Corrosion Protect of Brass Tubes Heat Exchanger by using CuO Nanocoating with Thermal Pyrolysis Techniques

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Abstract

In this paper, thermal pyrolysis nanocoating technique was used to coat the brass alloy (grade B-111) of heat exchanger that used in Midland Refineries Company-Iraq. The nanocoating specifications and surface characterization have been made by using many measuring techniques; Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), and X-ray Diffraction (XRD). From AFM results, it was observed that the particle size of nanocoated brass substrate was 70 nm. From XRD results it was showed high crystalline thin films. On the other hand, the SEM results showed good smooth surface morphology films. The corrosion behavior of with and without nanocoated brass tubes achieved by study the open circuit potential, corrosion current density and corrosion potential which are used to determine the corrosion rates in 3.5M of sodium chloride solution. The results indicated that nanocoated substrate showed insignificant weight losses in comparison to that of uncoated substrate. So minimum weight loss with CuO nanocoating with thermal pyrolysis technique at 0.04M was 2.5*10^{-2} mm/year.

Keywords: Heat exchangers; Petroleum refinery; corrosion, Nano-coating.

I. Introduction

Corrosion is regarding the main problem in most heat transfer equipment, many hundreds of million dollars are loss every year due to corrosion problem in the industry. In Iraq petroleum refinery, the efficiency of heat exchanger is mainly depending on fouling rate because the fouling has low thermal conductivity and the accumulation of fouling have a negative effect on the operational efficiency of the process and this cause surface corrosion.

Fouling can be defined as the deposition undesirable materials such as suspended solids, and insoluble salts on the internal or external surfaces of heat transfer equipment (Mostafa, 2011),this regarded a major problem and should be reduced. Such problem effects lead to loss of energy, increased maintenance cost, and lowering of heat transfer. The thermal conductivity of the fouling layer or layers which is generally lower than the thermal conductivity of the fluids or conduction.
wall. Then, the overall thermal resistance to heat transfer is increased and the effectiveness and thermal efficiency of heat exchangers are reduced (Ibrahim, 2012). Using of nanotechnology considered as one of the most important method to overcome this problem and it will be regarded a good choice (Hussein, et al., 2005). Nanotechnology is becoming vitally important in many industrial fields, offering significant wealth creating opportunities and massive improvements to standards of living (national nanotechnology 2006). Recent advances in nanotechnology have allowed development of a new category of protective nanomaterials containing particles that are significantly smaller than 100 nm (Taniguchi, 1974). The use of nanotechnology to coat surface heat exchanger regards as a promising solution due to the nanomaterials possess hydrophobic properties (Pastorello & Bonanno 2015 and Wolfgang, 2014) and that mean self-cleaning of the surface. (Parkinet al., 2005 and Nun et al., 2002).

II. Experimental work

Materials

In the present investigation was utilized the brass alloy (B-111) substrate that used in tube of heat exchanger in oil refineries of Iraqi midland refineries company. The dimensions of the brass substrate are a square plate (15*15) mm and the thickness is 2.5 mm. The experimental work which includes using thermal pyrolysis technique to produce copper oxide nanocoating layer on brass surface substrate.

Nanocoating Technique

In the present investigation was mixed 0.04molar concentrations from copper (II) chloride dehydrates (CuCl₂, 2H₂O) with 100 ml of water (Chafi et. al, 2016) and in ultrasonic to be homogenous. The aqueous solution of coating material was sprayed of the heated brass substrate and keeping the sprayer on for 10 minutes to supply a required amount of Nano-material to the coated surface, thermal pyrolysis required a special procedures and equipment to gain a nano-structures of the brass substrate surface as figure (1).

Several instruments were used to characterize the nanocoating of brass substrate such as Atomic Force Microscopy (AFM), x-ray Diffraction (XRD) and scan electron microscopy (SEM).

Corrosion Rate Measurement

Potential static polarization was carried out in Sodium chloride salt with concentrate 3.5 M at temperature of 25°C±1°C for both an uncoated and coated specimen for various time intervals as in figure (2). All the potential measurements were made with reference to a standard calomel electrode (SCE). A platinum rod was used as counter electrode and Potential static (WENKING M lab multi channels and SCI-M lab corrosion measuring system from Bank Electronic-Intelligent controls GmbH Germany) was used for conducting the polarization experiment.
Potentiostat polarization was started from an initial potential of 200 mV, the current was recorded with respect to the potential. The test was conducted at a scanning rate of 2mV/sec. All test was held at College of Science, Chemistry Department / University of Baghdad. Use the OCP-time measurement to understand the corrosion behavior of the coated and uncoated specimens under equilibrated conditions in the sodium chloride salt solutions. Open-circuit potential, Ecorr changes were measured.

Figure (1): Thermal Pyrolysis Devises

Figure (2): polarizationmeasurements

Complete system against a standard saturated calomel electrode. In open circuit experiments curves of potential versus time were obtained. The OCP-time measurement is considered as an important parameter for evaluating the stability of the passive film of the specimens.

The specimens were immersed into the electrolyte and the potential was monitored with respect to a standard calomel electrode (SCE), until the potential reached a stable value.

In Tafel Extrapolation method uses data obtained from cathodic and anodic polarization measurements. Cathodic data are preferred, since these are easier to measure experimentally. To determine the corrosion rate from such polarization measurements, the Tafel region is extrapolated to the corrosion potential. At the corrosion potential, the rate of hydrogen evolution is equal to the rate of metal dissolution, and this point corresponds to the corrosion rate of the system expressed in terms of current density (Fontana and Greene, 1984). In order to evaluate the
corrosion rate by the electrochemical techniques, Tafel plots can provide a direct measure of the corrosion current, which can be related to corrosion rate. The corrosion rate in milli-meter per year (mpy) can be determined from following Equation (Faraday's law) (Denny, 1996).

### III. Results and Discussion

#### Characterization of Nanocoated Brass Substrate

From Figures (3 and 4) showed the AFM test for coating brass substrate by copper material and thermal pyrolysis technique with 0.04M concentration where the light-colored areas are tops of nanoparticles while the dark areas of the scan area indicate the shallowest parts. The polycrystalline nature of coating CuO is clearly. Figures (3) indicated the roughness average was 0.943 nm also obtain the nanoparticles dimeter of nanocoating layer was 70 nm. While figure (4) showed the threedimension of coating substrates and it show the good Surface topography and the dark areas it was clear but not more.

Figure (5) showed the x-ray diffraction patterns of CuO thin films sprayed by thermal pyrolysis technique and the range of the diffraction angle (2θº) was (20º - 80º). According to this figure the presence of sharp peaks was shown and reveals that the sprayed CuO thin films with Three highly intense diffraction peaks observed at angles 72.6o, 49.2o and 42.8o. The intensity of XRD peaks was related to many factors, which include crystallization quality, density, and thickness of thin films (Chang K. 2005). On either side of the Bragg angle, the diffracted beam will destructively interfere and result in a sharp peak (Hall et al 2000).
Figure (3): Two-dimension atomic force microscopy by thermal pyrolysis technique with copper nanocoating at concentration 0.04 M
Figure (4): Three-dimension atomic force microscopy by thermal pyrolysis technique with copper nanocoating at concentration 0.04 M

![Figure 4](image4.png)

Figure (5): X-ray Diffraction (XRD) test by thermal pyrolysis technique with copper nanocoating at concentration 0.04 M

![Figure 5](image5.png)

From figure (6) the SEM results are shown with magnification 20 000× and it is easy to notice that the examined particles consist of a number of smaller objects of 0.5 μm. From maximum resolution image obtain. The nanocoating copper oxide with thermal pyrolysis technique with 0.04 showed good clarity of morphology also much distributing of dark and bright areas represented a good nano-morphology where the bright area represented the tops of Nano-structures and the dark areas represented the valleys between them.
Reduction of Corrosion Rate by Nanocoated

In this heat exchanger case study, the brass tube is permanently exposed to water and it will be affected by salt medium and with time it will be corroded. The corrosion is the most dangerous problem which is effect in heat exchangers and that will cause frailer to the system and it will be stopped to be repaired or exchanged the tube, that will increase additional cost and time lost, by using nanomaterial coating is minimums these problems.

From The experimental part the corrosion behaviors of brass substance with and without coating at different conditions were studied with potential static polarization measurements. The potential static polarization for brass material with and without coating were presented in Figures (7and 8) which show
Figure (7): Corrosion test of brass substrate without nanocoating

Polarization curve as a plot of the electrode potential versus 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 ($I_{corr}$) and corrosion potential ($E_{corr}$) (Sami et al 2014). From these figures, it observes the coating substrate have lesser weight losses than uncoated substrate. So, from figure (7) showed the brass substrate without coating and it was indicated the weight loss rate was 0.229 (mpy) while the figures (8) showed minimum weight losses with nanocoating copper oxide with thermal pyrolysis and it was 2.5*10^-2 (mpy). Also from table (1) was shown the corrosion rate of brass substrates with and without coating.

From these figures and table, it found the coated specimens are more noble than that uncoated specimen. 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.
Figure (8): Corrosion test of nanocoating copper oxide with thermal pyrolysis technique

or in the negative end for this reason the electrochemical chain gives 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.

Table (1) showed the corrosion rate of brass substrates with and without coating

| Nanocoating Material | Method | OCP   | $E_{corr}$ (mV) | $I_{corr}$ (A/cm$^2$) | Corrosion Rates (mpy) |
|----------------------|--------|-------|-----------------|-----------------------|------------------------|
| Copper Oxide         | TP     | -377  | 214.9           | 2.15                  | 2.5*10$^2$             |
| Without coating      | -      | -233  | 212.8           | 19.66                 | 0.229                  |

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IV. Conclusions

Many conclusions were obtained from the results of the present study as the following:

1. It was concluded from the results of (XRD, AFM and SEM) that the nanocoting with copper oxide (0.04 M) attributed to the high adhesion ability of nanofilm and small average particles size of 70 nm.

2. It was concluded from corrosion results the corrosion rate decreases to the half and that means the life of brass tube to be longer. The coated specimens are more noble than that uncoated.

V. Notation

\begin{itemize}
  \item mpy: Milli meter per year,
  \item Icorr: Corrosion current density (A)
  \item E.W: Equivalent weight of the corroding species, (g/y).
  \item d: Density of the corroding species, (g/cm³)
  \item A: Area of the sample in Cm²
\end{itemize}

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