

The effect of potential scan rate and temperature at aluminum passive state in borate buffer solution

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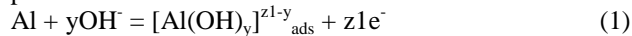
At the present work it was investigated aluminum (Al 99.99%) anodic behavior in borate buffer solutions (0.2M H₃BO₃ + 0.05M Na₂B₄O₇, pH 8.4) under different potential scan rates (4 - 100 mV/s) at temperature interval (20-70°C). Reliability of experimental results was attained by use of a complex of independent physic-chemical methods (voltammetry, chronoamperometry, optical microscopy (MBS-2 (x7) and MIM-7 (x500)), scanning electronic microscopy (SEM, x1000) with JEOL-6380LV and energy-dispersive X-ray analysis (EDXA) with INCA Energy-250).

The research of aluminum anodic behavior in borate buffer solutions has shown that under anodic polarization metal surface is in passive state under all studied scan rates of potential and all studied temperatures.

According to the obtained data the shape of anodic polarization curves changes with increase of potential scan rate. At $v \geq 30$ mV/s on voltamperograms appear the anodic peak at potentials (-370) ÷ (-380)mV (NHE). The dependence $\lg i_{\max} = f(\lg v)$ is linear, and criterion of Semerano [1] is 0,71, therefore limiting stage of the studied process is adsorption.

The experimental results have shown that rate of anodic process aluminum in borate buffer solutions exponentially increases with temperature growth, following Arrhenius-type plot. The effective activation energy value for passive state is $W = 52.4$ kJ/mol) and chemical or electrochemical reaction is limiting stage [2].

The generalization of experimental data and well-known from literature information [3,4] permitted to suggest the following mechanism of aluminum passivity process in borate buffer solution:



Thus both reactions (1) and (2) proceed at the same time in free corrosion conditions with formation of a passive film of the mixed type (oxide-hydroxide and salt at the same time). At interaction of passive metal with borate-ions are formed the superficial adsorbed complexes [AlHB₄O₇]²⁺ because of borate-ions are built into a hydroxide film, that promotes additional stabilization of aluminum passive state. High values of currents of

passivation on anodic polarization curves confirmed existence of salt passivity.

According to this mechanism in borate buffer solutions the reaction (2) addition stabilizes of a passive film, and this reaction is limiting stage of the studied process.

The indirect proof of the offered mechanism are results of EDXA method which have fixed element B on aluminum surface film. This confirms existence of adsorbed B-containing complex on passive aluminum surface, which may be superficial complex [AlHB₄O₇]²⁺_{ads}. The received results have been interpreted on the basis of "hard and soft acids and bases" (HSAB) conception [5]. According to conception HSAB this compound is stable so as it is formed by hard acid and the hard basis (within the limits of Pearson's principle Al³⁺, Al₂O₃ are hard acids, and borate-ions are the hard bases).

References

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