Full Paper

The Role of Nano-scale Grain Refinement on the Vacancy Diffusion Coefficient in the Passive Layer of Pure Copper in 0.1 M KOH Electrolyte

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Abstract- Passive film of nano-grained pure copper was examined for semiconducting behavior in comparison to annealed pure copper. Mott–Schottky analysis revealed the vacancies behavior through the passive layer, and the Point Defect Model (PDM) put an accurate interpretation on the survey data. The findings clarify that the vacancy of copper is the main in the passive layer on both annealed and nano-grained pure copper formed anodically in 0.1 M KOH electrolyte. Also, calculations based on PDM showed that the diffusion coefficient of the copper vacancy for nano-grained sample reached to $17.11 \times 10^{-17}$ cm$^2$/s from $12.05 \times 10^{-17}$ cm$^2$/s of the initial annealed one.

Keywords- Pure copper, Nano-grained, Mott–Schottky analysis; Diffusion coefficient, Copper vacancy

1. INTRODUCTION

The grain refinement process in most metals and alloys is actually of a great importance [1,2]. Regarding its effect on strength and ductility, grain refinement process has absorbed many researchers interest in applying various sever plastic deformation like accumulative roll bonding (ARB) [3], in bulk or on the surface, to obtain the ultrafine-grained materials and materials with grains in nano-scale.
Copper and its alloys, between the most applied engineering substances in petrochemical and chemical industries, have a significant role. According to the demands and great interests, the absolute study of copper passivation in alkaline electrolytes is necessary [4–7]. Despite some studies published on the electrochemical response of pure copper [8–10], more detailed information is still required on the role of copper grain refinement on its formed external oxide layer semiconducting properties (especially diffusivity of point defects). Actually, to describe the transportation of point defects and therefore the passive layer growth kinetic, the point defects diffusivity is considered as an important parameter [11–13].

The main objective of this research is to know the impact of nano-scale grain refinement on the semiconducting response of passive layers formed on pure copper. To serve the purposes, the Mott–Schottky (M–S) analysis of annealed and ARB-processed (ARBed) specimens in 0.1 M KOH solution in conjunction with the PDM was performed and concentrations of defects were calculated as the effect of grain refinement and passive film formation.

2. EXPERIMENTAL PROCEDURES

The detailed procedure of ARB processing and sample preparation is published elsewhere [7-9]. Pure copper with nano-scale grains successfully made by nine-cycle ARB process. To study the microstructural evolution of the annealed and ARBBed samples, an optical microscope (OM) and transmission electron microscopy (TEM) was applied, respectively. The detailed procedure of sample preparations of OM and TEM observations is published elsewhere [7-9]. Before any electrochemical experiment, both samples were grounded in 5000 grit and then washed by deionized water. After that, using a flat cell with three electrodes (pure copper samples as work electrode, counter electrode of Pt and reference electrode of Ag/AgCl saturated in KCl), all the tests were carried out. In this flat cell, 0.1 M KOH solution was used at 25±1 °C and all set was run by the µAutolab Type III/FRA2 system.

After 0.5 h rest at the open circuit potential (OCP), the potentiodynamic polarization (PDP) curves were measured during the test, starting from -0.5 to 0.9 V$_{Ag/AgCl}$ with the scan rate of 1 mV/s. However, prior to PDP and M–S experiments, for the oxidation contaminants removal, the samples were cathodically polarized at a potential of −0.8 V$_{Ag/AgCl}$ for 180 s. Anodic polarization at various potentials (0.1, 0.2, 0.3 and 0.4 V$_{Ag/AgCl}$) was performed for 1 h, so that we have a steady-state conditions of passive layer formation. Then, M–S measurements were provided by measuring the frequency response at 1 kHz during a 25 mV/s potential scan from −0.4 to 0.8 V$_{Ag/AgCl}$ [10].
3. RESULTS AND DISCUSSIONS

The optical micrograph of annealed pure copper shown in Fig. 1 illustrates a homogenous equiaxed microstructure with the average grain size of 26±1 µm. Fig. 2 depicts the TEM micrograph and related selected area diffraction (SAD) pattern of ARBed pure copper after 9 cycles. The average grain size of this specimen is 85±5 nm, which shows a drastic grain size reduction. The SAD pattern of this specimen is developed into ring shapes consisting of discrete spots that clue us in on many nano-grains with various orientations [7,9].

Fig. 1. Optical micrograph of annealed pure Cu

Fig. 2. TEM micrograph and SAD pattern of nano-grained pure Cu

OCP-time curves of both annealed and nano-grained pure copper specimens in 0.1 M KOH electrolyte are demonstrated in Fig. 3(a). These curves show that within 0.5 h a complete stable condition is achieved to implement the electrochemical tests. Fig. 3(b) is the PDP plots demonstrating the annealed and nano-grained pure copper specimens in 0.1 M KOH electrolyte. An active–passive–transpassive corrosion behavior showed by both samples is connected to the duplex passive layers formation. Similar duplex passive behavior was in accordance with the records in alkaline electrolyte [7,8,10].
Fig. 3. (a) OCP-time and (b) PDP curves of both annealed and nano-grained pure Cu in 0.1 M KOH solution

The variation of the corrosion potential ($E_{\text{corr}}$) and the corrosion current density ($i_{\text{corr}}$) of both annealed and nano-grained pure copper specimens in 0.1 M KOH electrolyte are shown in Table 1. The corrosion potential of annealed pure copper specimen was more cathodic than that of nano-grained pure copper specimen. In addition, the corrosion current density of nano-grained pure copper specimen decreased compared to the annealed specimen.

Table 1. Variation of the corrosion potential and the corrosion current density of both annealed and nano-grained pure copper specimens in 0.1 M KOH electrolyte

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{corr}} / V_{\text{Ag/AgCl}}$</th>
<th>$i_{\text{corr}} / \mu A \text{ cm}^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annealed pure Cu specimen</td>
<td>-0.194</td>
<td>0.94</td>
</tr>
<tr>
<td>Nano-grained pure Cu specimen</td>
<td>-0.199</td>
<td>0.45</td>
</tr>
</tbody>
</table>

During the polarization process, the mixture of the first passive layer of Cu$_2$O and CuO/Cu(OH)$_2$ as the second passive layer are generated in the respective potential range. The first layer is appeared on the Cu substrate surface and the final passive layer is formed on the surface of Cu$_2$O layer. As the grain size varies, the PDP curves exhibit a small change. The
difference of corrosion potential \( (E_{\text{corr}}) \) for both samples is not considerable. This confirms the same active dissolution ability in both pure copper specimens. Broadly, it is noted that the grain size alterations affect the passive process of annealed and nano-grained pure copper. Although the primary passive potential \( (E_{\text{pass}}) \) increase is insignificant, the critical current density \( (i_{\text{cr}}) \) of annealed pure Cu is notably greater than that of nano-grained pure Cu. This signifies that passivation in nano-grained pure copper sample occurs easier than annealed pure copper specimen. The findings suggested that the passivation was prone to take place on surface nanocrystalline lattice defects [14]. In the current work, the nano-grained pure copper in comparison with the annealed pure copper, contains high intergranular defects volume fraction (i.e., grain boundaries or triple junctions) associated with the nano-size grain. The passivation layer was developed in particular areas on the nucleation sites (i.e., grain boundaries) when the nano-grained pure Cu electrode was in contact with the 0.1 M KOH solution. Then, gradually the Cu surfaces were covered by Cu_2O layer with the potential increase to the higher range.

All along that passive films were forming on both pure copper electrodes, current density as the result of different potentials application was recorded. Generally, the current density diminishes over a period of time till a constant value is appeared and a steady-state quantity is recorded. Fig. 4 is the demonstration of the steady-state passive current density \( (i_{\text{ss}}) \) values versus the formation potential. The mean steady-state current density for both pure copper specimens extracted from Fig. 4 are \( 0.66 \times 10^{-6} \) and \( 0.53 \times 10^{-6} \) Acm\(^{-2}\), respectively. The illustration of Fig. 4 shows that the steady-state current density for both pure copper samples in 1 h duration was independent of the film formation potential, which is in close accordance with the PDM postulation.

![Fig. 4. Steady-state passive current density obtained during the potentiostatic growth of the passive layers; at different film formation potentials for 1 h](image)

In order to determine the notable effect of the grain refinement and film formation potential on the passive layers formed on both pure copper specimens in 0.1 M KOH electrolyte, the capacitance \( C \) at semiconductor/solution was measured and M–S curves \((1/C^2 \text{ vs. } E)\) were provided. The followed formulation, resulted from the experimental records, easily helps to determine the acceptor density \((N_A)\) \([7,10]\):

\[
\frac{1}{C^2} = -\frac{2}{\varepsilon \varepsilon_0 e N_A} \left( E - E_{fb} - \frac{k_B T}{e} \right)
\]

(1)

Here, \( \varepsilon \) denotes the passive layer dielectric constant (taken as 12 for copper \([7,8]\)), \( \varepsilon_0 \) shows the vacuum permittivity, \( e \) is the electron charge, \( k_B \) and \( T \) stand respectively for the Boltzmann constant and absolute temperature. An obvious decrease in the capacitances caused by grain refinement is shown in the M–S plots of both pure copper samples in 0.1 M KOH electrolyte, Fig. 5.

![M–S plots of (a) annealed and (b) nano-grained pure Cu samples in 0.1 M KOH solution.](image_url)

**Fig. 5.** M–S plots of (a) annealed and (b) nano-grained pure Cu samples in 0.1 M KOH solution.
Moreover, the observations suggest that the film formation potential increase, decreases the capacitance of both pure copper specimens. According to the Fig. 5, in one region, $C^{-2}$ and $E$ show the linear relationship. M–S plots obtained on pure copper in alkaline solutions are also similar [7, 8]. Considering the slopes of the M–S plot, an estimation of acceptor density ($N_A$) is calculated by the equation below:

$$N_A = \frac{2}{\varepsilon_0 \varepsilon} \left[ \frac{d(C^{-2})}{dE} \right]^{-1}$$

The illustration in Fig. 6 is the calculated acceptor density of both pure copper specimens in 0.1 M KOH electrolyte as the formation potential function. Generally, depending on the oxide film thickness and the consumed electrolyte, the literature recorded value for $N_A$ is in the range of $10^{18}$ to $10^{23} \text{ cm}^{-3}$ [15].

Fig. 6. Calculated acceptor density of the passive layers formed on both annealed and nano-grained pure Cu samples in 0.1 M KOH solution

Acceptor densities measured in this procedure are in the order of $10^{21} \text{ cm}^{-3}$ and also comparable to the recorded values in the literature [7,8,10]. Widely, this kind of high dopant levels are not accessible in bulk oxides and this can be ascribed to the degeneracy. Indeed, the passive layer produced on copper in alkaline electrolytes has been described as a bilayer. The barrier layer of Cu$_2$O adjacent to the metal and a Cu(OH)$_2$ outer layer [10]. We can observe the grain refinement process impact as an obvious reduction in the calculated value of $N_A$. Fig. 6. Acceptor density decline tends to restrict the electron transfer and as a result of the described limitation, the electrochemical reactions can be impeded. So due to the mentioned result, the dissolution of the passive film is decelerated [16,17] and successively, there are fewer defects and superior protective capacity. The lower defect concentration, results in lower mass transport and therefore higher corrosion resistance will appear.
By Fig. 6, it is notable that while the film formation potential increases, the acceptor density of both pure copper samples decreases exponentially. Xu et al. [10] showed that along with increasing the potential, acceptor density of pure copper in 0.1 M NaOH tends to decrease exponentially. Giving enough attention to the potential-dependent $N_A$ jointly with the potential-independent current ($i_{ss}$) is essential as they both could entail that $N_A$ at the metal/oxide interface has specific influence on the current density [15]. Entirely, due to the grain refinement, there is a distinct decrease in acceptor density in each film formation potential. This is a remarkable improvement indication of the passive layer protective effect on the nano-grained pure copper.

Based on PDM, change in the defect density is generally because of the non-stoichiometry defects in the passive layers. In Fig. 5, with the demonstration of p-type behavior for pure copper in 0.1 M KOH electrolyte, the copper vacancy function as electron acceptors and therefore lead to positive conduction type (p-type) in the passive film [10]. The main cause of high values of the acceptor density is ascribable to a higher density of copper vacancy in the passive layers. The values gained through M–S analysis showed that grain refinement is the decrease reason in acceptor density of pure copper samples (Fig. 6). According to the PDM and by the theoretical calculations, the followed equation can be developed to describe the relation between acceptor density and the film formation potential. The relevant equation, as a description of dependent quantities shows the acceptor density in relation with the formation potential Eq. (3), where $\omega_1$, $\omega_2$ and $b$ are constants determined by the experimental data [10]:

$$N_A = \omega_1 \exp(bE_f) + \omega_2$$  \hspace{1cm} (3)

Considering the software nonlinear fitting of the data during experiments, the exponential relation between the acceptor density and the film formation potential is concluded as Eq. (4) and (5) for annealed and nano-grained pure copper, respectively:

$$N_A = 9.0263 \times 10^{20} \exp\left(-7.0553E_f\right) + 3.585 \times 10^{20} \left(cm^{-3}\right)$$ \hspace{1cm} (4)

$$N_A = 3.7757 \times 10^{20} \exp\left(-2.8947E_f\right) + 2.0261 \times 10^{20} \left(cm^{-3}\right)$$ \hspace{1cm} (5)

The calculation of the diffusion can be done using Eq. (6) as follows [10]:

$$D_0 = \frac{i_{ss}RT}{4eF\omega_2\varepsilon_L}$$ \hspace{1cm} (6)

Here, $F$ and $R$ are the Faraday constant and the ideal gas constant respectively. Substitution of $i_{ss}$, $\varepsilon_L (\sim 6.11 \times 10^5 \text{ V/cm} [10])$, and $\omega_2$ into Eq. (6) yields $D_0 = 12.05 \times 10^{-17}$ and $17.11 \times 10^{-17} \text{ cm}^2/\text{s}$ for annealed and nano-grained pure copper, respectively. Under consideration of the error caused by the presumption of $\varepsilon_L$ in Eq. (6), copper vacancy
diffusion coefficient in the formed passive layer on both pure copper in 0.1 M KOH solution is estimated to be in the range of $10^{-17}$ cm$^2$/s, set in the order of the results recorded for defects diffusion coefficient in the passive layer on copper in 0.1 M NaOH solution [10]. Also, this result showed that the diffusion coefficient of copper vacancy was increased with grain refinement. Unlike the traditional coarse-grained materials, nano-grained materials present exclusive physical, chemical and mechanical qualities. This is attributed to their high volume fraction of grain boundaries resulting from the nano-size grains [18-20]. In general, nano-grained structures are anticipated to impact on corrosion resistance both positively and negatively. It depends on the sufficient concentrations of passive elements that take part in the insoluble passive film growth [21,22]. In case that formed passive layer was soluble, the corrosion resistance would be diminished by nano-size refinement, and vice versa. In this research, the nano-grained structure is advantageous to the pure copper corrosion resistance, since the grain boundaries high density can function as short diffusion routes for passive elements and therefore, facilitate the stable passive layer formation.

4. CONCLUSION

Results revealed that the acceptor densities were in the range $10^{21}$ cm$^{-3}$ and declined as the sample grain size decreased. Moreover, it was presented that the calculated acceptor density for both annealed and nano-grained pure Cu samples reduces exponentially with increasing formation potential. Calculation based on the PDM confirmed that the diffusion coefficient of copper vacancy for nano-grained sample reached to $17.11 \times 10^{-17}$ cm$^2$/s from $12.05 \times 10^{-17}$ cm$^2$/s of the initial annealed sample. This indicated that the diffusion coefficient of copper vacancy was increased with grain refinement.

REFERENCES