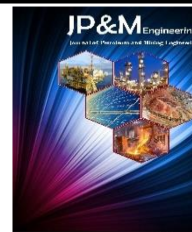
JP&M Engineering

Journal of Petroleum and Mining Engineering




# Improving Corrosion Resistance of Copper by Forming Super Hydrophobic Layer on Surface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## Abstract

Improving corrosion resistance of copper is often associated with the presence of cuprous oxide (Cu2O) films on the surface. Many surface modification techniques such as chemical etching, oxidation, inhibitors, electro deposition and sol-gel could be employed

In the present work a film of Cu2O, which is considered to be protective and strongly adherent to the substrate, is formed. Experimental technique includes etching of copper specimens in ammonia solution, calcination, and then modified in ethanol solution of stearic acid for different times was employed

Etching of copper for 60 h in 10 wt. % ammonia solution exhibits a contact angle of 135˚ but the formed layer, which is CuO, has poor adhesion.

Modifying of etched-calcined copper in 0.1 mol/L ethanol solution of stearic acid for 3 h shows a superhydrophobic film (Cu2O) with a high contact angle of 160˚, good adhesion and lowest corrosion rate. The contact angle was measured at ambient temperature.

The surface morphology and chemical compositions of the samples were investigated with a scanning electron microscopy, EDX and an X-ray diffraction. Electrochemical corrosion behavior was conducted in 3 wt. % NaCl aqueous solution at room temperature. The contact angle was measured using Attension Biolin device (Theta Optical Tensiometers) Also Thickness (using Tooke Inspection Guage OG204 according to ASTM D4138) and adhesion (using X-Cut Tape Adhesion test according to ASTM D3359) of formed films were determined



**Keywords**

Copper; Surface modification; Superhydrophobic films; Cupric and Cuprous oxides; Contact angle.


## Introduction

Copper due to its good electrical and thermal conductivities, and high mechanical properties (malleability, ductility, formability, machinability, and strength when alloyed, except at high temperatures) [1-4] has been widely used in military, various instruments of the elastic element, tubing, pump, medical equipment, optical instruments, decorative materials, metal artwork and a variety of household appliances, constructions such as roofing and plumbing , industrial machinery such as heat exchangers, steam condensers, distribution systems for industrial and potable water, where they generally give reliable performance , power generation and transmission, electronic product manufacturing, heating and cooling systems, transportation of water for domestic and industrial uses, and telecommunications links used every day in homes and businesses. [5-10].

The main disadvantage of copper is its corrosion in natural water and corrosive media such as acidic or alkaline solution, or the presence of a strong oxidizing. Thus, the corrosion problems of copper have attracted great attention [3, 11-13]. Many surface modifications techniques such as chemical etching [14], oxidation [15], inhibitors [16], sol-gel [17, 18], and electro-deposition [19, 20] could be used to improve the corrosion resistance of copper.

This work was aimed to fabricate a superhydrophobic layer on the copper substrate using an environmentally friendly compound.

## Materials and Methods

### Materials

The analysis of the used copper was conducted by X-ray fluorescence (XRF) Spectrometer Model NITON XL3 T980 GOLD, as shown in Table 1, And it received in form of free cutting copper rods with 11.5 mm diameter. The rod was cut into specimens with area of 1 cm2 cross section and 1 cm height for the microscopic investigation and electrochemical experiments.

**Table 1** Chemical composition of pure copper

| Element | Cu | Fe | In | Sn | Pb |
|---|---|---|---|---|---|
| **Composition wt.%** | 99.9 | 0.014 | 0.012 | 0.031 | 0.023 |

### Specimen preparation

Specimens were ground progressively using wet silicon carbide (SiC) emery papers with grit number starting with 600-grit and proceeding to 2000- grit papers. Water is used to keep specimens cool and to flush away loose particles of metal and abrasive. Final polishing is performed on a low speed wheel covered with micro-cloth using 0.05 µm Alumina suspension (Al2O3) Thereafter, samples were rinsed using distilled water and acetone, and air dried.

### Applied surface modification techniques

#### Etching

Copper samples were etched with a 50 mL ammonia solution (10 wt. %) at room temperature for different times, and then samples were washed by distilled water, and dried. Then corrosion resistance is characterized by scanning electron microscope (SEM), X-ray diffraction (XRD), water contact angle, potentiodynamic polarization metallography, adhesion and layer thickness.

#### Calcination

Some etched samples were calcined in air using an electric resistant furnace of type (Nabertherm) at 350◦C for different times. Then corrosion resistance is characterized by scanning electron microscope (SEM), X-ray diffraction (XRD), water contact angle and adhesion.

#### Immersion in stearic acid

Some etched-calcined samples were modified in a 0.1 mol/L ethanol solution of stearic acid at room temperature for different times. Then copper samples were washed with distilled water and then dried for further characterization.

### Characterization

The surface morphologies and chemical compositions of the samples were investigated using an optical microscope (OPTIKA), a scanning electron microscopy (SEM, FEI Inspect S50), and X-ray diffraction (XRD, Bruker, discover D8 Advance). The contact angle was measured by Attension Biolin device (Model: Theta Optical Tensiometers), and the drop size was 5 µ litre of double distilled water at ambient temperature. Electrochemical corrosion behavior was conducted in 3 wt. % NaCl aqueous solution at room temperature via versa stat device. The work station was equipped with a standard three-electrode system: graphite electrode was used as the counter electrode, and the calomel electrode (SCE) and the copper sample were used as the reference electrode and working electrode, respectively. Before electrochemical experiments, these copper samples were immersed in the NaCl solution for 20 min. to achieve a stable open circuit potential (OCP vs. SCE). The potentiodynamic polarization curves were measured between −0.15 V and 0.15 V (vs. OCP) with the scanning rate of 0.5 mV/s. Thickness measurements were carried out using Tooke Inspection Gauge OG204according to ASTM D4138[21]. And the Adhesion was carried out using Tape adhesion Test (X-Cut) ASTM D3359 [22]

## Results and Discussions

### Contact Angle Measurement

The contact angle determined at different times of the three treatment conditions (etching, etching-calcination, etching- calcination and modifying in 0.1 mol/L ethanol solution of stearic acid).

The results reveal that, in etching treatment the contact angle increases to reach the maximum at 60 h etching to be 135˚ then decreases again with increasing time, it could be related to the formation of different compounds in each time (from reaction of copper with excess amount of ammonia), Figure 1.

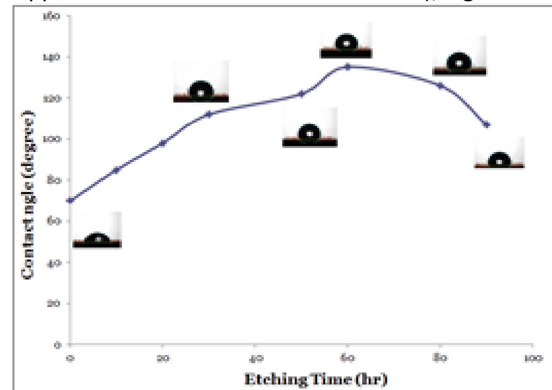


**Figure 1** Shows the effect of etching on contact angle at different times.

When etched samples were calcined at 350˚C for 20 min, the contact angle values decrease to be about 70˚, as shown in Figure 2.

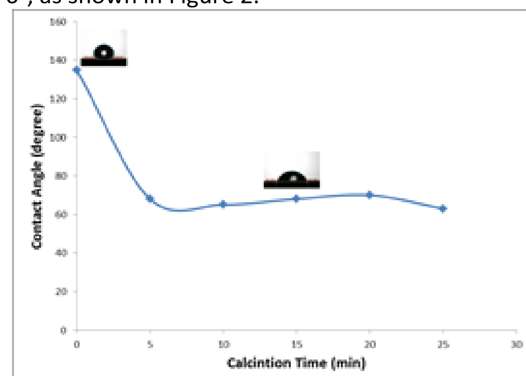


**Figure 2** Shows the effect of calcination after etching on contact angle at different times.

After modified etched- calcined samples in 0.1 mol/L ethanol solution of stearic acid, the contact angle increases again to be about 160˚ at 3 h, Figure 3, that's prove a superhydrophobic layer is formed on the surface of substrate, then decreases and this is could be related to the formation of another compounds (from Cuprous and stearic acid) over the layer of $Cu_2O$ previously formed.

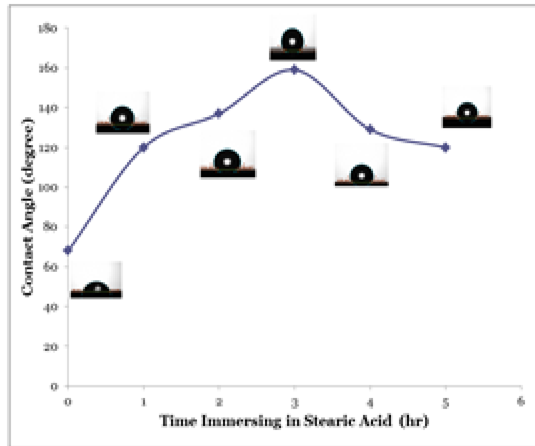


**Figure 3** Shows the effect of stearic acid on contact angle after etching-calcination process.

## Corrosion test

Results of the potentio-dynamic polarization tests of all etched and etched- calcined and then modified in 0.1 mol/L ethanol solution of stearic acid specimens are given in Tables 2, 3 and illustrated in Figures 4, 5 respectively. It could be observed that etching for 60 h and modified etched- calcined samples in 0.1 mol/L ethanol solution of stearic acid for 3 h, Figures 6, 7, 8 gave the lowest corrosion rate which is confirmed the results of contact angle measurements.

## Surface morphology

### Etching in 10% wt. ammonia solution

The geometrical characteristics of the surfaces before and after etching were investigated by SEM images. **Figure 9 (a)** shows the morphology of Cu surface without any treatment. It is very smooth with a Contact Angle of 70◦. After the etching treatment (60 Hr. in 10 wt. % ammonia solution), it could be observed that the surface was covered by a layer with a contact angle of 135˚, as shown in Figure 9 (b).

EDX investigation, Figure10, showed that the formed film is mainly consists of copper, oxygen and nitrogen due to the reaction of ammonia with copper surface.

**Table 2** Corrosion parameter of etched samples at different times

| Condition | | $E_{corr}$ (V) | $β_a$ (V) | $β_c$(V) | $i_{corr}$ (μA) | C.R (mpy) |
|---|---|---|---|---|---|---|
| Pure | | -0.255 | 0.688 | 0.466 | 32.623 | 14.928 |
| Etching in 10 wt.% ammonia solution | 10 hr | -0.171 | 0.785 | 0.66 | 41.646 | 19.057 |
| | 20 hr | -0.075 | 0.183 | 0.142 | 22.922 | 10.489 |
| | 30 hr | -0.101 | 0.1896 | 0.0299 | 22.216 | 10.166 |
| | 40 hr | -0.493 | 8.746 | 0.756 | 18.347 | 8.396 |
| | 50 hr | -0.033 | 0.542 | 0.339 | 14.159 | 6.479 |
| | 60 hr | -3.235 | 119.342 | -3.516 | 2.283 | 1.045 |
| | 70 hr | -0.322 | 3.914 | 1.376 | 19.552 | 8.947 |
| | 80 hr | -0.092 | 0.391 | 0.0434 | 23.532 | 10.769 |

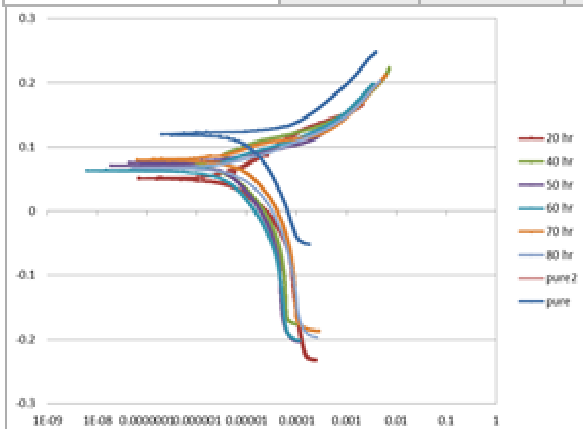


**Figure 4** Polarization curves of etched samples at different times.

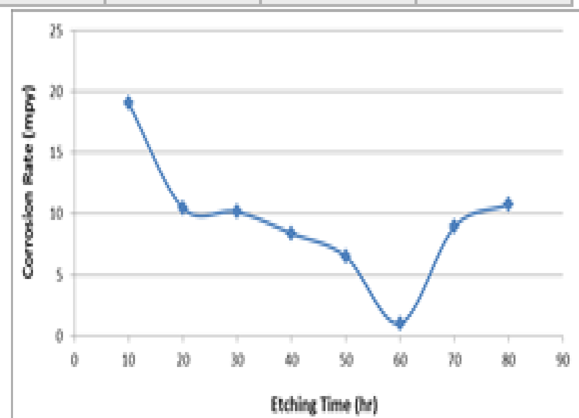


**Figure 5** Variation of corrosion rate of copper after etching in 10 wt. % ammonia at different time .

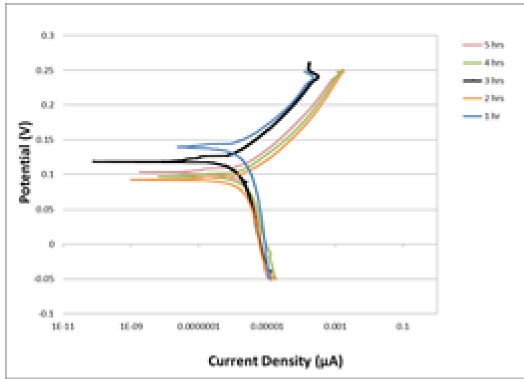


**Figure 6** Polarization curves of modified samples in stearic acid after etching- calcination process at different times

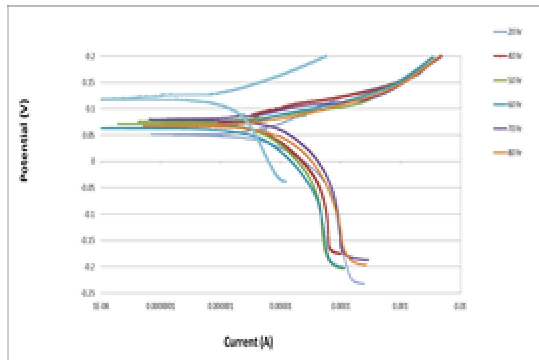


**Figure 7** Polarization curves of etched samples at different times and immersing in stearic acid 3 h

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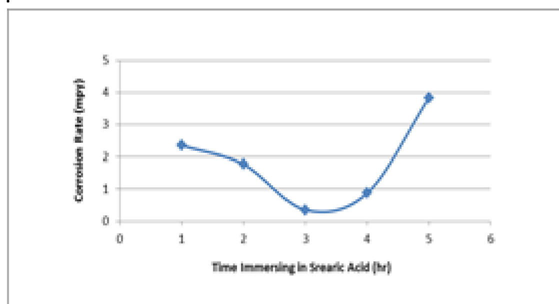



**Figure 8** Variation of corrosion rate of etched- calcined then immersing in stearic acid copper samples with time.

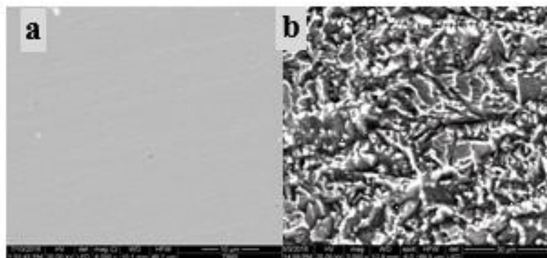
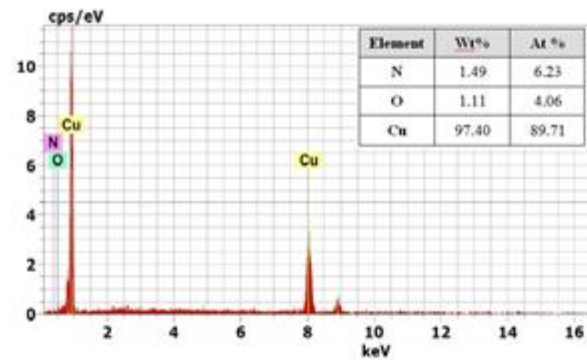



**Figure 9** SEM images of bare copper (a) and etched copper with 10 wt. % ammonia solution (b).

**Calcination**

After the calcination treatment, a more rough structure can be formed on the substrate, as shown in Figure 11.

EDX results showed that, the formed film Oxygen Wt. % increased while Copper Wt. % decreased due to the oxidation process which has carried during calcination, as shown in Figure 12.




| Element | Wt% | At % |
|---|---|---|
| N | 1.49 | 6.23 |
| O | 1.11 | 4.06 |
| Cu | 97.40 | 89.71 |

**Figure 10** EDX analysis of etched sample with 10 wt. % ammonia solution for 60 h.

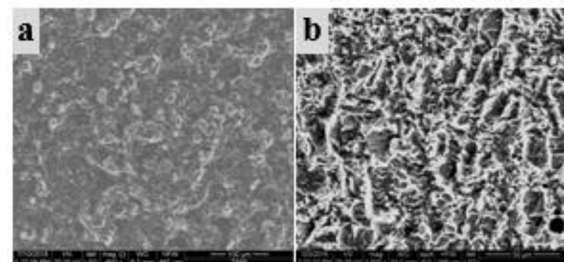
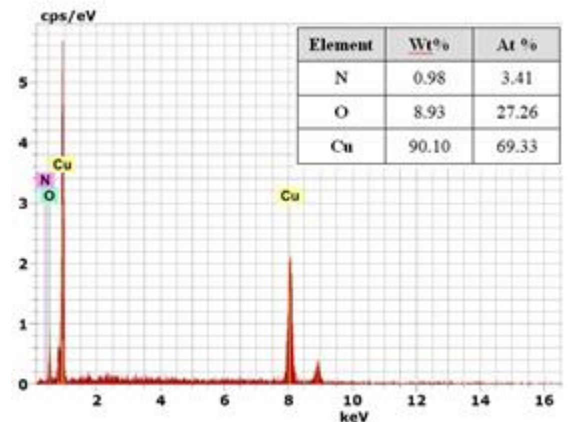



**Figure 11** SEM images of etched- calcined samples for 20 min at 350˚C (a) low magnification (b) high magnification.




| Element | Wt% | At % |
|---|---|---|
| N | 0.98 | 3.41 |
| O | 8.93 | 27.26 |
| Cu | 90.10 | 69.33 |

**Figure 12** EDX analysis of etched-calcined sample at 350˚C for 20 min.

**Etched- calcined samples immersing on 0.1 mol/L ethanol solution of stearic acid**

Once the etched- calcined samples were modified in an ethanol solution of stearic acid for 3 h, copper oxides which formed during etching and calcination rapidly reacted with stearic acid and form a new layer which could be cuprous oxide Cu2O, as shown in Figure 13, which is insoluble, strongly adherent and provides corrosion protection and showed Super-hydrophobic characteristic.

**Table 3** Corrosion parameter of etched- calcined and modified in 0.1 mol/L ethanol solution of stearic acid samples at different times.

| Condition | | $E_{corr}$ (V) | $\beta_a$ (V) | $\beta_c$(V) | $i_{corr}$ (μA) | C.R (mpy) |
|---|---|---|---|---|---|---|
| Modified in stearic acid After etched-calcined treatment | 1 hr | -0.081 | 0.677 | 0.786 | 5.151 | 2.357 |
| | 2 hr | -0.064 | 0.417 | 0.041 | 3.869 | 1.771 |
| | 3 hr | -0.456 | -0.410 | 9.828 | 0.765 | 0.350 |
| | 4 hr | -0.848 | -0.388 | 12.64 | 8.388 | 3.838 |
| | 5 hr | -0.066 | 1.48 | 1.567 | 1.916 | 0.877 |

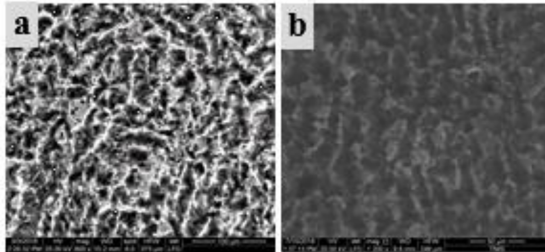
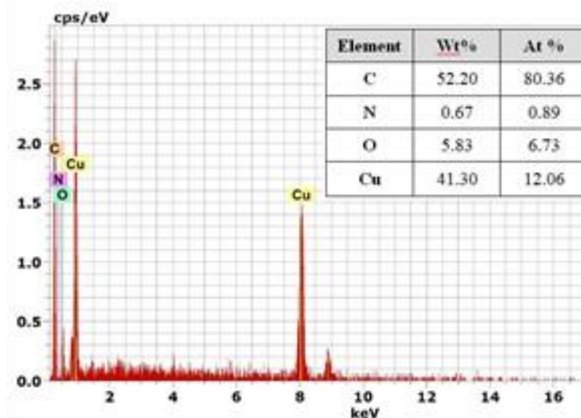



**Figure 13** SEM images of etched- calcined and immersing in stearic acid samples.

The EDX scan analysis reveals that cuprous oxide film is formed after modified etched-calcined samples in 0.1 mol/L ethanol solution of stearic acid sample for 3 h, since the atomic weight of copper is twice the atomic weight of oxygen as shown in Figures 14.



| Element | Wt% | At % |
|---|---|---|
| C | 52.20 | 80.36 |
| N | 0.67 | 0.89 |
| O | 5.83 | 6.73 |
| Cu | 41.30 | 12.06 |



**Figure 14** EDX analysis of etched-calcined and immersing in a 0.1 mol/L ethanol solution of stearic acid sample for 3 h.

## X-Ray Diffraction

From different X-ray diffraction patterns for the specimens in conditions; etching, etching-calcination, and Etching - Calcination followed by immersion in stearic acid, It was observed that, this is no change in the XRD when the 2θ ranged from 10º to 100 º, Figure 15. This prove that the formed layers were very thin and less than 20 microns.

So low angle XRD diffraction carried out and resulted in formation of cupric oxide CuO in the surfaces of etched and etched– calcined substrate, and cuprous oxide Cu2O in the condition of modifying the etched- calcined samples in 0.1 mol/L ethanol solution of stearic acid, shown in Figure 16 (a, b, c).

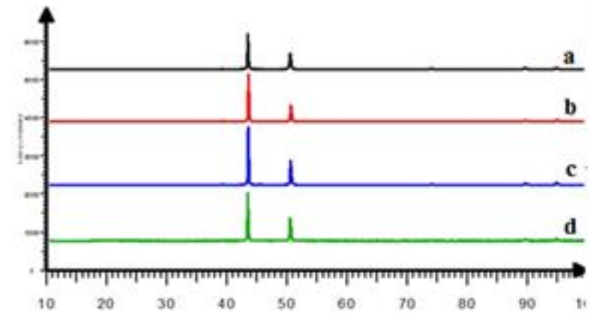



**Figure 15** XRD pattern of, pure copper (a) etched copper surface with 10 wt.% ammonia solution (b), calcination of copper surface after etching(c) and etched-calcined and modified in stearic acid (d).

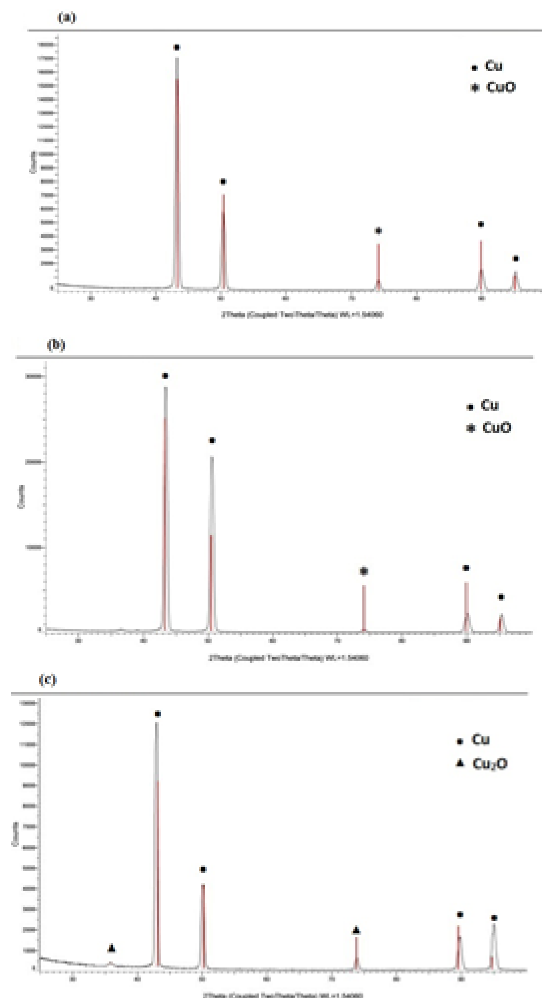



**Figure 16** Law angle XRD pattern of etched (a), etched-calcined (b) and etched- calcined then modified in stearic acid (c) samples.

## Adhesion Test

The adhesion tape test carried out on the 3 conditions and results on

### Adhesion of etched samples

Figure 17 (a,b) show the result of adhesion test that carried out on etched samples in 10 wt % ammonia solution for 60 hrs.

It can be observed that, although the surface in this condition had a very good result on contact angle determination and corrosion rate test but it loose as shown.

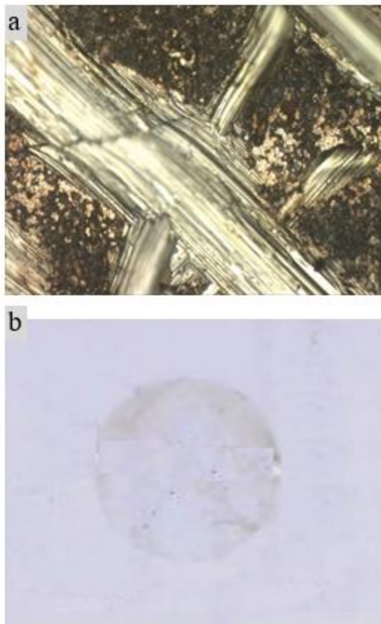


**Figure 17** Shows optical images of etched samples after tape adhesion test (a) and result of test (b).

### Adhesion of etched- calcined samples

From Figure 18, we could be observed that the adhesion of the surface of etched- calcined sample is better than the etched one.

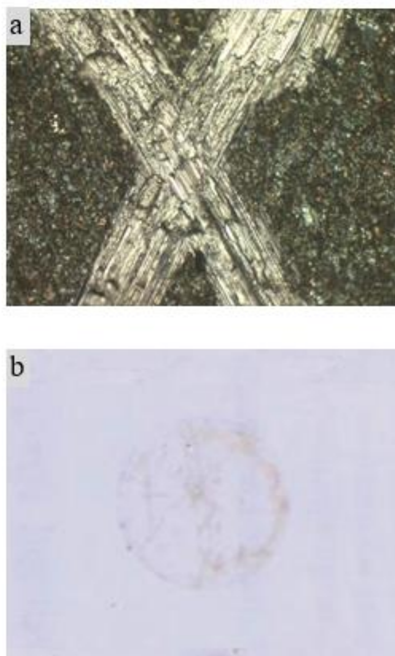


**Figure 18** Shows optical images of etched-calcined samples after tape adhesion test (a) and result of test (b).

### Adhesion of samples immersed in stearic acid

The Adhesion of $CU_2O$ film is better than etched and etched- calcined samples as shown in Figure 19.

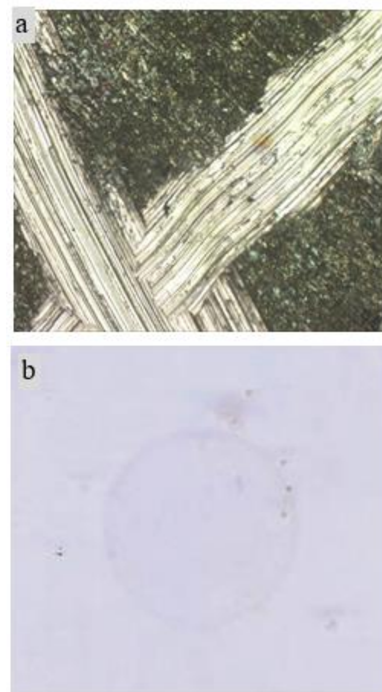


Figure 19 : Shows optical images of etched-calcined and immersing in stearic acid samples after tape adhesion test (a), and result of test (b).

## Layer thickness determination

### Etching in 10 wt. % ammonia solution

Table 4 and Figure 20 show the variation of layer thickness with etching times. It could be observed that layer thickness reached 15 micronsafter 60 hr etching in 10 wt% ammonia solution.

**Table 4** Shows variation of layer thickness with etching time.

| Etching Time (hrs) | 20 | 40 | 60 | 80 |
|---|---|---|---|---|
| Layer Thickness (micron) | 6 | 12 | 15 | 9 |

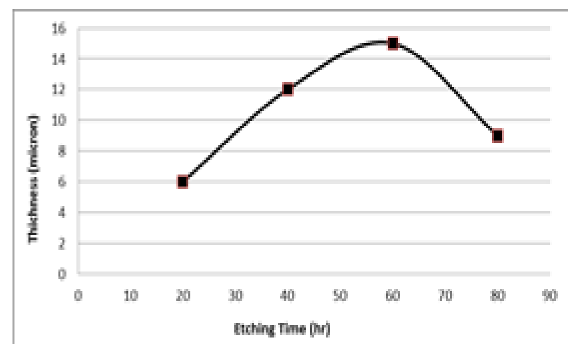



**Figure 20** Shows variation of layer thickness with time of etching.

**Immersing in 0.1 mol/L ethanol solution of stearic acid**

This is gradually increased in layer thickness with increasing time of immersing etched- calcined samples in 0.1 mol/L ethanol solution of stearic acid, as shown in Table 5 and Figure 21.

**Table 5** Shows variation of formed layer thickness with time immersing in stearic acid.

| Immersing in stearic acid (hrs) | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Layer Thickness (microns) | 7.5 | 12.5 | 15 | 17.5 | 17.5 |

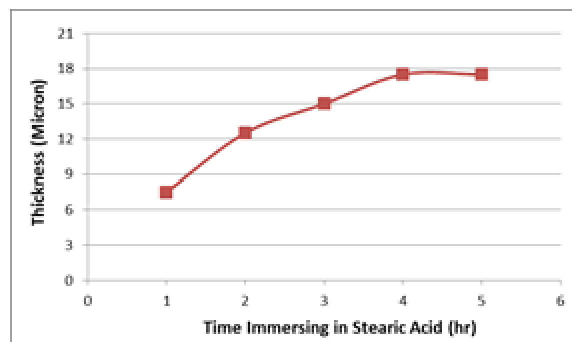



**Figure 21** Shows variation of layer thickness with time of etching- calcined and immersing in stearic acid samples.

We were discussed some suggested reactions which lead to form cuprous and cupric oxides and didn't reach to specific mechanism.

So, explain kinetics and mechanisms of these phases need more additional intensive work with professors of organic chemistry.

## Conclusions

Etching of Pure copper in 10 wt. % ammonia solution for 60 h forms a layer of contact angle 135˚, Unfortunately, The adherence between this layer and substrate is poor and can be easily removed.

When Etched samples calcined at 350˚C for 20 min., the contact angle decreases.

After modified etched-calcined samples in stearic acid, the contact angle of the surface increases to about 160˚. That's means a superhydrophobic surface is formed on the substrate.

From EDX and XRD, It could be observed that, the Cuprous Oxide ($Cu_2O$), which is the most protective layer, is formed.

The corrosion rate of pure copper decreased from about 15 mpy to about 0.3 mpy after modified etched-calcined samples in stearic acid.

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