Journal of Petroleum Research and Studies

Open Access
No. 34 Part 2, April 2022, pp. 290-301

P- ISSN: 2220-5381
E- ISSN: 2710-1096

DOI: http://doi.org/10.52716/jprs.v12i1(Suppl.).638

Studying the effect ZnO_{NP} Deposited on ST37-2 by Pulse Laser Depositions Technique for Corrosion Protection Using in Oil Storage Applications.

Ahmed S. Abbas, Iman Adnan Annon, Firas. F. Sayyid
Production Engineering & Metallurgy Department - University of Technology / Baghdad - Iraq.
Corresponding Author E-mail: 70017@uotechnoogy.edu.iq

6th Iraq Oil and Gas Conference, 29-30/11/2021

Abstract

In the study, zinc oxide nanoparticles (ZnO_{NP}) were coated on carbon steel substrates via pulse laser deposition (PLD) process, in order to achieve passive layers of nanocoating. ST37-2 a type of steel is used in the manufacture of tanks that are used in oil applications, which suffers from corrosion, this will lead a large losses. Electrochemical technique (Tafel polarization completion) has been carried out for study the corrosion behavior of this steel coating type. The specimens of steel were examined in aqueous solution containing about 3.5 wt. % NaCl using polarization method, with power of hydrogen (pH) held to value 4.0, in order to evaluated the corrosion rate. $ZnO_{NP.}$ Characteristics and topographic nanocoating by PLD technique were evaluated by Field Emission Scanning Electron Microscope (FESEM) and X-ray Diffraction (XRD) tests. Where semi uniform nanoparticles of ZnO_{NP} were achieved with a nanoscale approximately ranging from 33-56 nm, While XRD pattern indicated the presence of ZnO_{NP} with different crystal structures. In other side the input parameters of (PLD) technique were substrate temperature, number of pulse and fluencies energy have been examined, in order to study their influence on the rate of corrosion reduction. The results indicate that number of shoots pulse has a significant effect the corrosion rate in operation of PLD technique, which is highest among the contributions of the other parameters. Enhancement about 56% is achieved of ST37-2 coated with (ZnO_{NP}) deposition, as compared with uncoated steel.

Keywords: ZnO, nanocoating, ST37-2, PLD, Corrosion rate.

دراسة خصائص اوكسيد الزنك النانوي المطلي على الفولاذ نوع 37-2 للحماية من التآكل والمحضر بتقنية الترسيب الليزري النبضي والمستخدم في تطبيقات الخزن النفطي.

الخلاصة :

في هذه الدراسة ، تم ترسيب دقائق من أوكسيد الزنك النانوية على اساس من الفولاذ الكاربوني نوع 37-2 بأستخدام تقنية الترسيب الليزر النبضي وذلك لاعداد طلاء مقاومة للتآكل.
أستخدمت الطريقة الكهروكيميائية (استكمال منحني تافل) لدراسة سلوك التآكل لطلاءات اوكسيد الزنك النانوي على

Open Access
No. 34 Part 2, April 2022, pp. 290-301

P- ISSN: 2220-5381
E- ISSN: 2710-1096

الفولاذ . تم تقييم العينات المطلية بماء البحر وبنسبة 3.5 ٪ من محلول كلوريد الصوديوم باستخدام تقنية الاستقطاب مع ضبط الأس الهيدروجيني إلى 4.0 لتحديد معدلات التآكل. حيث تميزت العينات المرسب عليها أغشية أوكسيد الزنك الرقيقة بتقنية الليزر النبضي بمقاومة تأكل جيدة مقارنة بالعينات الاساس بدون طلاء بحدود 56%. تم دراسة طوبغرافية وخصائص الطلاء باستخدم المجهر الماسح وحيود الاشعة السينية , حيث أشارت النتائج إلى أن متغيرات الترسيب النبضي بالليزر من درجة حرارة و عدد نبضات وطاقة يؤثر على خصائص الطلاء لكن عدد النبضات شكل العامل الاكثر اهمية من بينها.

الكلمات المفتاحية: معدل التآكل، الفولاذ الكاربون نوع 37-2 طلاء نانوي، اوكسيد الزنك.

1. Introduction

The corrosion problem is one of the most important industrial problems in oil sectors, which costs money, maintenance, effort and time, in addition to monitoring [1]. Oil and gas transport pipelines and tanks are exposed to damage due to corrosion, which draws great attention from researchers, educational and research institutions, in addition to private companies [2]. Particular in Iraq, due to the types of soil and cruel climatic conditions, large parts of oil and gas transport pipelines and tanks are exposed to damage [3]. Carbon steel, whether was medium or low, is commonly used in oil applications such as, pipelines or tanks, because of its good properties and availability, in addition to low cost [4]. It is very common to use ST37-2 in tanks and drums in Iraqi Factories and Petroleum refinery [5]. This type of metals are affected by corrosion, especially the external areas, so precautions, must be taken to maintain [5]. Unluckily oil or gas tanks life can be dramatically limited by corrosion and this represented a serious problem for many years [6]. Many researchers have drawn a big attention to this topic and implanted many conditions conventional corrosion protection systems such as coatings, cathodic protection, and inhibitors and even are not active enough, having a short service life, or cannot be applied. E. Ya. Lyublinski et al [7] applied cathodic protection combination with soluble corrosion inhibitors. M. J. Kadhim et al [8] deposited titanium oxide on the surface of the steel type A106-B which, commonly used as an oil pipe via PLD technique. On the other side, the importance of nanotechnology rise as a hope representing the new era in the protection of petroleum applications [8, 9]. This paper describes impact of ZnO_{NP} on ST37-2 to obtain a distinctive and nano textured implanted by PLD technique that, gives good surface characteristics to protect against corrosion.

Open Access
No. 34 Part 2, April 2022, pp. 290-301

P- ISSN: 2220-5381
E- ISSN: 2710-1096

2. Material and processes

1.1 Base Metal

The material substrate that used in this work St37-2carbon steel has been analyzed in the (Al-Nabaa Co. Engineering Services Ltd.) using spectrometer type (Pmi Master Pro) optical emission spectrometer (OES) (S.N52Q0089) robust mobile model, German manufacturing under conditions at the temperature of 20 ºC and the humidity of 63%. The results of the analysis have been illustrated in the Table (1), which includes the stander and actual and measured values of chemical compositions belong to material substrate.

Table (1) Shows the standard and actual chemical compositions values of steel carbon steel type 37 - 2 [10].

Chemical compositions %	Stander Values	Actual Values
C	Max. 0.21	0.17
Mn	0.29–1.70	0.86
Si	Max.0.60	0.16
P	Max. 0.065	0.010
S	Max. 0.065	0.020
Cr	Max.0.40	0.01
Ni	Max.0.40	0.09
Mo	Max.0.15	0.01
V	Max.0.08	0.004
Cu	Max.0.40	0.03
Fe	Remaining.	Remaining.

2.1 Carbon steel (ST37-2) microstructure test

The microstructure examination of the base metal was carried out in steps represented by following stages. The first, which was the process of grinding the surface, this operations via abrasive sand papers with different number of grains per square inch including 120, 320, 500, 1000 and 2000 grit .While the second stage was polishing using alumina particles with soft cloth, until the surface sample becomes somehow similar to mirror. Then the microstructure is should applied to a chemical treatment known as etching process using Nital (2% $HNO3$ + 98% Alcohol), then microstructure imaging using an optical microscope (carlzeiss jena) type with a digital camera arrangement. The microstructure represented by areas of dark color

Open Access
No. 34 Part 2, April 2022, pp. 290-301

P- ISSN: 2220-5381
E- ISSN: 2710-1096

known as Pearlite phase (α + Fe_3C), and, on the other side were more bright colored areas founded are known as ferrite (α-Iron phase), and through the volume fraction, it clear that this type of carbon steel is medium, and the Figure (1) depicted that friction area consists of ferrite to pearlite.

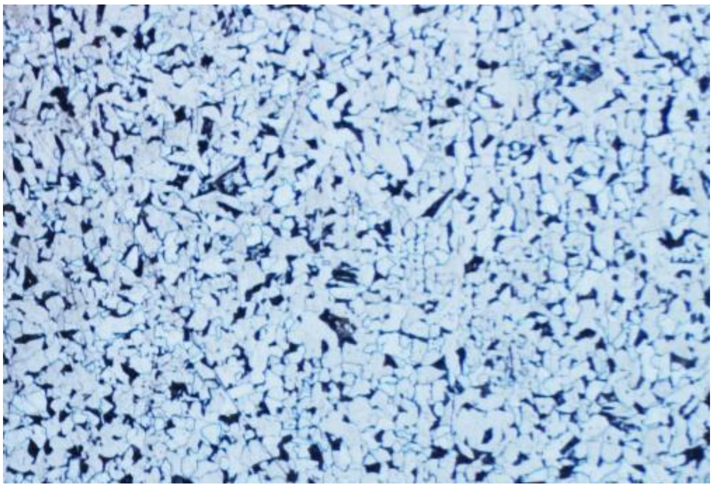

Fig. (1): Microstructure of St37-2 carbon steel used in work.

3.1 ZnO powder

Zinc oxide powder (ZnO) has been used as a metallic powders in this work. The physical properties and specifications of ZnO powder are illustrated in Table (2), which fabricated by Nanjing Nanotechnology Co. Ltd.

Table (2) Specifications of ZnO nanoparticle.

Property	The value	Units
Average particle size	< 100	nm
Purity	97.98	%
Specific surface area	15 - 25	m^2 /g
Bulk density	0.25 - 0.4	g / cm^3
True density	5.61	g / m^3
Color and Form	off-white powder	-

Open Access
No. 34 Part 2, April 2022, pp. 290-301

P- ISSN: 2220-5381
E- ISSN: 2710-1096

While temperatures of evaporation and melting belong to nanomaterial under various circumstances are listed in Table (3).

Table (3) depicted the temperatures of melting and evaporation, which refers to ZnO_{NP}.

Metal	Density bulk g / cm^3	Melting temperature, $^{\circ}C$	Temperature & Vapor pressure (Torr).
			10^{-4}
ZnO_{NP}	5.61	1975	1800

4.1 ZnO_{NP} Powder

X-Ray diffraction of ZnO NP Powder is presented in Figure (2) based on comparing the results obtained from miller indices and angles of the XRD, corresponding to the strong peaks of the zinc oxide nano powder. The values are stated in according to standard numbered card # 36-1451 issued by the Joint Committee on Powder Diffraction Standards, (JCPDS) (the new name is international center for diffraction data, ICDD) [Ref.]. The results were well matched in terms of miller indices with a slight match in the diffraction angle values. The crystal does not exceed the same angle value for a number of distinctive peak positions, as shown in Table (3). These peaks are belonged to zinc oxide. the crystalline structure of ZnO_{NP} denoted the recognize peaks at angles 31.88°, 34.57°, 36.35, 47.70°,56.602° and 62.862° refer to the nano oxide zinc powder with structure (100), (002), (102),(110) and (103) respectively [ref].

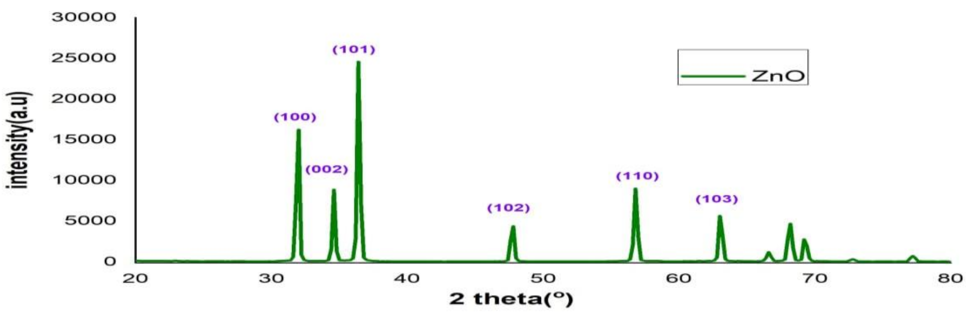

Fig. (2): XRD pattern of ZnO_{NP} powder as received.

Open Access
No. 34 Part 2, April 2022, pp. 290-301

P- ISSN: 2220-5381
E- ISSN: 2710-1096

2.5. Thin Film Preparation Procedure with PLD

2.5.1 Target Preparation for PLD

Zno nanoparticles were compressed into a disc form of 25mm diameter and thickness of 6mm using a uniaxial press with ability (1400 kg/cm^2), as depicted in the Figure (3) below, which described the punch, die and uniaxial press, so as to implement the zinc oxide target. While Figure (4) shows the dimensions and shape belong to the (ZnO) PLD target.

Fig. (3): Illustrates the uniaxial press instrument

After that the pellet is sintered at 450°C, in furnace for 1 hour in order to be used as a target for the PLD.

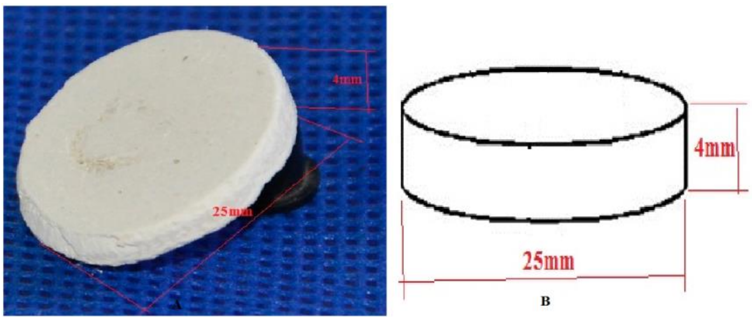

Fig. (4): Showing (A) the actual photo of ZnO target pallet,(B) shape and geometry of ZnO target pallet

Open Access
No. 34 Part 2, April 2022, pp. 290-301

P- ISSN: 2220-5381
E- ISSN: 2710-1096

2.5.2. Pulse Laser Deposition (PLD) system

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 fluencies energy 1 J/cm ^{2}. The distance kept constant between ZnO target and laser source by 5 cm. where the other PLD working conditions illustrate in the Table (4).

Table (4) Variables and conditions involved for PLD

parameter	The value	Units
The initial substrate temperature	27	ºC
Frequency	1	Hz
Energy	1	J
Pulse duration	3×10^{-9}	sec
Deposition time	1	

Figure (5) shows the photograph of the excremental work unit with PLD system. Then, the chamber was evacuated using a rotary pump with the aid of a turbo molecular pump to arrive the required operating pressure, until the pressure reaches 0.00075 torr, which is equivalent to 1×10^{-3} millibars (mbar). While the time required for depositions with this technique at rate one pulse for every second. The average number of pulses was applied on the ZnO disc are 300. The films were grown on the substrate of the ST37-2 material. During coating process the substrate temperatures was 300 º C. On the other hand, the repetition rate was 5 Hz and the operating pressure was kept constant at 10^{-2} mbar. Temperature at 300 ºC, number of shoots are 300, and fluencies energy 1000 mJ/cm^2 considered as optimal conditions to minimize corrosion rate are.

Fig. (5): Illustrated the PLD system used in study

Open Access
No. 34 Part 2, April 2022, pp. 290-301
P- ISSN: 2220-5381
E- ISSN: 2710-1096

2.6. Corrosion Study

In order to study the corrosion behavior of ST37-2 and ZnO_{NP} coated on this type of steel a solution of sea water was prepared from a 3.5 wt.% NaCl solution with pH kept to 4.0 by adding 35 grams to one liter of NaCl to distilled water. The test implanted by using potential static device polarization model DY23OO as depicted in Figure (6).

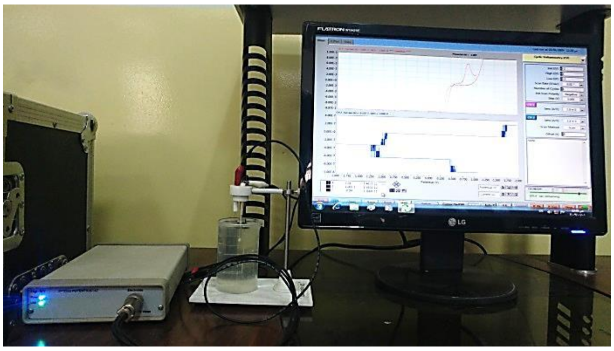

Fig. (6): Polarization instrument used in this work

3. Results and Discussion

3.1 (ZnO) nanocoating

The effect of PLD conditions including (substrate temperature, number of shoots and fluencies energy) on formation of ZnO_{NP} thin film growth have been analyzed. It was noted; that the numbers of pluses shooting of the PLD process have the most influencing factor on the substrate is determined by the time duration of the PLD. In other hand the appearance of the coating seemed uniform and dark, with a color that, tends to gray as shown in the Figure (7).

Fig. (7): Depicted specimen surface, (A) before coating, (B) after PLD coating

Open Access
No. 34 Part 2, April 2022, pp. 290-301

P- ISSN: 2220-5381
E- ISSN: 2710-1096

3.2. XRD analysis

XRD patterns of the ZnO_{NP} on ST37-2 metal substrate using the PLD technique at conditions (substrate temperature 300 ºC, number of shoots 300, and fluencies energy 1000 mJ/cm^2 are depicted in Figure (8) below. It is clear that, black lines in modify XRD pattern diagram indicted the strong peaks at angles 29.67°, 44.9° and 65.2° having crystal structures (111), (110) and (200) respectively ,corresponding to the Iron (Fe) in ST37-2(Ref .PDF #006-0696), while, red lines shows ZnO_{NP} strong peaks at angles, 30.91°, 33.66°, 36.49° and 66.37° (Ref. PDF #2111486).

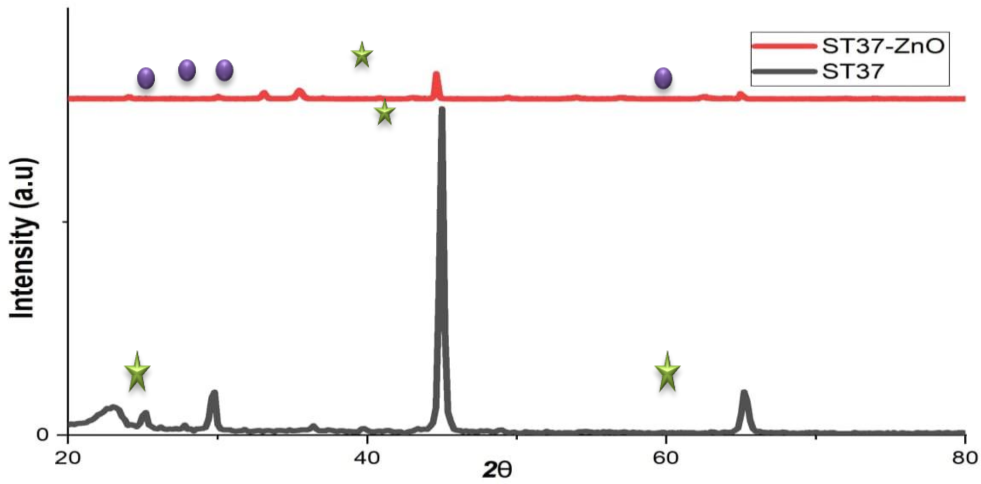

Fig. (8): XRD pattern of ST37-2 and ST37-2 coated ZnO_{NP}

3.3. Surface morphology results

The surface prepared by PLD technique was investigated by FESEM in order to know, more details about the shape and size of nanoparticles. Figure (9) imaging the morphology, of the surface topography, after, the PLD, coatings. Based on the substrate surface characteristics and the conditions of PLD process, like (substrate temperature, number of shoots, and fluencies energy, it was observed that the surface topography appear as valley and hill with spread of hillock. Thus affected the increase in the collision between the nanoparticles of the deposited ZnO, a small grains formed from those particles to accumulate together to become so larger grains. a dense layer is distinguished on the surface topography also, noted that a small semi spherical nanoparticles are observed homogeneously and uniformly distributed over the ST37-2 surface area. Figure (9) demonstrated the topography of ZnO_{NP} surfaces. Aggregations of zinc oxide particles were also observed, with sizes ranging from approximately 33-56 nm, Due to the

Open Access
No. 34 Part 2, April 2022, pp. 290-301

P- ISSN: 2220-5381
E- ISSN: 2710-1096

nature of deposition by the PLD method, the mechanism is based on the ablation of the metal atoms not evaporating them, from the metal target in non-equilibrium state, in addition to the fact that the target is zinc oxide, not pure zing element, which causes accumulations and gatherings in some areas.

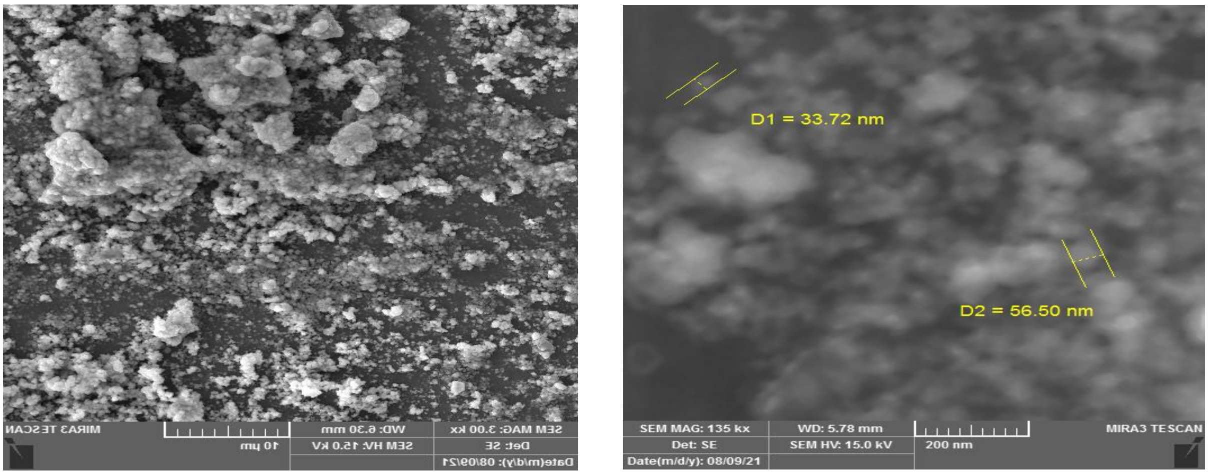

Fig. (9): FESEM images depicted the surface morphology of ST37-ZnO_{NP}

3.4 Corrosion rate results

Results of corrosion examine at PLD parameters of ZnO_{NP} coated on ST37-2 are showed in Table (5). While the corrosion behavior of uncoated sample, as compared with coated sample clearly observed, and the corrosion characteristics including corrosion current, corrosion rate and corrosion resistance are illustrated in the Table (5), clearly improvement in the corrosion resistance was noted about 56% .The corrosion resistance of all prepared coated samples ,demonstrated higher values than that of the parent metal (ST37-2). Figure (10) illustrates the comparison between them.

Open Access
No. 34 Part 2, April 2022, pp. 290-301

P- ISSN: 2220-5381
E- ISSN: 2710-1096

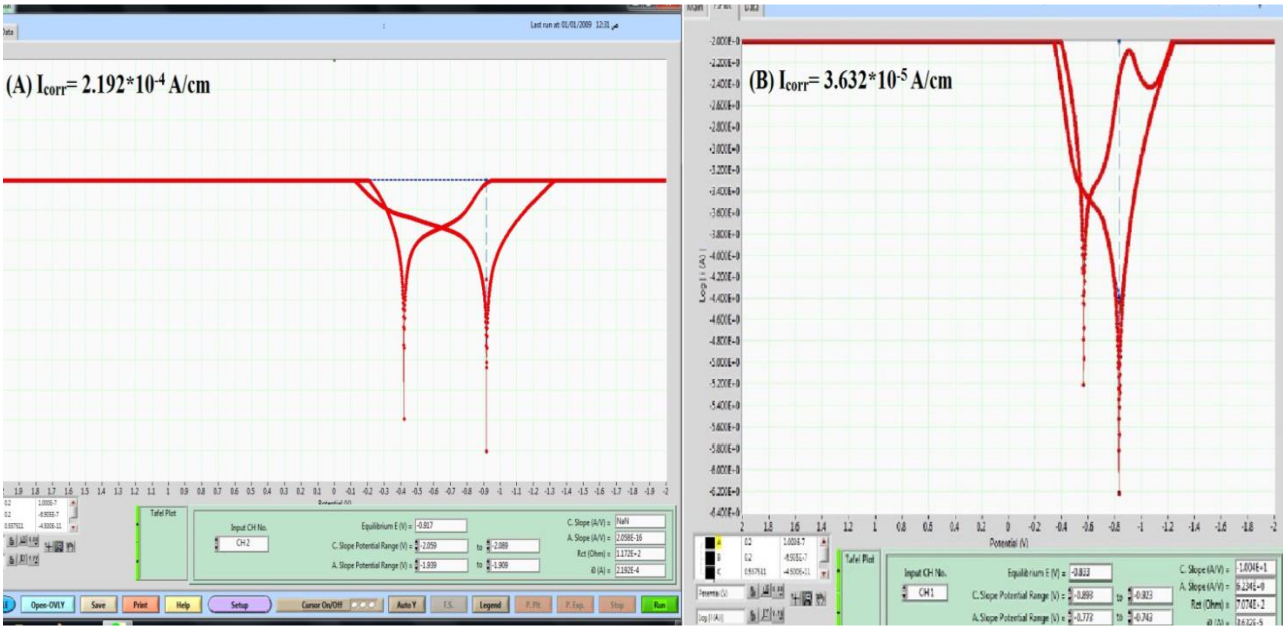

Fig. (10): polarization behavior of (A) ST37-2 , (B) ST37-ZnO_{NP}

Table (5) Results of corrosion tests

Samples	$I_{corr} \times 10^{-6}$ A/cm^2	Corrosion rate (mpy)	*Corrosion resistance*	Enhancement
ST37-2	2.192*10^{-4}	2.026*10^{-4}	4935.834	56%
ST37-ZnO	3.632*10^{-5}	8.906*10^{-5}	11228.385	

4. Conclusions

In this study, zinc oxide nanoparticles were deposited on carbon steel of type 37-2 by PLD technique and under working conditions substrate temperature at 300 ºC, number of shoots is 300, and fluencies energy 1000 mJ/cm^2.

A homogeneous and regular texture was obtained from zinc oxide nanoparticles with nano size ranging from 33-56 nm, which led to an improvement in the surface characteristics of corrosion resistance at a rate compared to the base metal, where the results showed a clear improvement about 56%.

Open Access
No. 34 Part 2, April 2022, pp. 290-301

P- ISSN: 2220-5381
E- ISSN: 2710-1096

References

[1] Bahadori, Alireza. Essentials of coating, painting, and lining for the oil, gas and petrochemical industries. Gulf Professional Publishing, 2015.

[2] Miesner, Thomas O., and William L. Leffler. Oil and gas pipelines in nontechnical language. PennWell Books, LLC, 2020.

[3] Sulaiman, Qasim, Ali Al–Taie, and Dahlia Mohamed Hassan. "Evaluation of sodium chloride and acidity effect on corrosion of buried carbon steel pipeline in Iraqi soil". Iraqi Journal of Chemical and Petroleum Engineering 15, no. 1 (2014): 1-8.

[4] Usman, AMINU D., and LINUS N. Okoro. "Mild steel corrosion in different oil types." International journal of scientific research and innovative technology 2, no. 2 (2015): 9-13.

[5] Abdullah, Hiba Anwer. Corrosion behavior of steel (St 37-2) by using natural products as Inhibitors In Petroleum Medium. Diss. Department of Materials engineering, University of Technology, 2014.

[6] Beavers, John A., and Neil G. Thompson. "External corrosion of oil and natural gas pipelines." ASM handbook 13, no. 05145 (2006).

[7] Clark, Peter D., David R. Hornbaker, and Thomas C. Willingham. "Preventing corrosion in sulfur storage tanks." Alberta Sulphur Research Ltd Quarterly Bulletin 45, no. 2 (2008): 1-20.

[8] LYUBLINSKI, E., Yu I. Kuznetsov, Marcelo Schultz, and Yefim Vaks. "Corrosion protection of tank product side bottoms." International Journal of Corrosion and Scale Inhibition 2, no. 2 (2013): 150-161.

[9] M. J. Kadhim , A. S. Abbas and K. A. Sukkar, "Investigation Nano coating for Corrosion Protection of Petroleum Pipeline Steel Type A106 Grade B; Theoretical and Practical Study in Iraqi Petroleum Sector." Engineering and Technology Journal 35.10 Part A (2017).

[10] Schweitzer, Philip A. Metallic materials: physical, mechanical, and corrosion properties. Vol. 19. CRC press, 2003.

[11] Saji, Viswanathan S., and Joice Thomas. "Nanomaterials for corrosion control." current science (2007): 51-55.

[12] Matteo, Cocuzza, Pirri Candido, Rocca Vera, and Verga Francesca. "Current and future nanotech applications in the oil industry." American Journal of Applied Sciences 9, no. 6 (2012): 784.