The investigation of copper anodic oxidation in alkaline solutions in presence of β-alanine by ellipsometry

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Earlier [1, 2] it was found out the double influence of β-alanine on copper anodic oxidation in alkaline electrolytes. Accordingly to experimental data small additives of amino acid (to 1×10^{-3} mpl) increased the copper passive state stability, but, on the contrary, high additives (under $C\geq1\times10^{-2}$ mpl) acted as activators. In the last case metal is exposed to local corrosion. These effects were interpreted with position of competitive adsorption and complex formation theories. Present work, in which electrochemical investigations were supplemented with ellipsometry, was carried out with aim to confirm or to contradict this explanation.

Decision of these tasks was realized in two series of experiments.

1. Combined electrochemical and ellipsometric measurements. Before each measurement the electrodes were subjected to catholic reduction pretreatment (E= -1.000 V, τ=10 min). After that potensiostatic investigations were carried out with 0.050 V interval up to potential of oxygen evolution. The main ellipsometry parameters were the angles Δ and Ψ [3, 4], which were measured by ellipsometer RR2000.

2. Research of β – alanine's adsorption on interface copper/alkaline solution. These experiments were carried out on the preliminary oxidized copper surface

(E=-0.15 V, τ=120min.) using the same method.

Accodingly to changes of ellipsometric parameters amino acid effects on the electrochemical behavior of copper already on the initial part of polarization curve. And the largest influence of amino acid is observed in zone of metal passivity. Thus, angle Δ changes in 1×10^{-2}M NaOH $+1\times10^{-4}$ M β-alanine solution are more in comparison with pure alkaline. And common film thickness in these systems are 4 nm and 3,1 nm respectively. Therefore, the inhibition effect of small additives of β-alanine can be connected with film thickness increase. It is possible at the expense of β-alanine's adsorption on the film or formation of combined insoluble surface complexes. The corresponding experiments were carried out for confirmation of β-alanine adsorption. On the basis of experimental data (about changes of angel Δ in dependence on β-alanine concentration) isotherm of adsorption was constructed, which was corresponded to Frumkin isotherm [5] ($\Delta G_{ad.}$= -30,4±0,4 kJ/mol).

Another effect is observed in the systems with high additives of β-alanine. According to obtaining angle Ψ changes it can be assumed that the composition of formed film on copper in these solutions is different from one formed in solution with small additives of β-alanine. Under the kinetics investigation of film growth, angle Δ increases. The last one points out to dissolution of metal surface, that has not been observed in solutions with small additives of β-alanine.

Analysis the electrochemical and ellipsometric data permits to conclude that the inhibition effect of small additives of β-alanine is explained by its adsorption and formation of combined insoluble surface complexes. Volumetric copper complexes predominate in systems with high additives of β-alanine, that leads to copper local corrosion. At the same time present investigation confirmes opportunity to use ellipsometry method for determination of passive layers' thickness on metal and for research of adsorption kinetics.

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