle was compressed into a disc form of 20mm diameter and thickness of 6mm using a uniaxial press (1500 kg/cm^2). After that the pellet was sintered at 1100 '^{0}C' in muffle furnace for 4 hours and used as a target for the PLD.

The PLD unit included vacuum system consists from vacuum pump and vacuum chamber constructed from high temperature Pyrex-glass. The pulse laser source is Nd:YAG laser with a frequency second radiation at 1064 nm at various fluencies energy 0.8, 0.9 and 1 J/cm ^{2}. The distance kept constant between TiO_2 target and laser source by 4.5 cm. Figure 2 shows the photograph of the excremental work unit with PLD system. The sintered TiO_2 disc was used in the PLD chamber. Then, the chamber was evacuated using a rotary pump with the aid of a turbo molecular pump to arrive the required operating pressure.

The average number of pulses was applied on the TiO_2 disc at 300-500 layered thin films. The films were grown on the substrate of the A106-B material. During coating process the temperatures of evaporation varied between 100 '^{0}C' to 300 '^{0}C'. On the other hand, the repetition rate was 5 Hz and the operating pressure was kept constant at 10^{-2} mbar.

Figure 2: The thin film preparation unit using PLD technique.

III. Taguchi Design of Experiments

Taguchi analysis program is used in the present investigation to predict an orthogonal-array and signal-to-noise analysis. Three main factors (substrate temperature, numbers of shoots per time and fluencies energy) with three levels were selected as main parameters. Table 3 summarized the main factors and levels.

Table 3: The main factors and there levels that used in this study.

No.	Control factors	Level 1	Level 2	Level 3	Units
1	Substrate temperatur e.	100	200	300	^0C
2	No. of pulses	300	400	500	-
3	Influences energy	800	900	1000	mJ/cm^2

The selected levels and factors were applied to design a mathematical orthogonal array $\mathbf{L_9}$ $\mathbf{(3^3)}$ for experiments. In the experimental design a nine Taguchi tests were done twice in order to be sure from the experimental results. In such cases, the errors cannot be eliminated because of the characteristics variations. So that, any increase in the variation of corrosion resistance will be worked on the lowing the type and quality of coatings. Therefore, in order to minimize the effect of the variation of corrosion resistance on the analysis process, it is suggested to use of the signal-to-noise ratio (S/N). This step will be converting the required trials information into a value that determine and analysis the coating quality.

IV.Corrosion Study

The corrosion solution comparable to sea water with little acidic was prepared through a 3.5 wt.% NaCl solution with pH level 4.0 by adding 35 grams to liter of NaCl to distilled water with the addition of hydrochloric acid (HCl) at room temperature. The potential static polarization carried out using potentiostate model DY23OO as shown in figure 3 scanned on the range of (-2.0V to +2. 0V) with a scan rate of 0.10 V/s.

Figure 3: Potential static polarization device.

V. Characterizations

In the present investigation different measuring techniques and instruments are used to characterize of nanomaterials and thin films. X-ray diffraction (XRD) studies were carried out using Shimadzu 6000-XRD. The surface morphology was studies by AFM (SPM-AA-3000), and SEM (Tescan-VEGA 3). Also, FTIR (Shimadzu-Type 8400S) was used to determine the functional groups.

3. Results and Discussion

I. XRD and FTIR Analysis

XRD spectrum of the TiO_2 coatings with Cu Ka radiation (E=1.0454A°) at a scanning rate of 10deg.per sec. ranging from 20 to 80.Figure (4-A, B, and C) shows the X-ray patterns of crystalline structure of TiO_2. Figure (4-A) indicted the strong peaks at angles 44.9 ^{o} and 65.2 ^{o}, corresponding to the iron in mild steel substrate without coatings (Ref .PDF #00-006-0696), while, Figure (4-B) shows TiO_2 thin films strong peaks at angles, 44.52 ^{o}, 64.79^o (Ref. 21-1276+PDF #211276) which indicate the Rutile structure of TiO_2. Also, the Anatase phase indicated at peak angles 24.73 ^{o} - 29.32 ^{o} with tetragonal structure (101) (Ref.21-1272+PDF #211272). As shown in (Fig. 4-C) the strong peaks at angles, 44.48 ^{o}, 64.88 ^{o} (Ref. 21-1276+PDF #211276) belong to Rutile phase, while, peaks at angles 24.57 ^{o} 29.17 ^{o} belong to Anatase phase (101).The XRD results showed that is the major phase in coating of TiO_2 Rutile and the films also were polycrystalline with tetragonal structure (210) (310).

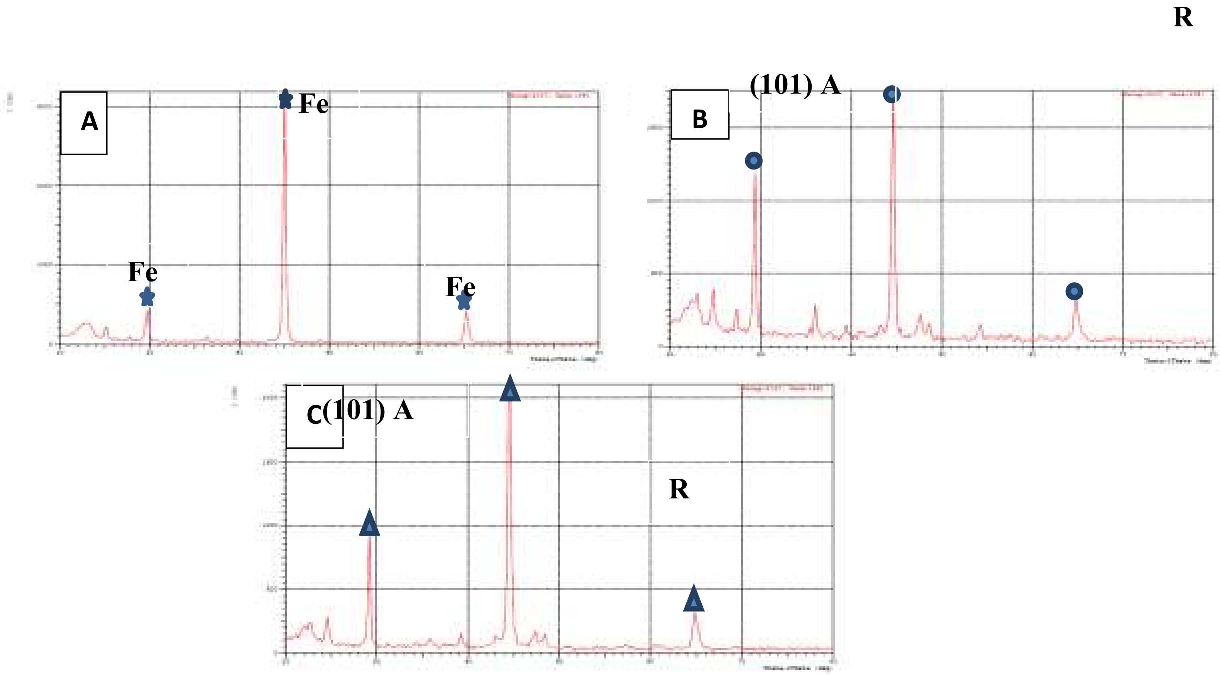


Figure 4: XRD pattern of the (A) steel substrate (uncoated), (B&C) TiO_2 deposited on steel at substrate temperature of 300, 100 ’^{0}C’ No.of pulses 500,400 and1000, 900 mJ/cm^2 respcativly

Figure (5-A) shows FTIR spectra of TiO_2 that affected by substrate temperature at 200^{0}C’. The lowest substrate temperature was at 100 ’^{0}C’ as shown in figure (5-B). It is noted that the TiO_2 film growing by increasing the temperature. This will lead to change in the characteristics of morphology (especially the roughness) resulting a slight change in spectral optical transmittance in wave length.

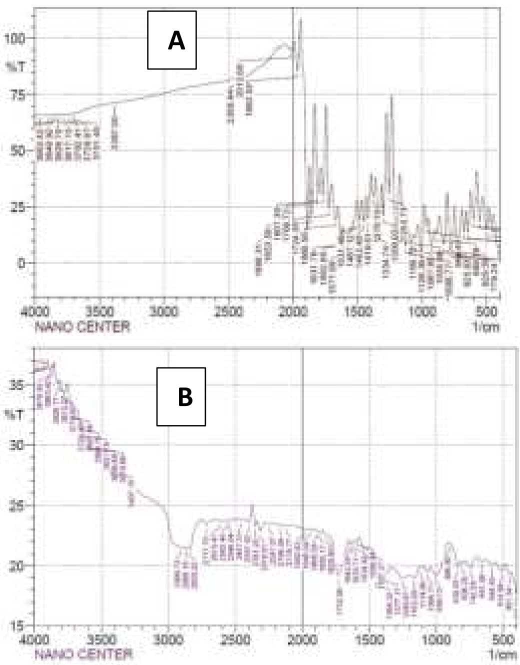


Figure 5: Transmission spectrum of TiO_2, (A): at substrate temperatures of 200’^{0}C’, (B): at substrate temperatures of 100’^{0}C’.

II.AFM and SEM

The surface roughness and topographies of the prepared thin films were examined by AFM. Figures (6, 7, 8 and 9) show the AFM images of the TiO_2 thin films that were prepared at different substrate temperatures 100, 200 and 300 ’^{0}C’ at constant deposition pressure of 10^{-2} mbar for all runs. From the topographic results it can be noted that the substrate temperature plays an important role affected by both grain size and surface roughness. The roughness increase with increases temperature when TiO_2 film grown constant target to substrate distance of 4.5 cm **[8].** The results pointed to that the topography of the films prepared at 100 ’^{0}C’ shows more uniform as compared to the topography that prepared at 300 ’^{0}C’. Then it was concluded that the temperature variation is very significant in topography changes. Such results is related to the effect of the surface mobility of the adatoms is higher at high temperate in which lead to generate high surface diffusion length, island separation, and lateral size. When island separation length is greater than lateral size of the island, terrace and stairs topography are usually preferred. Moreover, surface mobility of the adatoms decreases at lower temperature, islands are more closely spaced. On the other hand, if the island separation is smaller than the island lateral size, it is expected more uniformed growth of the prepared thin film is dominate [**8**].

Table (4): AFM morphology characterization of TiO_2 .

No. of	PLD parameters			Average grain size (nm)	Roughness average (nm)	Root mean square (nm)
	Temp. ^0C	No. of pulses	Fluencies energy MJ/cm^2			
1	100	200	800	280.00	11.3	19.5
2	200	500	1000	303.33	15.7	21.9
3	300	300	850	314.94	14.7	22.3
4	300	200	1000	287.96	14.3	20.5

Also, figure (10) shows the SEM of TiO_2 at different temperatures (100, 200' and 300'^{0}C'). From this figure it is noted that the temperature is highly effected on the particles distribution surface of thin film. It is important to mention here that the substrate temperature and kinetic energy of the particles qualified as remarkable energy sources during PLD film growth and influenced on both film morphology and crystalline structure. It was concluded that the grain dimensions and film roughness increase with increasing temperatures. An increase of the substrate temperature will lead to increase the surface mobility of clusters at the film surface. Such case encourages coalescence of cluster to form larger clusters **[9].**

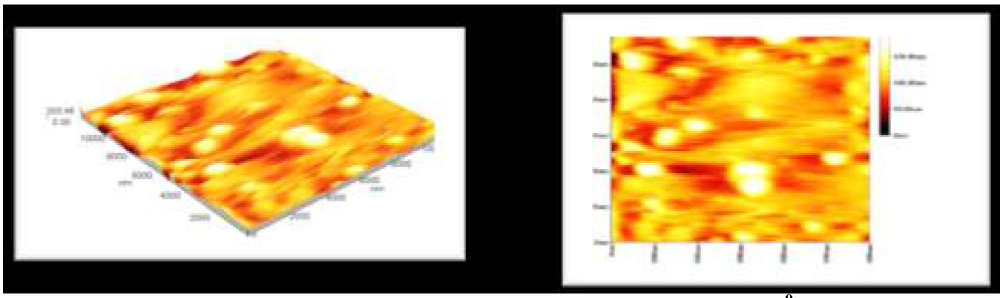


Figure 6: AFM images of TiO_2 at substrate temperature 200'^{0}C', 500,1J

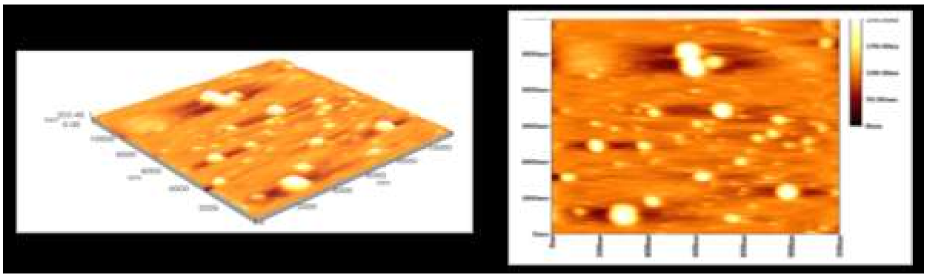


Figure 7: AFM images of TiO_2 at substrate temperature 100'^{0}C', 200, 800mJ.

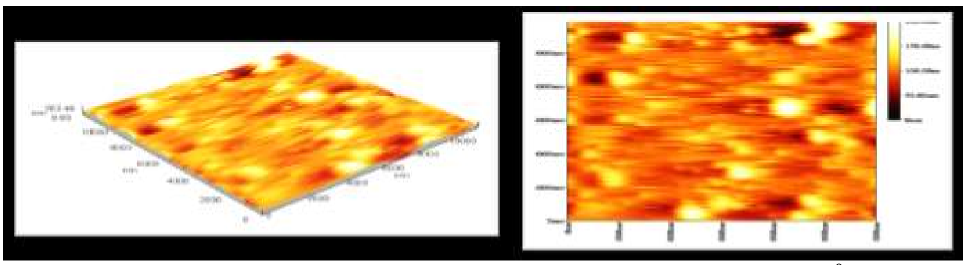


Figure 8: AFM surface images of TiO_2 at substrate temperature 200'^{0}C', 300, 1J.

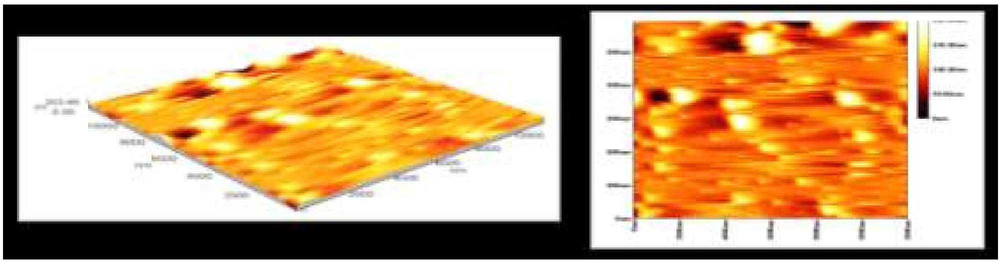
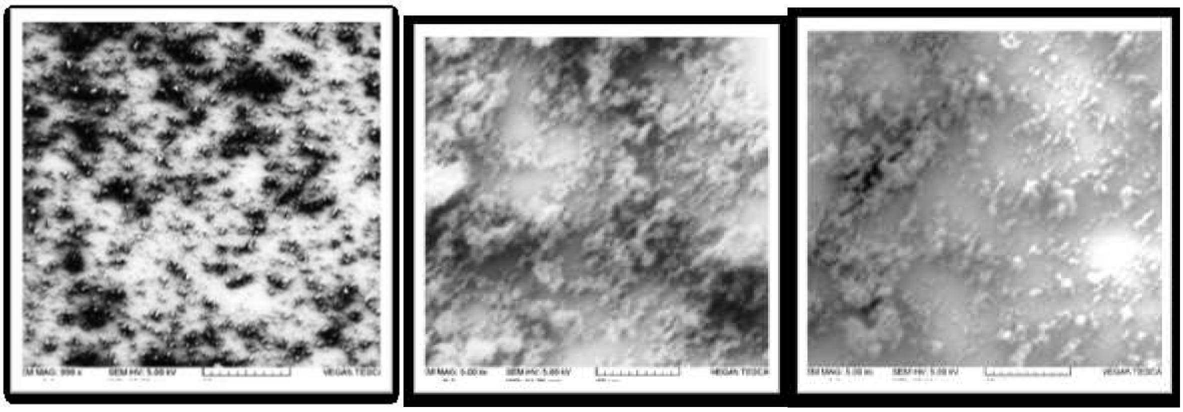


Figure 9: AFM images of TiO_2 substrate temperature 300’^{0}C’, 300, 900 mJ.



(A) (B) (C)

Figure 10: SEM images of TiO_2 at different substrate temperatures A) 100’^{0}C’, B) 200’^{0}C’ and C) 300’^{0}C’.

III.Corrosion Rate

Results of potentiostatic corrosion tests at different PLD parameters of Titanium oxide deposited on steel A106-B are show in Table 5. The corrosion resistance of all prepared samples of coated A106-B show higher values than that of the parent A106-B. **[11]**. Figure (11) illustrates the comparison between the results of the uncoated (polarization without coating A and B) and coated (with TiO_2 at 100’^{0}C’ substrate temperature, 200 pulses number and 800 mJ/cm^2 fluencies energy).

Table 5: Taguchi design results.

	Virtual Factors			**Actual Factors**			**Output**		
No.	A	B	C	Temp.	No. of shoots	Fluencies energy	Corrosion rate (1)	Corrosion rate (2)	Mean
1	1	1	1	100	300	800	0.0000890	0.0002118	0.0001504
2	1	2	2	100	400	900	0.0000662	0.0000947	0.0000805
3	1	3	3	100	500	1000	0.0000770	0.0000903	0.0000837
4	2	1	2	200	300	900	0.0000500	0.0000537	0.0000519
5	2	2	3	200	400	1000	0.000075	0.0000725	0.0000742
6	2	3	1	200	500	800	0.0000721	0.0000697	0.0000709
7	3	1	3	300	300	1000	0.0000046	0.0000077	0.0000062
8	3	2	1	300	400	800	0.0000611	0.0000441	0.0000526
9	3	3	2	300	500	900	0.0000890	0.0001455	0.0001173

Table 6: Results of potentiostaticic corrosion tests for comparison.

Samples	I corr × 10^{-6} A/cm^2	Corrosion rate(mpy)	*Corrosion resistance*	Enhancement
A106-B-1	$5.16*10^{-4}$	$4.77*10^{-4}$	2096	99%
Optimized coating-1	$1.88*10^{-6}$	$4.61*10^{-6}$	216919	
A106-B-2	$5.66*10^{-4}$	$5.24*10^{-4}$	1908	99%
Optimized coating-2	$3.16*10^{-6}$	$7.75*10^{-6}$	129032	

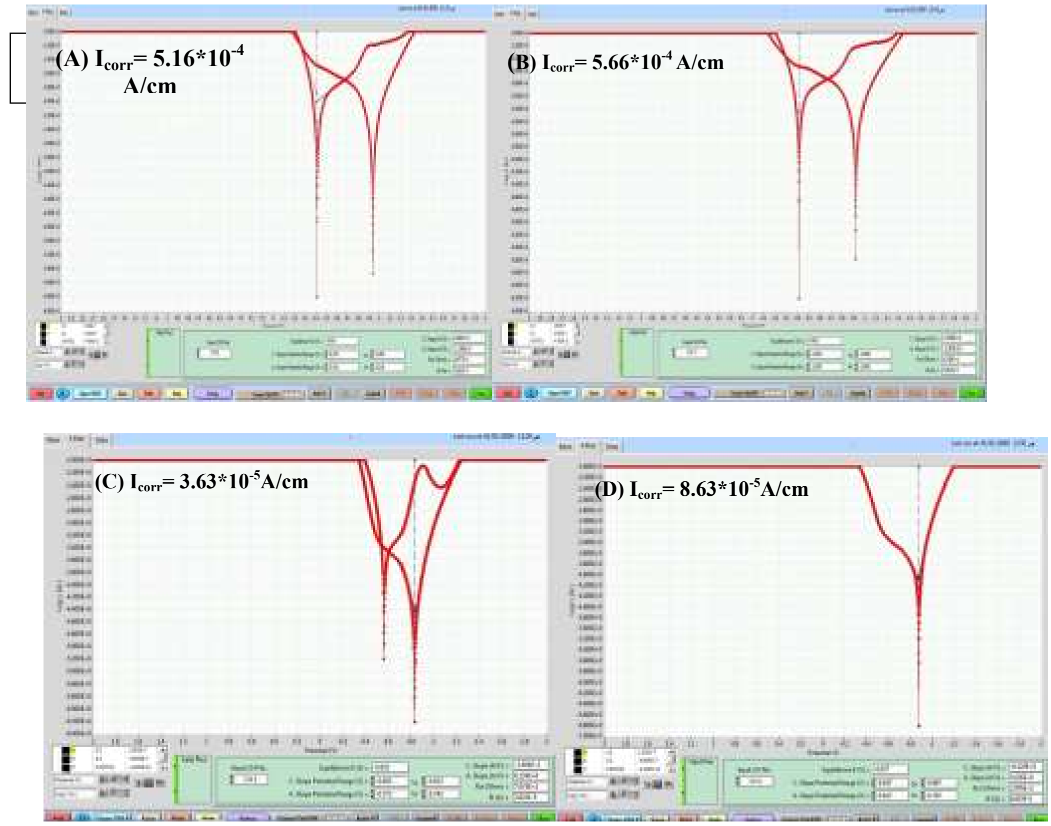


Figure. 11: Potentiostatic polarization behavior of (A): uncoated A106-B, (B): uncoated A106-B, (C): TiO_2 deposit on steel A106-B, (D): TiO_2 deposit on steel A106-B.

III. Effect of substrate temperature, number of pulse shoots and fluencies energy on corrosion rate:

Substrate temperature plays an important role on the morphology, structure of the TiO_2 films, also coating adhesion .Number of laser shoots and influences energy density leads to thigh kinetic energy of particles ejected from the target which facilitates the growth of the grains and crystallization on TiO_2 film. However, increment of energy density may increase the size and the density of the droplets of TiO_2 films. It's evident that in the figures (12, 13) shows the PLD parameters effected on corrosion rate. It can be seen that the raise in substrate temperature leads to minimize corrosion rate, because this range of temperature effected on morphology characterization of TiO_2 film. Reduction in number of laser pulses minimizing corrosion rate. Increasing number of laser pulse encourages obtain non-homogeneous distribution of nanoparticle associated with substrate temperature and fluencies energy. The raise of influencing energy leads to reduce the corrosion rates in addition to deposition rate grows with the fluencies energy too, as the number of pulses progresses, this trend is more important In order to see the efficiency of material deposition obtained from the ablation process, the deposition rate equalized to the fluency which represented against the fluency **[10, 11].**

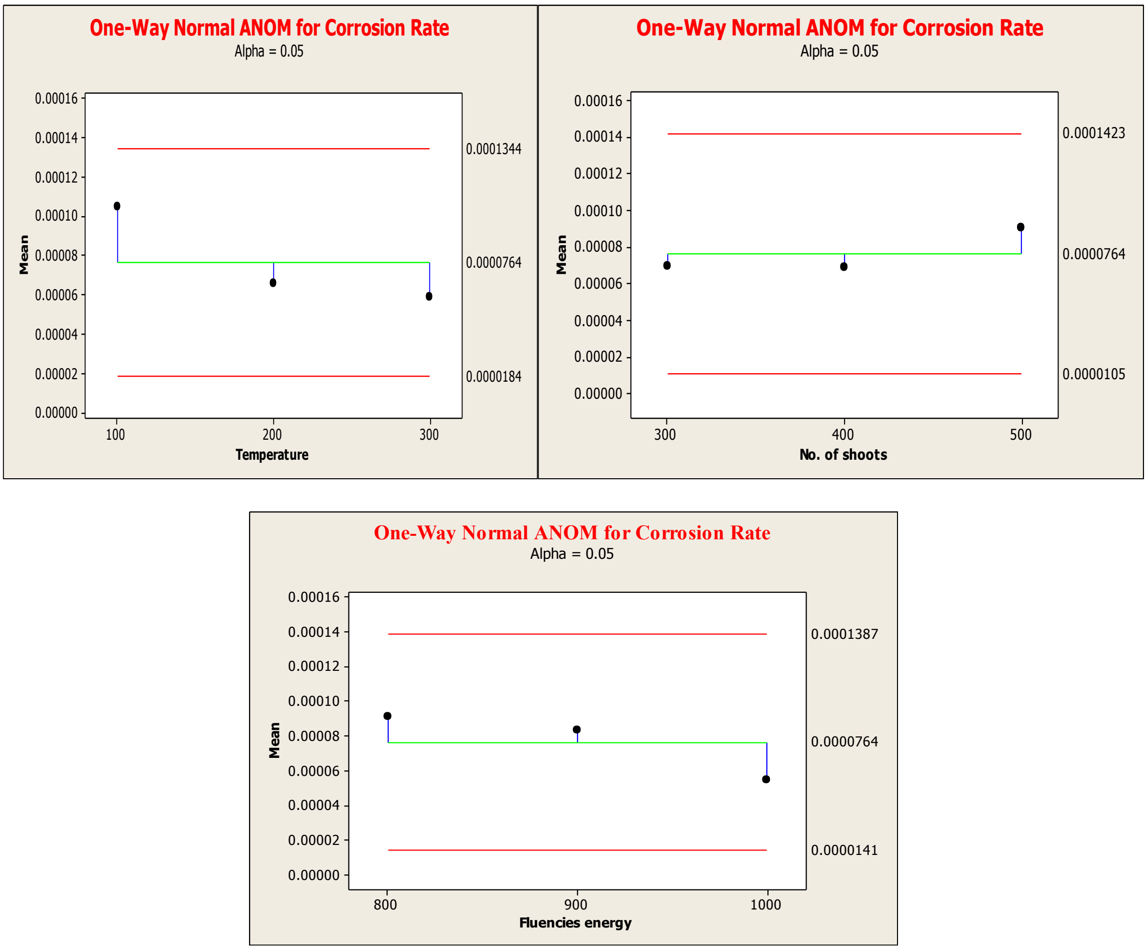


Figure. (12): Analysesis of mean for (A) substrate temperature, (B) number of pulse shoots and (C) fluencies energy.

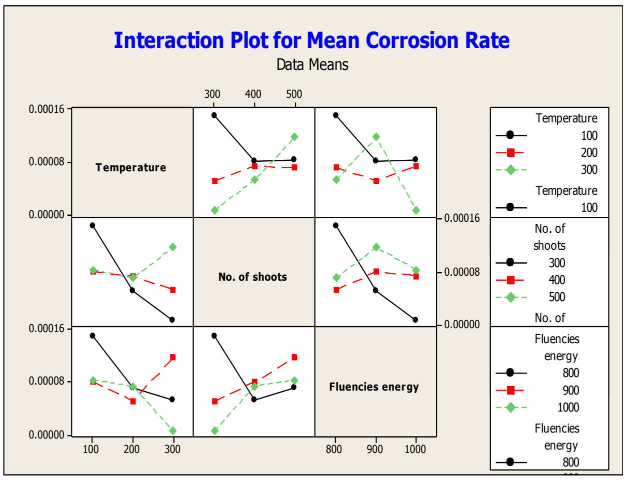


Figure. 13: Interaction plot mean corrosion rate in PLD technique.

IV. Analysis of Variance for corrosion rate

Analysis of variance (ANOVA), results was performed to evaluate the source of parameters during the PLD process for TiO_2 coatings in order to identify the factors significantly affecting on TiO_2 coatings and their contribution for these factors to the corrosion resistance of the coatings.

The results of the ANOVA for corrosion rate are given in Table (7) and figure (14) that shown pie chart based on this analysis. The analysis was carried out for a significance level of α=0.05, i.e. for a confidence level of 95%. From these results it is clear that the number of shoots pulse significantly effect on the corrosion rate, which is highest among the contributions of the other parameters. So, the important conditions are No. of shoots (58.03%) which is about three times of the fluencies energy (19.12%). The substrate temperature has a few influences with (4.22%). In general as the substrate temperature increases more than 300 ^{0}C used in this study will lead to increment in surface roughness, and as we know the corrosion rate effected by this morphology property, Moreover the limitation substrate temperature in the pulse laser deposition system was used in this study.

Table 7: Analysis Variance for Corrosion Rate.

Source of variance	DOF	Sum of Square	Variance (V)	F	P %
Temperature	2	3.1	1.5	0.13	4.22
No. of shoots	2	42.47	21.23	4.15	58.03
Fluencies energy	2	13.99	7.00	0.71	19.12
Error	2	13.62	6.81		18.61
Total	8	73.18			100

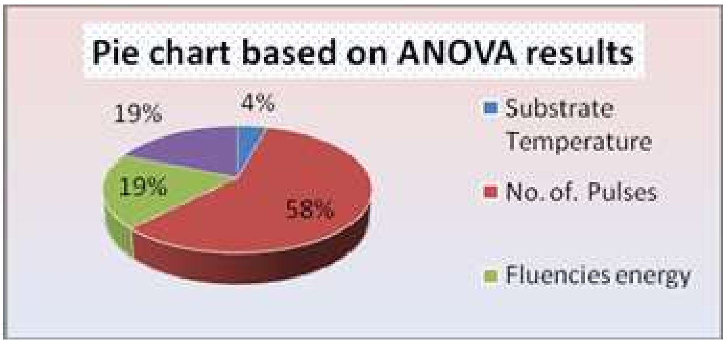


Figure 14: PLD parameters distribution based on ANOVA.

V.Optimum Design Conditions for Corrosion Rate

Plots are used for determining the optimum design conditions to have the optimal corrosion rate and conditions of PLD is "Minitab 16 program". Figure (15) explain effect of corrosion rate and input parameters process. This figure explains differences for the responding of the three input parameters, (i.e. substrate temperature, number of pulse shoots and fluencies energy). The optimum conditions to minimize corrosion rate are: temperature at level-3 (300 ’ºC’), number of shoots at level-1(300), and fluencies energy at level-3 (1000 mJ/cm^2). Also, figure (16) shows three dimensional plots of PLD parameters. It was noted that the numbers of pluses is the highly affective parameter in minimizing corrosion rate with optimal parameters that was used which is (98.6).

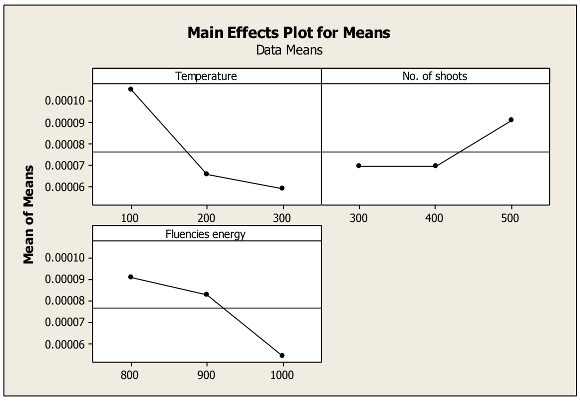


Figure 15: Dependences of the mean corrosion rate on the: (a) substrate Temp., (b) No. of laser shoots and (c) fluencies energy.

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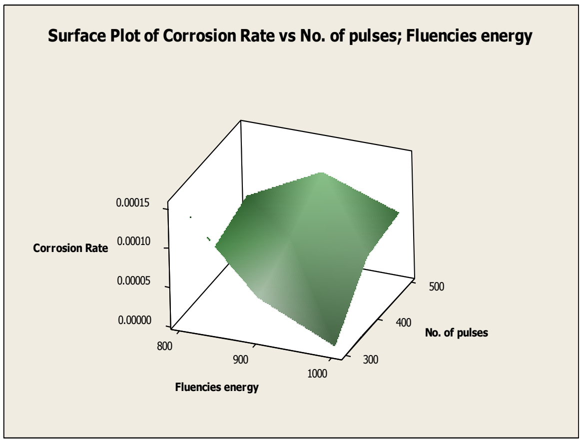

Figure 16: The interaction between PLD parameters and their effect on the corrosion rate.

4. Conclusions

In this paper TiO_2 thin film deposited on steel A106-B by PLD technique was achieved successfully. The results of the Taguchi analysis showed that the numbers of laser pulses considered the most important factor on corrosion rate. Also TiO_2 coated with PLD parameters at level 3 has the best properties of TiO_2 thin-film coatings that possess high corrosion resistance. Moreover, the uniform and roughness prepared thin film improve the corrosion resistance of the A106-B. The Taguchi analyses of experiments design simplify the arrival process to the optimal parameters of the PLD process. It was concluded that the number of laser pulses is the major parameter affecting on the corrosion behavior of the coating. The fluencies energy coating rate found to be the second important factor affecting the corrosion resistance of the coating, while the substrate temperatures have weaker effects on the corrosion resistance. The contribution percentages of the substrate temperature, number of pulse laser, and fluencies energy to the corrosion resistance are 4.22%, 58.03%, and 19.12%, respectively. The optimized processing parameters are as follows: 300 '^{0}C' for the substrate temperatures, 300 for numbers of laser pluses, 1000 mJ / cm^2 for fluencies energy. The corrosion resistance of the optimized coating is roughly 99 times higher than parent metal.

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