

Localized Corrosion Research Since 1960

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This presentation will compare and contrast two research themes in localized corrosion that have been prominent during the past 40 years. There will be a strong focus on stainless steels, since the author can speak (he thinks) with some authority on those materials. Aluminum and other metals will be introduced where they help to illuminate some general theme, or where they reveal that some process occurring in stainless steel is specialized to the FeCr system, or to commercial alloys, and does not extend to pure metals.

The first theme is the initiation of localized corrosion, and the role of the passive film and of chloride ions in initiation processes. For pitting at plane surfaces, kinetic laws were proposed based on the induction time for pit nucleation, a convenient quantity for representing the inverse “rate” of passivity breakdown. The work of Hoar and Jacob, while not the first example of this approach, was notable in that a specific complexation process was cited on the basis of kinetic relationships. This was essentially a film-dissolution concept. Other authors who have extended this approach have come under some pressure to justify the use of the induction time itself. I personally have difficulty with the kind of experiment where chloride is injected into the solution after some period of pre-passivation. Authors rarely measure the current sensitively and rarely determine the actual pit nucleation rate in the altered solution. To my knowledge, no-one has exactly repeated classical work (based on induction times) using sensitive instrumentation that can record metastable pitting events, especially under conditions where stable pitting is greatly delayed. Such experiments might counter or confirm the suggestion that the induction time is simply the inverse of the pit nucleation rate and has no other fundamental significance.

Theories of pit initiation based on commercial alloys are vulnerable to any demonstration that pitting occurs exclusively at inclusions that provide geometrical, chemical (sulfur) and perhaps other congenial conditions for pitting. In the case of FeCr alloys, it has been shown (by Ryan and others including the author) that it is questionable whether pitting is even possible on smooth surfaces without inclusions, unless the Cr content is so low that a tunnel-like corrosion occurs, leading to the creation of occluded cavities on an imperfectly passivated surface. This places the emphasis firmly on the creation of an occluded cavity within which concentration of dissolution products can occur. An unresolved issue, for example in “pure” iron or aluminum, is whether a low population of particles can give the observed number of pitting events (probably not, at least in the case studied by Bardwell, where iron was subjected to potential steps into the pitting region that were terminated after short periods followed by microscopic examination. Pit densities were much too high to be ascribed to particle nucleation.).

I have focused on film dissolution, but of course a proper accounting of research in this area has to include “mechanical” or “chemical-mechanical” modes of film breakdown. Amongst mechanical aspects is the

electrostriction effect of anion adsorption. This is a real, demonstrable effect, and may act in concert with other, more critical events. A powerful experimental approach by Burstein and others has led to the conclusion that the fundamental event in pit nucleation is the formation of a (ferrous) chloride salt under the passive film, followed by rupture of the latter by volume expansion due to the larger molar volume of the salt. This needs to be confirmed in systems that are not so sensitive to non-metallic inclusions as stainless steels. For those seeking the true origin of pitting, such theories displace the main mystery back one step, to the formation of the salt island under the passive film. Perhaps the film becomes an anion-selective membrane locally, to such an extent that chloride ingress into a hydrated salt island is easier than proton egress. Finally, the point defect theory postulates creation of a vacancy cluster or small void under the passive film, which nucleates film collapse and pit initiation. This is a true nucleation theory, and probably has not yet been subjected to a careful attempt at falsification. In its most general form, it does have some dubious aspects, such as the claim that alloying elements promote or retard pit nucleation by altering the point defect population of the passive film. There is no evidence for this proposition.

Many scientists believe that crevice corrosion initiation is a mature area and that mathematical modeling has confirmed the notion of passive dissolution leading to gradual acidification. This is not the case. It is still unclear which crevices obey this “Oldfield and Sutton” or “Greene” or “Crolet” mechanism, and which are dominated by metastable pitting or some chance occurrence of adjacent metastable pitting events within the crevice. To my knowledge, no-one has attempted to initiate crevice corrosion on inclusion-free stainless steels, which might be one test of the importance of pitting.

In contrast to the slight confusion about pit initiation, the propagation of localized corrosion is a rather mature area. The main area of disagreement, and a focus of this presentation, is the extent to which pit “initiation” is really governed by the stability of propagation, but in a very small cavity. Even before 1960, Edeleanu had shown the basic features of localized corrosion chemistry in aluminum, using a divided cell approach and microscopic observations of tunnel propagation. It was obvious that Edeleanu thought stability of propagation was sufficient to explain localized corrosion. Modern mathematical methods have enabled the advanced propagation of crevice corrosion to be modeled rather accurately, and understood on several levels. A more controversial claim, by Galvele (1976) was that pitting at plane surfaces simply reflected the stabilization of a critical chemistry in a minute cavity such as a crack in the passive film. This, in my view, is the single most important advance in corrosion theory in the past 40 years. Of course the theory had flaws, mainly the optimistic assumption that thermodynamic stability of dissolved products relative to solid ones was sufficient to explain the passage of extraordinary anodic current densities. The fact that this is *not* a sufficient condition explains why real pits nucleate in pre-existing cavities, or perhaps in special underfilm geometries as proposed by Burstein. The author with N.J. Laycock has made some progress in applying Galvele’s concepts quantitatively to stainless steels: the results tend to confirm that practical effects of alloying or environment have nothing to do with the composition, structure or electrical properties of the passive film.