

### Aluminum anodic behavior under halogenide and oxygen-containing anions action

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Aluminum and its alloys are widely used in various industries. The main problems of the aluminum equipment application are connected with its local destruction. This type of corrosion is caused different factors, but at the present work the anionic composition and solution pH were investigated.

The experiments were carried out on a stationary electrode (Al of 99.99 %) in media with various nature additives anions: inorganic (class of halogenides -Cl<sup>-</sup>, Br<sup>-</sup> and oxygen-containing ions - NO<sub>3</sub><sup>-</sup>) and organic (CH<sub>3</sub>COO<sup>-</sup>) ions. 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).

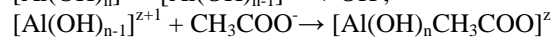
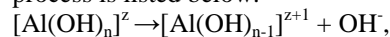
The obtained data have shown that in media with inorganic ions, aluminum is in passive state or it is exposed to local activation. For example, in water solutions of KNO<sub>3</sub> (C<sub>NO<sub>3</sub><sup>-</sup></sub> = 1·10<sup>-4</sup> - 1·10<sup>-1</sup> M; pH = 4.6-5.4) and in KNO<sub>3</sub> solutions with the fixed pH value (C<sub>NO<sub>3</sub><sup>-</sup></sub> = 1·10<sup>-4</sup> - 4·10<sup>-2</sup> M; buffer solution - 0.1 M NaHCO<sub>3</sub> (pH 8.4)) on an aluminum surface wasn't revealed local destructions. Rate of anodic process in both cases slightly changes with concentration nitrate ions at an invariable form of anodic polarization curves. It is possible to assume that in water solutions the passivation layer, owing to high chemical affinity of aluminum to oxygen, is formed at metal interaction with water [1]. In case of weakly alkaline solutions, as in present investigation, is observed competitive adsorption of HCO<sub>3</sub><sup>-</sup> ions -stabilizing process - and NO<sub>3</sub><sup>-</sup> ions -stimulating it, compensating each other.

Anodic behavior of aluminum is absolutely other in systems with additives of halogenide-ions where metal is exposed to steady local activation. Under this limits of pitting formation in the water solutions, containing Br<sup>-</sup> or Cl<sup>-</sup> -ions, are slightly differ (C<sub>Cl<sup>-</sup></sub> ≥ 1.7·10<sup>-4</sup> M, C<sub>Br<sup>-</sup></sub> ≥ 5·10<sup>-4</sup> M). Depth of pittings in the studied systems varies from 3 to 12 μm with increasing in concentration of activators. At that time the local activation mechanisms by Br<sup>-</sup> and Cl<sup>-</sup> -ions are similar [1,2] and correspond to the nucleophilic substitution

model [3,4]. Under this Cl<sup>-</sup> -ions are more aggressive than Br<sup>-</sup> -ions. This fact is confirmed with a complex of physic-chemical methods of research and correlates with the «hard and soft acids and bases» (HSAB) conception [5]. According to literature data Cl<sup>-</sup> -ions are the hard bases which forms with the aluminum oxidized surface (hard acid) the steady adsorbed complex compounds (possibly, Al(OH)<sub>2</sub>Cl [1]). The last is soluble therefore these complexes to pass in electrolyte volume that facilitates pitting formation process. According of HSAB conception Br<sup>-</sup> - ion represents the intermediate basis [5], therefore it is less aggressive in comparison with chloride ion.

Interesting results were obtained under anodic polarization of aluminum in hydrocarbonate solutions with pH = 8.4, containing of organic acetate-ions additive. In these systems the metal surface is exposed to local activation only in the narrowest concentration interval of the organic activator (8·10<sup>-3</sup> - 3·10<sup>-2</sup> M CH<sub>3</sub>COONa) and also it is in a passive state beyond indicated limits. Under this pittings depth doesn't change (9 μm), but their diameter undergoes extreme changes, reaching the maximum value (20 μm) at C<sub>CH<sub>3</sub>COO<sup>-</sup></sub> = 1·10<sup>-2</sup> M with the subsequent reduction to 15 μm at C<sub>CH<sub>3</sub>COO<sup>-</sup></sub> = 3·10<sup>-2</sup> M.

Corresponding mechanism of local activation process is listed below:



The comparative analysis of experimental data has shown that depending on the nature of electrolyte anion aluminum both is in a passive state, and is exposed to local activation, demonstrating variety in regularities of these processes.

### References

1. T.A. Borisenkova, S.A. Kaluzhina // Condensed matter and interphases. **13**, 136 (2011).
2. A.T. Chikova, T.A. Minakova, S.A. Kaluzhina // PRiME Meeting ECS. 2476 (2012).
3. Yu.I. Kuznetsov, O.A. Lukyanchikov, N.N. Andreev // Electrochemistry. **21**, 1690 (1985).
4. Yu.I. Kuznetsov, I.A. Valuyev // Electrochemistry. **20**, 424 (1984).
5. Yu.I. Kuznetsov // Protection of metals. **30**, 341 (1994).