Metastable Pitting – Occurrence and Significance for Passive Metals

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Introdction

Many investigators have observed that passive film breakdown and repair events can occur at potentials far below the critical pitting potential required for stable pitting (1-8). Under potentiostatic conditions these events result in current transients.The resulting transients differ widely with respect to the peak current height as well as life time. Small current transients in the pico- and femtoampere range, corresponding to pits of micro- and nanometer size can be detected only when applying micro- and nanoelectrochemical methods (9). Increasing the potential generally leads to larger current transients with higher peak currents and longer lifetimes, indicating an extended period of pit growth.

Results from Investigations of Stainless Steels

Recent microelectrochemical investigations of localized corrosion processes on stainless steel showed, that the oxidizing dissolution of MnS-inclusions acts as pre-cursor process for pitting corrosion. The size and the geometry of active inclusions as well as the presence of mechanical stress (10) are important parameters for metastable pitting as well as for the transition to stable pitting. Measurements using a capillary tip of 2.5 µm in diameter revealed that the interface inclusion/steel is the weakest zone of a MnS inclusion. Additional investigations with a modified microcell containing a pH sensor inside the microcapillary showed that in presence of shallow inclusions, where only metastable pitting is observed, the pH decreased only to values beteween 2 and 4. However in presence of deep inclusions where stable pitting occured the pH decreased to values ≤2 (11). Furthermore these findings were confirmed by numerical simulations using a finite difference model (10).The simulation predicted that in a typical deep crack or crevice, the combination of a pH of around 2 and a chloride concentration of about 6 M led to stable pitting. These results clearly indicate, that the occurence of metastable pitting as well as the transition to stable pitting depends decisively on the mass transport conditions at the pit nucleation site.

Additional studies on stainless steels with high chloride concentrations (>5 M Cl^-) and at high temperatures (90°C) where mass transport processes are less decisive, showed that metastable pitting was rarely found below the pitting potential. One of the first pit initiation process produced stable pit growth (12). Under these conditions strong concentration- or resistance polarization effects are not required for the simultaneous co-existence of passive and active electrode states as already discussed by Osterwald (13) about 20 years ago.

Results from Investigations of Aluminum Alloys

The heterogeneous microstructures of many aluminum alloys have primarily been optimized for desirable mechanical properties, but such heterogeneities may render the alloys more suceptible to localized corrosion. In case of Al-2024-T3 alloy AlCuFeMn inclusions are more noble than the Al-matrix and act as cathode whereas AlCuMg inclusions are less noble than the Al-matrix and act as anodes (14-17). The onset of pitting at single inclusions of the aluminum 2024-T3 alloy showed that the pit initiation process started only at a few AlCuMg inclusions (18). It was found that pit initiation occurs at the adjacent matrix of AlCuMg inclusions. Compared to AlCuMg inclusions the onset of pitting at AlCuFeMn inclusions took place at potentials 200 to 600 mV more positive. The onset of pitting at areas without inclusions occurred at potentials higher than +500 mV_{SCE}. If copper was homogeneously dissolved in the matrix the resistance against pitting was strongly improved.

In a recent study using a 3 µm microcapillary different spots of the matrix near a AlCuMg inclusion could be investigated. The polarization curves were taken at different distances from the matrix/inclusion interface. The results clearly show that the pitting potential increases approximately linearly with increasing distance from the interface. A pitting potential of over 1000 mV_{SCE} is attained at a distance of about 40 µm. This is completely different from stainless steels where already at a distance of 5 µm the bulk properties are measured and no pitting was observed anymore. Further local surface analysis have to be performed on Al-2024-T3 to see whether these findings can be explained for instance by a copper depleted zone around the inclusion, since dissolved copper strongly affects the pitting behavior of aluminum. Contrary to stainless steels local concentration gradients in the pit electrolyte are probably less important to stabilize the active metal dissolution of these alloys. Metastable pitting was therefore hardly observed during microelectrochemical measurements.

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