Copper oxide nanowhiskers: structure, growth mechanisms, and associated stresses

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Abstract. A detailed study of the structure of nanowhiskers and the processes accompanying their growth during thermal oxidation are presented. The structure of nanowhiskers is studied by scanning and transmission electron microscopy and X-ray diffraction. The role of internal stresses in the substrate on the growth of nanowhiskers is shown, and the stress state for various configurations of the copper/copper oxide system is calculated. The sorption, catalytic, electrochemical, and mechanical properties of oxide nanowhiskers are described. The areas of the practical application of copper oxide nanowhiskers such as water purification systems and lithium batteries are shown.

1. Introduction

First reports on the observation of the growth of copper oxide nanowhiskers during the thermal oxidation of copper can be found in the works of the 1950s [1 - 2]. This phenomenon turned out to be a simple and effective way of producing copper oxide nanowhiskers, which are already widely used in various fields, such as photocatalysis [3], solar panels [4], lithium batteries [5], etc. However, the issue of a selective method for producing such nanowhiskers has not yet been resolved. To develop a selective method (for example, in terms of size) for producing nanowhiskers by thermal oxidation, a clear understanding of the nature of the processes accompanying the formation and growth of nanowhiskers is required. Many phenomenological models are describing the growth of whiskers: dislocation, diffusion, stress-stimulated, etc. [6 - 9]. Summarizing the known facts and factors indicated in the aforementioned models, it should be noted that thermal oxidation is a complex process, and to understand its nature and modeling, it is necessary to take into account the interrelation of individual processes (diffusion, thermal expansion, phase transformations, and stress state). The chemomechanical approach to this problem makes it possible to take into account the effect of stress state on chemical processes, in particular, phase transformations: copper - copper oxide.

In our previous works [3], [6], we estimated the stress state during annealing for continuous electrolytic coatings deposited on a mesh substrate as well as individual particles. Note that the growth of whiskers is observed experimentally not only on cylindrical or spherical objects of the core-shell type. Therefore, in this work, we have estimated the stresses in flat copper layers subjected to thermal oxidation.
2. Material and methods

A rolled plate of the stainless steel mesh (type AISI 321) with thickness 700 μm was used as a substrate. The metal electrodeposition method was employed to coat the plate with a bulk copper layer as described in [10]. The copper deposition was conducted from the sulphuric electrolyte in a potentiostat regime. The duration of the electrodeposition was 30 minutes under the overvoltage of 200 mV. The regime resulted in a continuous coating with a thickness of 50-60 µm that was subsequently mechanically separated from the substrate. Thermal oxidation of the samples was conducted in a muffle furnace with a programmable process controller under a heating rate of 15 °C/min.

Morphology of copper and oxide layers was investigated by scanning electron microscopy (SEM, TESCAN Mira 3, and JEOL JCM 6000). The experimental analysis of the phase transformations accompanying the growth of nanowhiskers was carried out by X-ray diffraction (X-ray diffractometer Shimadzu XRD 7000). To study all samples diffraction patterns were taken in the range 20 ° –120 ° with a step of 0.02 ° and a scanning speed of 2 °/min. An X-ray tube with a copper anode with a power of 1.5 kW was used while the tube voltage and the current were set to 30 kV and 30 mA respectively.

3. Results and discussion

During the oxidation process, the oxide film and substrate can be modeled as a thin film/substrate system with a moving boundary, as shown in figure 1. To simplicity and due to the symmetry of the problem, we considered half systems.

![Figure 1](image_url)

**Figure 1.** Scheme of the stress-strain state in the plane copper oxide/copper system, $t$ is the thickness of the oxide film as a function of time, $\sigma_{CO}$ and $\sigma_{C}$ is the average biaxial stress in the oxide layer and copper, $T$ is the initial thickness of the samples relative to the symmetric axis.

It is assumed that the oxide film is well bonded to the substrate. Taking into account the geometric symmetry of the system, the deformation in the oxide and the substrate satisfies the compatibility condition.

After analyzing the three stages of oxidation, the chemical mechanic’s equation is proposed in a dimensionless form:

$$\dot{i} = \frac{B\beta\Delta C}{i} e^{\tilde{\sigma} \tilde{t}}$$

$$\left(\frac{M(1-\tilde{t})}{\tilde{t}} + \tilde{t} \tilde{\sigma} + \left(A(1-\tilde{t}) + \frac{\tilde{\sigma}}{1-\tilde{t}}\right)\tilde{t}\right) \tilde{t} = 0$$

where $M = \frac{M_C}{M_{CO}}$, $A = \frac{M_C D_{CO} T}{\sigma_0}$, $B = \frac{R^2}{T^2}$, $\tilde{\alpha} = \frac{\alpha \Omega \sigma_0}{R \theta}$, $\tilde{\sigma} = \frac{\sigma_{CO}}{\sigma_0}$, $\tilde{t} = \frac{t}{T}$, $M_C$ and $M_{CO}$ are the biaxial moduli of the copper base and the copper oxide layer, respectively, $D_{CO}$ is the coefficient depending on the microstructure of the oxide, $\beta$ is the coefficient taking into account the substance and the reaction (copper oxidation), $\Delta C$ is the difference in oxygen concentration at the boundary of gas/oxide and oxide/copper, $\alpha$ is a positive dimensionless constant, $\Omega$ is the molar volume of oxygen, $R$ is the gas constant, $\theta$ is a temperature.
The initial conditions of the problem are written in the form:

\[
\begin{align*}
\tau &= 0 \\
\sigma &= 0
\end{align*}
\]

For numerical calculations, the following parameters were selected: \( M = 0.8, A = 500, B = 500, \alpha = 2.5, \beta \Delta C = 1.6 \cdot 10^{-7} \). The calculation results are shown in figure 2. It should be noted, one can take into account the defect structure by writing down the initial conditions, for example, indicate the stresses of the defects present in the sample.

![Figure 2](image)

**Figure 2.** Kinetics of oxidation of a flat copper sample, \( a \) and \( b \) show the dependencies of the dimensionless stress in the oxide layer and the dimensionless thickness of the oxide layer on the dimensionless time respectively.

According to the theory of reactive diffusion [11], when copper is oxidized in air, from the beginning of the process, a two-phase diffusion zone is formed, consisting of layers of Cu$_2$O and CuO. During the formation of a two-phase diffusion zone, the thickness of the CuO phase layer is much less than the thickness of the Cu$_2$O layer and the CuO layer grows at a rate almost an order of magnitude lower than the growth rate of the Cu$_2$O layer. This is probably the reason that at the initial stages of thermal oxidation when the thickness of the diffusion zone is small, it is not possible to detect the CuO phase by X-ray phase analyzes as shown in figure 3. However, the presence of the CuO phase on the surface, starting from the beginning of oxidation, can be judged by the black color of the sample characteristic of CuO. This color of the surface is retained during long-term oxidation when the presence of the CuO phase is also detected by X-ray phase analysis.

4. Conclusions

Thus, it can be argued the oxidation of copper at atmospheric air pressure begins with the formation of the thinnest layer of the CuO phase on the sample surface. This is followed by the formation of the Cu$_2$O phase between the CuO layer and the copper substrate, which in all cases is the main oxidation product and grows at a much higher rate than the CuO phase.

It was shown that a noticeable yield of bivalent copper oxide CuO at a heating rate of 15 °/min begins to form at a temperature of 400 °C. At this time, in addition to the growth of whiskers, active growth of the CuO layer occurs. However, the temperature of the beginning of the formation of whisker structures is 250 °C.

In general, the temperature and duration of the heat treatment process have a significant effect on the oxidation of copper. It has been revealed that, upon oxidation of copper in air, from the beginning of the process, a two-phase diffusion zone is formed, consisting of Cu$_2$O and CuO layers. Of these, the primary is the CuO phase. In this case, the oxidation of copper at the initial stage is accompanied by
Figure 3. X-ray diffraction pattern of the thermal oxidation of a copper plate heated up to 400 °C and holdup time 4 hours, 1 is original copper, 2, 3, and 4 are heating in air to 250, 300, and 400 °C respectively, 5 is annealing at 400 °C for 6 hours.

...an intensive growth of only the Cu$_2$O phase. Compressive stresses formed in the oxide layer are the driving force behind the release of copper cations to the surface, where these are oxidized with oxygen and ensure the growth of nanowhiskers.

The proposed equations of chemomechanics make it possible to estimate the stress state of the substrate during the growth of nanowhiskers in the process of thermal oxidation.

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