Relationships Between Pitting Corrosion and Crystallographic Orientation, An Historical Perspective

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Over the past half century numerous authors have reported relationships between pitting corrosion and crystallographic orientation of the metal substrate. These observations can generally be divided into two categories: 1) relationships between pitting susceptibility (nucleation) and crystallographic orientation and 2) relationships between pit morphology (propagation) and crystallographic orientation. This paper will review the published literature on the topic and present a model for crystallographic pitting which describes dissolution of the active interface in terms of bonding in the crystal.

Pit nucleation & orientation For bcc Fe single crystals in distilled water, Kruger demonstrated that pit density decreased in the order {110}>{100}>{111}.[1] This relationship was preserved in large grain polycrystalline material. Although no explanation was given for the observed trends in pit densities, one might conclude that it is easier to nucleate pits in {110} Fe planes as compared to the other low indices planes examined. For the Ni chloride system, MacDougall and Cohen proposed that the susceptibility to pit nucleation (characterized by pit density measurements) was related to misorientation between the oxide film and metal substrate.[2] It was shown that the oxide film on Ni was (111) "like." MacDougall and Cohen proposed that the misorientation of the oxide with the surface resulted in defects in the passive film (to accommodate the misorientation). Thus, the observed rates of breakdown on {111} surfaces were slower than other low index planes owing to few misorientation defects.

Later studies used pitting potential as an indication of susceptibility to pit nucleation. Yasuda *et al.* showed that the pitting potentials for single crystal fcc Al decreased in the order {001}>{011}>{111}.[3] The results were rationalized in terms of a competitive film dissolution / film formation mechanism; the rate of active dissolution for the single crystal surfaces was theorized to increase in the order {001}<{011}<{111}. Unfortunately, no dissolution rates in simulated critical pitting solutions were measured. Treacy *et al.* rationalized the variation in Al pitting potential with differences in surface energy and cathodic reaction rate.[4] Yu *et al.* used XANES to measure chloride content of the passive film on Al single crystals.[5] During anodic polarization of {110} surfaces Yu found that chloride adsorption, absorption, and migration increased at potentials near the pitting potential. Contrary to pitting potential results, the total chloride content of the oxide film on {111} was lower than that of the oxide film on {110} surfaces.

While breakdown of the oxide film has been used widely to explain relationships between crystallographic orientation and breakdown susceptibility, it has one major flaw. Exposing bare metal surface to chloride solution, either naturally via metastable pitting activity or artificially in straining experiments, does not influence the breakdown potential. In addition, metastable pitting activity below the pitting potential for single crystal beryllium is greatest for samples with the highest pitting potential. This observation combined with the finding that these events re-occur at the same site indicates that pit morphology plays an important role in the transition to stable pitting and thus the pitting potential.

Pit propagation & orientation Faceted corrosion pits are widely observed and may be more common than smooth hemispherical pits. Faceted pits were probably first observed in dislocation etch pit experiments. While there is ample evidence in the literature to demonstrate that etchants may be used to produce pits in metal surfaces at the location where a dislocation penetrates the free surface (several reviews have been written by Ives[6]), there is no relationship between the movement of the dislocation (or dislocation pile-up) through the lattice and pit geometry.

The most common explanation for preferentially oriented pits / propagation is surface energy. Surface energy is a fairly general term to describe dangling bonds at a free surface - more closely packed surfaces often having lower surface energy as they loose the fewest number of bonds per unit area when the new surface is formed. However, this simple "hard-sphere" model of the surface does not adequately describe the lattice and does not predict the observed trends in pitting potential or pit morphology in some systems. This does not mean that bonding as a model is incorrect, rather, that our concept of surface energy needs to be modified.

In the hcp system pit morphologies for Be and Zn are sharply different yet the trends in surface energy are the same.[7] Differences in pit morphology may be explained by examining the electron density maps (EDM) for the materials. EDM are generated from x-ray diffraction data and map the distribution of electron density (and, therefore, bonding) in the crystal lattice. The EDM for $(11\bar{2}0)$ in Be is characterized by a maximum in density at the tetrahedral sites and a minimum at the octahedral sites.[8] A volume depleted of charge extends along the *c*-direction encompassing the octahedral holes. For Zn the maximum in density occurs between atoms in the *a*-direction, eliminating the volume of depleted charge seen in Be.[8,9] These charge density distributions correlate directly with pit morphology. This observation combined with metastable pit data suggests that exposing a sufficient area of susceptible low index planes may be the necessary criterion for pit stability where crystallographic pitting is observed.

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