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Developing of Corrosion Resistance Nano Copper Oxide Coating on Copper Using Anodization in Oxalate Solution

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P A P E R I N F O

A B S T R A C T

The excellent heat transfer properties of copper it is the reson behind its use in the manufacturing of various equipment of heat transfer applications. However, contamination of water by copper in water circulation systems is one of the serious industrial problems [1]. This contamination commonly results from copper corrosion reactions in boiler feed water environment. The contamination of copper could be reduced by improving copper corrosion resistance in water. This research studies the developing of copper corrosion resistant by using anodization technique. The anodization experiments are conducted in oxalate solutions of concentrations from 0.1 to 0.5 M, at a temperature range from 24 to 0 ℃ and applied potential from 7.5 to 9 V. Anodized coating was analyzed using field emission scanning microscope, energy dispersive X-ray spectroscopy, and X-ray diffraction. Characterization results referred to the formation of copper oxide anodized coating with grain size range from 25 to 68 nm. The tests of the corrosion resistance of the anodized copper samples were carried out in simulated boiler feed water. The results show the enhancement of corrosion resistance of anodized samples. The corrosion protection efficiencies for the anodized coating increased 86.2% and 74.5% in testing solutions contains 3.5% NaCl, and 2 mg/l NH3, respectively.

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1. INTRODUCTION

Copper alloys are the most common materials used in the manufacturing of heat exchangers, tanks, and cooling towers due to its excellent heat transfer and corrosion resistance properties [1]. The anodized coating protects the copper from corrosion in the water environment and minimizes undesired copper contamination. Nano-copper oxide is used in various applications such as gas detection sensors, super hydrophobic surfaces, and solar cells [2-4]. Moreover, it is used as anode materials for LIBs because of its high capacity, environmental benignity,
safety and low-cost [5]. The recent discovery of the antimicrobial activity of nano-copper oxide towards microbial agents, make it more preferred in the food industry [6]. The hardness of nano-copper oxide makes it efficient for using in friction-reduction and anti-wear

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of the machinery parts [7]. Finally, the nano-copper oxide was used for increasing the thermal conductivity of nanofluids [8-10].
The effect of acidity of the oxalate solution on copper dissolution was studied by Lowalekar [11]. It was found that the stability of various copper species changed according to the amount of dissolved copper in solution. It was also reported that the dissolved copper concentration in solution increased when the line of stability between Cu^{2+}/CuO was shifted from pH 7 to 4. They concluded that the stability region of cupric oxide (CuO) would be expanded at higher pH solution [11]. Many other researchers [12-14] studied the synthesis of nanostructure oxides coating on metals. In these studies, various nanometal
 oxides, including copper oxide, were synthesized using the electrochemical method. After that, many researchers fabricate nanostructured thin films of copper oxide on copper foil using anodization technique [15-17]. In these studies, the coating was synthesized using anodization in different aqueous solutions at room

temperature. Another researcher on the same subject reviewed the characteristics of the copper oxide formed by electrochemical anodization in caustic soda (NaOH) solution at 90 ºC [16]. The copper anodization in oxalic acid containing solution also was studied by some researchers [17, 18] to form a passive copper oxide coating on the copper surface to prevent further dissolution of copper.

This study presents the experimental results for the effects of the anodized copper coating on the corrosion behavior of copper in a simulated boiler feed water containing sodium chloride and ammonia.

2. MATERIALS AND METHODS

The experimental work planned to study the effects of the anodized coating in simulated boiler feed water environment, as shown in the block diagram Figure 1.

Copper oxide coating using anodization technique was carried out in oxalate solution. The coating was conducted on pure copper foil (purity 99.5%) from R&M chemicals, with a thickness of 0.12 mm. The copper samples were cut to 1cm x1cm dimensions. Then, they were polished, cleaned, and washed with distilled water, and acetone. Finally, samples were dried in air at room temperature. The surface of samples was dried and smoothened before the experiments. Figure 2 shows an illustration of the anodization experimental cell. It consisted of; (a) electrolyte, (b) counter electrode, (c) reference electrode, (d) working electrode, (e) copper sample holder, (f) stirring magnetic bar, (g) heater, (h) cooling jacket, (i) inlet coolant tube, (j) outlet coolant tube, (k) jacket temperature indicator, (l) electrolyte temperature indicator, (m) potentiostat. The experiments were performed using Ag/AgCl (SSE) as the reference electrode and Platinum foil as the counter electrode. Anodization measurements were performed by Auto Lab Potentiostat/ Galvanostat, PGSTAT AUT86037 supported with (NOVA 1.10 Software).
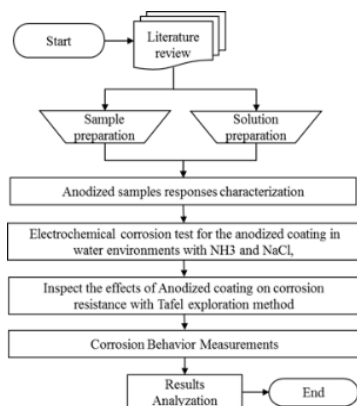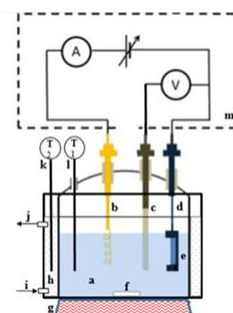

Figure 2. Anodization Experimental cell

The anodization experiments were conducted using Linear Voltammetry (LSV) method, at 0.02 V/S scan rate. Anodization electrolyte solutions were prepared with oxalate concentration range between 0.1 to 0.5 M. Anodization temperatures were at a range between 0 to 24 ºC, and potentials range between 7.5 to 9 V.

Corrosion resistance tests for the anodized and non-anodized samples were carried out at room temperature in two aqueous solutions containing 3.5% NaCl and 2 mg/l NH_3, respectively. These experimental tests were performed in a conventional three-electrode cell assembly using Auto Lab Potentiostat/ Galvanostat, PGSTAT AUT86037 (NOVA 1.10 Software).

3. RESULTS AND DISCUSSIONS

3. 1. Synthesis of Anodized Coating   The anodized copper coating was successfully synthesized on copper substrates using anodization technique. The copper anodization was conducted in oxalate containing solutions at various concentrations, temperatures, and applied voltage.

Energy Dispersive X-ray Spectroscopy (EDX), X-ray diffraction (XRD) and (FESEM) were used to study the surface morphology of the anodized layer and its composition. The (EDX) spectral result in Figure 3 shows the increase of the oxygen content in the anodized coated surface, Figure 3b, as compared with that in the uncoated sample, Figure 3a. This result was an indication of the formation of copper oxide phase on the copper surface.

The X-ray diffraction, XRD pattern graph shown in Figure 4, which resulted from the reflected spectrum on the anodized samples revealed diffraction peaks identical with the spectral peaks of cupric oxide (CuO) according to the standard card JCPDS 05-0661.

The positions of the X-ray spectrum peaks referred to the formation of monoclinic phase of cupric oxide CuO on the anodized sample surface. The peaks in the XRD pattern for the anodized coated samples indicates the deposition of a single-phase monoclinic crystalline lattice structures of cupric oxide with preferred orientation plans (111).
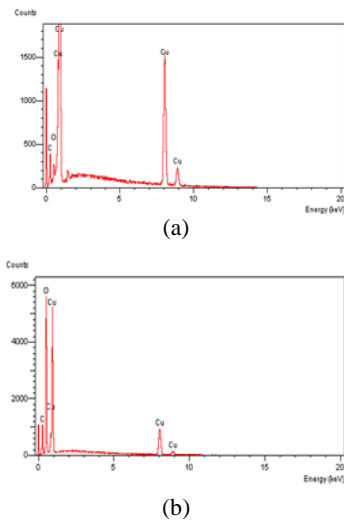

Figure 1. Experimental work block diagram

(a)

(b)

Figure 3. Energy Dispersive X-ray Spectroscopy (EDX) spectra distribution for a: uncoated, b: coated, copper sample
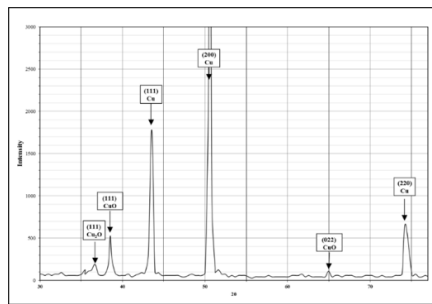

Figure 4. XRD Analysis of anodized copper samples

Moreover, the average crystallite size of the (CuO) coating surface was 32.6 nm based on the X-ray diffraction spectral peak employing Debye-Scherrer's formula using the full width at half maximum method [19], and X'Pert High Score software.

3. 2. Morphological Analysis   The morphological investigation of the anodized coating samples was performed by the Field Emission Scanning Electron Microscope (FESEM). The FESEM results were analyzed using Image J software to investigate the effect of temperature on the grain size and porosity of the coating. The results show that the grain size of the coating was in the range between 25 and 68 nm and the porosity of the coating was between 0.59 and 16.5%. The results show that the grain size and the porosity of the coating increase with the increasing of anodizing temperature. The coating anodized at 0 °C in the anodizing solution contains 0.5M oxalate concentration, was of smaller and more uniform grain size with fewer voids, as shown in Figure 5.
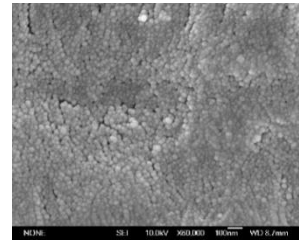

Figure 5. The microstructure of coating anodized at 0 °C

While the coatings anodized at higher temperatures of 8 and 16 °C have larger grain size and higher porosity, in the same anodizing solution and applied voltage, as presented in the Figures 6 and 7.

From the results below, it was observed that grain size and porosity of the coating was increased with increasing of anodizing temperature in the same anodizing conditions of 0.5 M oxalate concentration and 9 volts, as illustrated in Figure 8.

From this observation, was concluded that the anodization temperature is an affecting parameter on the coating microstructure.
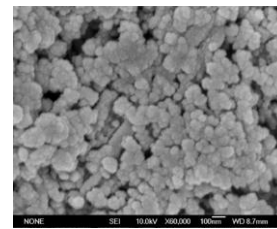

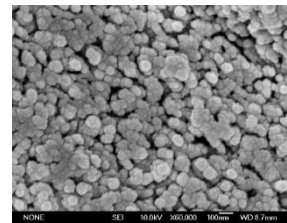**Figure 6.** The microstructure of coating anodized at 8 ° C

Figure 7. The microstructure of coating anodized at 16 ° C
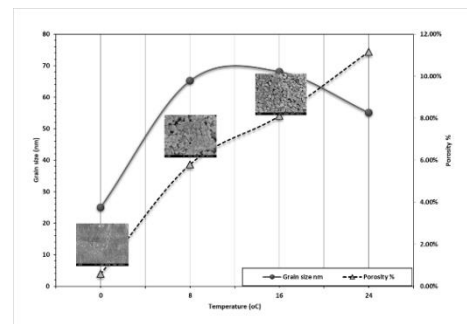

Figure 8. The grain size and porosity of the coating as a function of the anodizing temperature

The coating of minimum grain size and lowest porosity was obtained at lowset anodizing temperature.

The adherence resistance of the anodized coating with the base metal was tested using Peel adhesion testing method. The tests were conducted by pulling the tape from the surface at 90 &180 degree. The results showed a relatively good adherence for the anodized coating to the base copper, with no loss when adhesive tape was peeled from the surface, nor any loss by rubbing the surface with a cotton swab.

3. 3. Corrosion Behavior of the Anodized Coating
The experimental tests of the corrosion behavior for the anodized and non-anodized samples was carried out in simulated boiler feed water. The tested anodized samples were chosen according to the higher polarization resistance values, which was found at the anodizing condition of 0.5 M oxalate concentration and 0 °C anodizing temperature and 9 V applied voltage. Tafel Potential dynamic curves for the anodized and non-anodized samples were obtained in (3.5% NaCl) and (2 mg/l NH$_3$) aqueous solutions as shown in Figures 9, a and b, respectively.

These results showed that the corrosion potential (Ecorr) of the anodized copper was more than that for the non-anodized copper sample, while the corrosion current density of the anodized copper samples is lower than that of the non-anodized copper specimens.
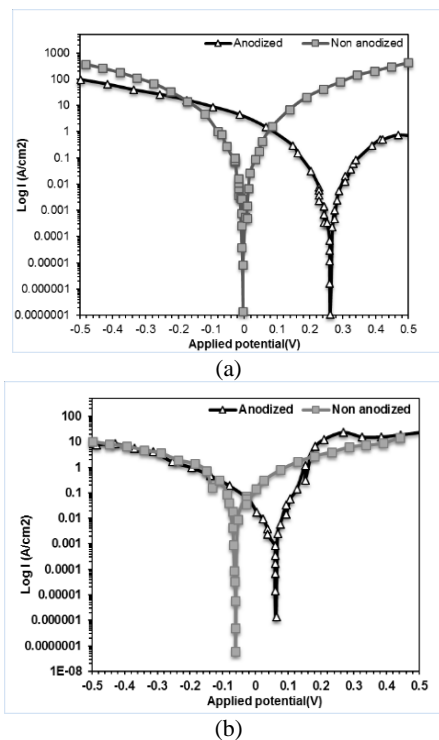

(a)

(b)

Figure 9. Potentiodynamic curves of anodized and non-anodized copper samples in, a: (3.5%l NaCl), b; (2 mg/l NH$_3$) water solution

Thus, the anodized copper sample could be corroded only at a relatively higher potential with a lower corrosion rate than that for the non-anodized copper specimen. The corrosion rates (C.R) in mm/year for the corroded samples were calculated by using the following relationship Equation (1) [20].

$$C.R = 3268 \times \frac{(Icorr \times MW)}{\rho \times z} \qquad (1)$$

where; Icorr represents the corrosion current density in (mA/cm^2), MW is the molecular weight of the specimen (g/mole), ρ the density of the sample (g/m^3), and z the number of electrons transferred in the corrosion reactions. The coating corrosion resistance efficiency CCP % was measured according to Equation (2), from the corrosion rates values of non-anodized sample (CRo) and corrosion rate of anodized sample (CR1), by using the following relationship; [20].

$$CCP(\%) = \frac{CR0 - CR1}{CR0} \times 100 \qquad (2)$$

The measuring results of the corrosion rates of the anodized and non-anodized samples in (3.5% NaCl) and (2 mg/l NH$_3$) aqueous solutions, and the corrosion protection efficiencies (CCP %) of the anodized coating are listed in Table 1.

The previous results were an indication of the enhancement of the corrosion protection efficiencies (CCP %) for the anodized coating in (3.5% NaCl) and (2 mg/l NH$_3$) aqueous solutions, as these efficiencies were 86.2% and 74.5%, respectively. The results showed that the corrosion resistance increased about seven times in (3.5% NaCl) aqueous solution and about four times in (2 mg/l NH$_3$) aqueous solution as compared with the corrosion resistance of the non-anodized samples in the same environments.

From the previous results of the corrosion tests, it was observed that the resistance to the transfer of ions and electrons through the anodized coating was higher than that for the non-anodized sample.The corrosion potential of the anodized coated sample was more positive than that of the non-anodized sample. The increase in the corrosion potential indicates that the anodized coatings have an effective inhibition influence on the anodic reaction. The increasing of the corrosion potential is associated with the porosity of the coating.

TABLE 1. Experimental results of corrosion rates for anodized and non-anodized copper samples

Environment	Material	Corrosion rate (mm/y)	CCP (%)
3.5% NaCl	Non-anodized	0.083	86.2
	Anodized	0.011	
2 mg/l NH$_3$	Non-anodized	0.070	74.5

Anodized	0.017

Where the coating of more porosity, allows a higher current to pass through it. Moreover, the corrosion current density decreases with the increase of the corrosion potential. Therefore, the higher polarization resistance (Rp) for the coated samples indicated to the lower corrosion currents and corrosion rates.

The maximum coating corrosion resistance efficiency was observed when the coating conducted at the lowest anodizing temperature of 0 °C. This result was due to the formation of a coating with smaller grain size and lower porosity at this condition. The corrosion resistance of the anodized samples was enhanced because of the blocking and insulating effects of the coating that makes the anodized coating surface passive; so, it protects the copper surface from ionization and dissolution. This result confirms that the anodized coating of copper oxide improves the corrosion resistance of the copper surface in the water environments.

4. CONCLUSIONS

From the above results, the following main points were concluded:
- ❖ The nano-copper oxide coating was successfully synthesized using the anodization technique in oxalate solution at various temperatures.
- ❖ The anodized coating of finest grain size and lower porosity was obtained at the lower anodizing temperature.
- ❖ The corrosion resistance tests for the anodized and non-anodized samples in (3.5% NaCl) and (2 mg/l NH_3) aqueous solutions show that the corrosion protection efficiencies of the anodized coating in these environments were 86.2% and 74.5%, respectively
- ❖ The anodized copper coating increases the copper corrosion resistance about seven times in (3.5% NaCl) aqueous solution and about four times in (2 mg/l NH_3) aqueous solution as compared with the non-anodized samples in the same environments.
- ❖ The best coating corrosion resistance in these environments was obtained for the coating anodized at the lower anodizing temperature.
- ❖ The coating passivity of the anodized coating protects the copper surface from further ionization and dissolution.

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چکیده

خواص عالی انتقال حرارت مس، آن را در تولید تجهیزات مختلف برنامه های کاربردی انتقال حرارت استفاده می شود. آلودگی آب توسط مس در سیستم گردش آب یکی از مشکلات صنعتی جدی است [1]. این آلودگی معمولا ناشی از واکنش خوردگی مس در محیط آب خوراکی دیگ بخار است. آلودگی مس با افزایش مقاومت خوردگی مس در آب کاهش می یابد. در این تحقیق، بهبود مقاومت به خوردگی مس با استفاده از روش آنودیزاسیون مورد بررسی قرار گرفته است. آزمایش های آنودیزاسیون در محلول های اگزالاتی از غلظت های 0.1 تا M 0.5 در محدوده دما از C° 0 تا 24 و پتانسیل اعمال شده از 7.5 تا V 9 انجام می‌شود. پوشش آنودایز با استفاده از میکروسکوپ اسکن انتشار میدان، اشعه ایکس پراکنده انرژی طیف سنجی و پراش اشعه ایکس بررسی شد. نتایج توصیفی به شکل گیری پوشش آنودایز اکسید مس با محدوده اندازه دانه از 25 تا 68 نانومتر اشاره کرد. آزمونهای مقاومت خوردگی نمونه‌های مس آنودایز در آب خوراکی دیگ بخار انجام شده است. نتایج نشان دهنده افزایش مقاومت به خوردگی نمونه‌های آنودایز است. راندمان محافظت در برابر خوردگی برای پوشش آنودایز در محلول های آزمایش حاوی 3.5 درصد اسید کلریدریک و mg / 1 2 آمونیاک به ترتیب 86.2٪ و 74.5٪ افزایش یافته است.

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