

The Effect of the Oxygen Evolution Reaction on Corrosion: Ni-Cr-Mo Alloy

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Ni-based alloys are known for their excellent mechanical properties and corrosion resistance and are used in many demanding industrial environments. Ni is commonly alloyed with Cr and Mo, where Cr is known to improve the corrosion resistance due to the formation of a Cr₂O₃ oxide film on the surface, while the role of Mo is debated. Due to the amorphous nature of the protective film, the structural and chemical changes during corrosion are notoriously difficult to study using standard surface science techniques. Moreover, commonly used electrochemical techniques for studying passivity breakdown may not be applicable to Ni-Cr-Mo alloys since the measured electrochemical current is not only due to corrosion reactions [1]. Ni and Mo are good catalysts for the Oxygen Evolution Reaction (OER) [2, 3], which is known to be coupled with dissolution and degradation [4]. A fundamental understanding is missing regarding how the chemistry and structure of the passive film on Ni-Cr-Mo alloys evolve in realistic aqueous conditions and how that correlates with the onset of dissolution, which determines the breakdown of passivity.

Here we present a comprehensive study combining several techniques to study the surface region of a Ni-Cr-Mo alloy in NaCl solutions in situ during electrochemical polarization. XRR and AP-XPS were used to investigate the thickness and chemistry of the passive film. GI-XRD was used to determine the change in the metal lattice underneath the passive film. XRF was used to quantify the dissolution of alloying elements. X-ray Absorption Near Edge Structure (XANES) was used to study the chemical state of the dissolved species in the electrolyte and the chemical state of corrosion products formed on the surface.

Growth of the passive film and enrichment of Mo⁶⁺ oxide was observed in the passive range below 800 mV vs Ag/AgCl, followed by a drastic increase in the electrochemical current coupled with the formation of a thick hydrous film of MoO₃, and Cr(OH)₃, as seen from the AP-XPS data in Figure 1 b). The current increase at potentials above 800 mV vs Ag/AgCl coincided with the dissolution of Ni²⁺, Cr³⁺, and Mo⁶⁺. Quantitative analysis revealed that a substantial part of the measured current was due to oxygen evolution. The experimental techniques and the unique information they provide will be discussed, as well as the role of OER on the passivity breakdown of the Ni-Cr-Mo alloy.

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