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Anodized Nano-coating of Copper Material for Thermal Efficiency Enhancement

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Abstract:

This paper presents the effects of Nano-coating process parameters on the thermal efficiency enhancement of copper substrate material. A comparison experimental results of Nano copper oxide coating prepared in oxalate solution at various operating conditions with different porosities and grain sizes. The study evaluate the effects of the Nano coating on the enhancement of heat transfer of copper substrate. Effect of oxalate concentration on the grain size and porosity of coating was investigated at various operating conditions of temperature and agitation. The Nano copper oxide coatings were conducted at the ambient temperature and below, in range of oxalate concentration between 0.1 - 0.5M using linear sweep voltammetry (LSV) method. The coating was performed in Auto lab Potentiostat with scan rate 0.02 V/Sec. the coating's characterization was done using Field Emission Scanning Electron Microscopy (FESEM). The thermal effects of the Nano anodized coating was evaluated according to the coating's grain size and porosity, which formed at various oxalate concentrations. The result shows that Nano anodized coating improves the thermal efficiency of copper by 96.5 % as a result of the increment in the heat transfer surface area around 350 times.

***Keywords:** Copper; Nano-coating; Surface Area, Thermal Efficiency.*

I.INTRODUCTION

Copper is safer and more corrosion resistance for using in industrial water environments, than aluminum. It is more thermally conductive than aluminum and Stainless steel [1]. Therefore, copper alloy considered the best material used for manufacturing heat exchangers and boilers because of its excellent corrosion resistance and heat transfer conductivity. Grain size and porosity of any coating are the most effective properties in the surface area of any substrate material. The grain size is the size of the partitions of the particles on the surface of the material. Porosity of coating is measured from pores percentage area on a selected area of the coated surface. In lower grain sizes and porosity, the particles of materials separated into smaller partitions. This clarifies the inverse relationship between the grain size and surface area [2] and [3]. Therefore, the surface area can be controlled by the adjusting physical characteristics of porosity and particle size that play an important role in particle arrangement on the surface.

Metal copper anodization is a conversion coating used to convert metal surface into oxide coating using various electrochemical treatment. The general classification metal coating is illustrated in Fig. 1. In 2011, researcher [4] study the copper anodization coating and reported the advantages of this coating in enhancing metal surface hydrophobicity [5] hardness [6] corrosion resistant and heat transfer [7].

The Grain size and porosity the anodized coating is the most effective parameter on the surface area of any material hence its thermal transfer efficiency. Therefore, controlling the grain size and porosity of the surface considered as a successful method for enhancing the hardness, corrosion resistance, and thermal properties of the material.

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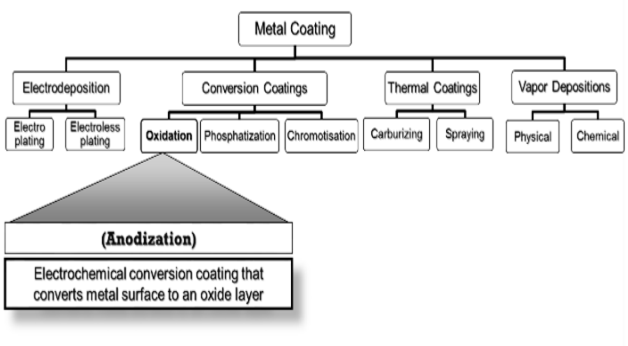

Fig. 1.Classification of anodization for metal coatings

Nano-copper oxide is used in manufacturing various applications such as gas sensors, hydrophobic surfaces, solar cells, energy storage and memory devices [8], [9].

Development of copper oxide nanostructure using coating is useful in a wide range of scientific applications like, heat transferring devices [10], gas sensors [11], hydrophobic surfaces [12] solar cells [13], energy storage [14], and memory devices [15].

Many investigations were conducted in the formation of anodized copper coating by the anodization method in various solutions [16] and [17]. Characteristics of anodized coating depend on the anodizing parameters like anodizing temperatures and anodizing solution. Another researcher [18] study the anodization of copper in the 0.1M NaOH using cyclic voltammetry. The Nano scale grain size of the metal surface can enhance the characteristic properties of the materials by the enhancing of the surface to volume ratio and increasing the quantum effect which controls the material properties.

Another researcher [19] has studied the development of high absorbing cavity porous cupric oxide (CuO) coating for electrical substitution detector used at liquid nitrogen environment. In this study, it was reported that the thermal conductivity of the coated samples was around 370 $Wm^{-1}K^{-1}$. The reported results in the recent research study [20] and [21] showed the successful fabrication of Nano copper oxide coating at various operating conditions with different, grain sizes and porosities. This research paper presents the effects of surface grain size and porosity of the copper oxide Nano-coating on the thermal efficiency of copper material.

II.EXPEREMENTAL WORK

Anodized coatings were performed on a copper using electrochemical anodization technique in oxalate solution. The effects of process parameters on the grain size and porosity of coating was evaluated using Taguchi design of the experiment method.

The anodizing parameters were in the ranges of, 0 – 24 ºC, 0.1 - 0.5 M oxalate and 7.5-9 volts. These parameters were selected to reach the optimum grain size and porosity of coating suitable for best heat transfer efficiency. Four levels and three factors were used for evaluating the impacts of the coating parameters on the anodized coating through the effect of grain size and porosity of the coating. Taguchi’s Design of Experiment (DOE) is a Statistics analysis method used to evaluate the effects of parameters on the resulted characteristics. It is an experimental strategy where the effects of multiple factors are studied. This research was based on L16 orthogonal array which represent the results of sixteen planned experiments.

To study the effect of oxalate concentration on the thermal transfer through its effect on the coating’s grain size and porosity. anodization experiments was conducted on pure copper foil with thickness of 0.12 mm and dimensions 1 cm × 1 cm. The experiments were performed with an electrochemical cell of three electrodes using Auto Lab Potentiostat PGSTAT AUT- 86037. All experiment con-ducted using linear sweep voltammetry method (LSV) at 0.02 V/Sec scan rate. The surface of copper samples was chemically cleaned in an acid bath before the coating, then it washed with ace-tone, distilled water and finally, it was dried in air at ambient temperature.

Fig. 2 illustrates the three-electrode cell of the anodization experiment. It consists of; (a) electrolyte container, (b) counter electrode, (c) reference electrode, (d) working electrode, (e) holder, (f) magnetic stirrer, (g) heater mantel, (h) circulating cooling water jacket, (i) inlet of cooling water, (j) outlet of cooling water, (k) temperature indicator of cooling water, (l) temperature indicator of solution.

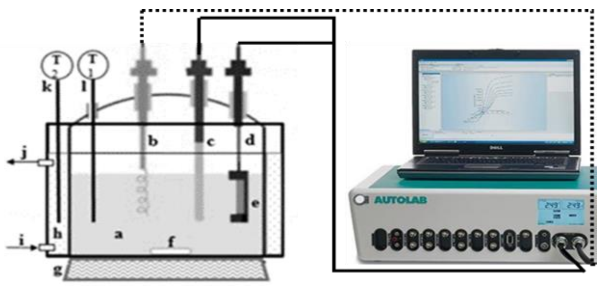

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Fig. 2. Experimental cell for anodized coating with three-electrode

The grain size and porosity of the anodized coatings formed under various conditions of temperature and oxalate concentration were characterized using Field Emission Scanning Electron Microscopy (FESEM). Linear intercept analyzing method, ASTM E112 was used to measure coating grain size. The measurements were made by means of image analyzer software on four straight lines with a total length (L). The straight lines on the sample surface were taken at (0°, 45°, 90°, and 135°) directions. In this method, the first stepis to set the line spacing in the directions horizontal, vertical and 45 degrees. The spacing of the 45-degree line was measured as (vertical /0.7) to plot lines of equal length in all directions, where the perpendicular distance between lines defined as (sin 45°= 0.707). The number of grains which its boundary intercepted with the selected line. The smaller measured grain size less than 3 pixels was eliminated and excluded from the calculations. The grain size, d was determined according to the following equation:

$$d=l/n \quad (1)$$

Where;
l; is the real lengths of the selected line,
n; is the number of grains which intercepted with the selected line.
The Pores percentage area of the anodized samples were measured according to ASTM E2109 - 01(2014) Standard Test Methods. This measurement was done by measuring the percentage of pores area on a selected surface area using image analyzer software. The pores of small sizes, less than one pixels, were excluded from the calculations and considered as noise.
The effect of the anodized coating on the thermal transfer through the copper pipe was investigated using an experimental testing sys-tem Fig. 4. This system consists of the copper pipe manufactured from high purity 99.99% copper alloy, with outside diameter 3.18 mm, inside diameter 1.55 mm, and wall thickness 0.81 mm. The copper pipe was bent into six paths passing through three sections, adiabatic, condensation, and evaporation. The condensation section consists of cooling water circulating bath, while the evaporation section consists of electrical heating mantel controlled by an adjust-able power supply. The six paths of the bent pipe were supported with eighteen temperature indicators to record the temperatures of each section of the pipe, as illustrated in Fig. 4.

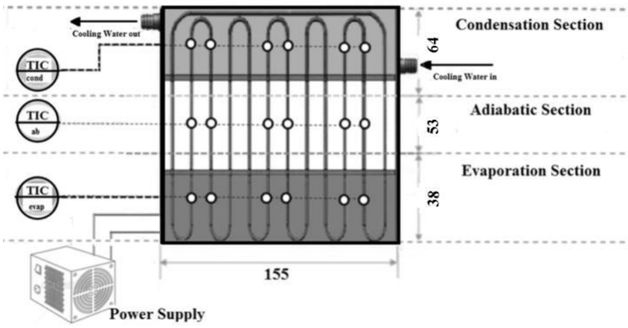

Fig. 4. Experimental set-up for Thermal Transfer System

Experimental tests were performed for the coated and non-coated pipe. The pipe in the evaporation section started heated up using a heating mantle when the cooling zone reached the steady-state temperature at 20 ^{o}C. The temperatures difference in the three sections of the pipe were recorded. Average temperature differences for each path were calculated.
To compare between the heat transferred through the coated and uncoated samples at same temperature difference (40 ^{o}C), and same samples dimensions (0.5×0.5×1) cm, the heat transferred measured according to the following equation;

$$Q=k\times Ac\times(\Delta T/Th) \quad (2)$$

Where;
Q; is the heat transferred in watt
k; is the thermal conductivity of samples material W/m.K
Ac;is the sample cross section area
ΔT; is the temperature difference
Th; is the sample thickness

The area of heat transfer (SSA) for coated and uncoated samples was calculated from the specific surface area per unit mass according to the following equation:

$$SSA=A/(V\times\rho) \quad (3)$$

Where:
A; is the area of heat transfer
V; is the volume of specimen
ρ;is the material density

The average grain size of the coated sample was 45 nm, and the average grain size of the uncoated sample was 15 micrometer. The calculated specific surface area of the coated and uncoated samples were 22.5 and ~0.045, m^2/g, respectively.

The specific surface area per unit volume (Sv) can be calculated from dividing the surface area of a single sphere;

$$Sv=\pi\times x^2 \quad (4)$$

Where x; is the average diameter of the particles. The specific surface area for a single spherical practical can be calculated according to the following equations:

$$Sv= (\pi\times x^2)/ ([\pi\times x]^3/6) \quad (5)$$

$$= 6/x \quad (6)$$

The specific surface area per unit mass Sw for a single practical can be measured by divide previous value by the material density ρ as the following equation

$$Sw= Sv/\rho \quad (7)$$

$$=6/x\times\rho \quad (8)$$

To evaluate the capability of effective heat transfer through the coated sample. Effective thermal conductivity at the specific heating fluxes was measured from the following equations;

$$Keff= (Q \times Leff)/ (\Delta T \times Ac) \quad (9)$$

$$Leff = (Le/2) +La+ (Lc/2) \quad (10)$$

Where;
Keff; is the effective thermal conductivity W/m.k
Ac; is the total cross-section area of the tested samples cm^2
Leff; is the total effective length
(Le, La, Lc); are the lengths of the evaporation, adiabatic, and condensation sections of copper samples.

The heat fluxes was measured from the following equations;

$$q =((Keff)/ (Leff))/((\Delta T\times Ac)) \quad (11)$$

$$q =Q/Ac \quad (12)$$

Where;
q; The heat flux, or the rate of heat transfer per unit area, (W/m^2)
Q; transferred heat joules (J)

III. RESULT AND DISCUSSION

Analyses of FESEM micrographs shown that the average grain size of the anodized coating was ~44 nm, and the average pores percent-age area of coating was ~8.5 %. Effects of the anodizing parameters on coating grain size and porosity were investigated using signal to noise ratio method. The evaluation results obtained fromsignal-to-noise ratio analyses showed that the anodizing temperature was the most affecting parameter on the grain size and porosity of the anodized coating and oxalate concentration was the second affecting parameter, as shown in Fig.5,Table. Iand Fig. 6,Table. II, respectively.

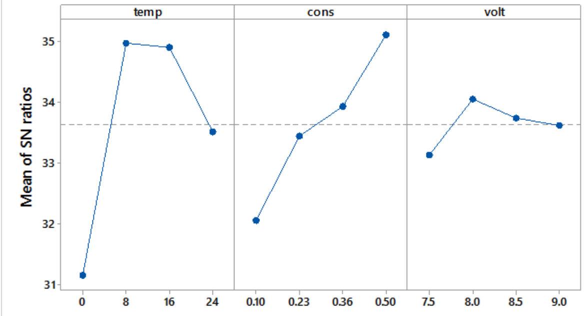

Fig. 5. Signal to noise graphs showing the effects of anodizing parameters over the grain size of coating

Table.I: Values of signal - to - noise ratio considering coating grain size

Level	Temperature	Concentration	Voltage
1	31.15	32.06	33.13
2	34.98	33.44	34.06
3	34.91	33.93	33.75
4	33.51	35.12	33.61
Delta	3.84	3.06	0.93
Rank	1	2	3

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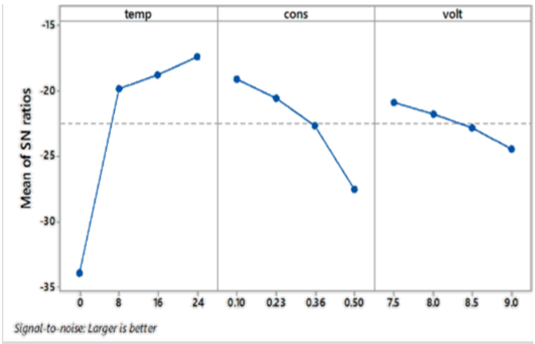

Fig. 6. Signal to noise graphs showing the effects of anodizing parameters over the coating porosity

Table .II: Values of signal - to - noise ratio considering porosity of coating

Level	Temperature	Concentration	Voltage
1	33.98	19.08	20.86
2	19.83	20.57	21.74
3	18.73	22.68	27.54
4	17.33	27.45	24.43
Delta	16.64	8.46	3.57
Rank	1	2	3

The increasing of oxalate concentration increases the conductivity of the anodizing solution, which increases the coating growth rate to form a thicker coating with organized Nano grain sizes and lowest porosity. Fig. 7 shows a comparison of different coatings formed at various oxalate concentrations.

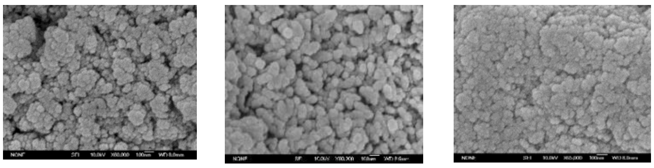

Fig. 7. FESEM image at 60 kx magnification of anodized copper coating prepared different oxalate Concentrations a: 0.1M, b: 023M, and c: 036M

From the previous resultsit can be observed that the increase of oxalate concentrationin the same operating conditions makes the coating to become uniform, compact, and denser. The effect of temperature and oxalate concentration on coating grain size and porosity are shown in the Fig. 8 and 9 respectively.

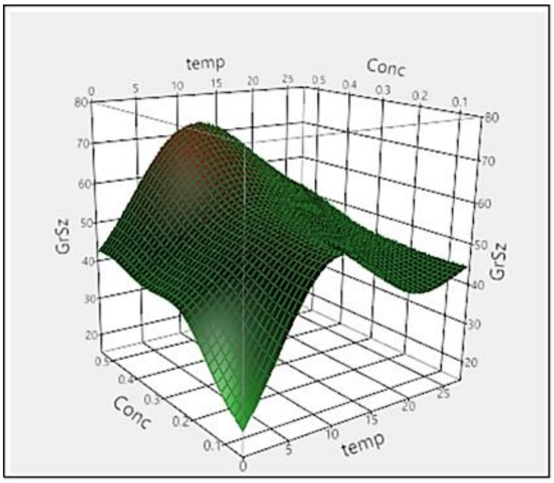

Fig. 8. Average grain size of anodized coating as a function of oxalate concentration and anodizing temperature

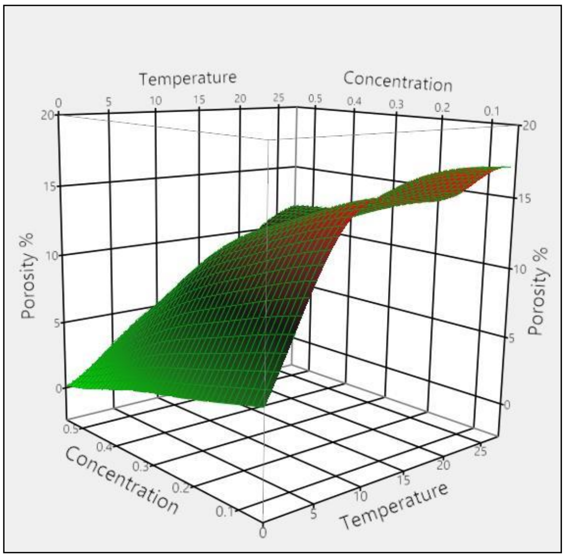

Fig. 9. Average porosity of anodized coating as a function of oxalate concentration and anodizing temperature

In Fig. 8, it showed that the increases of the coating grain sizewith the increasing of oxalate concentration in the anodizing solution.

This result was due to the increase of the solution conductivitywith the increases in oxalate concentration, leading to increasingthe rate of anodizing and forms larger grain sizes. Therefore, thesmaller grain size of the coating was obtained in solutions of loweroxalate concentration, and it increased with the increasing of theoxalate concentration in the anodizing solution. Whereas, coatingwith smallest grain size was formed at lower anodizing temperatures.

The reducing of the grain size with the decreasing

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of the temperatureis due to the decreasing of ionic mass transfer through theanodizing solution with the decreasing of the temperature. At lowionic mass transfer, the coating deposition rate reduced leading toform a coating of smaller grain size

Fig. 9 showed the porosity of anodized coating as a function ofthe oxalate concentration and anodizing temperature. From Fig. 9, the less porous coating was formed in the highest oxalate concentrationand lowest anodizing temperature. Whereas, the increasingof oxalate concentration increase the conductivity of anodizingsolution leading to increasing the charge transfer through the anodizingsolution. Increasing charge transfer through anodizing solutionleads to form a large grain sizes coating with few pores.

The grain size and porosity considered as the essential materialproperties which effects on the surface area. Where the material ofsmaller grain size has a higher surface area compared with thehigher grain size. This due to the partition of surface material particlesinto smaller parts leading to increase the total surface area. The increasing of surface area results in enhancing the surface to volumeratio and increasing the quantum effect which controls materialproperties. Therefore Nanotechnology contributed to the enhancementof materials heat transfer performance and improve its mechanicalproperties, and corrosion resistance.

Comparison experiments were carried out for coated and uncoatedsamples of various surface grain sizes, to evaluate the variation inthe surface area with the grain size before and after the coating. Fig. 10 illustrate the variations of the surface area with the variationof surface grain size of coated and uncoated samples.

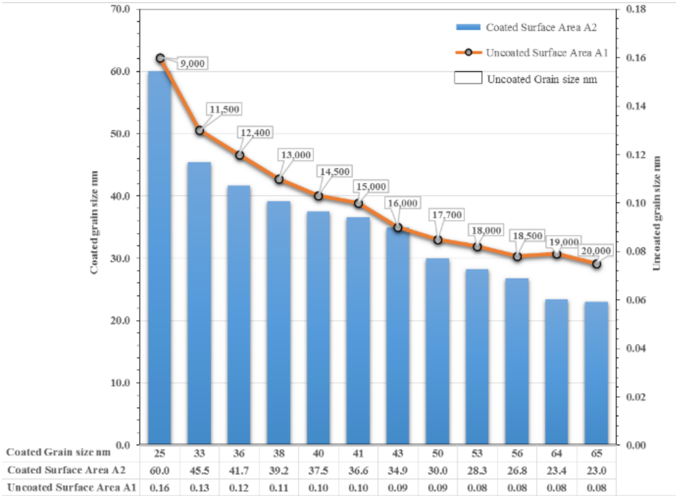

Fig. 10. Surface Area of coated and uncoated samples as a function ofgrain sizes

Results show that the surface area was increased dramatically withthe reducing of coating grain sizes as shown in the Fig. 10. From the previous figure it can be observed that the surface areaof samples was increased after the anodized coating and it wasreduced for both coated and uncoated samples with the increasingof surface grain size. Results also show that the area of heat transferincreased 352.6 times after the anodized coating which wasmeasured from the ration of uncoated surface area (A1) and coatedsurface area (A2). This increase in the surface area led to increasingthe heat transfer through coated samples by 29 times which wasmeasured from the ratio of heat transfer of coated (q2) anduncoated copper surface resulting in enhancement of heat transferefficiency by 96.56 %, as listed in the Table III.

Table- III: Comparison results of thermal calculations for heat transferred through copper-coated and uncoated samples

Copper sample	**Area**	**Heat transferred**	**Heat transfer Efficiency**	Area ratio	Heat ratio
	m^2	***KW***	%	%	%
Uncoated	0.10067(A1)	161(q1)	96.56 %	352.63	29.09
Coated	35.5004(A2)	4,686(q2)			

In a nutshell, it can be said that the enhancement of copper's thermaltransfer property after the anodized copper oxide coating is prominentdue to the enhancement of surface to volume ratio and increasingthe quantum effect which controls material properties.

IV. CONCLUSION

From present study, the following conclusions can be drawn:

1. The fabricated of Nano copper oxide coating was successfully achieved on a copper substrate using anodization method in oxalate containing solution.
2. The increasing of oxalate concentration increases the conductivity of the anodizing solution, leading to increase the coating grain sizes and decrease porosity.
3. The increasing of oxalate concentration increase the coating grain sizes and decrease porosity. This due to the effects of increasing of oxalate concentration on the increasing of the anodizing solution conductivity which lead to increase the charge transfer through coating solution. Hence form a coating of large grain sizes with few pores.
4. The coating with Nano scale surface grain sizes enhanced thermal transfer property, as a result to the enhancing of the surface to volume ratio. This enhancement was due to the improvement of the quantum effects that controls the material properties.
5. Anodized coating improved the heat transfer efficiency of copper by 96.5 % as a result of increasing active surface area around 352 times after anodized Nano-coating on substrate material.

This investigation result of the advantage of the anodized copper coating in the increasing of heat transfer efficiency, can serve and contribute to developing a variety of industrial challenges especially, in the design of heat exchanger, solar cell and energy storage device.

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