

A Current Transient Analysis on the Influence of Mo on Pitting Corrosion of Model Fe-Cr Base Alloys

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Molybdenum is the most important and most well-known alloying element in stainless steels, which counteracts pitting corrosion in Cl⁻ containing solutions. The role of Mo has been studied extensively in numerous publications since a long time. Nevertheless, there still exists some ambiguity on the exact mechanisms and hence different models have been proposed to explain the influence of Mo [1]. Mo has been reported to modify the passive film rendering it more stable against breakdown caused by the attack of aggressive Cl⁻ ions [2-4]. On the other hand, repassivation, or deactivation of growing pits, is improved significantly by the presence of Mo in the alloy.

Mo can easily dissolve in aqueous solutions at relative low potentials due to formation of soluble MoO₄²⁻ species [5]. The potential region for this reaction is situated in the passive region of Fe base alloys. It therefore is possible that MoO₄²⁻ may play an important role in the inhibition mechanism of pitting corrosion and it already has been shown that MoO₄²⁻ in the electrolyte inhibits pitting corrosion of stainless steels. [6-9]

In our experiments, Na₂MoO₄ has been added to the Cl⁻-containing electrolyte in order to study the influence of molybdate anions on the pitting behaviour of Fe-Cr alloys. By varying the Mo content in the Fe-Cr alloy it is possible to obtain two-fold information: on the one hand the influence of Mo in the alloy, on the other hand the effect of MoO₄²⁻ in the electrolyte. Since it has been shown previously that pitting corrosion preferably initiates at inclusions or impurities such as MnS [10-13], experiments are also carried out on Fe-Cr alloy with different MnS contents.

Information on pit initiation, pit growth and repassivation is obtained with standard electrochemical methods such as potentiodynamic and potentiostatic measurements.

Metastable pitting events, observed as current transients are analysed in regard of their number, height, shape and lifetime enabling the elucidation of the role of solution chemistry as well as alloying elements in the pit initiation and repassivation processes.

Mo as well in the alloy as in the form of MoO₄²⁻ in the electrolyte has a great impact on the process of pitting corrosion of the Fe-Cr alloys. In both cases the pitting potential could be raised to significantly higher values with augmenting the Mo/MoO₄²⁻ content. Even small amounts of MoO₄²⁻ (• 0.002 Mol/l) can significantly affect the pitting

behaviour of the alloys. The higher the Cr and Mo content in the alloy, the less molybdate is needed in order to increase the pitting potential, whereas MnS inclusions have a destructive effect so that pitting takes place at much lower potentials. But also with the alloys containing a high number of MnS inclusions, the addition of molybdate into the solution again increases the pitting potential.

Metastable pitting events (observed as current transients) in MnS containing alloys are strongly affected by the presence of MoO₄²⁻ in the solution. The number and size of current transients, observed in the passive region at potentials below the pitting potential, significantly decrease with molybdate in the solution. The effect of externally added, i.e. MoO₄²⁻ in the electrolyte is much more efficient than Mo in the alloy. A statistical analysis of single transients regarding number, shape, height and lifetime clearly demonstrates the effect of Mo / MoO₄²⁻ in the process of pitting corrosion.

Microelectrochemical experiments [12, 13] will be carried out in order to distinguish, if the interaction of the alloy constituents and solution chemistry takes place on a uniform scale (passive surface) or locally on/at inclusions or in the growing pit.

References

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