Metallic Corrosion

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The aqueous corrosion of metals was among the first electrochemical phenomena to be investigated, by Faraday and others, and retains a remarkable scientific appeal as well as obvious practical importance. Most industrialized countries have done a corrosion cost estimate, and generally the result is several percent of the gross domestic product (GDP). Some expensive forms of corrosion failure are also unsolved scientific problems of considerable complexity, and they occur on interfaces that are hard to observe. Now that techniques for study of the interfacial realm are available, there is hope for satisfying progress.

Corrosion in aqueous solutions proceeds by the coupled electrochemical dissolution of metal and reduction of agents in the environment (oxygen, water, chlorine, and so on). Current flows in the metal from sites where reduction predominates (cathodes) to those where oxidation predominates (anodes). The circuit is completed by ionic current flow in the solution (electrolyte). Atmospheric corrosion is just like immersed corrosion except that the liquid layer is thinner or discontinuous, or both. Normally we might expect that a more oxidizing condition would result in more severe corrosion, but passivation often intervenes: the formation of a nanometer-thick oxide film that reduces the corrosion rate to minuscule levels (stainless steel in tapwater, for example, corrodes at less than 0.1 μm per year). The exact nature of such films and how they break down, leading to pitting or cracking, has been a major focus of corrosion research.

Atmospheric rusting of iron is the most common corrosion process and is enhanced by wet-dry cycling. Until recently, rusting had been neglected since the pioneering work of Evans (*1*), who showed that the mechanism was electrochemical and that the fastest metal loss occurred during drying; his model included cycling of iron between the +2 and +3 oxidation states. The electrochemical kinetics of rusting have now been measured directly by Stratmann and colleagues (*2*), who combined differential pressure measurement (to follow oxygen uptake, that is, corrosion rate or current) with a noncontact Kelvin probe to measure the Volta potential, which is related to the electrode potential under the thin liquid layer. Mössbauer spectroscopy can be used to follow the corresponding structural chemistry of the rust, and all these techniques were shown to work equally well in the presence of an organic coating. Several aspects of Evans' model have been confirmed and greatly extended. Weathering steels contain copper to improve atmospheric corrosion resistance under wet-dry conditions; Stratmann's work has shown that, depending on its concentration in the steel, the copper can either reduce the kinetics of oxygen reduction during drying (a paradoxical result, considering that copper normally enhances this reaction) or densify the dry rust film.

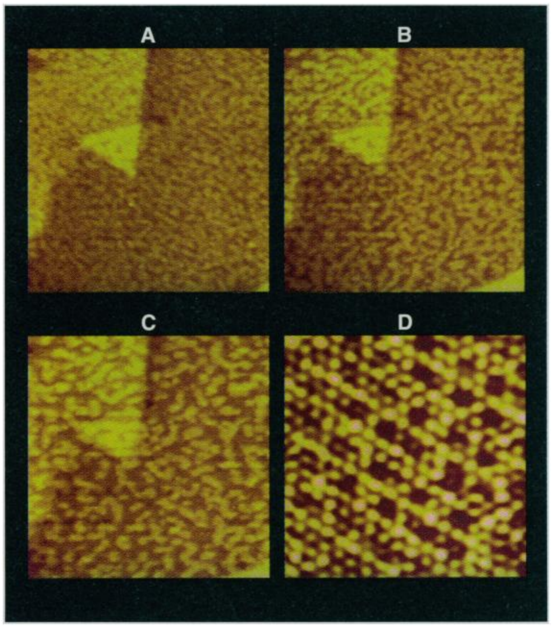

Fig. 1. A time sequence of STM images showing aging of the gold residue on a lightly corroded 60% gold–40% silver (111)-oriented alloy surface (*4*). The lightest areas are topographically highest, and each variation in shade corresponds to exactly one monolayer (0.256 nm) of height variation. (**A**) Immediately following exposure; (**B**) after 1 hour in air; (**C**) after 5 hours; and (**D**) atomic-resolution image of one of the 2-nm-wide gold ligaments pictured in (C), showing that a surface reconstruction has occurred owing to the corrosion process. The image width in (A) to (C) is 207 nm.

Many corrosion problems are mitigated by the use of alloys. During alloy corrosion there is a surface enrichment of more noble (unreactive) alloy components; an understanding of this process could lead to cheaper corrosion-resistant materials because in principle, a minor alloying element could cover the surface completely. Recently, the tool for this particular job has been developed: the electrochemical scanning tunneling microscope (STM). Atomic or near-atomic resolution can be obtained, either in air or in solution, with electrochemical control (*3*).

Figure 1A shows the surface structure of a 60% gold–40% silver alloy after a corrosion process that removed silver from several atom layers (*4*). The remaining gold has reorganized itself by surface diffusion into an interpenetrating solid-void microstructure, reminiscent of patterns seen in microemulsions and porous glasses. Similar patterns have also been observed by transmission electron microscopy (*5*). The surface morphology coarsens with time by further surface diffusion (Fig. 1, B and C). Atomically resolved pictures of the corroded structures have been achieved (Fig. 1D). The coarsening process is affected by the environment; in particular, adsorption of chloride ions increases the diffusion rate.

When selective dissolution has proceeded to a considerable depth and starts to produce a three-dimensional nanoporous structure, it is called de-alloying. This process has a long pedigree: Early Andean metalsmiths adorned the surfaces of their artifacts in gold using a de-alloying process now known as depletion gilding (*6*), and Raney catalysts are made by the de-alloying of aluminum from systems such as Ni-Al. Sieradzki (*7*) has recently explained the evolution of de-alloying microstructures in terms of a dynamic roughening transition attributable to competition between curvature-dependent dissolution and surface diffusion. The governing differential equation is similar to equations describing the development of surface morphologies during thin film growth (*8*). The evolution of the porous microstructure can now be studied by in situ small-angle neutron scattering (Fig. 2) at the National Institute of Standards and Technology (*9*). After only 10 min of immersion, there is a scattering peak, which represents the emergence of a well-defined length scale (the pore or ligament size). Later, the scattering intensity increases and the scattering peak shifts to smaller values of the scattering wave vector *Q*, indicating an increase in the characteristic length. Such structures have potential commercial value as membranes or as substrates for electrochemical sensors.

Porous layers seem to play an important role when fracture is induced by a reactive environment: stress-corrosion cracking. Materials like copper and brass, which have

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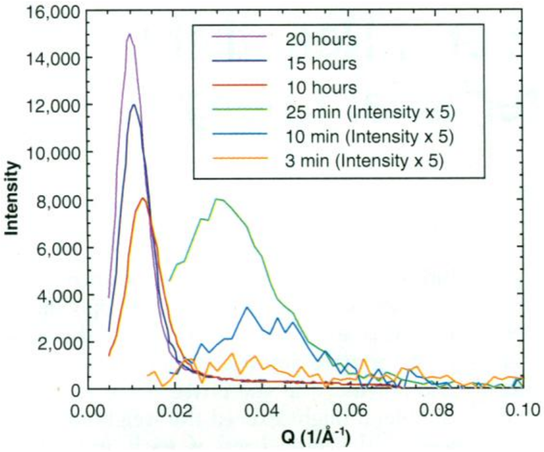

Fig. 2. In situ small-angle neutron scattering intensity versus scattering wave vector (*Q*) from a 35% gold–65% silver alloy undergoing corrosion in concentrated nitric acid for the indicated times (*9*). Silver is selectively removed from the alloy, creating a connected porous structure with a dominant length scale, as evident from the scattering peaks.

face-centered-cubic crystal structures, are ductile. However, environments that cause little or no uniform corrosion can cause stress corrosion by a series of small brittle events (*10, 11*). In many cases, the only effect of the environment is to produce a de-alloyed layer less than 100 nm thick at the crack tip. Evidently, the dynamic fracture of such a thin, brittle layer can inject a crack into the substrate metal that does not stop for several microns (*12, 13*). There is no agreement on the mechanism of such a process, but ductile-brittle transitions in disordered solids have been observed experimentally (*14*) and predicted analytically (*15*). This phenomenon illustrates the interdisciplinary nature of corrosion science: To understand stress corrosion cracking fully, we need new knowledge in many disciplines, such as electrode kinetics, surface diffusion, and mechanical properties of random media.

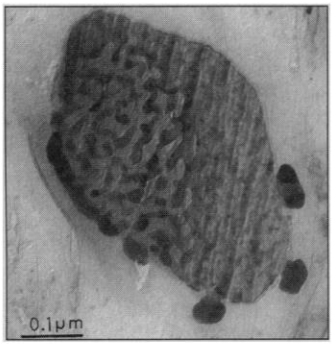

Fig. 3. Transmission electron microscopy of corrosion processes in Al-Cu alloys (*21*). A CuAl$_2$ intermetallic particle in the center of a pit on aged 95% Al–5% Cu after atmospheric corrosion by chloride ions, showing de-alloying of aluminum from the particle (compare with Fig. 1) and enrichment of nearly-pure metallic copper (dark blobs).

Synchrotron radiation has made useful contributions to corrosion science. Many x-ray methods are not inherently surface-sensitive, so experimenters have devised clever techniques using thin-film specimens and specially designed electrochemical cells for in situ studies (*16*). The resulting data indicate that the passive oxide film on iron is none of the known oxides or oxyhydroxides. A detailed analysis indicates that the iron in the film is surrounded by six oxygen atoms in a distorted octahedral arrangement, and that these octahedra share edges and faces, perhaps forming sheets or chains. A current challenge is to achieve time resolution in structural studies; time-resolved chemical information is already available for stainless steel passivation, confirming that both iron and chromium are selectively oxidized whereas nickel is retained at the metal-film interface (*17*). The STM is also making a key contribution with evidence for epitaxial oxides on pure nickel (*18*) but a range of more-or-less disordered oxides on Fe-Cr alloys (*19*). These latter films show remarkable recrystallization with time. Neutrons can also be used as a structural probe (*20*).

Conventional microscopy allied to novel specimen preparation has greatly advanced the study of filmed metals. For example, transmission electron microscopy has been used by Thompson and Gibbins (*21*) to visualize the copper enrichment process that occurs during pitting corrosion of two-phase Al-Cu alloys (Fig. 3).

Pitting is a common disease of passive metals exposed to chloride ions. Owners of dishwashers know that pits grow at around 1 mm per day, whereas the passive surface dissolves at less than 1 mm per millennium. Recently, the trigger events for pitting of stainless steel have been measured electrochemically at the picoampere level and seem to indicate a catastrophic mechanical event (*22*). One possible explanation is that cation vacancies generated by anion absorption at the film-solution interface coalesce near the metal-film interface and nucleate a crack in the film (*23*). Once a pit is growing, it sustains a remarkable local environment that is acidified by cation hydrolysis; great advances have been achieved in the modeling of such localized corrosion cells (*24*). Oscillatory and chaotic behavior have been reported in pits, and this complex dynamical behavior is now being modeled successfully. Electrochemistry provides very good model systems for such studies, as the kinetics are continuously registered by the electric current.

The next few years will see exciting developments in corrosion science. All of the modern techniques mentioned in this article will progress, and atomic force microscopy will also thrive. In situ synchrotron radiation studies and neutron scattering will benefit from the intense sources now becoming available for materials research. Scanning laser microscopy using photocurrents or thermal effects will advance our knowledge of local processes on filmed metals (*25*). The scanning near-field optical microscope may have interesting imaging and analytical applications. Advances in organic and metallic coatings (such as electropolymerization and unbalanced magnetron sputter deposition) and in the protection of steel in concrete will have major economic impact, and alternatives to toxic treatment chemicals such as chromates will be commercialized. Techniques are not everything, and corrosion still provides a rich field for modelers who are not afraid of complexity in physical systems.

References

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