

Progress in Understanding the Pitting of Corrosion

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During forty years of studies, significant progress was made in several fields of pitting and crevice corrosion:

- As a result of works of many researchers on metastable pit formation and growth, the critical pitting potentials are now better defined. Because of knowledge of the properties of metastable pits, the growth of stable pits below the pitting potential and the lower critical crevice potential than the pitting potential is explained.
- The kinetics of small hemispherical pits growth is established, but there is no agreement if pit growth occurs under ohmic or diffusion control. The kinetics of large pits growth with a different shape was not studied.
- The most complete investigations were done on the effect of alloy composition and on the effect of inclusions in iron-base alloys on pitting. It is noted that many recent papers either repeat previously done experiments using often better experimental methods or provide information that is not very substantial.
- There are several hundred papers examining the inhibition of pitting by organic and inorganic species. Until now, for practical purposes, the inhibitors are mainly chosen by empirical tests. However, there are studies trying successfully to explain the behavior of the inhibitors on the basis of a hard and soft acid and base principle (HSAB) (hence taking into consideration the electronic structure of adsorbate and adsorbant). Surprisingly only a few researchers were investigating the adsorption of Cl⁻ on a hydroxylated passive film. The above experiments indicate the existence of the dependence between pitting potential and the potential of zero charge and the isoelectric point of the oxide.
- Numerous theories on pitting have been proposed over years of investigation: penetration of Cl⁻ through the passive film, adsorption of Cl⁻ on the passive film, mechanical disruption of the passive film, and the metal vacancy production at the metal/oxide interface. It needs to be emphasized that none of these theories explain all experimental data. However, in any particular case the data obtained can be explained by one of the existing models.