The Pearson's Principle for the Analysis of the Processes of Copper Local Activation under the Organic Additives Influence.

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Copper and it's alloys are widely used under decision of the modern electrochemical and corrosion problems: the optimization of electropolishing processes, the depassivation of copper anodes in the bath for electroplating, the inhibition of metal's electrodissolution [1].

The solutions with organic additives in representing cases are used as quality wide-spread environments. In this case the organic additives in dependence from their concentration in the electrolyte and temperature are able to be activating or inhibiting particles [2]. In connection with this the information about the real role additives in any situations, taking into account the composition of solution and thermal conditions is very important.

In this work the data which are proving a possibility of using the Pearson conception - " hard and soft acids and bases" (HSAB) in analysis of copper local depassivation under the action of the organic additives (formic, citric) in different thermal conditions are represented.The experiments were carried out on plant with stationary copper electrode with using complex of physic-chemical methods in hydrocarbonate solutions with formic- and citric-ions (C = 5×10^{-3} - 2×10^{-2} mpl) and temperature range from 20^{o} to 80^{o}C.

The results of this investigation have shown that the nature of ion-activator, his quantity and thermal conditions have a large influence on an ability of copper to local activation (LA). The concentration borders of formic ions in 0,1 M $NaHCO_3$ where copper surface undergoes to LA were determined. These ones were 0,0025-0,010 mpl for 20^{o}C and 0,001-0,040 mpl for 80^{o}C. Local activation potential (E_{LA}) is 0,910 - 1,060 V (NHE) (at 20-80^{o}C respectively). The concentration increasing of this additive from 0,01 to 0,02 mpl leads to inhibiting of copper local activation process and stable passive state of metal is keeping to oxygen.evolution's potential value. Temperature increase stabilizes the metal protecting it from local destruction. In the presence of citric ions the breakdown of copper passive state is observed when the concentration of activator is 0,005 mpl at E_{LA} = 0,080 V (NHE).The increasing contents of organic additive and temperature leads to increasing LA rate and reduction of the resistance copper to LA.

This experimental results are interpreted from the position of HSAB theory, according to one all reactions are passing by mechanism from which "hard acids" are preferably bounding with "hard bases", but "soft acids" - with "soft bases". According to the HSAB principle LA of copper under formic ions action (E_{la}= 0,910 V) is happening as a result of " hard- hard" interaction but the breakdown of copper passive state in the citric ions presence (E_{la}= 0,080 V) – because of "soft-soft" interaction. On the basis of represented analysis the copper local activation are passing in correspondence with the theory of Kuznetsov's nucleophilic substitution the passive particles in adsorption complex on metal surface by aggressive anions [6].

Taking into account the revealed regularities the control methods of LA processes in studied systems were proposed (the varying the solution's composition and thermal conditions on the interface border) and the possibility of HSAB conception's using in the analysis of copper anodic-anion activation under the organic additives was proved.

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