

In Situ Corrosion Studies

In situ techniques to understand passivation and corrosion

by Alison J. Davenport

The corrosion of metals has a major economic impact, yet the underlying processes that control the phenomenon are very difficult to study. Removal of a corroded sample from its wet environment can change it, so the results of subsequent ex situ characterization may be artifacts. In recent years, there has been considerable interest in the development of in situ techniques that allow examination of metal surfaces during the corrosion process; a few examples of such studies are given here.

The structure of the passive film on iron.—Investigations of the ability of iron to resist corrosion predate Faraday, although he was the first to suggest that the phenomenon, termed passivation, was due to oxidation of the metal surface. However, despite many measurements using a great variety of techniques, it was only recently that the structure of the film was determined unambiguously with an in situ technique: synchrotron X-ray diffraction (1). FIGURE 1 shows a diffraction peak from the passive film.

Although the film is very thin (a few nm) it is possible to extract a considerable amount of information from the diffraction pattern. The passive film has a spinel structure, related to, but distinctly different from, maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and magnetite (Fe_3O_4), and has a strong orientational relationship with the underlying metal. It contains far more defects than these two structures: the occupancy of octahedral and tetrahedral cation sites are only 80% and 66%, respectively, compared with magnetite, and cations occupy 12% of the available interstitial positions.

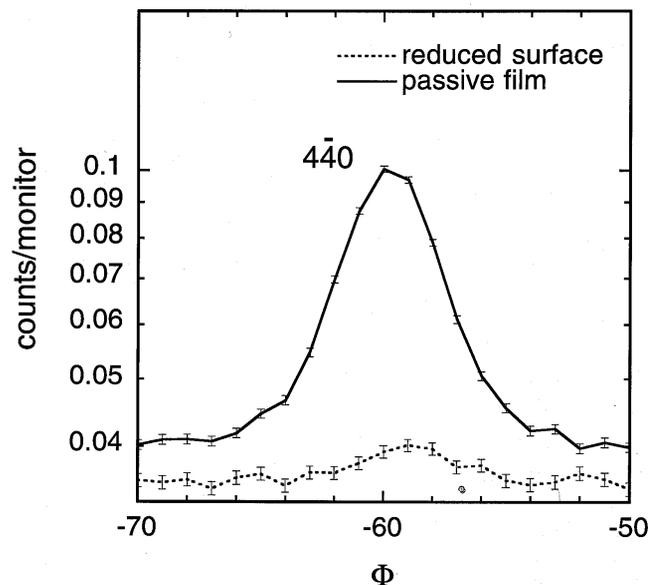


FIG. 1 The (440) reflection from the passive film grown on Fe(110) in borate buffer at +0.4V(MSE) compared with the data collected after electrochemical reduction of the surface.

The stoichiometry of the film is close to Fe_2O_3 , consistent with data from in situ X-ray absorption spectroscopy (e.g. Ref. 2, 3), and the local structure determined with in situ scanning tunneling microscopy (STM) (4) correlates with the orientation relationship determined from X-ray scattering.

Critical chromium concentrations for passivation of stainless steel.—It has been known for the best part of this century that it is necessary to add about 13% Cr in order to make FeCr alloys corrosion-resistant. However, it is not understood why this amount is critical for prevention of corrosion under conditions where the metal is already covered with an oxide film (either an air-formed film or a passive film). When the ferric oxide component of the film is reduced to ferrous oxide and dissolves away, the exposed underlying iron corrodes.

A synchrotron-based spectroscopic method, X-ray absorption near edge structure (XANES) is able to give information on both the valence state of species in passive films, and the amount of each element with submonolayer reso-

lution during film formation and dissolution. Recent investigations have shown that passivation in mildly acidic solutions results in no detectable dissolution of Cr, but a small quantity of Fe is lost, the amount increasing slowly with decreasing Cr content of the alloy. During reduction of the oxide, the Fe loss appears to increase significantly below about 13% Cr. These measurements are being used to test the hypothesis that the extent of reactivation is controlled by the Cr content of a stoichiometric passive oxide layer that forms under a Cr-rich porous oxyhydroxide layer resulting from passivation (5).

Newman and co-workers have found a different critical threshold at 17% Cr for passivation of oxide-free stainless steel surfaces, which they have modeled using an approach based on percolation theory (6). Both the value and sharpness of the threshold were verified using another synchrotron-based technique, the X-ray microprobe, which uses photons to excite the characteristic X-rays of each element in a sample (7). Rather than making a whole series of samples

with compositions close to the 17% threshold, a single thin film sample was sputter-deposited with a continuous lateral variation in Cr content by sputtering from adjacent Fe and Cr targets to give a linear variation in composition of about 10%, and a resolution in composition of about 0.01%.

The crystallinity of passive films can also be correlated with the percolation-based view of the passivity of FeCr alloys.

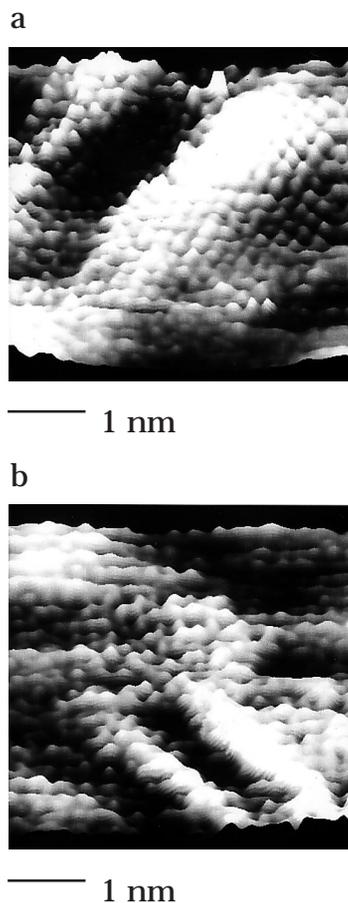


Fig. 2 In situ potential-controlled STM images of (a) Fe-13.8Cr and (b) Fe-16.5Cr in 0.01 M H_2SO_4 at +400 mV (SCE) after about 1 hour of passivation (8).

Using in situ STM, Ryan et al. (8) found that the passive film on a sample containing 13.8% Cr showed long range crystalline order (FIG. 2a), whereas that on a sample with 16.5% Cr was more disordered (FIG. 2b). According to the model, the passive film formed from an alloy with a lower Cr content is more open, so it can crystallize more readily.

Localized corrosion.—While passivation depends upon behavior on an atomistic scale, localized corrosion is affected by heterogeneities in engineering alloys, so it is important to carry out studies on length scales that corre-

spond to the alloy microstructure. This is most easily achieved with the range of techniques based on scanning probe microscopy (SPM), such as STM and atomic force microscopy (AFM). A good example of this is provided by the corrosion of aluminum alloys. In situ AFM has been used to demonstrate that corrosion of commercial aluminum alloys is due to local attack at a variety of intermetallic particles with much greater anodic and cathodic activity (9,10).

It has long been known that corrosion pits in stainless steels are associated with manganese sulfide inclusions. For example, Suter and Böhni (11), using a silicone coated pipette, have examined masked areas of stainless steels only a few microns in diameter and correlated initiation events with the sulfur content of the steel. However, the exact mechanism of pit initiation has remained elusive; there is a need to explain how local conditions of low pH and very high chloride content can evolve on a surface where the average passive current density is on the order of $nAcm^{-2}$. Williams et al. (12,13) have recently used scanning electrochemical and photoelectrochemical microscopy to demonstrate that pit initiation is a result of chloride-catalyzed dissolution of MnS inclusions. This can take place at extremely high current densities ($>1 Acm^{-2}$), forming a crust of elemental sulfur that restricts diffusion, allowing establishment of the local acidic conditions that allow dissolution of the steel. These results are consistent with earlier AFM observations of the build-up of deposits on and around inclusions (9).

The propagation and repassivation of pits is better understood than their initiation. However, some questions still remain. It has long been known that the concentration of dissolution products in a pit can become so high that a salt film precipitates on the dissolving surface. The composition of salt films is quite impossible to determine ex situ, as the salt film dissolves immediately when the potential is removed. However, with X-ray microprobe, analysis can be carried out in situ, and it has been determined that the composition of the salt film on stainless steel is not the same as that of the alloy, but is strongly enriched with iron (14).

Kelvin probe studies of paint delamination.—For many practical applications, corrosion of metals is prevented by the application of organic coatings. The corrosion failure of coated metals is a complex process, and is particularly difficult to study because the initiation step takes place under the coating in a wet environment, a particularly inaccessible place for most char-

acterization techniques. Recently, the Kelvin probe, which is able to measure the corrosion potential of the metal under an intact wet coating, has been used to demonstrate that the delaminated area is a local cathode, whereas the defect is the local anode (15,16). At the local cathode, a highly alkaline solution develops, leading to failure of the metal/polymer interface as a consequence of oxygen reduction, leading to formation of reactive species such as $\bullet HO_2$, H_2O_2 , and $\bullet OH$.

In situ techniques have much to contribute to elucidation of the mechanisms of corrosion reactions and solving practical problems. With the variety of probes available, and the possibilities provided by SPM control systems, the development of new techniques and greater understanding of corrosion is limited only by the ingenuity of those carrying out the research. ■

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