Corrosion Reduction for Brass Alloy by Using Different Nano-Coated Techniques

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Abstract

In the present investigation the corrosion resistance of brass tubes heat exchanger that used in Midland Refineries Company-Iraq were improved dramatically by using nanocoating of brass substrate. Two nanocoating techniques were used to coat the brass alloy (B-111): Physical Vapor Deposition (PVD) and Pulse Laser Deposition (PLD). Copper (Cu) and aluminum (Al) metals were selected to be the coating material for the brass substrate.

The nanocoating specifications and characterization of surface have been tested by using many measuring tests; SEM, AFM, and XRD. From AFM results, it was observed that the nanocoated particle diameter of brass substrates in the range of (60 - 90) nm. From XRD results it was concluded that the PLD technique represents the best nanocoating process for the brass and it was showed high crystalline thin films. On the other hand, the SEM results showed that the PLD techniques with Copper nanocoating is good comparison with other PVD technique and aluminum nanocoating material.

After identifying the characterization of brass substrate, it was studying the corrosion potential, open circuit potential, and corrosion current density that used to estimate the corrosion rates in sodium chloride solution. The results indicated the minimum weight loss with copper nanocoating with PLD technique was 4.48*10^-2 mm/year.

Keywords: corrosion; Nano-coating, characterization

Introduction

Nanocoating has been used to protect the several metals and alloys from corrosion [I-VII] and the corrosion is regarding the main problem in most heat...
transfer equipment [VIII-X]. such problem, leads to the interruption work and take of the unit service to be disassembled and cleaned and it can be very costly [XI]. In Midland Refineries Company-Iraq, the efficiency of the heat exchanger is mainly depending on fouling rate because the fouling has low thermal conductivity and the accumulation of fouling have a negative influence on the efficiency of the operational process [XII]. Most tubes heat exchanger are made of brass material and it has good corrosion resistance [XIII] and is specially used for heat exchangers in oil refineries, in which corrosion from sulfur compounds and other fouling material [XIV-XVI]. Using the nanotechnology to coat the heat exchanger tube will be considered a good choice due to the properties of nanomaterial such as a hydrophobic property [XVII-XIX] that made the surface be resists the corrosion. The latest advances in nanotechnology have showed improvement of a new category of nanomaterials which include particles that are smaller than 100 nm [XX]. Various methods like chemical, thermal, spin coating, pulsed laser deposition, physical and etc. these have been developed to coat nanoparticles in a form of thin films on solid supports such as metal, metal oxides, glass or thermally stable substrates [XXI-XXIII].

I. Experimental work
II.i. Materials

In the present investigation, brass alloy (B-111) substrate is used in tube of heat exchanger in Iraqi midland refineries company and chemical composition of brass was determined by x-ray fluorescence test as shown in table 1.

Table (1) Chemical composition of brass alloy (B-111)

|  Cu  |  ZN  |  Pb  |  P   |  Sn  |  Mn  |  Ti  |  Fe  |
|------|-----|------|------|------|------|------|------|
| 73.32| 25.08| 0.0084| 0.0017| 0.001| 0.006| 0.0042| 0.09 |
| Sb   | Mg  | Al   | Si   | Cd   | V    | Zr   | Ni   |
| 0.001| 0.032| 0.057| 0.0026| 0.003| 0.0021| 0.02  | 0.097 |
| Nb   | Mo  | W    | Cr   | Co   | As   | Ag   | S    |
| 0.0021| 0.175| 0.021| 0.0579| 0.045| 0.0005| 0.0011| 0.002 |

The dimensions of the brass substrate are a square plate with length (15*15) mm and the thickness is 2.5 mm.

II.ii. Preparation and Experimental Setup

The specimen surface condition considered as an important role in a quality of coating and corrosion resistance. Substrates were prepared in order nanocoating processes and corrosion study. Firstly, mechanical Polishing is used to preparation the specimens then etching (Mixing 5 g Ferric Chloride...
and 10 ml Hydrochloric Acid with 100 ml water and the specimen is immersed.

In the experimental work, two types of nanocoating material are used and they are copper (Cu) and Aluminum (Al) with two different coating techniques, pulse laser deposition (PLD) and physical vapor deposition (PVD). After the specimen’s preparation of metal tube, these techniques and different materials have been used in coating processed and have been tested by AFM, XRD and SEM to choose the best material and best technique specimens of the brass substrate.

- **pulse laser deposition (PLD)**
  It used to prepare very thin layer on the surface of the substrate. The laser deposition system consists of a neodymium-yag laser at 10 nanoseconds with wavelength of 1.6 micrometer. The operated power (100-800) mJ and works using a nonlinear crystal to give another wavelength 532 nm with a glass of Pyrex chamber shown in the figure (1).

  In this method, it is used two materials copper (Cu) and aluminum (Al) as a powder and each one was pressed in the metal template. target (metal template) had been put in the chamber and had been evacuated and Laser had been illuminated on the target through a quartz window then plasma plume from the target had been evaporated and had been deposed in the surface of the heated specimen which had created a thin membrane on it.

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• Physical vapor deposition (PVD)

In this method, it has been used powder materials aluminum and copper as a target in a boat inside a vacuum chamber and high temperature was applied above the melting point of the target till the target evaporated and deposited on the surface specimen and created a thin layer on it as in figure (2).

II.iii. Characterization Measurements

In order to characterize the nanocoating of brass substrates several tests were utilized. For measurements of practical diameter, roughness, morphology of the surface, and structures. Therefore, Atomic Force Microscopy (AFM), X-Ray Diffraction (XRD) and Scan Electron Microscopy (SEM) were used.

II.iv. Corrosion Rate Measurement

In order to measure the corrosion rate used the potential static polarization so the brass substrates (uncoated and coated) put in sodium chloride salt with concentrate 3.5M with a temperature of 25°C±2°C at different time intervals. The tests were set of a primary potential at 200 mV and respect to this potential the current was recorded so the counter electrode used platinum rod while conducting polarization experiment used Potential static.

II. Results and Discussion

In the experimental part the samples (Brass) coated with two material copper and aluminum with two methods PLD and PVD then AFM and XRD were tested and the results showed as following

• Atomic Force microscopy (AFM)

The figures (3-6) showed the light-colored areas are tops of nanoparticles while the dark areas of the scan area were indicated the shallowest parts. the obtained results by AFM showed the quantitatively and qualitatively how that the surface properties (roughness and topography) vary with coating techniques and type of materials. The polycrystalline nature of coating Cu and Al thin films is clearly observable in all cases.

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From Figure (3.a) showed the AFM test for coating brass substrate by copper nanocoating and pulse laser deposition technique and it was indicated the roughness average is 0.559 nm and obtain the nanoparticles average diameter from the test was 60 nm. Also, it was showed the nanoparticle as needle structures. While figure (3.b) showed the three dimension of coating substrates and it gave indicator for the best coating topography of the surface beside that it found the surface more homogenies and uniform and the dark areas it was very little.

Figure (3): Atomic Force Microscopy by PLD with Copper Nanocoating (a) Two Dimension (b) Three Two Dimension

From Figure (4.a) showed the AFM test for coating brass substrate by copper material and physical vapor deposition technique and indicated the roughness average is 0.968 nm also obtain the nanoparticles average diameter from the test was 75 nm. From figure (4.b) showed the three dimension of coating substrates and it show the topography of the surface was good but less uniform and the dark areas it was clear.

Figure (4): Atomic Force Microscopy by PVD with Copper Nanocoating (a) Two Dimension (b) Three Dimension

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From Figure (5.a) showed the AFM test for coating brass substrate by aluminum material and pulse laser deposition technique and indicated the roughness average is 1.04 nm also obtain the nanoparticles average diameter from the test was 85 nm. From figure (5.b) showed the three dimension of coating substrates and it showed the topography of the surface was not good and the dark areas it was very clear.

Figure (5): Atomic Force Microscopy with Aluminum Nanocoating by PLD Technique (a) Two Dimension (b)

Figure (6.a) showed the AFM test for coating brass substrate by aluminum material and physical vapor deposition technique and indicated the roughness average was 2.14 nm also obtain the nanoparticles average diameter from the test was 90 nm. From figure (6.b) showed the three dimensions of coating substrates and it showed the topography of the surface was worst for and the dark areas it was very clear and the pours very spaced.

Figure (6): Atomic Force microscopy with Aluminum Nanocoating by PVD Technique (a) Two dimension (b) Three dimension
X-Ray Diffraction

X-ray diffraction test, that is an easiest test and one of the most important measurement and consider as useful tool in nanomaterial research field. X-ray diffraction tests were carried out on the specimen brass with and without coating to determine the existing phases of the surface in each substrate (brass substance). The diffraction angle range was from (20° to 80°), The intensity of XRD peaks was related to many factors, which include crystallization quality, density, and thickness of thin films [XXIV]. The differences in peak in these methods occurred because of a relatively different coating condition, which will cause difference growth of the phase in nanoparticles.

On either side of the Bragg angle, the diffracted beam will destructively interfere and result in a sharp peak while an increase in the width of the diffraction causes decrease in the crystallite size [XXV]. The intensity of peak decreases with increase d spacing of atom according to Bragg’s law.

From Figure (7) showed the XRD test for coating brass substrate by copper material with pulse laser deposition technique and physical vapor deposition technique and it observed four peaks by using PLD methods with copper material with angles 72.952, 71.821, 49.793 and 42.9734 so it has two strong peak and that it had been showed the strong layer of coating with this method. The sharp peaks presence was as shown in this figure that thin films are polycrystalline in nature. In this method have minimum d spacing 1.29574, while in PVD methods the three peaks at angles 73.0738, 49.9681 and 43.1085 and the strengthen peak at angle 73.0738 with high intensity but in broadened peaks and two weak peaks with minimum d spacing 1.29388.

![Figure (7): XRD Test Copper Material with Pulse Laser Deposition Technique and Physical Vapor Deposition Technique](image-url)
From Figure (8) showed the XRD test for coating brass substrate by aluminum nanocoating with pulse Laser deposition technique, physical vapor deposition technique and thermal pyrolysis and it observed three peaks by using PVD methods with Aluminum material with angles 43.16, 50.0537 and 73.131 it had two peaks was weak and that it had been showed the weak layer. Only one beak was high intensity the presence of sharp peaks while other peaks a broadened peak. While in PLD methods showed the XRD test for coating brass substrate and it observed three peaks by using with angles 42.5338, 49.3695 and 72.5436 and from the figure it observes the coating PLD better than PVD the three peaks had somewhat strong.

Figure (8): XRD Test Aluminum Material with Thermal Pyrolysis, PLD and PVD
Tables (2) were indicate for three methods with copper were compared and observed at the powder diffraction standard card of JCPDS, copper file No. 04–0836. While table (3) showed three methods with Aluminum were observed and compared with the standard powder diffraction card of JCPDS, aluminum file No. C 13.44.

Table (2): The Diffraction Angles of Experimental Work and Compared with The Standard Powder Diffraction Card of JCPDS, Copper File No. 04-0836.

| Experimental diffraction of 2 theta angle (in degrees) | Standard diffraction angle 2 theta JCPDS Copper: 04-0836 |
|-------------------------------------------------------|--------------------------------------------------------|
| PLD | PVD |
| 42.9734 | 43.1085 | 43.297 |
| 49.7933 | 49.9681 | 50.433 |
| 72.9523 | 73.0738 | 74.130 |

Table (3): The Diffraction Angles of Experimental work Compared with The Standard Powder Diffraction Card of JCPDS, Aluminum File No. C 13.44

| Experimental diffraction angle [2theta in degrees] | Standard diffraction angle [2theta in degrees] Aluminum: C 13.44 |
|--------------------------------------------------|----------------------------------------------------------|
| PLD | PVD |
| 42.9734 | 43.1085 | 45.11 |
| 49.7933 | 49.9681 | 48.85 |
| 72.9523 | 73.0738 | 72.13 |
Scan Electron Microscopy

The scan electron microscopy as used to study the morphology of surface and these images depict surface morphology and explain the manner in which the nanoparticles are spread across the surfaces on the nanocoated brass substrate also provide image of nanoparticle and their agglomerate in the sufficient resolution. Depending on the size of the piratical and the microscope used a certain imagination has to be used to provide images clearly identified particle. To give an overview of the sampling petrean also magnification series should be provided for a complete analysis of the substrate. From figure (9 to 12) the results are shown with magnification 20 000X and it is easy to notice that the examined particles consist of a number of smaller objects of 0.5 μm to few micrometers in size. From maximum resolution image obtain from the test showed. Copper nanocoated with PLD method showed good clarity of morphology also much distributing of dark and bright areas represented a best nano-morphology where the bright area represented the tops of nano-structures and the dark areas represented the valleys between them.

Figure (9): SEM Test Copper material with PVD

Figure (10): SEM Test Copper material with PLD
Reduction of Corrosion Rate by Nanocoated

From the experimental part, the corrosion behaviors of brass substances with nanocoating at different conditions were studied with potential static polarization measurements. The potential static polarization for brass material with nanocoating was presented in Figures (13 to 16) which show polarization curve as a plot of the potential electrode contra the logarithm of current density so cathode and anode polarization curves and the cross of these curve is Equilibrium potential point and through it that can determine corrosion current density (Icorr) and corrosion potential (Ecorr) [XXVI].

Figures (13) and (14) indicated the weight losses for copper nanocoating with PLD and PVD with the weight loss rate 4.48*10^-2 (mpy) and 5.09*10^-2 (mpy) respectively. From figures (15 and 16) showed Aluminum material coated with the two methods and they have the weight loss rate 5.97*10^-2 (mpy) and 5.76*10^-2 (mpy), for PVD and PLD respectively.

From these results that observe the copper nanocoating was better than Aluminum nanocoating so it obtains good corrosion rate for all nanocoating in two techniques. From table (4), it was shown the corrosion rate of brass substrates with nanocoating.

From these figures and table, it found the coated with copper nanocoating was better nanocoating for brass substrate. There is a relation between the susceptibility of metals to corrosion and their place in the electrochemical chain, so it found non-corroded metals like gold and platinum are at the end of the chain or in the positive end while reactive metals that rapidly decay are located at the top of the chain or in the negative end for this reason the electrochemical chain give an idea about the extent and ability of metal to corrode, and this
result approved that the copper material is located in the end of electrochemical chain as mention previously.

Figure (13): Corrosion Test of Copper Material with PLD Technique

Figure (14): Corrosion Test of Copper Material with PVD Technique
Figure (15): Corrosion Test of Aluminum Material with PLD Technique

Figure (16): Corrosion Test of Aluminum Material with PVD Technique

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Table (4): Corrosion Results of Brass Substrates

| Nanocoating Material | Techniques | OCP  | $E_{\text{corr}}$ (mV) | $I_{\text{corr}}$ (A/CM$^2$) | Corrosion Rates (mpy) |
|----------------------|------------|------|------------------------|----------------------------|----------------------|
| Copper               | PLD        | -421 | -252.8                 | 4.16                       | 4.84*10^{-2}         |
|                      | PVD        | -392 | -220.8                 | 4.37                       | 5.9*10^{-2}          |
| Aluminum             | PLD        | -407 | -226.6                 | 4.95                       | 5.76*10^{-2}         |
|                      | PVD        | -362 | -200.5                 | 5.13                       | 5.97*10^{-2}         |

III. Conclusions

1. It was concluded from the results of (XRD, AFM and SEM) that the copper nanocoating is the best for coating brass tube of heat exchanger. This attributed to the high adhesion ability of nanofilm and small average particles size of 60 nm in compassing with Al nanocoated tubes.
2. It was concluded the copper nanocoated specimens are more noble than that Aluminum nanocoated.
3. PLD technique showed the best corrosion resistance than that other nanocoating Techniques.

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