Physics of corrosion

A metal is often protected from further attack by a film of the reaction product, but localized forms of corrosion—pitting, cracking—continue to be problems for researchers.

David A. Vermilyea

Most metals have a strong affinity for oxygen. Just as a great deal of energy must be supplied to ores to separate the metal from the oxygen, the refined metal has a strong tendency to revert to an oxide form by corrosion.

Two general exposure situations are important in corrosion:

- The metal surface is in direct contact with the environment.
- A layer of the product of the metal with environmental oxygen separates the metal surface from that environment.

In the latter case the metal is protected from further attack, which is of tremendous importance in corrosion control. The color photo on the cover of this issue of PHYSICS TODAY shows such a reaction-product film.

In this article I consider the phenomena, at the atomic scale, of the corrosion of metals immersed in liquid ionizing media such as water or alcohol; behavior, accordingly, at temperatures below a few hundred degrees Celsius. A special emphasis will be on such localized forms of attack on the metal surface as pitting, intergranular attack and those disastrous cases in which the concerted action of stress and corrosion speeds the formation of cracks. Figure 1 shows a laboratory test of stress–corrosion cracking, directed towards solving problems of cracking in components of light-water nuclear reactors.

Removal of ions at bare surfaces

Although essentially all engineering metals are normally protected against environmental attack by a layer of reaction product, corrosion does occur at bare surfaces, especially during localized attack as in pitting and stress–corrosion cracking. Understanding and dealing with corrosion therefore requires knowledge about corrosion in the absence of reaction products. Such corrosion, which is often called "active" corrosion, almost always occurs by the separate removal of ions of the metal and of electrons. The metal ion is evidently removed at kink sites in atomic steps, in the manner proposed originally by William Burton, Nicholas Cabrera and Charles Frank.

The rate i of the fundamental ion-transfer steps depends strongly on the electrical potential difference across the metal–solution charge double layer. This dependence is expressed by an equation of the form

$$i = i_0 \exp\left(\frac{\alpha z F \eta}{RT}\right) \qquad (1)$$

for potentials more than about 100 mV from the reversible potential. In equation 1, i_0 is a rate constant containing frequency, entropy and activation-energy terms, α a constant with a value of 0.3–0.7, z the ionic charge, F Faraday's constant, R the gas constant and T the absolute temperature. The overpotential η is the difference between the electric potential and the equilibrium potential.

Values for the exchange current densities for metals in aqueous solutions range from several amperes to a few microamperes per square centimeter; it is therefore relatively easy for the metal ion to change its binding state from metallic to solvated, and hence corrosion at bare surfaces is fast. For example, for a rather sluggish metal with $i_0 = 10^{-6}$ A/cm^2, $z = 2$, $\alpha = 0.5$ and $\eta = 0.3$ V, the corrosion rate is 0.1 A/cm^2, which corresponds to a surface recession rate of roughly 10^{-5} cm/sec—far too high for practical applications.

The detailed steps involved in active corrosion may be quite complicated, and we have relatively little firm data and less understanding of the phenomena. Protons, for example, play a retarding role in the dissolution of iron and an accelerating role in the dissolution of titanium, and it has been postulated that surface hydroxyl complexes may be involved on iron and adsorbed protons on titanium. Anions also exert significant effects on the reaction rates; for instance, in retarding the active dissolution of iron. These effects of solution composition are relatively small, usually less than a factor of ten. Defects in the metal crystal evidently do not play important roles, probably because lattice steps can readily be generated at crystal edges. Cold work or plastic deformation during dissolution therefore has little effect on the active corrosion rate; rates may be increased by factors of two or three but not much more.

Removal of electrons

Electrons are usually removed from the metal in the reduction either of oxygen to form hydroxyl ions or of water to form hydrogen. An equation such as 1 will describe the current–potential relationship, provided transport is not slow. Hydrogen evolution proceeds by discharge of protons to form adsorbed hydrogen, followed by surface recombination or by a second discharge reaction, "electrochemical desorption," which forms hydrogen molecules directly. On some metals (mercury, lead, tellurium, cadmium, zinc) the discharge reaction is slowest and therefore rate-determining, and the surface concentration of adsorbed protons is low. The rate constants for hydrogen evolution on these metals are relatively low (10^{-15}–10^{-7} A/cm^2) and their good corrosion resistance results in

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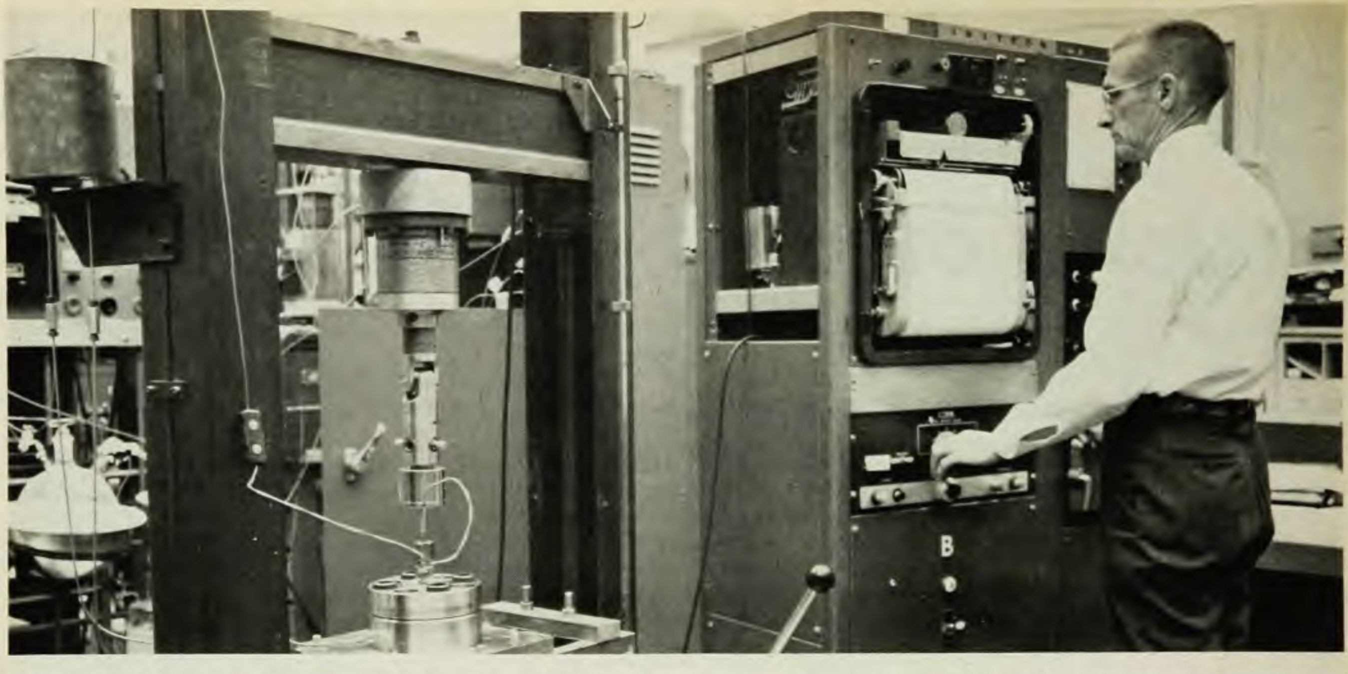


Break . . . corrode . . . break . . . The author, David Vermilyea, is here shown simulating conditions that might lead to stress–corrosion cracking of iron–chromium–nickel alloys used in nuclear reactors. The sample, autoclaved in aqueous solution at high pressure and temperature, is subjected to tensile strain by a steady downward motion (about 10^{-6} cm/sec) of the lower cross beam. Figure 1

part from their resistance to hydrogen discharge.

On transition metals the rate-determining step may be either slow discharge or electrochemical desorption. Generally, rate constants for hydrogen evolution are higher (10^{-8}–10^{-5} A/cm^2) on transition metals, which are therefore less well able to resist active corrosion in acid solutions. When electrochemical desorption is rate-determining, the concentration of adsorbed protons is relatively high and protons may be transferred into the metal, causing hydrogen embrittlement. Sulfides exacerbate this tendency to adsorb hydrogen, and the sulfide-containing environments found in oil wells therefore are often very detrimental to the steels used.

The reduction of oxygen is much more complicated than is hydrogen evolution, and the detailed mechanisms are still obscure. Reduction rate constants are almost invariably low, but the thermodynamic driving force for reduction is usually large, so that the reduction is fast. For iron corroding in water the corrosion rate is determined by the rate of transport of oxygen to the surface, each molecule being reduced rapidly because of the large overpotential. For typical conditions corrosion rates of 0.1 cm/yr can be anticipated.

The metal–solution double layer

Any potential difference at the metal–solution interface is distributed across a double layer of charge, comprising a Helmholtz layer (the first atomic layer in the solution) and the diffuse layer (with its characteristic Debye length). In principle, there are several roles the double layer might play in corrosion phenomena at bare surfaces:

- The fraction of any applied potential influencing charge-transfer reactions depends on the potential distribution in the double layer.
- The solution composition near the surface depends on the magnitude of the metal–solution potential and on its relationship to the potential at which the metal is uncharged (the point of zero charge).
- The adsorption of neutral organic substances from solution is known to be greatest at the point of zero charge, so that possible inhibition of corrosion by such substances will be greatest near this potential. Despite these possibilities, there is little evidence in practice for any special effects of the double layer on corrosion phenomena.

When an alloy dissolves actively, considerable complexity can be expected because the components will differ both in their thermodynamic tendencies to dissolve and in their rate constants for dissolution. As a result, there may be surface enrichment of one or more of the components. Such surface enrichment does occur in practice, for instance in the "dezincification" of brass; it can leave a porous, non-protective layer of the less reactive metal, which can grow to thicknesses of several millimeters. Two mechanisms can lead to the development of such layers:

- Both components can dissolve, with redeposition of the less reactive.
- When the rate of dissolution of the less reactive metal is extremely low, the porous layer can form by a mechanism, discovered by Howard Pickering and Carl Wagner,[2] that involves volume diffusion of divacancies.

In this mechanism the more reactive metal is rapidly dissolved from kink sites, leaving a surface with no reactive metal ions in position to be dissolved. Dissolution can only continue if the driving force present is high enough to remove reactive ions directly from completed atomic layers, in which case vacancies are left behind. These vacancies join to form divacancies, which are believed to be sufficiently mobile to migrate into the solid even at low temperatures, transporting the more reactive metal to the surface. A rugged interface, and eventually a porous layer of the less reactive metal, forms at the boundary.

Although most engineering metals are alloys, our understanding of alloying effects on dissolution appears to be very meager and inadequate. Studies with new surface analytical techniques should prove rewarding.

Product-covered surfaces

Useful metals are covered with a film in their normal state. The corrosion rates of film-covered metals may be smaller by as much as nine or ten orders of magnitude than those of the corresponding active metals under similar exposure conditions. Metals exhibiting such low corrosion rates are said to be "passive." Vlasta Brusić[3] has recently reviewed the literature on passivation. Not all reaction products convey inert behavior. During electropolishing, for example, metal surfaces are covered with highly soluble reaction products, which allow corrosion at rates as high as several amperes per square centimeter. Much remains to be learned about the formation, compositions, structures, chemical and mechanical properties, and ion-transport characteristics of reaction products.

An old and simple example—the electrochemical polarization of iron in sulfuric acid—will serve to introduce some of the fascinating phenomena that occur at film-covered electrodes. When pure iron is exposed in sulfuric acid, ferrous ions enter the solution and protons are reduced to hydrogen, the rates balancing at the corrosion potential. Upon positive polarization the dissolution rate increases, reaching values of 0.1 to 1.0 A/cm^2. At about those dissolution rates the solubility product of ferrous sulfate is reached near the surface, and crystals of that compound nucleate and spread over the surface. Despite the saturation in the solution near the surface, the sulfate layer remains porous and allows the reaction to proceed.

Continued polarization to about +0.6 V relative to a standard hydrogen electrode in the solution results in the sudden replacement (within milliseconds) of the sulfate layer with an oxide layer. The growth of oxide is accompanied by a decrease of reaction rate by a factor of 10^6, and the metal becomes passive, as figure 2 indicates. Further polarization does not change the steady corrosion rate but does thicken the film slightly. Whereas the sulfate layer might have been thicker than 10^{-4} cm, the thickness of the passive film is less than 10^{-6} cm. Polarization at very high positive potentials results in oxygen evolution and an increase in the rate of dissolution of the metal; this so-called "transpassive" corrosion is not well understood.

Figure 2 also shows current–potential curves for stainless steel and its constituents, all of which exhibit spectacular changes in activity. Such active–passive transitions are not easily observed with such metals as aluminum, tantalum, zirconium and titanium, which are nearly always passive, and it is less spectacular with copper-base alloys. The data in this figure show that nickel behaves like iron, while chromium is more easily passivated.

The addition of nickel to the iron–chromium alloy to form an austenitic stainless steel has a remarkable effect in lowering the maximum active corrosion rate, thereby facilitating passivation, as shown in figure 2. There is no satisfactory explanation of the mechanism by which nickel is able to promote passivation of the iron–chromium–nickel alloys. Iron–nickel binary allows behave roughly like iron and nickel, neither of which are especially easy to passivate. Addition of molybdenum to Fe–Cr–Ni alloys further facilitates passivation, again for obscure reasons. Nickel and especially molybdenum are found by Auger spectroscopy to be depleted in the film, so they do not facilitate passivity by forming films containing nickel or molybdenum oxides. Chromium, by contrast, is relatively concentrated in the reaction product. The explanations for the superior performance of nickel- and molybdenum-containing Fe–Cr alloys and for the fact that at least 10% chromium is needed to cause a significant improvement in binary iron–chromium alloys are presumably to be found in the detailed structures of the films and the kinetics of their formation.

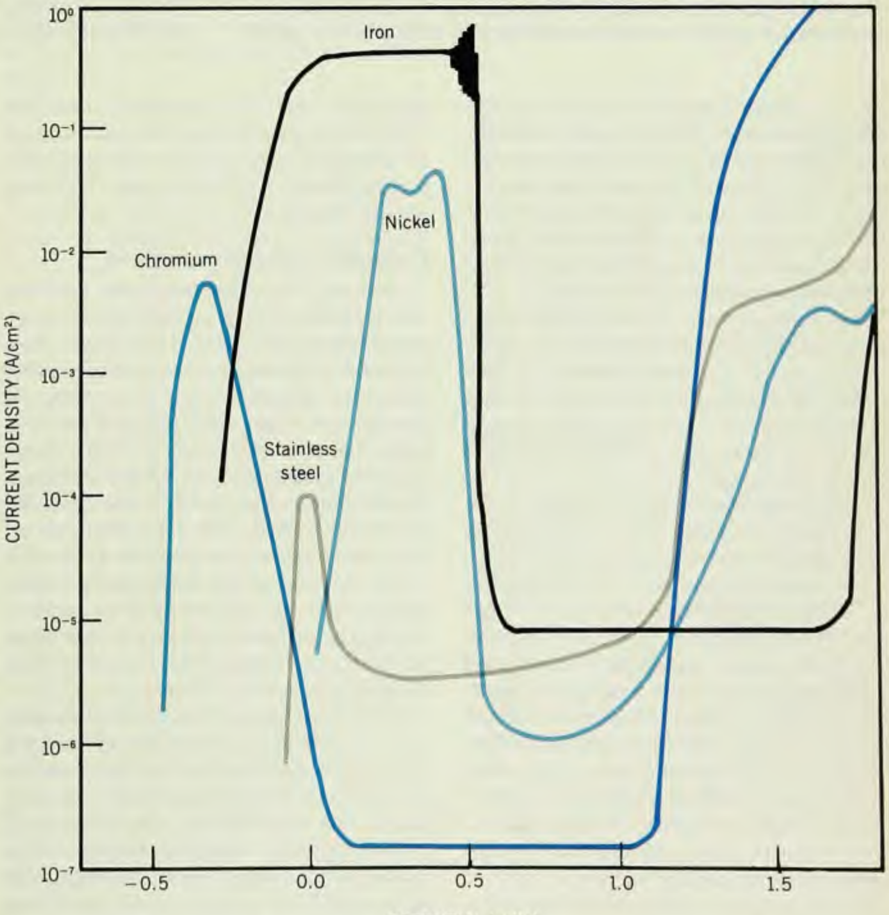
Characteristics of reaction products

The layers of highly protective products formed on many metals range in thickness from a few molecular layers to about 10^{-6} cm, as determined by optical and electrochemical measurements and from dielectric properties. Figure 3 shows two transmission electron micrographs of reaction-product films grown on stainless steel under different conditions.

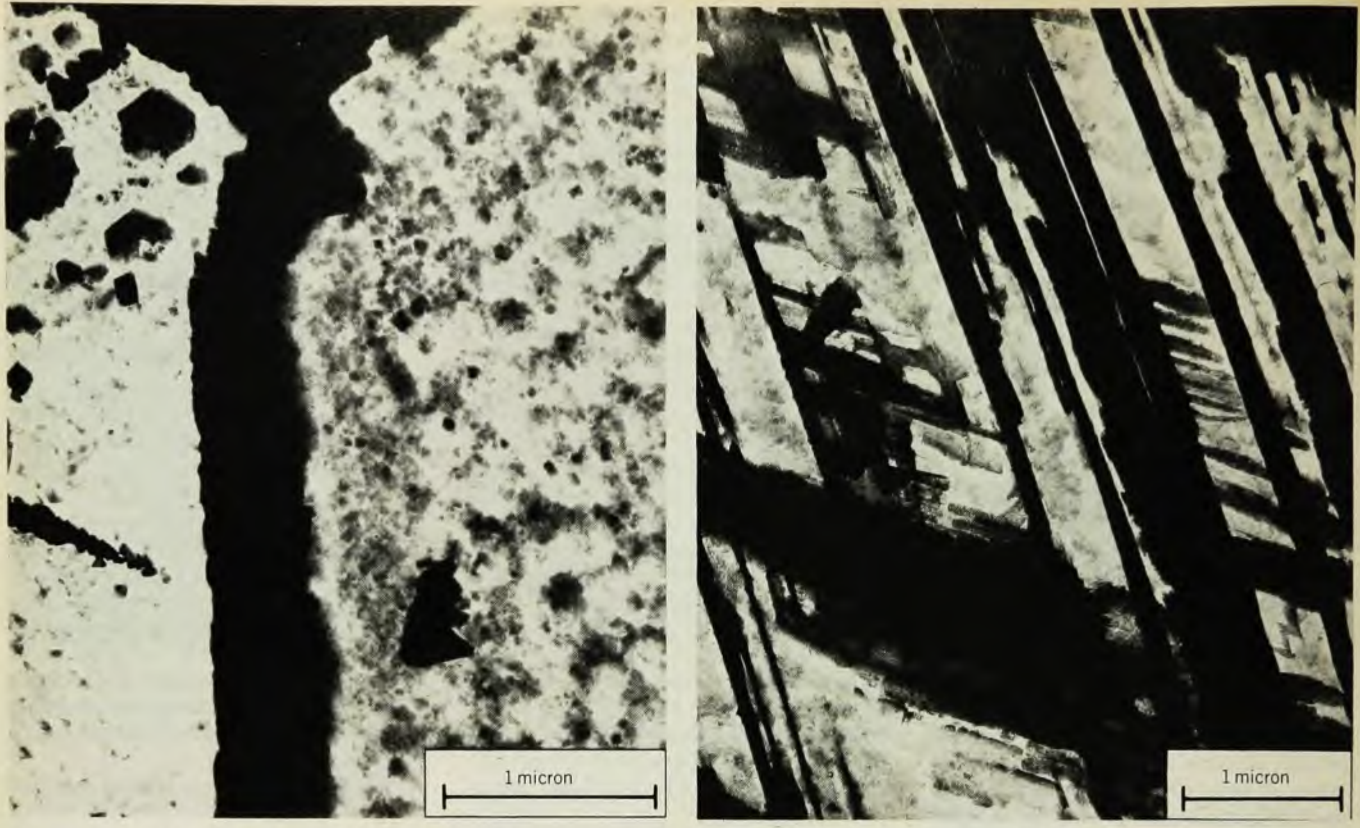
Films formed on iron and zirconium have been reported to be crystalline, while films formed on aluminum, tantalum and titanium are usually amorphous. Probably both amorphous and crystalline products can be formed on most metals. There is evidence for hydroxyl groups and water in the films, and it is widely accepted that the films may be partially hydrated oxides or even solid gelatinous substances. Thicker anodic films formed on aluminum and tantalum are known to contain components of the solution in which they are grown, phosphates and borates being readily incorporated. There is little evidence about such incorporation in films less than 10^{-6} cm thick, although Go Okamoto has reported the presence of sulfate in passive films on stainless steels.

The mechanical properties of these reaction products are sometimes very different from those of corresponding bulk phases. For example, films formed on tantalum are remarkably ductile, plastic strains greater than 0.1 having been observed. Studies of very thin films on several metals have shown that plasticities are quite variable, ranging from very low for a film on an alloy of 80% Ni and 20% Cr to large for tantalum oxide. Passive films formed on iron–chromium–nickel alloys exhibit appreciably different plasticities, large values being found near the iron end and lower values near nickel.

The elastic properties of the reaction



Passivation in four metals. The product of the reaction between metal and solution forms a film that sharply reduces the current density. As the metal potential (relative to a standard hydrogen electrode in the solution) is made more positive, the film thickens. With further polarization, oxygen is evolved and the metal again dissolves rapidly. Figure 2



Reaction products formed on type-304 stainless steel during a 48-hour exposure to pure water at 289°C. The specimen on the left had been heat treated to precipitate chromium-rich carbides at the grain boundaries. That on the right had been cold worked; it shows thick films on martensite platelets. These transmission electron micrographs show the films after the metal was dissolved away. Figure 3

product formed anodically on aluminum are also peculiar. For example, the elastic modulus of such films decreases reversibly by a factor of ten from the value for sapphire as the humidity increases from vacuum to moist air. Furthermore, stress relaxation occurs in aluminum-oxide films when strong electric fields (about 10^6–10^7 V/cm) are applied. Fields of this magnitude are normally present in thin films and may play a role in plasticity. Evidently the mechanical properties of thin reaction-product films are quite unusual, but our understanding of these phenomena is very meager.

The characterization of reaction products should develop rapidly during the next decade as new surface analytical techniques are applied. Optical studies in which the reflection of polarized light is used (ellipsometry) have already contributed much new knowledge, and techniques for studies in times of milliseconds have been developed. Such studies permit determinations of film thickness and of optical constants, which provide clues to film composition, properties and structure. Reflection-infrared-spectroscopy studies are contributing new understanding, especially of organic inhibitors but also of film compositions. Measurements of electrical impedance continue to provide information on electrical characteristics of products. Surface analytical techniques such as Auger spectroscopy and electron spectroscopy for chemical analysis (ESCA) permit accurate determinations of compositions of very thin surface layers, promising a better understanding of film chemistry.

Formation of reaction products

Layers of reaction products, whether salt or oxides, form on bare surfaces by nucleation and spreading, and then thicken. The nucleation and spreading processes appear always to be fast, although not many detailed studies have been conducted on oxide growth. As an example of the speed of oxide formation, figure 4 shows the current–time behavior observed during the formation of an iron-oxide film in a sodium-hydroxide solution on a bare surface created by the rapid straining of a wire. The repassivation process is complete in a time equal to the time required to form the bare surface, which is 10^{-3} sec.

Once the surface is completely covered the new product can thicken either by a high-field ion-conduction process or, when the initial product is not the most stable one possible, by dissolution and reprecipitation. Many examples of the latter process, which is very common, are discussed in reference 1. A surprising feature of dissolution and precipitation phenomena is that the product formed never seems to become completely nonporous, so that it is primarily the inner, less stable film and its properties that determines the behavior of the metal.

High-field ion conduction obeys a law of the type

$$i = A \exp\left(\frac{\alpha E}{RT}\right) \qquad (2)$$

in which E is the electric field and A and α are constants for a particular temperature and metal. The high-field ion-conduction process has several remarkable features, which have been studied thoroughly in anodic oxides[4]:

- Current transients of several orders of magnitude take place during periods of seconds to minutes following potential changes.
- The steady-state value of α, which has dimensions of charge × distance, is too large to correspond to a simple single-ion process. On the other hand, the value of α calculated from transient measurements is about the right size for a single-ion process (about 1 electron charge × 1 Å = 1.6×10^{-27} coulomb meters), but it is a function of temperature, formation rate and film history.
- It is quite certain that the anion and the cation are about equally mobile in the films over the accessible ranges of temperature and electric field. Some process involving simultaneous motion of at least two oppositely charged ions appears likely to be involved in the conduction mechanism, but the details are obscure.
- The resistance to reduction already mentioned may have its source in the

growth mechanism. It has been suggested that the initial film is quite hydrous and that protons are removed by high-field conduction as the field grows. The shrinkage that would accompany such a process could account for the tensile stresses, which are normal in such films in the as-grown condition. Such dehydration could also make reduction difficult, for the local arrangements that accompany dehydration and the change of bonding from metal–hydroxide ion–metal to metal–oxide ion–metal could impede the reversal of the process.

Corrosion of film-covered metals

The rates of corrosion at metals covered with reaction products usually are in the range of 10^{-5} to 10^{-8} A/cm^2. The rate is almost invariably controlled by the rate of dissolution of the reaction product, and only rarely by the rate of removal of electrons. Very little is known about the mechanisms by which electrons are removed.

The mechanisms and rates of dissolution of ionic compounds are of great importance to the control of corrosion, and much remains to be learned. There is a general correlation between good corrosion resistance of the metal and the sluggish dissolution of its oxide. It is known that the corrosion rates depend sensitively on subtle chemical effects; for example, the oxides of the divalent cations MgO, ZnO, CuO and NiO, all with similar structures, binding energies and solubilities in water have dissolution rates in acid solutions that inexplicably vary over many orders of magnitude.

It is also known that oxides such as Al_2O_3, Fe_2O_3, Cr_2O_3, TiO_2, ZrO_2 and Ta_2O_5 are extraordinarily difficult to dissolve in most acids despite very large thermodynamic driving forces. For anodic Al_2O_3 films the dissolution rate is surprisingly independent of pH in the range of 1–10, and a rate-determining surface-hydrolysis step has been postulated.[5] While the study of oxide dissolution has been resumed after years of neglect, the effort is still very small. The subject has been reviewed recently,[6] but there is no theoretical understanding of the orders of magnitude of the fundamental rate constants for the reactions.

The inhibition of dissolution of ionic compounds is another area of interest. Studies of the dissolution of Al_2O_3 and MgO have shown that certain inorganic ions can slow the dissolution substantially—some by more than a factor of 100. The effective substances had nearly the same ratio of the charge to ionic radius as the oxide studied, and they had proton affinities similar to that of the substrate.[7] The bonding of such ions evidently follows crystal-chemical structural rules and is at least partially hydrogen bonding. Surface-active agents containing an effective inorganic group and an aliphatic hydrocarbon (for example, lauryl acid phosphate) were especially effective.

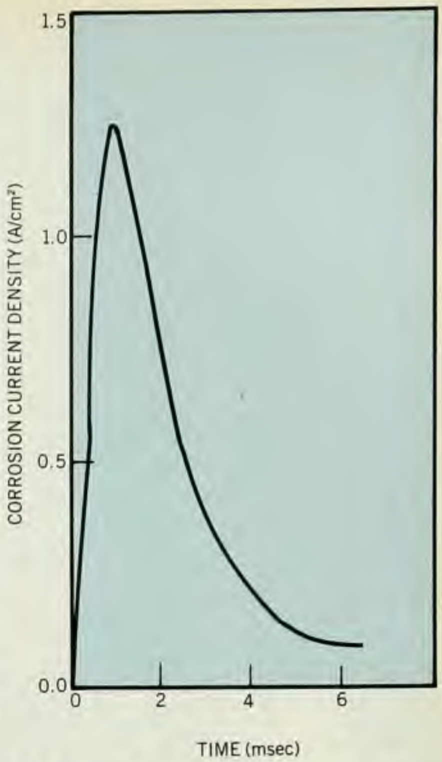
There is also a major need for information about the dissolution of films formed during electropolishing. The dissolution of metals covered with continuous films always results in a smoothing of the surface, but the surface-removal rate must be high to make the technique practical. Electropolishing solutions form products on the metal surface that produce the desired smoothing action while the metal dissolves at rates up to several amperes per square centimeter. Almost nothing is known about such films—their structure, composition and thickness remain mysterious. Similar films are probably also formed during some types of pitting and stress–corrosion cracking, and hence their study is important in corrosion research as well as in electropolishing technology.

Corrosion inhibition

The addition of substances to the environment to mitigate corrosion is one of the most important practical means of corrosion control. The subject is extraordinarily complex, involving both inorganic and organic substances and many different mechanisms that act on either the ion-removal or electron-removal process. Much is understood, but much still remains unexplained about inhibition; a review[1] and a recent book[8] contain further information on the subject.

The way that most *inorganic inhibitors* reduce the corrosion rate is probably by assisting film formation. One of the simplest functions of an inhibitor is buffering; the prevention of acid conditions can greatly facilitate film formation. Such materials as phosphates, silicates, borates and chromates probably participate directly in the film-formation process; chromium is known to be introduced into reaction-product films from dissolved chromate. Some soluble cations, such as Zn^{+2} and Mg^{+2}, precipitate at high-pH regions near the cathode, reducing the reaction rate there. The addition of inorganic substances can be extremely effective, reducing the corrosion rate by factors of 10^2 to 10^3 by keeping the reaction-product layer in good repair.

Organic substances may also inhibit corrosion, either by assisting the formation of reaction products (sometimes by being incorporated into the product) or by adsorbing at the surface. The list of effective organic substances is long—most substances have some effect. Action is greater: for larger than for smaller molecules; for aromatic than for aliphatic compounds; for molecules containing double bonds; for molecules containing sulfur or nitrogen groups, and for certain organic ions and molecules. Sophisticated analytical tools such as nuclear magnetic resonance and reflection infrared spectroscopy are being used to study the states of adsorbed substances, and good progress is being made.



The speed of passivation is illustrated by this graph of the transient accompanying the formation of an iron-oxide film. In this experiment, by Ronald Diegle, an iron wire was rapidly strained (to expose the bare surface) in a sodium-hydroxide solution. Figure 4

Inhibition by adsorption alone is much less effective than that by film formation; a typical adsorption layer may reduce the corrosion rate ten times, a factor of 100 being very exceptional. Because the binding energies of adsorbed substances to metal surfaces in aqueous solutions are only modest, the coverage is neither very complete nor very stable, and fluctuations that temporarily bare the surface allow continued corrosion at moderate rates.

Localized attack

The great reduction of the corrosion rate resulting from passivity makes it possible for the metal to be exposed at a potential far above its reversible potential—that is, at a much more aggressive potential in a thermodynamic sense. If a small region of the surface becomes bare under such conditions, the corrosion rate can be very high, although it is usually limited to 1–10 A/cm^2 by transport processes; this corresponds to metal-removal rates of 10^{-4} to 10^{-3} cm/sec. Passivity thus makes metals useful by preventing a rapid general attack, but sets the stage for localized destruction.

Even though a large local current density may exist at the attacked site, the total current at the site may be small because of its small area. The removal of the electrons corresponding to the localized ion removal can take place on the relatively enormous area still passive, and

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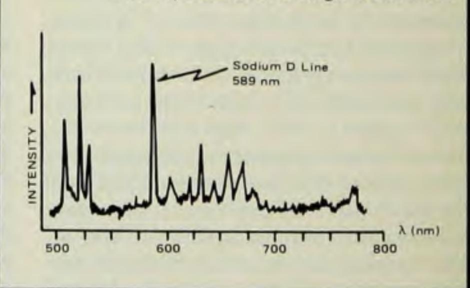
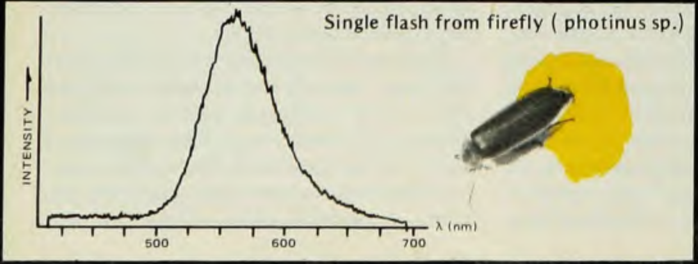


Single flash from firefly (photinus sp.)



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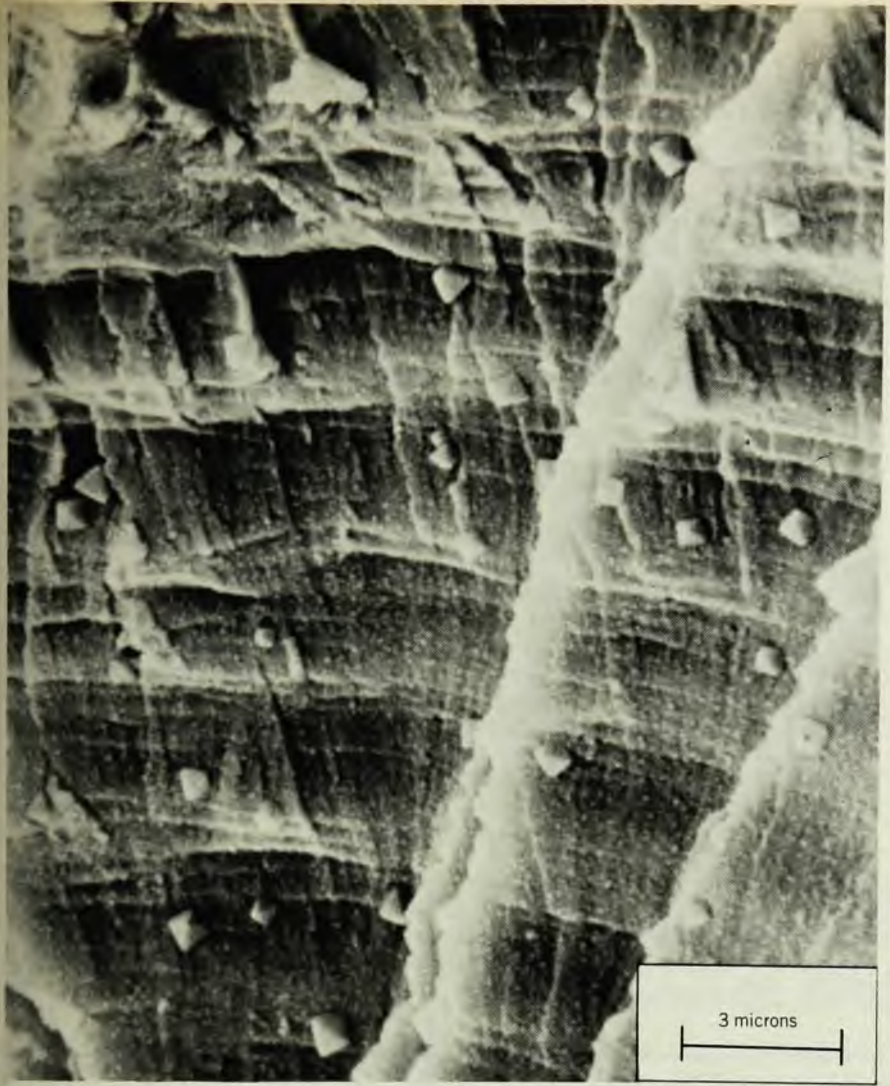

A scanning electron micrograph of the fracture surface of a specimen that failed by stress–corrosion cracking. The sample, of type 304 stainless steel, was subjected to a straining electrode test at 289° C in a sulfuric-acid solution of pH 2.5. The crack progressed from bottom to top in the photo; the horizontal striations are interpreted as positions at which the crack front halted momentarily in its motion. The photograph is therefore believed to support the film-rupture mechanism described in the text. The small polygonal particles are deposits of iron oxide that formed after the development of the crack. Figure 5

hence little change of the corrosion potential may occur. Pitting, intergranular attack and stress–corrosion cracking provide examples of such localized attack on passive metals. The phenomena are complicated; they are the subject of a recent book,[9] to which the reader is referred for details and literature.

The usual pit observed on working metal objects is a roughly hemispherical cavity covered with a complicated tubercle of corrosion product. In the laboratory, pits can readily be produced on most metals by anodic polarization in a medium containing one or more special ions to which the metal is sensitive. The pits produced in this way may or may not be covered. Solutions containing halides and sulfides are especially aggressive. Sulfate, perchlorate and carbonate ions sometimes cause pitting, while phosphate, chromate, nitrate and borate ions do not cause pitting—they may even protect against pitting in the presence of aggressive ions.

There is a general correlation with ionic properties: The larger ions with low ratios of charge to radius are aggressive; they can escape more readily from their hydration cages and interact with the metal surface. Larger ions that contain oxygen surrounding a very highly charged small cation (SO_4^{-2}, ClO_4^-, CO_3^{-2}) are in an intermediate category. Ions that may themselves form insoluble reaction-product films (phosphate, borate, chromate) are protective.

The variable that determines whether pitting of a given metal will occur in an aggressive medium is the potential. Pitting is always found to occur above some potential and can be prevented at more negative potentials; the behavior at intermediate potentials is complicated with dependences on surface preparation, time, potential history and fluid motion in the environment. The threshold potential for pitting is generally proportional to the logarithm of the concentration of aggressive ions in the medium.

What is the mechanism responsible for pitting? There is general agreement that the aggressive ion becomes concentrated in the flow-restricted region of the pit by mass-transport processes. Fluid flow may be restricted by reaction products that cover the mouth of the pit, by hydrogen bubbles in the pit or by the bypassing of certain regions of the metal, the attack proceeding underneath the surface. Very large potential differences, of the order of a volt, have been measured between the solutions outside and inside a growing pit. Such large potential differences are capable of causing very large changes in the activities of the ionic species and the water within the pit. The medium of the pit therefore may be very different from that outside so that passivation does not occur in the pit solution.

There is no consensus about the mechanism of aggressive action. One theory holds that the aggressive ions adsorb onto the metal within the pit and prevent passivation. Another theory proposes that the surfaces of the pit are covered with a highly defective metal-salt film, which forms above the potential at which the defective phase and the normal oxide have the same free energy of formation. Still another possibility is that the pit solution has been so modified that metal salt is formed in preference to the normal passive oxide. There is good evidence for all of these theories—at least for the occurrence of both bare and filmed pit surfaces.

The question of pit initiation is also controversial. Some authors have given evidence for initiation at film defects such as inclusions, fractures or differences in the character of the film formed over dislocations or crystalline defects; others postulate a penetration of the passive film by the aggressive ion. It is likely that pits do form at inclusions, but it is hard to discount the possibility of film penetration. The passive films have structures and properties different from those of bulk crystalline solids, and ion transport through them may occur even though the same ion might be unable to enter a bulk crystal of the same oxide.

Studies in this area that would be fruitful include determinations of the characteristics (structure, composition, dissolution rates) of films formed inside pits; measurements of the penetration of ions through passive films; detailed investigations of the effect of ion concentration on the pitting potential, and determinations of the thermodynamic parameters of very concentrated ionic solutions.

The grain boundaries of alloys are favored places for segregation of various kinds—thermodynamically driven differences in the binding of elements at structural defects; segregation caused by kinetic effects such as vacancy flows, and gross differences caused by the precipitation of second phases. There is clear evidence for an effect on corrosion only in the case of precipitation of a second phase.

A famous and particularly troublesome example is the intergranular attack on alloys of iron, chromium and nickel following the precipitation of chromium-rich carbides at the grain boundaries. Such precipitation depletes the region of the chromium near the grain boundary, lowering the local resistance to corrosion and allowing attack. The photo on the left of figure 3 depicts a reaction product formed on an alloy that had been treated in this way. This example of intergranular attack is reasonably well understood—to the point where alloys resistant to the attack can be designed on the basis of thermodynamics.

While we have no thorough understanding of the mechanisms of attack when precipitation does not occur, we know many examples of such attack. For example, again in the Fe–Cr–Ni system, we know that phosphorus and silicon in solid solution cause intergranular attack on solution-annealed materials exposed under strongly oxidizing conditions. The extent of any possible grain-boundary segregation and the mechanism of the attack are still not known. Enough is now known about nonequilibrium segregation to make predictions possible. Studies of corrosion at grain boundaries in alloys selected to show such segregation as well as pronounced corrosion differences should be very illuminating.

Stress–corrosion cracking

Of all the forms of localized attack, stress–corrosion cracking is by far the most serious and difficult to cope with. Here the applied static or dynamic stresses on the metal and its corrosive environment conspire to cause rapid failure, even though either condition alone would cause only negligible damage. There are at least two major fundamental ways in which such failures can occur. One of these involves a chemical change in the metal that facilitates mechanical fracture; hydrogen embrittlement resulting from the introduction of hydrogen into the metal is an example. Hydrogen-assisted cracking is very important and also very complicated, but does not involve corrosion in the crack advance, which is a mechanical step. I have chosen not to consider this type of stress–corrosion cracking and to confine this discussion to a mechanism involving corrosion in the fundamental cracking step.

This mechanism is one involving repeated rupture of the protective reaction product by plastic strain at the crack tip; it is often referred to as a "film-rupture mechanism," and it is thought to occur as follows: Suppose that the crack is growing and that the creep strain induced by mechanical forces has just caused the oxide film to rupture at the crack tip. The film rupture exposes fresh metal, which corrodes rapidly for a short time (10^{-3}–10^{-1} sec), after which repassivation occurs. The corrosion has moved the crack forward a small distance (10^{-7}–10^{-5} cm); consequently the material ahead of the new crack tip is exposed to higher stresses and begins to strain faster. The strain eventually becomes large enough to exceed the fracture strain of the reaction product, which ruptures again to begin the cycle anew. The scanning electron micrograph of a surface that failed by stress-corrosion cracking shown in figure 5 is believed to support the hypothesis of the film-rupture mechanism. The striations visible in the photo are thought to represent periodic interruptions in the crack's motion.

The strain per film-rupture event depends strongly on both the slope of the strain–distance relationship ahead of the crack (a function of the nature of the material and the applied stress intensity) and on the distance the crack moves each time the reaction product is ruptured. Both factors are empirically known to be important in controlling the rate of crack propagation. For example, there is a minimum stress intensity for crack propagation under certain conditions, the critical value depending on the metallurgical condition of the metal and on the exposure conditions. Changes in the metallurgical condition can affect both the response of the metal to stress and the corrosion behavior; changes in exposure conditions modify the extent of corrosion per film-rupture event. The effect of increased stress intensity often brings about a striking acceleration of the cracking rate.

The observations currently available support the general features of the film-rupture mechanism for many metals and exposure conditions. It it not possible, however, to make quantitative predictions of the effects of changes in such variables as stress intensity, metallurgical condition, applied potential or solution composition. The reasons such predictions can not be made are clear: The rate of crack propagation is very sensitive to the exact values of such factors as the strain–distance relation ahead of the crack tip, the transient strain response following stress changes, the fracture strain of the reaction product and the extent and velocity of corrosion following film rupture. Our knowledge of most of these factors is still too vague to permit an accurate prediction of the crack-propagation rate, although plausibility arguments can be made.

An alternative way of considering stress–corrosion cracking by the film-rupture process has been developed recently.[10] This new method, based on two fundamental conditions required to produce a crack, leads to the following two

Possibilities for research in corrosion physics

Research is needed in three areas—the nature of reaction products, stress–corrosion-cracking theory and pitting—which are not only of great importance but in which rapid progress may be possible because of recent advances either in understanding or in experimental techniques. Since several new techniques await application, the prospects for improving our general understanding of reaction products in corrosion are great. Stress–corrosion cracking and pitting are such important technological problems that progress either towards better theoretical understanding or towards means for control could make a tremendous impact on the uses we make of materials. Specific suggestions in these areas are:

The nature of reaction products

- Study the detailed structure and composition of products, and the roles of metal and solution compositions in controlling corrosion characteristics.
- Develop understanding of the circumstances in which substances from the solution are incorporated into the film and how these influence the properties of the film.
- Study the nature of electropolishing films.
- Investigate film plasticity.
- Study oxide and hydroxide dissolution and its inhibition.

Stress–corrosion cracking

- Obtain experimental verification of the theoretical conditions for stress–corrosion cracking to be possible: that films not be plastic, that strain in the metal be concentrated and that the crack-tip ratio of corrosion rate to strain rate exceed 2×10^{-7} cm.
- Develop understanding of the rapid variation of the stress-corrosion-cracking rate with stress intensity.
- Study the factors that influence susceptibility: the strain–distance relationship ahead of growing cracks, the transient creep rate, the fracture of corrosion products and the repassivation rate after film rupture.

Pitting

- Study ion migration through passive films.
- Investigate the nature of very concentrated aqueous solutions.
- Determine the nature and properties of films formed in pits.

Readers interested in further information about current research activities will find summaries of the programs of corrosion-research centers in the journal *Corrosion*, starting in the January 1973 issue (volume 29, number 1).

predictions of the characteristics necessary to permit stress–corrosion cracking: The mechanism must produce a crack that grows deeper more rapidly than it widens (otherwise the crack will become a pit or a groove), and each increment of crack advance following a film rupture must generate enough strain to cause a second film rupture.

A formulation based on these concepts has led to three important conclusions:

- Stress–corrosion cracking is not possible if the film is plastically ductile, for a thinning of the film at the crack tip results in insufficient crack advance.
- The strain must be localized on a small fraction of the crack-tip surface to concentrate the advance in the region just ahead of the existing crack. Such strain concentration can occur if the mode of deformation is planar glide, or it can result from deformation near grain boundaries.
- The ratio, at the crack tip, of corrosion rate to strain rate must exceed a critical value of 2×10^{-7} cm for this type of cracking to occur.

All of these characteristics can be determined quickly by experiments not involving stress–corrosion cracking.

Progress is rapid, not only in these studies but in the entire field of corrosion physics; we can reasonably expect that the next decade will produce significant advances in our knowledge of corrosion and the techniques for its inhibition.

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This article is an adaptation of a paper presented 3 February 1976 at the annual joint meeting of The American Physical Society and the American Association of Physics Teachers in New York City.

The kindness of Go Okamoto and Pergamon Press is permitting the use of figure 2 is gratefully acknowledged.

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