

## Effect of Anodic Additives on Passivation of Chromium-Iron Alloys

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Chromium-iron and aluminum alloys are the basis of a large group of structural materials used for operation in liquid corrosive media. Cr-Fe alloys are also promising as the basic material for protective coatings on carbon steel based equipment. However a number of limitations on their corrosion resistance (susceptibility to pitting, slot, intergranular corrosion and corrosion cracking) present new problems for scientists and engineers to develop effective means of their corrosion protection. Development of new methods for improving of the passivity and corrosion resistance of the Cr-Fe and Al alloys has always been challenging research subject. Alloying is an effective method for increasing of corrosion resistance. Cathodic alloying, of Cr and Cr-Fe alloys by addition of a small amount of noble metals (0.1-0.4 wt.% of Os, Ru, Ir, Pd, or Pt, or 1 wt.% Re), improves the self-passivation ability of the alloys and decreases their corrosion rate in sulfuric acid solutions by several orders of magnitude<sup>1</sup>. However, this is an expensive method and, therefore, a not often economical one. Alloying the passivable matrix of an alloy with anodic additives is more easily reached. Metals used as alloying anodic additives are the ones with lower electronegativity (according to Pauling), lower standard electrode potential ( $E_0$ ), and higher oxygen affinity ( $D$ ) than those of the basic metals. Positive effect of some elements on properties of metals and different binary alloys was also previously shown. However, influence of anodic additives on passivity and corrosion resistance of Cr-Fe and Al alloys of multipart compositions has not been sufficiently studied in the past. The objective of the present work is to study the effect of anodic additives on the passivity and corrosion resistance of Cr-Fe and Al alloys in aggressive liquid media.

Corrosion and electrochemical behavior of the high purity and commercial Cr-Fe alloys containing from 16 to 60 of wt.% of Cr alloyed with small additions of Al and some d-transition metals (La, Sc, Zr and Mn) as well high-strength Al alloys alloyed with small additives of Sc, Zr, Mn and other d-metals in aggressive liquid media was investigated by electrochemical and gravimetric methods. The structure of the alloys was investigated by electron microscopy and X-ray microprobe analysis. Surface elemental composition, before and after corrosion and electrochemical investigations was studied by Auger-electron spectroscopy. It was shown<sup>2</sup>, that passivation potential,  $E_p$ , critical passivation current,  $i_{cr}$ , and current of passive dissolution,  $i_p$ , in sulfuric acid solutions were distinctly decreased when alloying of the high purity and commercial Cr-Fe alloys containing 16 - 60 of wt.% Cr with small additions of Al and some d-transition metals. The addition of La, Sc, Zr and Mn also increased the passivability and corrosion resistance of rolled and annealed Cr-Fe-Al commercial alloys to pitting and intergranular corrosion in 3 M HClO<sub>4</sub> + 1 M NaCl solutions<sup>3</sup>. Similarly, cast and hardened commercial alloys, containing more than 27% Cr alloyed with anodic additives, exhibited a high corrosion resistance and ability to passivate in sulfuric acid solution after their wear

test under conditions of extrusion processing of polymers<sup>2</sup>. In both cases alloying by Al and small additions of La or Sc increased corrosion protection of the high-chromium alloys. Passivation and resistance of commercial Cr-Fe-Al alloys alloyed with anodic additives to total, pitting and intergranular corrosion in aerated a) 0.5 M H<sub>2</sub>SO<sub>4</sub>, b) 3% NaCl, c) 2 M HCl and d) 2M HClO<sub>4</sub> + 1M NaCl solutions were increased after wear resistance testing with contact with polymers<sup>3</sup>.

The mechanisms for improving of passivation and corrosion protection of alloys by anodic additives on the basis of component selective dissolution theory were proposed<sup>2</sup>. The suggested mechanisms of these additives take into account their ability for initial preferred selective dissolution that generates non-equilibrium surface vacancies, causing Cr atoms to come out on the surface. These Cr atoms, despite the partial dissolution, will accumulate in greater amounts, in the oxidized state, within the surface oxide layers compared to the alloys without the anodic additives. Moreover, by intensifying Fe-O bonds in the produced Cr and Fe complex oxides they facilitate passivation of the alloys. This is a general proposal of the action of La and Mn additives. Al, Zr and Sc, exhibiting high affinity to oxygen, are oxidized by oxygen from water and accumulated on the surface in the oxidized state. In this case, Al and Zr oxides with lattices similar to those of Cr<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> are included in the mainstay passive layer of chromium-iron oxy-hydroxides and are condensing it, and consequently improving its protective properties. Poorly soluble scandium oxide, having another type of lattice is accumulated as an individual thin layer. However, by mechanically blocking the surface, it also impedes the alloy dissolution and facilitated its passivation.

It was established that anodic additives are also increasing passivability and corrosion resistance of high-strength Al alloys in seawater. It was shown that total and pitting corrosion rates of high-strength Al alloys alloyed by addition of Sc and other d-metals were decreased under sea conditions in comparison with those of Al alloys not containing them.

As a result, the mode of corrosion protection of alloys is proposed. It is based on the metal passivation by means of alloying them with anodic additives. The fundamental scope for effective alloying of passivating alloys with small anodic additives is theoretically substantiated and experimentally verified for Cr-Fe and high-strength aluminum alloys. The mechanisms of passivation and protection increase in corrosion of alloys by anodic additives are proposed.

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