

Application of Various Experimental Approaches to Elucidate the Effects of Mo Species on Pitting Corrosion of Fe-Cr Alloys

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Pitting corrosion is an old and widely studied topic in the field of corrosion science. Especially technologically important alloys, which are well-known to suffer pitting corrosion in chloride-containing environments, such as stainless steels, have been intensively investigated. Therefore, detailed information is available on the influence of different internal and external parameters on the pitting susceptibility. Moreover, modern techniques have revealed insights into the pitting process, for instance as concerns the different stages of pitting: nucleation, initiation, propagation or repassivation of pits.

In the present work, we studied a classic system in the field of pitting corrosion: stainless steels with a variation of the Cr- and Mo-content and different impurity grades (Mn- and S-content). We compared the effect of alloyed molybdenum and molybdate species added into the electrolyte in hindering pitting corrosion. To obtain a more detailed understanding of the effects observed, we applied many different techniques with different time- and/or size-scales of observation.

The results clearly indicate that even though internal and external additions of molybdenum species into the system always lead to an increased resistance against stable pitting corrosion (measured as the value of the pitting potential), the way these species act is very different. An analysis of current transients corresponding to metastable pitting events indicate that molybdate in the electrolyte can strongly decrease the number of pit initiation events, whereas alloyed Mo is more efficient in retarding the propagation of metastable pits, and hindering the transition into stable pitting. Foil penetration experiments, which reveal information on the growth of stable pits, further indicate that alloyed Mo can efficiently slow down the kinetics of pit growth. Molybdate in

the electrolyte, however, shows almost no influence on pit growth as studied by the foil penetration technique. These and further findings clearly demonstrate that the external inhibitor molybdate is mostly efficient in surface-related phenomena, such as initiation events of pitting corrosion, whereas Mo as an alloying element is more efficient in processes taking place in the pits. This, of course, is related to dissolution and mass transfer related concentration effects on the surface and in the pit electrolyte. Raman spectroscopy indicates that the corrosion products in the pits and outside in the vicinity of the pits are of a similar (but not identical) chemistry for both alloyed Mo and molybdate in the electrolyte solution. The pH-dependent formation of various molybdate complexes seems to play a significant role in the pitting inhibition process. On the other hand, identification of the corrosion products may be used as an indication of prevailing pH-conditions in and around the pits.

The application of different techniques revealing information on the various stages of pitting corrosion is helpful, to obtain a better understanding of the complex mode of action of the species inhibiting pitting corrosion of stainless steels.