

EFFECT OF NATURAL CONVECTION ON METAL ANODIC DISSOLUTION

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The effect of natural convection on the metal anodic dissolution under the conditions of limiting diffusion current is considered by the example of tungsten dissolution in the alkaline solution: $W + 8 OH^- \rightarrow WO_4^{2-} + 4 H_2O + 6e$. This electrochemical system is characterized by a well-defined limiting current plateau in the polarization curve and the known condition of the limiting current origination (the near-electrode concentration of OH^- ions is zero). The advantage of this system over the well-known systems like $Cu/CuSO_4 + H_2SO_4$ and Cu/H_3PO_4 (the systems with more than two types of ions) is simpler theoretical calculation of the limiting current under the conditions of natural convection, because the concentration of ions of one type at the electrode surface is known. In other aforementioned cases, the limiting current is reached, when the solution near the anode surface becomes saturated with the product of metal dissolution. The concentration of saturated solution is not known, because it depends on the near-electrode concentration of electrolyte, H_3PO_4 , for example, which is not known beforehand. Natural convection is caused by the buoyancy force. In the case under consideration, the buoyancy force in near electrode boundary layer δ (Fig.1) is caused by the variations in the concentrations of both the reagent (alkali C_1) and the reaction product (tungstate C_2) near the anode. A decrease in the alkali concentration leads to a decrease in the solution density and will cause the solution flow upwards. An increase in the tungstate concentration causes the liquid flow downwards. The second factor prevails; therefore, the resulting liquid flow V_x is directed downwards (Fig.1).

For plane **vertical** tungsten electrode, the equation for an average limiting current under the conditions of natural convection is derived. In this equation, the contributions of both a decrease in the alkali concentration and an increase in the concentration of tungstate near the electrode are taken into account. In contrast to the majority of other available solutions of the problems on the limiting currents under the conditions of natural convection, this equation contains no transport numbers and takes into account the dependence of the limiting current on the diffusion coefficients of all three types of ions, which are present in the solution. The results calculated by this equation are compared with the limiting currents measured on the vertical electrode. Fig.2 gives the log of average limiting current density (A/cm^2) of tungsten anodic dissolution plotted against the log of KOH solution concentration (mol/l): (1) the measured and (2) the calculated results. The discrepancy between the experimental and calculated results is about 20%. Introduction of the corresponding numerical coefficient into the equation enables one to use it for sufficiently accurate calculation of the limiting currents in the system.

For the **horizontal** electrodes, different types of convective instability are obtained experimentally, and the results are discussed.

For the **inclined** electrodes, the experimental dependences of the limiting current of disk tungsten anode dissolution in alkali on the electrode's diameter and the

electrode slope in the gravity field are presented.

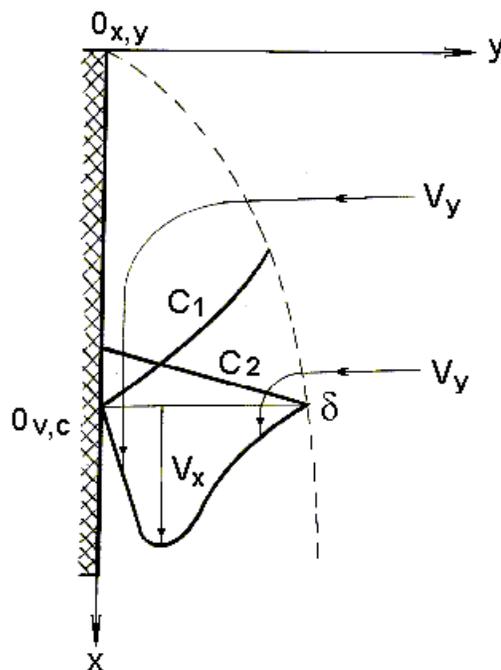


Fig.1

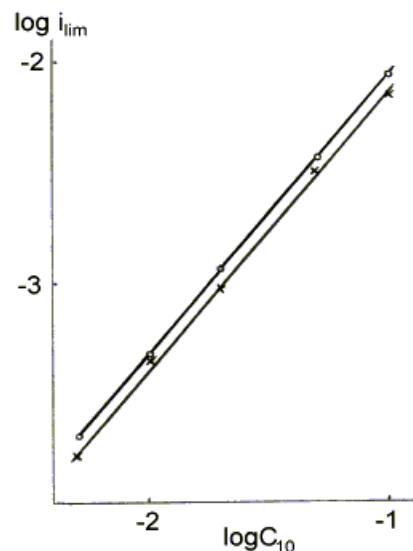


Fig.2