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DEPOSITION OF METALS (AL, ZN, SN) AND THEIR OXIDES TO PROTECT CARBON STEEL PIPES CARRYING CRUDE OIL FROM CORROSION

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Abstract

The vapor deposition method was used in a vacuum to paint samples cut from a carbon steel tube with an electric drill with a diameter of 25 mm. The students were using high-purity powders of aluminum, zinc, and tin. Then the samples were fixed in a closed crude oil recycling system. The flow inside the system was estimated at 2m3/h. Qayyarah crude oil was used in the study, and the oil in the system lasted one hour for each of the special experiments in minerals and their oxides. After the samples were exposed to crude oil, they are removed from the system and a cleaning process is performed for them. After that, structural tests are conducted, which included three Types of tests are (Xrd; Edx; SEM). Through these tests, a comparison was made between samples that were exposed to flow crude oil and their counterparts that were not exposed, as they were prepared in advance with the same practical conditions. From the comparison, we get to know the extent of the effect of crude oil runoff on the paint. And which types of coatings are more resistant to corrosion, as the coating with zinc metal was more resistant to corrosion than aluminum and tin metals, but in the case of coatings with oxides, tin oxide was the most resistant to corrosion than other oxides.

Keywords: Vapor deposition, Carbon steels, Crude oil, Structural tests, Corrosion

1. Introduction

Crude oil pipelines are subject to different types of corrosion, one of which is corrosion by stripping, which results in a gradual loss of material from a solid surface due to the mechanical interaction between that surface and a high-speed fluid, multi-component liquid, or solid particles accompanying the liquid, i.e. metal loss [1]. The damages caused by electrochemical corrosion are many and have multiple manifestations, so reducing this phenomenon is an industrial necessity [2]. Since the pipes are considered the main part of the equipment used in transporting oil from the oil wells to the storage depots and then to the operational units, therefore it is required to protect them from corrosion by using certain preventive measures, and among these measures is the use of paint appropriate to the nature of the pipe's work and its environmental surroundings. [3][4] The method of covering or coating by vapor deposition depends on liberating atoms of a certain solid or molten metal and depositing them on the surface of the metal to be covered, in a vacuum medium under very low atmospheric pressure, approximately ($760 * 10^{-5}$) atmospheric pressure. [5]. The metal's resistance to corrosion by

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stripping is greatly affected by the chemical components and hardness, in addition to the intrinsic corrosion resistance of this metal, The aim of this study is to compare the coating of three types of metals and their oxides on the base metal, carbon steel, and to find out which one is better in resisting corrosion and improving the surface properties of the metal.

2. Materials and experimental methods

2.1 Materials

2.1.1: carbon steel (A106) is an iron-based alloy that contains a percentage of carbon that does not exceed (1.4%), so if it contains the elements shown in Table (1), this type of carbon steel is used in the manufacture of the pipeline carrying crude oil from the Qayyarah fields to its refineries [6]

Table 1 Chemical composition of carbon steel (A106)

No.	Chemical composition	Wt %
1	C	0.2789
2	Si	0.2873
3	Cr	0.0237
4	Mn	0.3354
5	Fe	98.9895

2.1.2: The metals used in the coating

Metals that have the ability to gain inertness easily were used to resist corrosion [7], where aluminum, tin, zinc and their oxides were used in the coating of the base metal of the carbon steel tube, Where aluminum is considered one of the metals with high chemical activity, yet it is resistant to corrosion in many media, because it has the ability to form a layer of oxide in these media that adheres to its surface and protects it from corrosion [8], As for the zinc metal, it is used in coating steel to protect it from corrosion, as the steel in this case is called galvanized steel [9], Also in this study, tin metal was used in the coating because it is a relatively inert element in many mediums, and it is used in coating other metals, especially steel, because it provides the necessary protection from corrosion [10], After that, the metals used in the study were oxidized in order to form an oxide peel on the surface of the metal used, which is free of porosity and has good resistance against corrosion [11].

2.1.3 Crude Oil

One of the types of Iraqi oils was used, Qayyara crude oil, in this study, as it is characterized by its high sulfur content and high viscosity compared to other oils. The table(2) below shows the compositional specifications of the used crude oil[12].

Table 2 Qayyarah Crude Oil Specifications

NO.	TESTS	RESULTS
1	**Density @ 15 C°**	**0.9500-0.9700**
2	**API Gravity**	**14 - 17**
3	**Salt Content mg/l**	**6.0-9.0**
4	**R.V.P@ 37.7 C° Psi**	**3.0-4.5**
5	**B.S. and W by Content Wt.%**	**Nil-Trace**
6	**Sulphur Content Wt%**	**7.4 – 8.5**
7	**Kin. Viscosity @ 37.7 cst**	**190 -350**
8	**Pour Point C°**	**-15 -- -30**
9	H_2S **ppm**	**5.0 - 300**
10	**Asphaltenes Content wt%**	**16.0 – 19.0**
11	**Ash Content Residue wt%**	**0.02 -0.03**
12	**Ram. Carbon Residue wt %**	**6.0 – 12.0**
13	**Nickel ppm**	**20.0 -30.0**
14	**Vanadium ppm**	**50 – 80**

2.1.4 The samples used in the study

samples with an oval shape were used, and they were cut by an electric drill from a carbon steel tube. These samples were fixed after conducting cleaning operations for them and coating them with the appropriate metal. They are installed on the system for the flow of crude oil and ensuring exposure to it. Figure (1) shows the sample used in the experiment

Figure 1. The sample used in the experiment

3. Experimental methods

3.1. Clean up forms

The process of cleaning the samples in this study goes through two stages, the first before coating, where smoothing paper is used with different smoothing degrees to obtain a surface free of defects, and the second is after the samples are exposed to the flow of crude oil, so cleaning is done using acetone and cotton to wipe the surface of the sample from the remnants of crude oil.

3.2. **Sample coating method**

A thermal evaporation system was used in a vacuum to deposit thin films on the samples used in the experiment, as this method depends on liberating atoms from the base metal to be covered[13]., and the figure(2) shows the system used.

Figure2. The system used in coating samples

3.3 Crude oil recycling process

We designed a system for circulating crude oil in order to reach the flow of crude oil 2m^3/h. This system was equipped with all measuring devices and control valves, as shown in Figure) 3(.

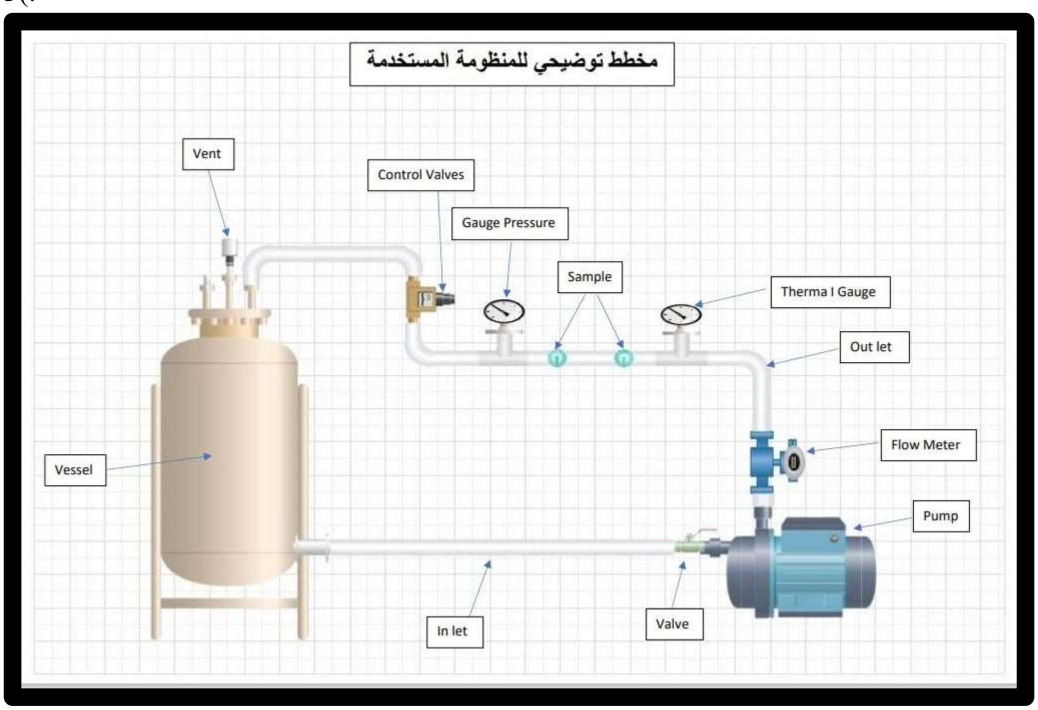
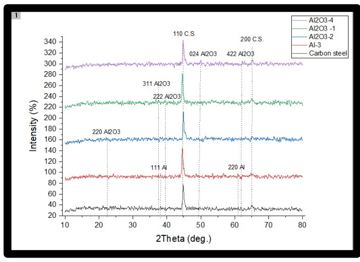
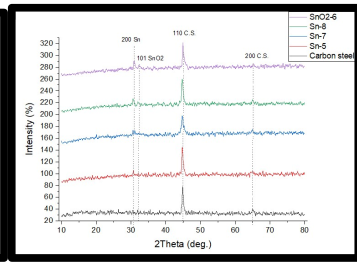


Figure**3.** Diagram of the experimental setup

4. Results and discussion

Through the use of the XRD test, it was found that the metals that were coated with had adhered to the sample, with no peaks resulting from the interaction of these minerals and their oxides with crude oil, and the original peaks remaining in their subjects. Therefore, it is difficult to rely on the XRD test to find corrosion rates, and the benefit from this test was limited to the presence of elements The paint in the metal and the figures (4,5,6) show the adhesion of the paint metal to the carbon steel base metal





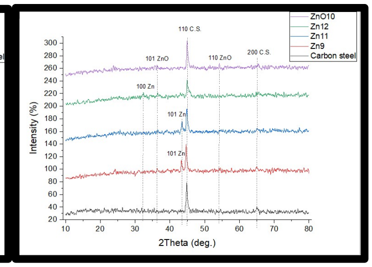
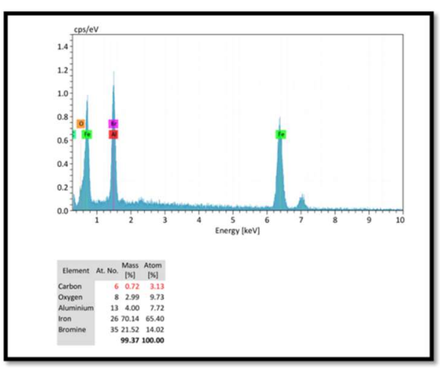


Fig (4) Fig (5) Fig (6)

Figure (4) shows the results of the (XRD) examination of the original metal and its aluminum and oxide coating, Figure (5) shows the results of the (XRD) examination of the original metal and its tin coating and oxide, Figure (6) shows the results of the (XRD) examination of the original metal and its coating with zinc and oxide

As for the results that prevent it from being obtained from the Edx examination, it gave an explanation of the percentages of lost atoms as a result of exposure through a comparison between samples that were exposed to flow crude oil and their counterparts that were not exposed, and the figures (7,8,9,10,11,12,13,14,15,16,17,18) show the percentages of loss in atoms according to the type of metal used in the coating



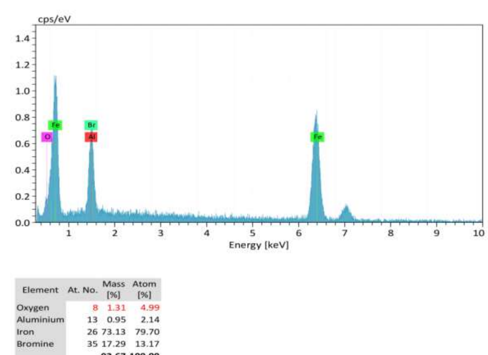


Fig (7) Fig (8)

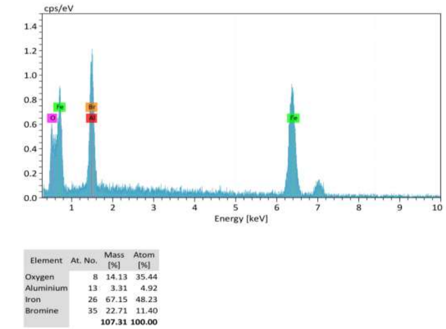


Fig (9)

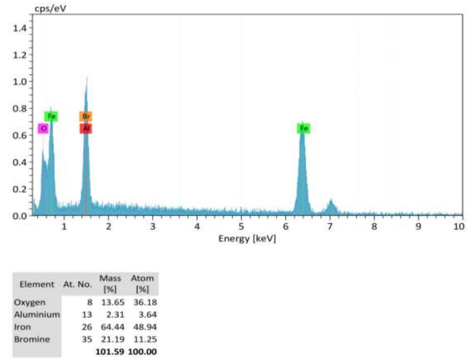


Fig (10)

Figure (7) Atomic ratios of the element aluminum before exposure, Figure (8) Atomic ratios of aluminum after exposure, Figure (9) Atomic ratios of the element Aluminum oxide before exposure. Figure (10) Atomic ratios of Aluminum oxide after exposure

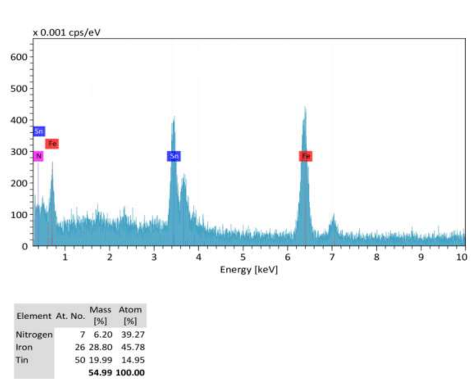


Fig (11)

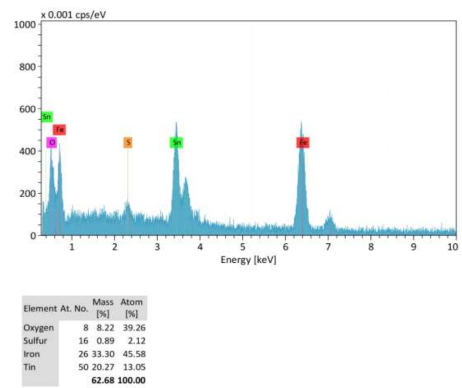
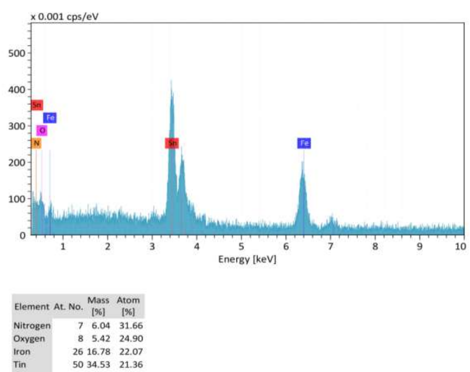


Fig (12)



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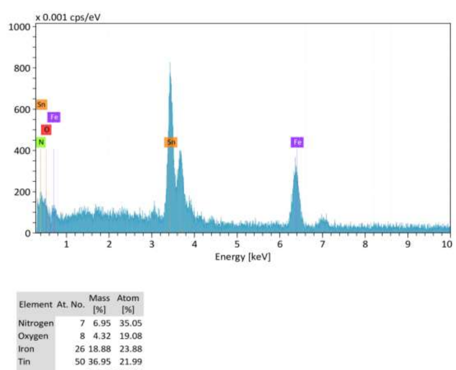
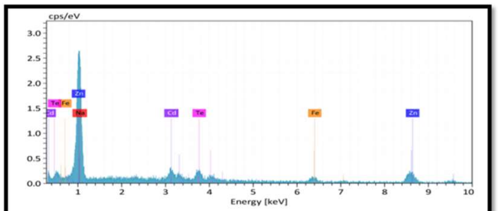


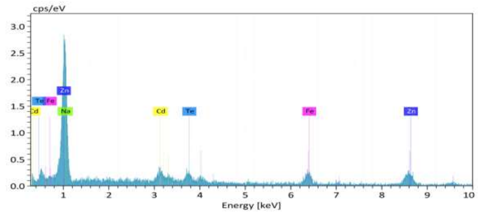
Fig (14)

Figure (11) Atomic ratios of the element Tin before exposure, Figure (12) Atomic ratios of Tin after exposure, Figure (13) Atomic ratios of the element Tin oxide before exposure., Figure (14) Atomic ratios of Tin oxide after exposure



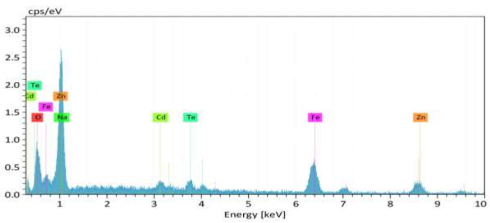
Element	At. No.	Mass [%]	Atom [%]
Sodium	11	18.45	52.17
Iron	26	5.14	5.98
Zinc	30	34.95	34.74
Cadmium	48	4.48	2.59
Tellurium	52	8.84	4.51
		71.87	100.00

Fig (13)



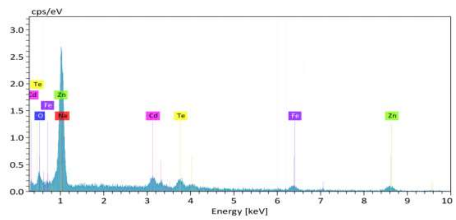
Element	At. No.	Mass [%]	Atom [%]
Sodium	11	17.07	49.64
Iron	26	10.94	13.10
Zinc	30	30.27	30.95
Cadmium	48	4.43	2.63
Tellurium	52	7.01	3.67
		69.71	100.00

Fig (14)



Element	At. No.	Mass [%]	Atom [%]
Oxygen	8	13.34	32.69
Sodium	11	14.60	24.89
Iron	26	26.96	18.92
Zinc	30	34.58	20.73
Cadmium	48	2.42	0.84
Tellurium	52	6.26	1.92
		98.16	100.00

Fig (15)

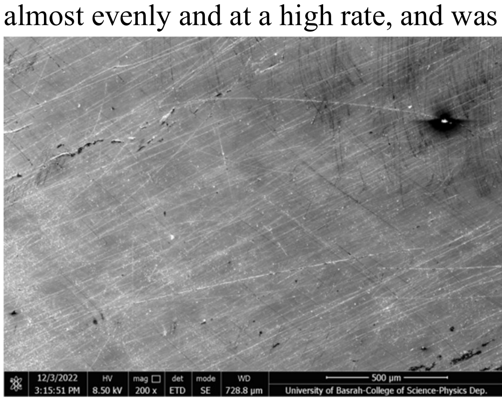


Element	At. No.	Mass [%]	Atom [%]
Oxygen	8	5.51	22.84
Sodium	11	14.62	42.19
Iron	26	5.28	6.27
Zinc	30	19.10	19.38
Cadmium	48	8.17	4.82
Tellurium	52	8.67	4.51
		61.33	100.00

Fig (16)

Figure (13) Atomic ratios of the element Zinc before exposure, Figure (14) Atomic ratios of Zinc after exposure, Figure (15) Atomic ratios of the element Zinc oxide before exposure. Figure (16) Atomic ratios of Zinc oxide after exposure.

And when using the scanning electron microscope (SEM) technique, these examinations gave images of the metal surface with high accuracy and a very high magnification size, through which it becomes clear the extent of the influence of crude oil on the samples used in the study, where the images in Figures (17,18,19,20) represent the sample that was coated with aluminum before and after exposure The other one is coated with aluminum oxide before and after exposure. It is clear from the pictures that the crude oil skimmed the outer surface of the metal almost evenly and at a high rate, and was unable to penetrate the surface.



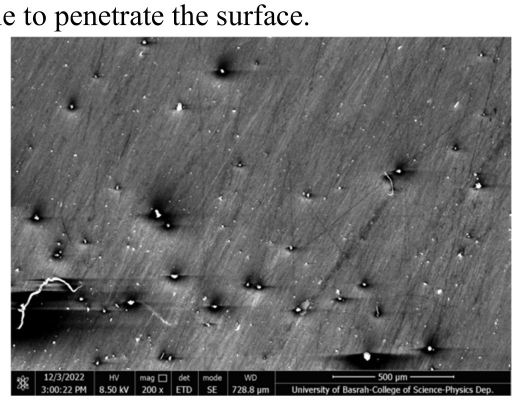
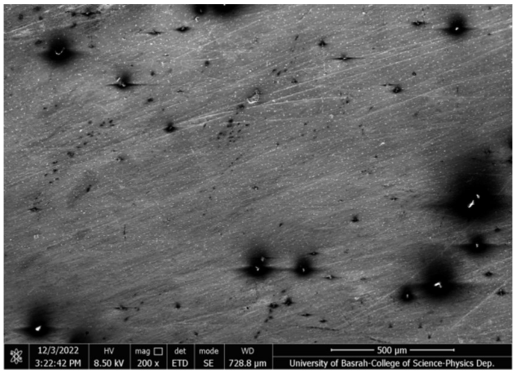


Fig (17) Fig (18)



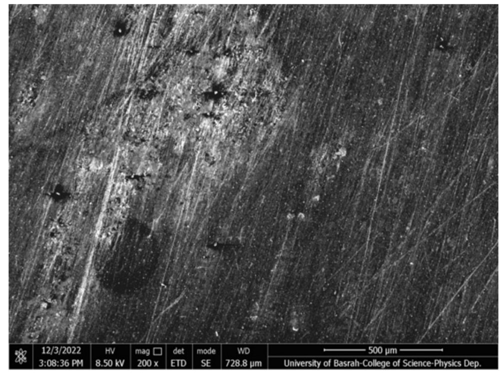
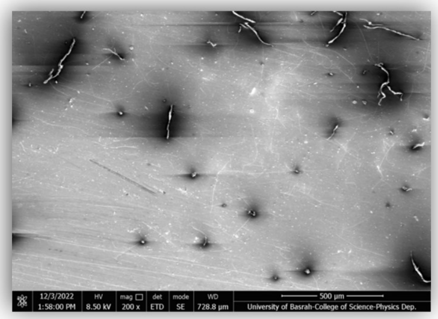


Fig (19) Fig (20)

Figure (17) of aluminum element before exposure, Figure (18) of aluminum element after exposure

Figure (19) of aluminum oxide element before exposure. Figure (20) of aluminum oxide element after exposure

When coating with tin and oxidation, the pictures in Figures (21,22,23,24) before and after exposure to crude oil showed that the crude oil when coated with tin metal cracked the surface, which led to the creation of large voids that enabled the crude oil to enter into the metal and disintegrate it. In the case of coating with tin oxide, the oxide was able to The metal maintains the shape of its outer surface compared to other oxides



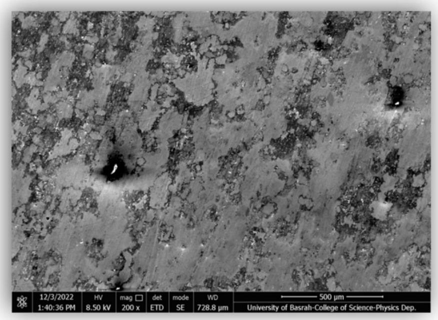
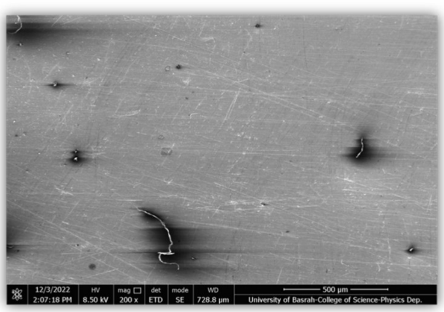


Fig (21) Fig (22)



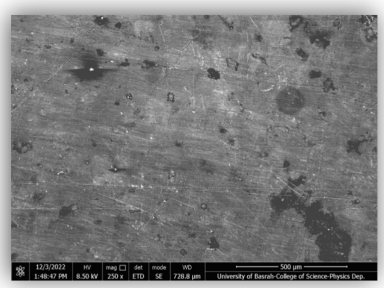
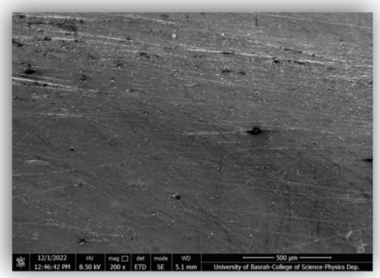


Fig (23) Fig (24)

Figure (21) of Tin element before exposure, Figure (22) of Tin element after exposure
Figure (23) of Tin oxide element before exposure, Figure (24) of Tin oxide element after exposure

In the case of plating with zinc metal and its oxide, the pictures in Figures (25,26,27,28) show that in the case of plating with zinc, the crude oil skimmed the surface evenly and was unable to separate parts of it or exploit the crystalline defects present in the metal to create voids and pits. In the case of coating with zinc oxide, the pictures showed the presence of hills And micro valleys Crude oil worked to remove the peaks and make the surface more smooth and was unable to penetrate the surface through the existing valleys



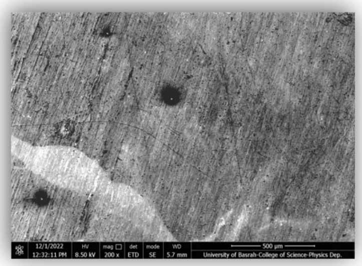
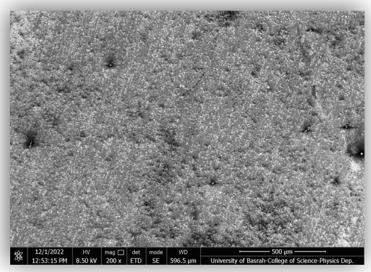


Fig (25) Fig (26)



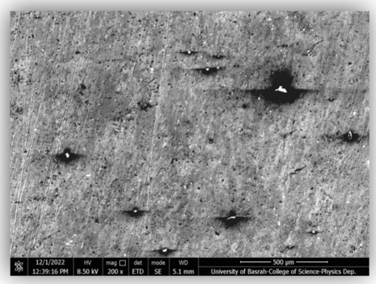


Fig (27) Fig (28)

Figure (25) of Zinc element before exposure. Figure (26) of Zinc element after exposure.
Figure (27) of Zinc oxide element before exposure. Figure (28) of Zinc oxide element after exposure.

Referring to the Edx technique, and by calculating the difference for the lost atoms as a result of exposure of the coating metal to crude oil, and from Table (999), it is clear to us that the coating with zinc is more resistant to corrosion than coating with other metals. In terms of oxides, the coating with tin oxide is more resistant to corrosion than other oxides.

Table 3 Percentage of missing atoms of minerals and their oxides

STATE	**ELEMENT**	**ATOM 1**	**ATOM 2**	**loss %**
Oxidizer	**AL2O3**	**4.92**	**3.64**	**26.01626**
annealed	**AL**	**7.72**	**2.14**	**72.27979**
Oxidizer	**SNO**	**21.99**	**21.36**	**2.864939**

annealed	**SN**	**14.95**	**13.05**	**12.70903**
Oxidizer	**ZNO**	**20.73**	**19.38**	**6.512301**
annealed	**ZN**	**34.74**	**30.95**	**10.90961**

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