

## CORROSION AND THE FAILURE OF METALS

By

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Corrosion is one of the greatest single factors in the failure of metals; no broad discussion of this topic could possibly be complete without reference to corrosion phenomena. The mechanical failures encountered in practice can often be ascribed to causes such as the faulty design of components, or the unreasonable stressing of parts, or the use of wrong or impure materials or of those which have received faulty metallurgical treatment, or to the incorrect operation of machinery or equipment; the metal may well be less to blame than the man who manufactures it or uses it. But a tendency towards corrosion, on the other hand, is an inherent characteristic of many metals, including those most widely in use, and often contributes indirectly to, or intensifies, the other forms of failure to which metals are susceptible. No excuse is needed, therefore, for introducing a review of the subject into this Symposium.

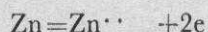
We all know how greatly corrosion affects some metals; we have positive evidence before our eyes every day. Nor is the reason hard to seek. Relatively few metals are found uncombined in nature; many of them are too reactive chemically for this to be possible. The existence in the free state is abnormal, and they tend continually to revert back to the combined condition. The resemblance between the corrosion products of certain metals and their ores has often been remarked upon. Corrosion, in fact, undoes all the work of mining and metallurgical production, and has been aptly described as "a major industry in reverse."

### THEORETICAL ASPECTS OF CORROSION

The processes involved in corrosion, although accelerated by heat, are capable of proceeding in the cold, and are able to bring about, a roundabout route, many chemical changes which could otherwise only occur at high temperatures. The rusting of iron, as we all know, occurs without warming; but the direct oxidation of iron takes place only at red heat. A chemical interaction, such as the latter, is not, of course, to be regarded as a corrosive process; the term corrosion is restricted to indirect reactions which lead to the destruction of metal.

The particular type of reactivity which permits corrosion to occur is essentially electrochemical in nature, and the basic analogy in corrosive processes is the short-circuited electrical cell. This may be exemplified by a system consisting of a piece of copper and a piece of zinc, both partially immersed in a solution of salt, and connected externally by copper wire. A potential difference will be found to exist between the zinc and the copper, and a current will flow through the connecting wire in one direction and through the electrolyte in the opposite sense. The potential difference between the zinc and the copper originates at the dry metallic junction between them, and depends on the relative "work functions" of the two metals; that is, the energy that has to be expended in removing an electron from an atom of either of them. The difference is such that copper tends to withdraw electrons from zinc, and this withdrawal will continue until a potential difference has been produced of such magnitude that the transference of further electrons is prevented. Electrons thus flow in the direction indicated by the arrow in Figure 1. Copper becomes the cathode in this system, and zinc the anode.

In the electrolyte, positively charged sodium ions will migrate towards the cathode. At the same time zinc atoms are deprived of electrons and pass from the anode into the solution in the form of ions.



The final result is a high concentration of zinc and chlorine ions around the positive electrode.

Alkali is produced at the cathode by the absorption of electrons, as shown in the equation :—

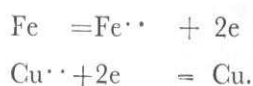
$$\text{O} + \text{H}_2\text{O} + 2e = 2(\text{OH})'$$

There are several highly important points to be noted ; the first is that the initial e.m.f. arises from the relative electron-absorbing tendencies of the metals concerned ; the second is that when dissimilar metals are in contact in the presence of an electrolyte the less noble is attacked; the third is that the presence of oxygen is necessary for the reaction to proceed at all (this can be quite easily demonstrated experimentally); and fourthly, that the amount of corrosion that occurs is directly proportional to the amount of current ("Corrosion current") which flows.

Although in the example just given *two* dissimilar pieces of metal in electrical connection with each other were the ultimate source of the potential difference, it should not be supposed that corrosion currents can arise only in this way. Any circumstance, either internal or external to the metal, which leads to a potential difference between one part of it and another part can equally well initiate the flow of a corrosion current should a conducting solution be present. The pre-requisite for corrosion is that differences between the availability of electrons at various points in the metal should arise from one cause or another.

The existence of cathodic and anodic areas on the surface of a single piece of metal can easily be demonstrated. If a copper plate, preferably sand-blasted or roughened with sand-paper, is carefully immersed in a neutral solution of salt containing a little phenolphthalein and left undisturbed, an alkaline reaction will be seen to occur almost immediately at several points on the surface of the copper. The effect can be shown still better if a piece of clean iron plate is placed in a flat dish and a hot solution of agar-agar containing sodium chloride, phenolphthalein, and a little potassium ferricyanide poured over it. A few hours later, when the agar-agar has set, cathodic areas will be revealed by a pink colour whereas the ferrous ions liberated at anodic areas will react with the ferricyanide to produce a blue colour. The mixture of salt, ferricyanide and phenolphthalein is known as the "ferroxyl indicator" and is of great use in this type of work.

Another possible type of corrosion-mechanism is the displacement of one metal from a solution of its salts by a baser metal. Thus metallic iron placed in a solution of copper sulphate will pass into solution whilst copper is deposited. In electrochemical terms, the iron is attacked anodically whilst the copper undergoes cathodic deposition:—



In the case of two metals whose normal potentials (that is, the potential of the half-cell formed by a metal in contact with a solution of its ions at normal activity) are not widely different, either metal will continue to displace the other until such time as an equilibrium is reached in which the potentials of both metals, each with respect to its own ions in the solution, are the same. This reaction does *not* require the participation of oxygen.

Similarly, when a metal is immersed in an acid solution, hydrogen is displaced and the metal passes into solution in equivalent amount until a concentration of its ions is attained such that its potential with respect to those ions is equal to that of hydrogen with respect to the hydrogen ions present. In the case of metals such as silver or copper this equilibrium is reached after an infinitesimally minute evolution of hydrogen; and these metals are not corroded by non-oxidising acids in the absence of oxygen or oxidising agents. On the other hand, for a base metal such as zinc the concentration of hydrogen required to achieve the equilibrium potential is greatly in excess of the amount which can be held in solution, so that hydrogen is evolved continuously and equilibrium cannot possibly be reached.

In practice over-voltage effects, the theory of which need not be discussed in a review of this sort, lead to the result that a potential in excess of the theoretical is required before hydrogen is actually liberated as a gas from metal electrodes. In the absence of oxidising agents this phenomenon results in a reduction in the amount of attack that might otherwise take place. Pure zinc,

for example, though theoretically more reactive than iron, liberates hydrogen from acids far more slowly. Gold, which has a low over-potential, greatly increases the corrosion of zinc when alloyed with that metal, whereas the much less noble cadmium, whose over-potential is high, increases the amount of attack upon zinc only to an almost negligible extent.

Where an oxidising acid is involved, the reaction which ensues depends on factors such as the nature of the metal and the concentration of the acid; thus a metal which will liberate hydrogen from non-oxidising acids may, when attacked by an oxidising acid, liberate hydrogen either free or in the combined state (as for example, in the form of ammonia, hydroxylamine, etc.) according to circumstances. But in the case of the noble metals (which are not able to liberate hydrogen directly from non-oxidising acids) the only possible cathodic reaction is the reduction of the acid.

The presence of an oxidising agent greatly assists in the attack of non-oxidising acids like hydrochloric acid upon metals, since the hydrogen produced is thus consumed immediately it is formed and no stable equilibrium can result; and there can be, moreover, no over-voltage effect. Thus nickel is much more readily attacked by hydrochloric acid in the presence of hydrogen peroxide than it is by hydrochloric acid alone.

The presence of impurities in the metal exercises an influence upon corrosion which varies with the nature of the attacking reagent. As indicated elsewhere in this paper, segregated impurities in a metal greatly accelerate corrosion in neutral salt solutions by the creation of local anodes and cathodes. But in acid solutions it is often observed that impure metals corrode slowly at first, the rate becoming more and more rapid as time goes on. This effect can be explained as follows: If the impurities are present not in discrete form but in solid solution, they are dissolved simultaneously with the bulk of the metal (or, if not soluble, they become physically detached from the rest of the metal) and are then redeposited or remain segregated on the surface and thus provide local cathodes. Their effectiveness as cathodes depends, however, on whether their over-potential is high or low; if the latter, corrosion of the main metal proceeds apace. The physical nature of the deposited impurities is also of importance; spongy material is much more effective in liberating hydrogen than is massive metal. On the other hand, impurities are relatively of little importance when metals are experiencing acid attack under oxidising conditions.

There is some evidence that grain boundaries in metals may react in a different electrochemical sense from the bodies of the grains. They are frequently anodic in character. The difference may arise from the existence of differential strains, but may also be due to the presence of impurities, which tend to accumulate at grain surfaces, often in the form of eutectics. Theoretically electrical energy or corrosion energy should not be obtainable from a completely homogeneous system but in the case of heterophase alloys there is the possibility that one phase may act cathodically with respect to another. The beta-constituent of alpha-beta brass appears, for example, to act anodically with respect to the alpha-constituent, which often remains relatively unaffected by salt solutions. In alpha-brasses containing not more than 30% of zinc corrosion by chloride solutions is not more than that undergone by pure copper, in fact the attack is often less; but brasses with a few percent more zinc than this often experience corrosion which is initiated at zinc-rich points on the grain boundaries—possibly traces of the beta phase, although theoretically this should be absent from alloys containing less than 39% zinc when in the equilibrium state. Alpha-beta brasses when heat-treated in a certain way may consist of alpha-grains surrounded by a network of beta-brass; such alloys may be very seriously attacked by sea-water, the attack being concentrated on the beta-phase, the metal sometimes disintegrating in consequence, with the alpha-grains falling away uncorroded.

Although the contact of dissimilar metals is a common cause of electrochemical corrosion it is by no means the only one. Other causes include:—differential variations in the structure of the metal and thus of its electrochemical behaviour, which often causes trouble in welded structures; differential stress or strain—exemplified particularly at the edges of a piece of metal, or at scratches or abrasions, all of which usually behave anodically to the remainder of the piece; differential concentration in the corroding medium, a matter of particular importance in the case of

copper; temperature differences between one part of the metal and another; whilst differential illumination has even been claimed to be a possible stimulant of corrosion.

One of the most important of these is differential aeration. A piece of metal which is well-aerated is cathodic to one which is less well-aerated, although in the case of the more noble metals, such as copper, the effect may be masked by other factors, such as ion concentration. The phenomenon was very clearly demonstrated by Evans many years ago. He constructed a cell containing potassium chloride solution and divided it into two parts by means of a porous partition. Similar pieces of iron were then placed in each half of the cell and were connected electrically via a milliammeter. On bubbling oxygen through one of the compartments a flow of current was registered by the milliammeter, the direction being such that the aerated piece of iron was the cathode. On stopping the flow of oxygen through the first compartment, and directing it instead through the other, the direction of the current became reversed. The effect is also noticeable on metal specimens which are half-immersed in a salt solution, as shown in Figure 2. The upper layers of the solution are more oxygenated than those below, so that the metal immediately at or below the air liquid interface is cathodic with respect to the portions lower down. This leads to the intensified attack a little way down the specimen, and is the basis of the common observation that corrosion is particularly severe near the water-line on half-immersed metals.

Even though differential aeration is very effective in promoting corrosion, and is responsible for much of the ferrous corrosion encountered in practice, it is not the governing factor in all instances. Interesting examples of the reverse occurrence—the behaviour of screened areas as the cathode and not the anode, as would be expected if differential aeration was the controlling influence—have recently been discussed in the technical press by J.T. Crennell, and provide a striking illustration, if any were needed, of the complexity of corrosion phenomena.

The first point to note is that painted areas of a piece of steel immersed in a solution of salt behave *cathodically* with respect to unpainted areas, despite the fact that the exclusion of oxygen from the surface of the steel beneath the paint film is practically complete. The potential difference involved is not inconsiderable; painted steel shows an equilibrium potential of about  $-0.4$  volt against a silver silver chloride electrode in seawater, whereas the potential of bare steel under the same conditions is  $-0.65$  volt. The current flowing between painted and unpainted areas of steel is very small initially, but as the resistance of the film of paint gradually deteriorates the amount of current increases and after several weeks may rise to as much as 50 microamps flowing between test panels  $2" \times 3"$  in size. This current can be maintained for many months.

It was later found that a similar result could be obtained, not only by placing a closely adherent film such as paint over the metal, but also by merely screening it mechanically with for example a sheet of glass, provided of course that the salt solution could still penetrate between the two. If we immerse a bare steel plate in salt solution and then press a piece of flat glass gently against it we shall find that the area which has been covered reacts cathodically towards the remainder.

The cause of this peculiar behaviour lies in the nature of the cathodic reaction. If a continuous current is to be maintained there must be, at the cathode, either the evolution of hydrogen, or the deposition of metal, or the reduction of an oxidising agent. As already described, the reaction which takes place in a neutral salt solution is the last of these—the reduction of dissolved oxygen to hydroxyl ions. Now it can easily be shown that only a small concentration of alkali is needed to produce marked passivity on an iron or steel surface. If, for example, one twelfth of the sodium chloride in a 3.5% solution is replaced by an equivalent amount of sodium hydroxide, the potential of an iron electrode immersed in it will change from about  $-0.65$  volt relative to a silver silver chloride electrode to approximately  $-0.5$  volt. If the conditions existing at the local cathodes are such that the hydroxyl ions cannot diffuse away from the surface—which is the situation which arises beneath a film of paint or behind a sheet of glass in loose contact with metal—then the whole area concerned will ultimately react cathodically. On the other hand, if the conditions are such that free diffusion of hydroxyl ions can take place, then the dominating

factor in corrosion is likely to be either the mutual interaction of localised anodes and cathodes or the differential aeration effect.

The reality of the above explanation is confirmed by the fact that alkaline fluid can often be detected in the blisters formed on painted iron that has been immersed in salt solution. The practical consequence of the phenomenon is that the interior of a deep crack or crevice in metal should, under stagnant conditions, be expected to behave cathodically if the above effect—which for want of a better title could perhaps be called the “partial screening effect”—is the only one operative in a particular case. It will have been realised from what has been said earlier that there are a number of competing influences in metallic corrosion, and that the prediction of which one will predominate in a given instance is not always easy.

Another factor which has an important bearing on the course of corrosive processes is the presence or absence of a film of oxide on the metal. The existence of an oxide film effects the electrochemical behaviour of metals, and thus their corrosion-resistance, to a very great extent. The wellknown passivating effect of strong nitric acid upon iron is an example of this. Whilst dilute nitric acid dissolves iron by ordinary acid attack, nitric acid of specific gravity 1.4 oxidises the surface layers of the metal to ferric oxide, which is insoluble and prevents further attack. Moreover, passivity remains after the iron has been removed from the strong acid; it is lost, however, whenever the protective oxide film is destroyed as it would be, for example if the passivated metal were made the cathode in a galvanic couple immersed in acid solution. Similarly aluminium, although its theoretical normal potential would place it among the more reactive metals, suffers relatively slow attack by acids because of the protective film of oxide which exists on its surface, under alkaline conditions, on the other hand, the oxide film is removed and attack readily ensues. The passivating effect of chromates upon iron and some other metals is basically due to their ability to repair damaged oxide films. The corrosion-resistance of stainless steels likewise resides in a stable and continuous oxide film; such steels withstand oxidising acids but are susceptible to attack by hydrochloric and sulphuric acids.

This leads directly to a consideration of chemical inhibitors in general. Inhibition depends upon the precipitation or absorption of an insoluble compound in immediate contact with corroding metal, thus stifling further attack by mechanically excluding corrosive liquid. An inhibitor may be anodic, in which case it forms a precipitate with the metallic ions passing into solution from the anodic regions of the metal which is being attacked; or it may be cathodic in which case it must form a precipitate with the alkali produced on the cathodic areas of the metal; or it may be of the absorption type, whose mode of action is rather more complicated. Sodium phosphate is an example of an anodic inhibitor for iron which is quite effective in the absence of much chloride. There is however a danger in relying upon anodic inhibitors for anticorrosive purposes in that if insufficient inhibitor is present to stifle the reaction completely, which means that the anodic areas will be only partly but not entirely covered, the attack will be concentrated on the relatively poorly protected parts, leading to deep pitting at localised points. Salts of metals which form insoluble hydroxides are useful cathodic inhibitors in neutral solutions, since they are precipitated by the alkali produced at the cathode. In practice they are rather less effective than anodic inhibitors but are safer in that if present in insufficient amount to give complete protection they do not lead to intensified local attack. Absorption inhibitors are usually complex organic compounds, many of them being colloidal in nature. Agar-agar, gum tragacanth and albumen belong to this class. They possess the ability to form films over both anodic and cathodic areas, though some act preferentially on one or the other. A number of pure compounds, such as di-ortho-tolyl thiourea and quinoline ethiodide, are also known to be effective inhibitors; it seems probable that they unite chemically with the metal through the nitrogen or sulphur atoms.

Whilst some compounds tend to inhibit corrosion, others possess the power to intensify it by stimulating the cathodic reaction; ferric salts, for example, accelerate corrosion because they are effective depolarisers, and chromates, although valuable inhibitors in neutral solutions, have a similar stimulating effect in acid media.

Solid surfaces are not equi-potential, and the fact that certain atoms or molecules in a solid

surface exist in a state of relative strain is responsible for much of the abnormal activity that solids sometimes display, such as catalytic ability and corrosion-susceptibility. Quite apart from the question of externally imposed strains, the sensitivity of metal crystals to corrosion is known to vary appreciably from face to face—sometimes by a factor of two. In this connection it is worth while referring to the properties of the amorphous layer produced on metals by polishing—sometimes known as the Beilby layer—since cold work, rolling drawing, etc., produce a somewhat similar, though smaller and usually much more localised, effect upon metal. The Beilby layer is found to be harder than the remainder of the metal ; it is usually more readily soluble ; and, what is of particular import to corrosion phenomena, its potential is moved in the anodic direction, so that it corrodes more readily. The heat of solution of the surface layers of polished, worked or drawn metal is greater than that of the metal in its normal condition, indicating that these processes, which cause the rearrangement of ordered crystal structures to a disorganised state, result in the accumulation of potential energy in the regions concerned. The disturbance of the microstructure that polishing produces is not, of course, limited to the immediate surface layers but extends with diminishing effect for considerable distances down into the body of the specimen.

The frequent observation that intensified corrosion takes place at points where metal has been cut, perforated or other deformed is a practical example of the anodic reactivity of worked metal. On the other hand, it is also frequently found that polished surfaces appear to resist corrosion better than roughened or unpolished surfaces do ; this despite the anodic character of the Beilby layer. The reason is that a polished surface being uniform throughout, there are no localised anodic and cathodic areas present.

After this review of the basic principles of corrosion we can proceed to a consideration of their practical implications. It is not, however, proposed to discuss atmospheric corrosion beyond mentioning that the attack is initiated in films of moisture condensed on the surface of the metal. Corrosion and rusting do not take place in completely dry air.

### STRESS-CORROSION

The behaviour of metal at the grain boundaries is of great importance in studies of metallic failures. In the first place, as mentioned earlier, the surfaces of the grains often behave in a different electrochemical sense from the remainder, frequently being anodic in character, so that corrosive attack becomes concentrated upon them.

The grain boundaries in a metal which is being subjected to corrosion thus represent weak spots in the structure. If, in addition, the metal is simultaneously undergoing stress, especially tensile stress, these weak spots are the first to suffer. The surface crevices become widened and deepened, the corrosive liquid thus gains access to regions further and further within the body of the metal, and the two effects—corrosion and stress—continue to reinforce each other until failure of the whole results. Tensile stress is more active in promoting corrosion than is compressional stress, which may even have the effect of reducing attack by closing up minute cracks in the surface of the metal.

Stress-corrosion was first recognised as an important factor in the failure of metals during World War I, when the extraordinarily short lives of steel cables used for towing certain minesweeping devices at sea caused serious concern. Since that time it has been recognised that stress-corrosion plays a leading part in the premature breakdown of many other mechanical items, including propeller shafts, boiler tubes, turbine blades, steel springs, pump components, and even steel railway sleepers. Fatigue-corrosion is also commonly encountered in ships plates at points where the hull is continually subjected to flexing as the ship rides over waves.

Stress can arise in metal from the application of external forces and also from internal residual strains set up as the result of cold work done previously on the metal. It was shewn many years ago, for example, that the outer surface of a cold-drawn rod is in tension whereas the interior is in compression.

Usually external stresses are far more important in causing failure than are internal stresses,

since in many cases the latter may be relieved by a relatively small readjustment of the metallic structure. Sometimes, however, the effects of internal stress combined with intergranular corrosion are far from negligible, and may even be striking. Brass if heavily cold-worked and under high internal stress, is particularly susceptible to intergranular attack by mercury salts. Under these circumstances brass rods will sometimes split up into fibres when immersed in a solution of mercurous nitrate, and cases have been reported where brass has disintegrated with an audible report when touched by a mercury salt.

Whenever a metal is stressed there is a tendency for the stress to be intensified around imperfections such as fine surface cracks. Additional local stresses may arise at such points and may lead to localised plastic deformation even though the metal as a whole is not strained beyond the elastic limit. If the applied stress is of an alternating character work-hardening may result round the cracks, thus raising the elastic limit and enabling the metal to endure continued stressing provided that this does not exceed a certain value. If, however, the stressing is too severe, then the effects of local work-hardening will be nullified and the crack will extend deeper and deeper into the metal. The great part played by surface cracks in initiating the fracture of solids is perhaps most clearly shewn in connection with a non-metallic substance—rock salt. This material can be bent and twisted without fracture if it is first immersed in warm water, which has the effect of dissolving surface imperfections.

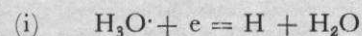
The cracks developed during stress-corrosion are most frequently intergranular in nature, whereas those resulting from corrosion-fatigue—that is, corrosion under alternating stress—are usually transcrystalline.

Corrosion which occurs before the metal is subjected to fatigue may also seriously impair its subsequent performance even if no further exposure to corrosive action occurs. It has been found that the weakening effect of corrosion pits is proportionately much greater in the case of metals of high tensile strength than it is in the case of metals of relatively low strength. Thus the advantages of using high quality material may be lost unless all possible precautions are taken to protect metal against corrosion before fabrication as well as afterwards.

A secondary effect that should be noted is that stress modifies the electrochemical behaviour of metals, and it is not necessary for the elastic limit to be exceeded before this can occur. The electrode potential moves in the basic direction, thus increasing the tendency to corrode, especially in cases where the stress is localised since the stressed area is then anodic to the remainder.

Where the corrosion-resistance of a metal depends upon a surface film of oxide, severe stressing, such as that involved in bending, may lead to the fracture of the film, especially on the convex side of a bend. If sufficient time is allowed for the film to repair itself before exposure to corrosive conditions occurs, the resistance of the metal may ultimately become as good as ever; but if this is not possible, accelerated failure is certain.

When metals are subjected to both acid attack and mechanical stress at the same time it is often found that a considerable amount of cracking occurs. While this may well be due to intergranular effects, it is also possible that the embrittlement of metal which results from the accumulation of hydrogen within the crystal lattice may assist the process. Iron and steel, for example, are known to occlude atomic hydrogen very readily at cathodic points when treated with acid. The production of molecular hydrogen occurs in two stages:—



On metals which display high overpotential either or both of these processes occurs slowly; if the second stage is slow, the absorption of considerable amounts of atomic hydrogen may occur. Iron has been known to absorb three times its own volume of hydrogen when treated cathodically in acid solution, and in this state will break under stresses which in the absence of occluded hydrogen would merely deform it. The explanation generally given is that deformation permits the escape

of hydrogen from the crystal lattice into minute rifts or pockets where the atoms react to form molecular hydrogen and the pressure generated deepens and extends the rifts leading to the formation of still more molecular hydrogen and the generation of still greater pressures. Such a process will be expedited if intergranular attack is taking place as well.

#### PRACTICAL EXAMPLES

Contact between dissimilar metals, which is such a fruitful cause of corrosion in neutral salt solutions, can usually be avoided in practice by an appropriate selection of constructional materials or even, as is sometimes necessary in aircraft and ship-construction, by actually interposing a layer of rubber or other insulating materials between them. Where, however, a metal contains inclusions of other metals as impurities, or one metal becomes deposited locally upon another, corrosion is very difficult to prevent. If the impurity is less noble than the rest of the metal corrosion will be focussed only on the impurity; but where the impurity is more noble, then the attack is concentrated on the surrounding metal whilst the impurity itself remains unaffected throughout. A good example of what can happen is afforded by the reduction of red lead to metallic lead on the submerged portions of ships' hulls, which sometimes occurs as the result of bacterial action. Lead is cathodic to iron, and the electrochemical attack is therefore concentrated on the iron in the immediate vicinity. This has been known to cause the perforation of ship's plates in a relatively short space of time. True, the lead in this case is derived from a source external to the iron; but the same thing would have happened if the lead had been present as a segregated impurity within the plating itself.

A specialised type of corrosion which is somewhat less common today than it once was is the so-called dezincification of brass. This can be quite a dramatic type of failure. Externally the brass loses its golden-yellow colour and becomes coppery-red. The dimensions of the metal do not alter, but the composition changes from the original brass to almost pure copper in a spongy condition. The loss of mechanical strength is catastrophic; cases have been reported where the tensile strength dropped to a tenth of its original value. Sometimes the dezincified area extends uniformly over the entire surface; sometimes it is initiated only at local points on the surface and the effected region extends vertically downwards deep into the metal, in the form of narrow plug. (See Figure 3.)

Copper alloyed with up to 30% of zinc does not corrode more than the original copper, but where the proportion of zinc is more than this—as of course it frequently is in commercial brasses—increased corrosion by salt water can occur. Corrosion in such cases is initially concentrated at zinc-rich areas, which are often found at grain boundaries. These areas are anodic to the remainder of the metal and both copper and zinc can pass into solution at such points. The copper tends to re-deposit on adjacent cathodic areas, making them still more cathodic in character, whilst of zinc cannot become re-deposited in this way. The spongy mass of deposited copper is not impermeable, so that the above process can continue beneath it, and the zinc ions gradually diffuse away. It seems that under some conditions the process is capable of being initiated in a slightly different manner, and that the first step may sometimes be the direct leaching-out of zinc, leaving copper ("residual copper") behind; but once free copper has been produced, by whatever mechanism, the subsequent course of events is the same.

The corrosion of zinc is largely controlled by differential aeration currents and in practice is almost independent of the concentration of zinc ions; the presence of oxygen raises the potential of zinc, thus most attack takes place under stagnant conditions. The removal of copper ions from solution on the other hand renders copper more anodic in character so that most attack occurs in the least stagnant places. Thus under conditions of little movement and unequal oxygen concentration the attack upon brass by salt solutions should favour the dissolution of zinc and the formation of residual copper or the redeposition of any copper which has passed into solution. Under conditions of rapid movement of liquid, however, copper ions may be swept away before they can be re-deposited; brass in these circumstances tends to corrode uniformly without dezincification, if it is attacked at all.

The situation of a brass securing-bolt in the hull of a wooden boat is almost ideal for the



occurrence of dezincification—stagnant conditions exist between the bolt and the hull and there is an appreciable oxygen gradient between the outermost and the inner portions of the metal.

In practice, dezincification is limited almost entirely to alpha/beta brass, and the addition of so-called dezincification inhibitors has little effect. Dezincification may also sometimes occur in alpha brass due to traces of the beta phase; but in this case metallurgical treatment to remove zinc-rich spots is a satisfactory remedial measure whilst arsenic added in quite small quantities to this type of brass—as little 0.02% will suffice—is also an extremely efficient inhibitor of dezincification. The available evidence suggests that the function of the arsenic is to produce an obstructive film over the susceptible areas.

Copper/zinc alloys for engineering purposes have been developed principally around two basic compositions, 70/30 Cu/Zn and 60/40 Cu/Zn; alloys containing less than 30% Zn are normally only used for decorative purposes whilst those containing more than 50% are too brittle, due to the presence of the gamma phase. Brasses with up to about 36% Zn are single phase (alpha), but those with over 36% and up to about 46% are duplex alpha plus beta types. As such, the latter are more susceptible to corrosion than the former. Single-phase beta brass can be produced but is rather brittle and variations in composition between individual grains being not uncommon, stress-corrosion often is found to occur in practice. Straight Cu/Zn brasses are, of course, rarely used and it is usual for various additions to be made to confer special properties. The “zinc equivalent” of the additions must be borne in mind in assessing the probable behaviour of brass with respect to corrosion.

The so-called “season-cracking” of brass is another type of intercrystalline attack which sometimes is produced when brass which has been severely worked and not properly annealed is stored under warm conditions, if the atmosphere contains traces of ammonia vapour; it may also occur under conditions which lead to the condensation of ammoniacal water vapour on the metal or, as is more common in industrial atmospheres, of moisture containing traces of ammonium salts. Annealing at 275°C., which eliminates internal stresses, for one hour usually suffices to render brass immune to this form of failure.

The intergranular corrosion of duplex brass has already been mentioned. It remains only to add that the unskilful welding of high tensile brass, a process sometimes used for building up and repairing large components made of that metal may lead to the production of the beta phase, within which stress corrosion is easily initiated, leading to deep cracking and failure.

Austenitic chromium/nickel steels if cooled from 1000-1200°C. and subsequently re-heated to around 700°C., are found to be highly susceptible to intergranular attack. This arises from the formation of chromium carbide at the grain boundaries, which thus become relatively poor in chromium and are then so easily attacked by some reagents that the metal is rapidly converted to the condition of a powder. Metallurgical treatment and cold-working in order to reduce the grain size has been found to lessen the amount of attack, the reason being that if the grain size is small chromium can diffuse more readily out from the interior of the grains into the zones that have been impoverished, thus to some extent restoring the original composition at the grain boundaries. The addition of titanium and other metals which have a higher affinity for carbon than chromium has also been effective, but sometimes other properties of the alloy are adversely affected; for example, in the case of titanium the ability to take a high polish is reduced. Sometimes this is acceptable, and the use of titanium alone may suffice; but if the metal is to be re-heated more than once—as in cross-welding and circumferential welds—the titanium may be removed by oxidation during the first weld, and some writers recommend the use of tungsten in addition to titanium in order to remove this defect. On the other hand some authorities maintain that the only remedy in the case of thick welds where much heating is involved is to quench from about 1100°C. The introduction of an alpha-iron phase into the austenite also tends to reduce intergranular attack. This may be due to the preferential formation of chromium carbide round the alpha grains; if these are present in numbers insufficient to form a continuous matrix throughout the metal then the extent of the attack will be limited. Silicon, molybdenum and tungsten produce this effect.

Certain types of light alloy are also liable to undergo intergranular attack, especially when

under stress. Where extremely high corrosion-resistance is a prime requirement, as it is in the case of alloys which are to be used for marine purposes the choice is largely limited to the magnesium/aluminium series. If however, the magnesium content of such alloys is more than about 5.5% they become heat-sensitive; the 7% magnesium type, for example, undergoes constitutional changes when heated to 75°C., an intermetallic compound being precipitated at the grain boundaries with the result that corrosion-resistance is seriously impaired. Other light alloys whose corrosion-resistance is extremely good provided that they have received suitable thermal treatment are the aluminium/magnesium/silicon and the aluminium/magnesium silicide types. These two materials resist corrosion much better in the solution-treated condition than they do after annealing or full heat-treatment. They should not be exposed to temperatures above 180°C.

Obviously heat-sensitive alloys of this type should not be used, if resistance to corrosion is an important requirement, in situations where they are liable to become heated in service; nor should they be subjected to high temperatures during fabrication or welded, since they will thereby become susceptible to corrosive attack.

We have seen how corrosion is essentially an electrochemical phenomenon. Whilst in ordinary corrosion the current is self-generated, corrosive effects will equally well take place if an external current is impressed upon a metallic system in contact with electrolytes. Leakages from power lines and electrical conductors of all sorts may cause wastage of metal which is all the more serious because it tends to be concentrated at points where the insulation has broken down. Leaden sheathing used for heavy cables is liable to suffer a form of intergranular attack under these circumstances, so that the amount of damage which results may be out of all proportion to the quantity of current that has passed. Apart from secondary effects of this sort, the direct action that occurs may be very serious in itself; a leakage of one ampere for a month would dispose of over six pounds of lead. Welding operations on board ship in which the hull is used as earth may lead to intense local pitting at points where the protective coating of paint is weak or has been damaged. It should be noted that the current densities involved in cases of leakage may be very much greater than those concerned in ordinary corrosion, with the result that the corrosion products may be quite different; lead peroxide may be found, for example, on cable sheathings through which current has leaked.

We have also seen that in any process of corrosion the attack is focussed on the anode, the metal of the cathode being unaffected. This fact offers us the possibility of protecting metal from corrosion by the simple procedure of making it the cathode in a galvanic couple a process which has received much attention in recent years under the broad title of "cathodic protection". As applied to ships, it takes the form of connecting the hull electrically to a magnesium anode which is immersed in the sea; all the corrosion then takes place on the magnesium, the hull (or at least those parts of it which are submerged) remaining entirely unattacked. There is little new in this idea, however, other than the use of magnesium; zinc blocks were fitted to iron ships for the same purpose over a century ago, and theoretically should have been quite effective since zinc is markedly anodic to iron. However the zinc available commercially in those days contained a number of metallic impurities, so that the zinc became largely wasted in self-corrosion.

The use of a dissimilar metal is an extremely convenient way of applying cathodic protection since once the system has been adjusted correctly it requires no further attention beyond the occasional replacement of the anode. The same result can, however, be equally well achieved by impressing an external current at low voltage upon the system which requires to be protected.

Cathodic protection is being used today to prevent the corrosion not only of ships but also of harbour installations, buried pipe-lines, and the like; it is applicable in all cases where metal is exposed to corrosive attack by solutions of salts. It does not, however, provide any protection against atmospheric corrosion.

### CONCLUSION

This review of the basic facts regarding corrosion, and of some of the ways in which corrosion can bring about the premature failure of metal has necessarily been brief and incomplete. It is

desired, however, to emphasize in particular the extreme importance of corrosion-fatigue.

Not only are the effects of corrosion fatigue far-reaching; they may also be insidious. As H.J. Gough has put it:— “ In many cases of corrosion fatigue, the amount of metal combining to form corrosion products is extremely small—to such an extent that certain fractured laboratory specimens retain undiminished their surface brightness, although their fatigue resistance has been considerably reduced. The serious damage sustained has been caused by the presence of sharp, deep pits or crevices, produced under the conjoint action.”

Studies of corrosion fatigue may lead us to revise our ideas as to what is the most profitable metal to use under a given set of circumstances, and may cause us to re-consider some of the ends towards which metallurgical research should be directed. It has, for example, been shewn that although alloy steels may possess high tensile strength and greater fatigue strength, their resistance to corrosion-fatigue may be little if any better than that of plain carbon steel ; a matter which should give us food for thought. It is obvious that in many cases designs should be based on corrosion fatigue strengths and not on fatigue strengths alone. The point was made extremely well by Evans when he said:—

“ Warnings regarding the danger of corrosion-fatigue are especially needed at a time when, owing to the more exact mathematical methods becoming available for the calculation of cross-sections theoretically necessary, there is a tendency to reduce the margin of safety. Such a reduction is perfectly justified, provided that the values adopted for the strength of materials allow for the chemical as well as the mechanical agents of destruction. If the values, however, are based on corrosion-free tests, the reduction may remove just that margin which in the past has enabled the engineer to neglect corrosion-fatigue with impunity.”