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جمعية كليات الهندسة اعضاء اتحاد الجامعات العربية

Nanoparticles Coatings to Reduce Corrosion of Carbon Steel in Artificial Seawater

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Abstract—Nanoparticles of Titania, Alumina, and Zirconia coatings were used on carbon steel specimens to test their ability for corrosion protection by using the atomization method. An airbrush was used with nitrogen gas to coat nanoparticles on carbon steel surfaces. The coatings percentage includes 100% nano Titania, 50% nano Titania – 50% nano alumina, and 50% nano Titania – 50% nano Zirconia. Field-emission scanning electron microscopy (FESEM) was used in this experiment. The particle size ranged from (28.42 - 44.31) nm, (34.77 - 47.15) nm, and (34.51 - 51.46) nm for titania, titania-alumina, and titania-zirconia coating, respectively. Furthermore, Energy dispersive X-ray spectroscopy (EDS) analysis used for the elemental analysis or chemical characterization of sample indicates that the highest percent of Fe was in titania coating compared with alumina and zirconia, other metals such as C, Si, and N appear because they present in the composition of carbon steel. Ti was recorded as 4.9, 23.4 and 29.26 wt% for coating by titania, titania-alumina, and titania-zirconia respectively. The corrosion test on specimens was performed. It showed that the potential–time measurement for uncoated and coated carbon steel recorded open circuit potential (Eoc) value of -0.6 V for uncoated sample, whereas the open circuit potential (Eoc) value was -0.313 V, -0.568 V and -0.572 V for coating by Titania, Titania-Alumina and Titania-Zirconia materials respectively. polarization curve for titania coated carbon steel indicating the lower corrosion rate which recorded 0.228 mm/y while the Titania-Zirconia coated carbon steel gave the highest corrosion rate of 2.511 mm/y followed by Titania-Alumina coating to give 2.187 mm/y compared with the rate of uncoated carbon steel sample which recorded 0.721 mm/y

Keywords—*Alumina, Carbon steel, Nano particles, Seawater, Titania.*

1. Introduction

Nanoparticle coatings can provide high protection layers on metals and alloys to solve corrosion problems [[22]22]. Vacuum and non-vacuum Nanocoatings can be made such as sol–gel, electrodeposition, atomization, and laser beam surface treatment [1]. Nanomaterials show excellent progress in preventing hightemperature oxide scale formation [10]. Nanomaterials have ability to fill the spaces leading to prevent of waterand air entry providing more efficient passive protection [9].

An appropriate design can minimize corrosion by selecting suitable materials [2]. Ceramic coatings based on thermal spray coating, dry-film lubricants, and other wet chemicals such as electrochemical coatings [19]. These types of coatings have some beneficial properties: such as the lifetime of the coated material increased, the corrosion rate reduced, and friction will be enhanced [5]. On the other hand, ceramic coatings have some disadvantages as well: they become brittle and difficult to repair; during the expansion and contraction, broken bonds can occur; at the cracks, corrosion easily occurs; they are larger than organic coatings [13]. Nanoparticle materials show promising advantages in preventing high temperature oxide scale formation [22]. Many works were done using nanoparticles in coating with different techniques such as nanostructured Al_2O_3-TiO_2 [24,25], nano alumina [21, 16], nano silica [15], nano alumina – hydroxyapatite [17], nano alumina -SiC and -ZrO_2 [7, 8], nano- and micro-composite coatings Al_2O_3–Y_2O_3 [14], MoO_4^{2-} loaded Micro/mesoporous ZIF67-MOF/multi-walled-CNT/APTES [3], nickel-graphene oxide-polypyrrole composite coatings on mild steel [23], Ni-Al polyvanadate layered double hydroxide with nanoceria [12]. This work aims to apply nano titania base coatings by atomization technique on carbon steel to investigate their role against corrosion in seawater at room temperature.

2. Experimental Work

2.1 *Material and Chemicals*

Specimens of carbon steel with chemical composition as shown in table (1) was used with dimensions of (10 mm× 10mm × 4mm) after grinding and polishing the specimens degreasing with ethanol. These specimens were prepared to achieve nanocoatings and corrosion tests in seawater (3.5 wt% NaCl solution)

Table 1: Chemical composition of carbon steel.

Metal	Wt%
C	0.115
Si	0.228
Mn	0.54
S	0.008
P	0.012
Ni	0.018
Cr	0.017
Al	0.067
Cu	0.022
Mo	0.013
V	0.008
Co	0.004
Fe	Bala.

These nano coatings included 100% nano TiO2, 50% nano TiO2 – 50% nano Al2O3 and 50% nano TiO2– 50% nano ZrO2. These materials were obtained from Guangzhou Jiechuang Trading Co., Ltd with particle size 10 nm for titania, 20-30 nm for Al2O3, and 40-50 nm for ZrO2.

2.2 *Air Atomizer Technique*

An air atomizer was utilized for the spraying method which is composed of a valve, solution container, flow tube, and a nozzle with a small orifice. The system of coating contains electrical heater to heat the sample to ≈150 °C controlled by thermocouple and nitrogen gas to push the coating solutions into the atomizer as shown in Fig. (1).

Figure 1: Coating system

Coating solution contains (5g nano titania in 25 ml ethanol, 2.5g nano titania+2.5g nano Alumina in 25 ml ethanol, and 2.5g nano titania+2.5g nano zirconia in 25 ml ethanol) all these three solutions were magnetically mixed followed by ultrasonic mixing for 30 min. as shown in Fig. (2)

(a) (b)

Figure 2: Mixing of coating solutions by (a)Magnetic and (b) Ultrasonic mixing.

2.3 *Characterization of Coated Samples*

(FESEM) is the focused electron beam that can intract with the sample atoms (i.e. excite the electrons) and because of the transition of electronos in the energy bands result in emtion of signals for creating detailed topographical maps samples synthesized were further morphologically analyzed using, (FESEM) were used to obtain high resolution imaging . FESEM can provide a spatial resolution of about 1.5 nm. In other words, 3 to 6 times enhancement compared with traditional Scanning electron microscopy [11]. Therfore, (FESEM) can be used to study the surface morphology and composition of a sample.

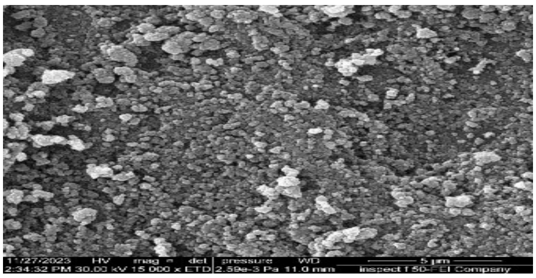
2.4 *Corrosion Test*

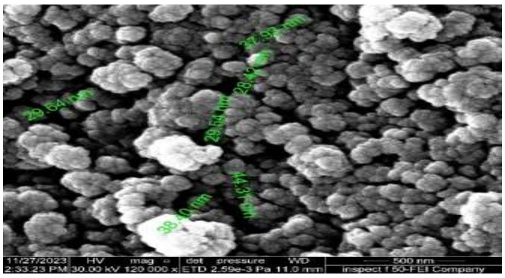
Corrosion test device was used for the electrochemical measurement from China with a standard cell with a capacity of 150 mL to test open circuit potential (Eoc) using three electrodes including working electrode (samples), an auxiliary electrode (Pt electrode), and reference electrode (as saturated calomel electrode SCE), in the first step of this measurement, the open circuit potential, and the polarization curve will start at the potential range about ±200 mV. Corrosion current density (i_{corr}) and corrosion potential values (E_{corr}) were determined from the polarization curve by Tafel extrapolation method.

3. Results and Discussion

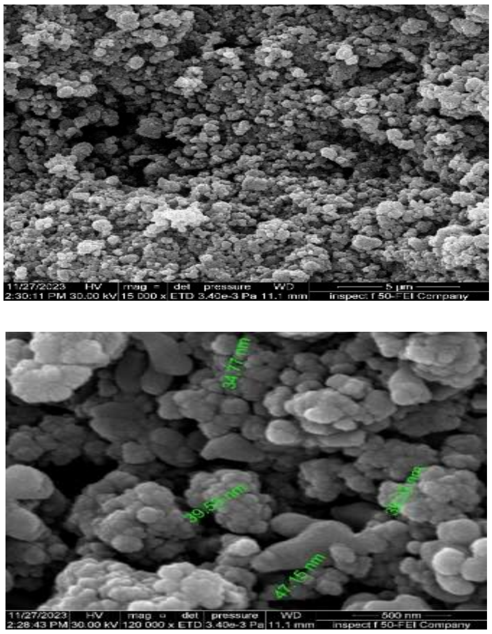
Field emission scanning electron microscopy examination is the first step was done to characterize the coated surfaces. FESEM images of nano titania coated sample indicate that the homogenously distribution of coating particle is clear with good coverage in addition to the clustering the particles in images with higher magnification illustrating the particle size of clustering to be ranged from 28.42 nm to 44.31 nm for titania coating, from 34.77 nm to 47.15 nm for titania-alumina coating and from 34.51 nm to 51.46 nm for titania-zirconia coating as shown in Fig. (3), these ranges were increased due to increasing in particle size of base materials. This higher range in particle size increases the roughness of the coated surface. As the size of nanoparticles increased the corrosion rate increased too.

To confirm the deposition of these coatings, Energy dispersive X-ray spectroscopy (EDS) analysis was examined for coated surface as shown in Fig. (4), Tables (2-4) indicate that the highest percent of Fe was in titania coating referring that this coating achieved the lowest coverage due to small particles compared with alumina and zirconia, others metal such as C, Si, and N are appeared because they present in the composition of carbon steel. Ti was recorded as 4.9, 23.4, and 29.26 wt% for coating by titania, titania-alumina, and titania-zirconia respectively referring to the titanium is enhancing to deposit by the presence other materials. The oxygen was recorded at 12.9, 39.9, and 34.2 wt%for coating by titania, titania-alumina, and titania-zirconia respectively and finally, Al and Zr have appeared in titania-alumina and titania-zirconia coating respectively.

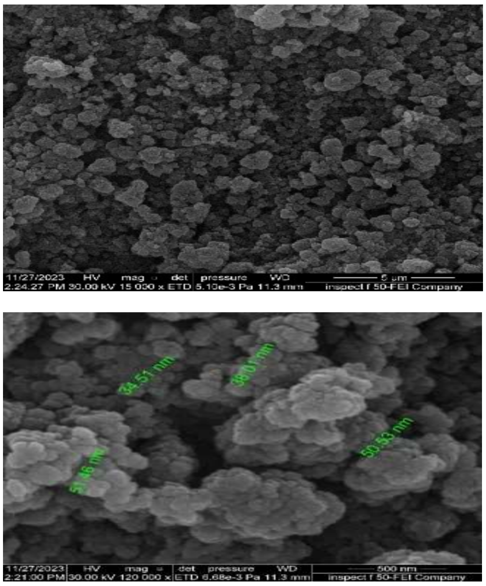




(a)

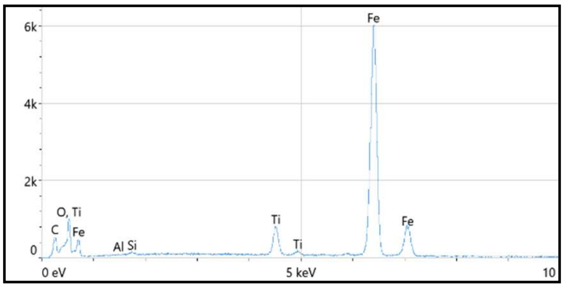


(b)

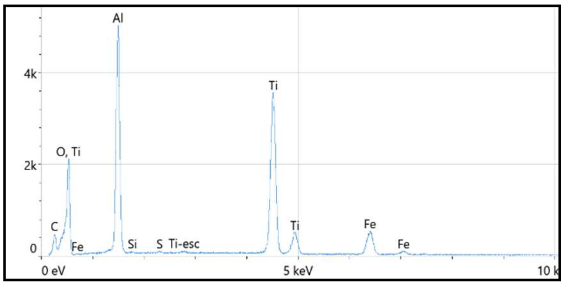


(c)

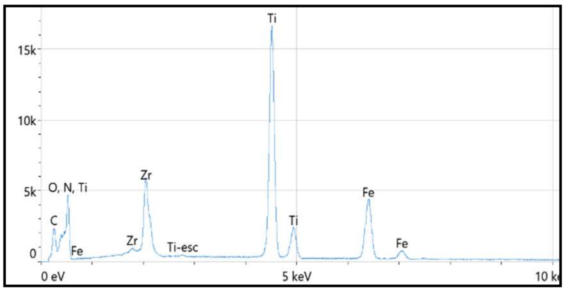
Figure 3: FESEM images for coated samples by titania (a), titania-alumina (b) and titania-ZrO2 (c).



(a)



(b)



(c)

Figure 4: EDS analysis for coated samples by titania (a), titaia-alumina (b) and titania-Zirconia (c).

Table 2: The surface composition for titania coating sample

Element	Weight %
C	11.5
N	1.3
O	12.9
Si	0.3
Ti	4.9
Fe	69.0

Table 3: The surface composition for titania-alumina coating sample

Element	Weight %
C	10.1
O	39.9
Al	20.7
Si	0.1
S	0.1
Ti	23.4
Fe	5.7

Table 4: The surface composition for titania-Zirconia coating sample

Element	Weight %
C	9.8
N	5.4
O	34.2
Ti	29.6
Fe	12.9
Zr	8.0

The important test for coated surfaces is the corrosion behavior, which can be formed by potential – time measurement to predict the stability of electrical double layer that formed at metallic surface – electrolyte interface as shown in Fig. (5) for uncoated carbon steel and coated samples that illustrate the shifting of this behavior to noble direction for coated surfaces compared with uncoated one which recorded (Eoc) value of -0.6 V, whereas the (Eoc) value was -0.313 V, -0.568 V and -0.572 V for coating by Titania, Titania-Alumina and Titania-Zirconia materials respectively.

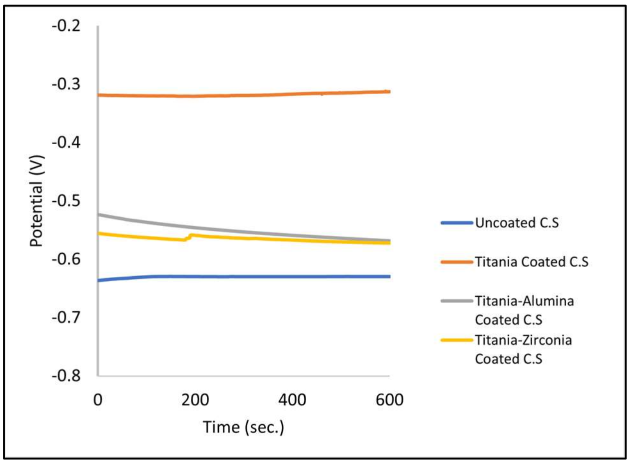


Figure 5: potential – time measurement for uncoated and coated carbon steel

Another test can be formed is Tafel plot or polarization curve that show the cathodic and anodic behavior of surfaces as illustrated in Fig. (6), where at anodic sites, the dissolution of metals take place especially for iron in carbon steel alloy as follow:

$$Fe \rightarrow Fe^{2+} + 2e \qquad (1)$$

At cathodic sites, the reduction of oxygen can occur due to neutral condition of seawater as follow:

$$O_2 + 4e + 2H_2O \rightarrow 4OH^- \qquad (2)$$

For titania coated carbon steel, it can be seen the shifting of polarization curve toward more noble direction and lower current density indicating the lower corrosion rate due to coverage of surface by titania layer to be barrier for reducing contact with corrosive medium, this coverage can be giving protection that calculate by the following equation [18, 4]:

$$Protection\ Efficiency\ \% = \left[1 - \frac{currentdensity_{(coatedsurface)}}{currentdensity_{(uncoatedsurface)}}\right] \times 100 \qquad (3)$$

The titania coating gave efficiency of 68.32%.

Other coatings shifted the polarization curve to higher current density because of the shrinkagecan occur between two different material (titania-alumina &titania-zirconia) during the heat treatment in the furnace in addition to the more roughness which produced as shown in FESEM images that create galvanic cells lead to acceleration of corrosion. Titania-Zirconia coated C.S gave the highest corrosion rate of 2.511 mm/y followed by Titania-Alumina coating to give 2.187 mm/y compared with the rate of uncoated C.S sample which recorded 0.721 mm/y that calculate using the following formula using corrosion current density values (icorr) [6, 20]:

$$Corrosion\ rate \left(\frac{mm}{y}\right) = 3.27 \times i_{corr} \left(\frac{e}{\rho}\right) \qquad (4)$$

Where e and ρ are equivalent weight (g/mol) and density (g/cm^3) of carbon steel respectively.

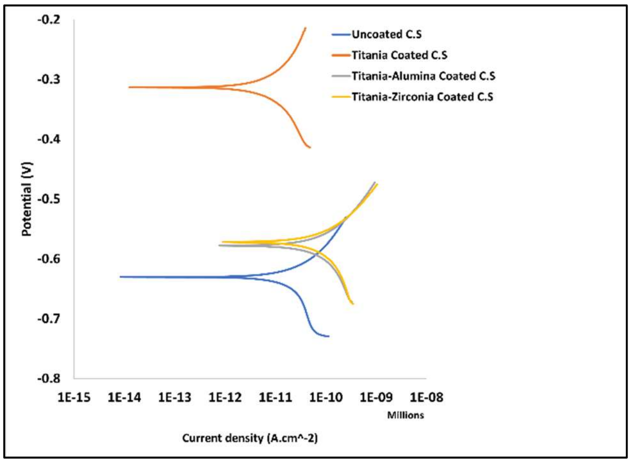


Figure 6: Tafel plots of uncoated and coated samples.

Table 5: Corrosion data of uncoated and coated samples.

Coating	E_{corr}(V)	$i_{corr}\times10^{-5}$ ($A.cm^{-2}$)	$-b_c$ ($mV.dec^{-1}$)	$+b_a$ ($mV.dec^{-1}$)
Blank	-0.63	6.146	407.07	139.86
Titania	-0.313	1.947	165.82	334.15
Titania-Alumina	-0.578	18.642	320.39	140.98
Titania-Zirconia	-0.572	21.401	447.57	139.7

4. Conclusions

Carbon steel has been coated with nanoparticles to estimate the corrosion rate in artificial seawater. The FESEM/EDS inspection illustrated the characterization of coated surfaces. Among three nanomaterial coatings (100%titania), (50% titania -50% Alumina), (50%titania-50%Zirconia), The titania coated carbon steel had the lowest corrosion rate while the Titania-Zirconia coated carbon steel gave the highest corrosion rate. The largest value of roughness was observed in nano Titania-Zirconia coating due to the aggregation of nanoparticles as found in the FESEM image

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طلاءات الجسيمات النانوية لتقليل تآكل الفولاذ الكربوني في مياه البحر الاصطناعية

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نشر في: 31 اذار 2024

الخلاصة – تم استخدام الجسيمات النانوية لطلاءات التيتانيا والألومينا والزركونيا على عينات الفولاذ الكربوني باستخدام طريقة التذرية. استخدم الرش الهوائي مع غاز النيتروجين لطلاء الجسيمات النانوية على الأسطح المصنوعة من الفولاذ الكربوني. تشتمل نسبة الطلاء على 100% نانو التيتانيا ، 50% نانو التيتانيا - 50% نانو الألومينا و 50% نانو التيتانيا - 50% نانو الزركونيا . تم استخدام FESEM في هذه التجربة. تراوح الحجم الجزيئي بين (28.42 - 44.31) نانومتر، (34.77 - 47.15) نانومتر، و (34.51 - 51.46) نانومتر للتيتانيا، وتيتانيا-ألومينا، وتيتانيا-زركونيا، على التوالي. علاوة على ذلك، يشير تحليل EDS إلى أن أعلى نسبة من الحديد كانت في طلاء التيتانيا مقارنة بالألومينا والزركونيا، وتظهر معادن أخرى مثل C وSi وN لأنها موجودة في تركيب الفولاذ الكربوني. تم تسجيل Ti كـ 4.9، 23.4 و 29.26 بالوزن% للطلاء بواسطة تيتانيا، تيتانيا-ألومينا وتيتانيا-زركونيا على التوالي. تم إجراء اختبار التآكل على العينات. بينت أن قياس الجهد للفولاذ الكربوني غير المطلي والمطلي سجل قيمة 0.6- (Eoc) فولت للعينة غير المطلية، في حين كانت قيمة 0.313- (Eoc) فولت، 0.568- فولت، و0.572- فولت لطلاء التيتانيا. ومواد تيتانيا-ألومينا وتيتانيا-زركونيا على التوالي. منحنى الاستقطاب للفولاذ الكربوني المطلي بالتيتانيا يشير إلى انخفاض معدل التآكل بينما أعطى طلاء تيتانيا-زركونيا CS أعلى معدل تآكل قدره 2.511 مم/ي يليه طلاء تيتانيا-ألومينا ليعطي 2.187 مم / سنة مقارنة بمعدل عينة CS غير المطلية التي سجلت 0.721 ملم / سنة

الكلمات الرئيسية –الألومينا،الفولاذ الكربوني، جزيئات النانو، مياه البحر، تيتانيا.