

Influences of temperature and heat-transfer on anodic behavior of copper in bicarbonate-thiocyanate solutions

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Copper is used as a main part for the technological equipment. Latter can be exposed to corrosion destruction. Its rational protection must be based on accurate description the copper anodic behavior under elevated temperature, positive thermal fluxes (PTF) and composition of aggressive solution. The system $\text{Cu}/0,1\text{M NaHCO}_3 + 0,1\text{M KCNS}$ was taken for analyses to continued the cycle investigations presented in papers [1]. The diapason of temperatures was $20 - 80^\circ\text{C}$ and the range of PTF was $Q=21,2 - 63,6 \text{ kWt/m}^2$.

The compared data were received on thermal equilibrium (TEE) and heat-transferring (HTE) electrodes used a complex plant. Its design, using methods were presented in early papers [1-3].

Experimental results shown that on anodic polarization curve (APC) in the potential range $(-0,040) - (-0,170)\text{V}$ (NHE) the anodic peak was presented. The role of thermal conditions consists in changing of current peak height, and wide of two potential ranges where current is independent from potential changes. The first (more narrow) potential range ($\Delta E=0,150 - 0,200 \text{ V}$) corresponds to the region where formation of an inner $\text{CuOH}/\text{Cu}_2\text{O}$ layer occurs. The second potential range ($\Delta E=0,500$ to $0,600\text{V}$ for TEE and $\Delta E=0,300\text{V}$ for HTE) comprises to zone of pitting repassivation [1]. Local activation (LA) is in zone of potential $E=0,00-0,26\text{V}$.

Control stages of anodic oxidation process were established on zones of active dissolution, passivation and LA of the metal. The exponential accelerations of anodic processes under temperature rising were marked on all stages of APC. The active dissolution of TEE is controlled by kinetic stage (real energy of activation $A=55,7 \text{ kJmol}^{-1}$), and for HTE process is happened by diffusion-kinetic control ($A=28,7 \text{ kJmol}^{-1}$). The fixed influence of PTF on regularity of control stage changing may be connected with alteration the composition and construction of double layer. Under heat exchanger condition the surface concentration of aggressive anions and degree of its cover the copper surface by adsorbed products are decreased in comparison with thermal conditions. As a result, the rate of anodic reaction on HTE is reduced. At that time, in the flow of diffusion the more active OH^- ions are blocked the delivery of aggressive anions to copper surface. Its effect leads to rising the diffusion limitations in system.

On the contrary, the anodic process on passive copper is controlled by diffusion-kinetic stages with predomination the transport limitation on TEE ($A(\text{TEE})=14,3 \text{ kJmol}^{-1}$, $A(\text{HTE})=20,7 \text{ kJmol}^{-1}$), and its rate is dependent from hydrodynamic condition.

Value of anodic current includes two main components. They are current connected with passive film formation and current stipulated for copper electro-dissolution from passive layer. The increase of process rate under higher temperature testifies about decrease the protecting effects of formed passive layer and increase the process of dissolution. Moreover, the protected characteristic of passive films on HTE is

decreased because of straining effect in the film. As a result, the anodic process on passive HTE is rise more effective than on TEE.

LA is controlled by solid phase diffusion. Its fact confirms by value of real energy activation ($A(\text{TEE})= 28,8 \text{ kJmol}^{-1}$, $A(\text{HTE}) = 14,3 \text{ kJmol}^{-1}$) and by absent the hydrodynamic condition influence on the process rate. The analysis of quantitative characteristic of LA was based on using the modern theory of pit initiation (presented in paper [1]). These results testify about solid diffusion control of metal cation from interface metal/film to interface metal/solution with passive film degeneration as a result of forming a "nucleus" CuX on copper surface, and CuX penetrates to the inside of film. Diffusion coefficient D_{Me^+} is sensitive to activator concentration near the surface electrode. And it is rise with its value. More significant effect is fixed on TEE.

Stability metal to LA is dependent from thermal conditions. The temperature increase of TEE is led to suppression LA. The heat-transfer conditions, on the contrary, are unstabilized the system. The reason for this effect is variation of grow and dissolution rates of solid "nucleus" on passive film. The relief of dissolution process for CuCNS under solution temperature increase is blocked the process of "nucleus" penetration to metal/film interface and increase the metal stability relative to LA. Dehydration of film makes this process more easily. Under heat-transfer conditions stability metal to LA is decreased because of rise the defects of protective layer, increase the process of CuCNS formation and decrease the rate of its dissolution.

References.

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