Electrochemistry of Pit Formation

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ABSTRACT

This paper discusses the processes by which pits are formed on metal surfaces by electrochemical means. Pitting corrosion is a remarkable electrochemical process phenomenologically. Pitting starts on a passive surface, often for which there appears to be no specific feature that could lead to non-passive behaviour. Yet, the process of pitting corrosion involves a very strong bifurcation of the surface into two different zones: one zone remaining passive, and the other dissolving at a very high rate. So bifurcated is the pitting surface, that the ratio of current density flowing from the pitting surface to that flowing from the passive surface can be many orders of magnitude. The reasons for this to happen on an apparently passive material, and the modes by which propagation occurs from this are the text of this paper.

Pitting is an electrochemical process in which small holes grow rapidly in a metal surface under the influence of a specifically aggressive electrolytic anion and an electric field. Most metal can be made to pit under appropriate conditions, but as an issue of corrosion engineering, some are much more susceptible to pitting than others. Electrochemically, the process is easy to examine. Pitting is normally a high-potential process, occurring at potentials higher than that at which passivation sets in. The reason for this is clear. For pitting to occur at all, the metal must be above its equilibrium oxidation potential, and it is therefore capable of oxidising over its entire surface. Pitting is a localized process, and only small regions of the surface dissolve at any instant. The rest of the surface, that surrounding the pits at that instant, is not pitting, and is thereby passive. Thus pitting and passivity are inextricably interlinked. If the remaining, non-pitting surface were not passive, it too would have to dissolve, and general corrosion (not pitting corrosion) would ensue. Thus pitting is a transpassive process, occurring at high potentials. In a polarization curve for the metal, a passive region exists below the potential at which pitting occurs, albeit that this might be a very small passive zone. The phenomenon has led to the notion of a pitting potential: the pitting potential is conventionally defined as the minimum potential below which the metal will not undergo pitting corrosion. From a mechanistic viewpoint, this definition is erroneous, since it can be shown that pits on many metals can be nucleated far below the pitting potential and may even propagate briefly there (1,2).

Three distinct stages in the development of a pit can be identified, perhaps a fourth too (3). The nucleation process is fast and brief, and can be detected as a discrete current transient showing a sharp rise followed by a decay. Many of these events show no sign of propagating at all, but die directly, with the current decaying back to the passive level. Some, however, propagate, and the current then rises again as the pit grows. There have been many reasons proposed for the origin of these events. They occur because of the action of a specific aggressive anion, commonly chloride, but not exclusively. The notion that Cl^- is comparable in size with the oxide and hydroxide anions, and the knowledge that some O^{2-} must transport across the passivating oxide to maintain the film, leads rationally to the proposal that Cl^- is also transported across the oxide in parallel. If Cl^- reaches the metal/film interface, it must cause the metal chloride to be formed there. The high molar volume of metal chlorides, and the presence of the salt at the metal/film interface must cause expansive stresses to form, ultimately to rupture the oxide as a nanoscopic explosion. This is nucleation. Once ruptured, the chloride dissolves in the incoming electrolyte to give a locally saturated solution. Most metal chlorides are highly soluble, so the solution becomes locally very concentrated. What happens form there, depends very strongly on the surface and pit geometries, particularly the degree of openness of the nucleated pit. Pit growth involves dissolution at the maximum rate, controlled by the outward diffusion of the metal cations from the nucleated site. This is necessary; if not under such diffusion control, the local solution must dilute to sub-saturation, and the pit repassivates. Propagation requires the aggressive concentrated local solution. Thus a less open site has a greater probability of pit growth because diffusion control requires a relatively smaller current. A more open site, otherwise identical, would require a larger current to reach diffusion control, and therefore a higher potential to achieve it. Diffusion control by the outwardly diffusing cation means that a high cation concentration exists within the so-called metastably propagating pit, and more Cl^- must enter the pit to maintain electroneutrality. Thus the propagating pit maintains the salt-saturated condition within. Stable pit growth occurs when the pit has grown so large that the pit depth alone can function as the diffusion layer thickness, and the original site geometry is then irrelevant. Because the diffusion-controlled reaction rate is fast, pits grow quickly. There are no slow ones. The dramatic bifurcation of the pitting surface arises because either pits grow rapidly, or they do not grow at all. There is also a further implication. If the conductance of the electrolyte is not very large, the surface cannot sustain many of these at any one time. Each pit that grows at its high rate depresses the potential of the surface by an amount controlled by that electrolyte conductance. Thus current measured from a laboratory specimen may show an ohmic relationship with the applied potential, even though individual pits propagate under diffusion control.

The origin of the nucleation site depends on the system. Starting from the premise that pits form where the aggressive anion can get to the metal/film interface, it is easy to see that some microstructural or microcompositional may induce pitting preferentially. This is consistent with the behaviour of stainless steels in chloride solution. However, if all that is required is the ability to get the aggressive anion there, then this is not a necessary mechanism. Ion migration under the electric field may be all that is required, and this may be evident for aluminum in chloride solution.

REFERENCES

1. H.S. Isaacs, Corros. Sci., **29**, 313 (1989).
2. G.T. Burstein and S.P. Mattin, J. Electrochem. Soc., **148**, B504 (2001).
3. S.P. Mattin and G.T. Burstein, Philos. Mag. Letters, **76**, 341 (1997).