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Corrosion Issues in Solder Joint Design and Service[1]

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Abstract

Corrosion is an important consideration in the design of a solder joint. It must be addressed with respect to the service environment or, as in the case of soldered conduit, as the nature of the medium being transported within piping or tubing. Galvanic-assisted corrosion is of particular concern, given the fact that solder joints are comprised of different metals or alloy compositions that are in contact with one-another. The (thermodynamic) potential for corrosion to take place in a particular environment requires the availability of the galvanic series for those conditions and which includes the metals or alloys in question. However, the corrosion kinetics, which actually determine the rate of material loss under the specified service conditions, are only available through laboratory evaluations or field data that are found in the existing literature or must be obtained by in-house testing.

Introduction

Addressing corrosion concerns is important when considering the design and service of products containing solder joints (Fig. 1). The consequences of solder joint corrosion are several. For example, solder joint corrosion can be detrimental to a product by deteriorating the latter's cosmetic appearance. The formation of corrosion by-products on exposed surfaces can reduce a product's sales appeal to the public; this is an important consideration in the jewelry trade. Functionally, however, it is the loss of material, be it the filler metal or the loss of nearby substrate material, that most significantly impacts solder joint performance and reliability. Material loss degrades the joint's capacity to support a mechanical load, provide hermetically for a container structure, or sustain continuity in an electrical circuit. One *cannot* assume that corrosion by-products that form in the joint are, themselves, structurally sound so as to replace the functionality of the original material. Uhlig provides a qualitative ranking of corrosion rates[1]:

Good corrosion resistance:	≤0.005 in./year (0.015 cm/year)
Satisfactory corrosion resistance:	0.005-0.050 in./year (0.015-0.15 cm/year)
Poor corrosion resistance	>0.050 in./year (>0.15 cm/year)

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Solder joints may experience corrosion activity when functioning in air, depending upon the local atmospheric conditions. This is referred to as *atmospheric corrosion.* Of course, the term atmospheric can be broadened to *environmental* so as to include corrosion by the metals and alloys when immersed in media other than air (gases and liquids). Corrosion mechanisms may be accelerated when dissimilar metals are in contact with one-another in the presence of moisture or other media; this circumstance is referred to as *galvanic-assisted corrosion* or simply, *galvanic corrosion.* The potential for galvanic corrosion is particularly high in solder joints because, by their very nature, solder joints are comprised of dissimilar metal or alloy components in contact with one another. Those materials include: (1) the substrate or base material(s), (2) protective and solderable coatings on the base materials, and (3) the composition of the solder. A third corrosion process is *voltage-assisted corrosion.* Corrosion processes may be accelerated or curtailed when the service conditions include an electrical potential being applied to, or across, the solder joint. A problematic consequence of this process in the phenomenon of electromigration in which the corrosion process causes the build-up of by-product material between two metal structures of different electrical potentials, resulting in a short-circuit. The occurrence of electromigration is of particular concern in electronic solder joints, but can be equally problematic in larger structures, particularly those that serve as an electrical ground. Corrosion processes that are also pertinent to solder joints is *stress corrosion cracking* and its companion process of *corrosion fatigue cracking.* As the terms imply, these processes involve corrosion activity that is accelerated by the presence of a monotonic load on the structure (stress corrosion cracking) or a cyclic load (corrosion fatigue cracking).

The generalized corrosion processes cited above (atmospheric or environmental corrosion, galvanic-assisted corrosion, stress corrosion cracking, and corrosion fatigue cracking) can manifest themselves into one or more, specific surface deterioration mechanisms. These mechanisms include: (1)*uniform corrosion*, (2) *pitting corrosion*, (3) *crevice corrosion*, and (4) *intergranular (interphase) corrosion.* Uniform corrosion describes the case in which material loss occurs homogeneously over a metal or alloy surface. Pitting corrosion is material loss on a very localized scale and manifests itself as small craters in the surface; the remaining surface shows little or no degradation. Because solders are multiphase materials, pitting can result from the preferential attack of one of those phases as opposed to the other phase(s). Crevice corrosion is material loss localized along the interface between two pieces of material that are physically next to each other, but do not have a filler metal in the gap. The materials need not be dissimilar for crevice

corrosion to occur. Although pitting and crevice corrosion are considered as localized mechanisms, they still take place on a relatively macroscale level. Intergranular corrosion is a microscale version of crevice corrosion, in which attack occurs along individual grain boundaries of the metal or alloy. In the case of multiphase materials, which represents a majority of solder alloy, preferential attack may also take place along interphase boundaries. The prevalence of each or combination of several of these mechanisms depends upon the local conditions (electrolyte, temperature, time) as well as the material properties such as alloy composition, oxide layer thickness, and physical dimensions of the parts.

Unfortunately, the topic of corrosion appears to have a rather paradoxical place in materials and joining technologies. On the one hand, it is probably the single most prevalent form of degradation in metallic structures and therefore, warrants considerable attention. On the other hand, however, corrosion degradation is a difficult problem to characterize, quantify; and lastly, eliminate. The predominance of one or more corrosion mechanisms, be it uniform, pitting, or crevice corrosion, as well as the rates of material loss, are very sensitive to the alloy properties (composition, phase distribution, oxide layer chemistry and thickness, etc.) and the service environment. In fact, a large extent of the difficulty in predicting corrosion behavior is associated with a poor understanding of the specific service conditions to which the particular metallic part will be exposed. Those conditions include: (1) relative humidity as well as airborne contaminants and their levels; (2) the species and concentration of a liquid electrolyte; (3) temperature conditions including maximums, minimums, and cycle frequencies; and (4) the overall time-of-exposure. Some of these variables have more impact on corrosion rates than others. Also, there can be synergistic effects between variables. Thus, it may be difficult to establish laboratory tests in order to obtain relevant data, thereby necessitating the need for more-costly field evaluations of corrosion rate.

A second aspect undermining the predictability of corrosion is its intrinsic nature to be *stochastic*. That is, corrosion often times appears to take place almost by random chance. The corrosion mechanism may appear at one particular location on a surface, but not at another, in spite of the fact that both areas were exposed to the same environment. This stochastic or random nature to corrosion is best illustrated by the pitting corrosion mechanism. The pits appear at random locations over the metal or alloy surface. Pitting corrosion has been traced to very localized defects in the surface passivation layer; however, it is the fact that these oxide layer defects appear to be random in-nature, themselves, that gives a stochastic nature to the pit locations.

It is paramount to identify specifically the environment to which the solder joint will be exposed. Corrosion data (potentials as well as rate kinetics) for the variety of commonly experienced environments can be very limited, particularly for the lesser used solder alloys. A large pool of such data can be found for the Sn-Pb solders and 100Sn[2,3]. In some instances, the 100Sn data has been used to predict the behavior of high Sn solders in similar environments. However, there is no underlying theory that supports this approach; in fact, past work has demonstrated that small alloy additions can dramatically impact the corrosion resistance of an alloy[4].

In the electronics industry, corrosion activity by flux residues has remained as an important concern for solder joint reliability and continues to be an area of active research, today. Manko has summarized the corrosion activity of Sn-Pb solders in the presence of chlorides since the latter substances have served as activators for flux chemistries[5]. Chloride ions (in water) attack the usually very protective PbO, resulting in the formation of a less tenacious $PbCl_2$ surface layer. The combination of water and CO_2 (from the air) converts the $PbCl_2$ into a powdery $PbCO_3$ compound. The latter layer provides no appreciable protection to the underlying Pb metal, causing the corrosion cycle to repeat itself and further increase the rate of material loss. Solder joint corrosion is of particular concern in the air conditioning industry. Aluminum-alloy tubing and fixtures have replaced similar Cu components because of manufacturing and cost advantages of Al alloys over traditional Cu alloys. However, a significant potential for corrosion activity exits in joints made between Al base metals and Sn-based solders; therefore; Zn-containing solders are preferred for such applications.

Clearly, predicting the occurrence and rates of corrosion activities for metal systems, under the pertinent environments, is an involved task. On the other hand, failure to address corrosion issues at the product design phase can result in significant cost penalties later-on, when the need arises to improve product reliability (or avert product *liability*). An awareness of potential corrosion issues at the engineering design stage of a solder joints is the important first step towards mitigating such concerns. Then, the need to acquire data, either through of literature searches, laboratory and field studies, or both approaches can be addressed. The following paragraphs will briefly describe the four corrosion processes noted earlier. Then, several approaches will be present by which corrosion processes can be mitigated.

Atmospheric (environmental) corrosion.

An understanding of the general concepts of atmospheric or environmental corrosion is needed as a foundation toward appreciating the other corrosion processes.

Atmospheric corrosion refers to process by which metal is converted into a corrosion by-product by the action of constituent contained in the atmosphere. Atmospheric corrosion can be generalized into environmental corrosion to include the case of other media such as water, acidic or alkaline solutions, etc. One or more of the aforementioned mechanisms (uniform corrosion, pitting corrosion, etc.) will provide the degradation. Aside from the environmental factors of corrosive strength, exposure time, or ambient temperature, the material composition is the determinant variable in corrosion behavior. Corrosion activity has two composition-related dependencies: (1) the intrinsic corrosivity of the exposed, bare metal or alloy and (2) the thickness and tenacity of the oxide formed on its surface. It is the latter factor, oxide formation and the oxide's capacity to protect the underlying base metal from attack by the environment, that most significantly affects corrosion behavior. Conversely, it is also the surface oxide that makes it difficult to predict corrosion activity from standard tables based upon the performance of bare metals, or to even corroborate benchtop experiments with actual field observations because oxide development is sensitive to slight differences in the environment.

Atmospheric corrosion of any metal or alloy requires that an *electrolytic cell* be established. The electrolytic cell is comprised of the metal member and the corrosive medium. An example would be that of an alloy immersed into water (the electrolyte). In the electrolytic cell, two half-reactions take place; they are called the *oxidation half-reaction* and the *reduction half-reaction.* They are termed "half-reactions" because when combined, they form the total corrosion process reaction. A metal or alloy exhibits "corrosion, " that is, a loss of material when it has the oxidation half-reaction. That material is called the anode of the cell. The oxidation reaction is the conversion of the metal from a neutral state (M^0) to a positive ion (M^+) by the loss of an electron (e^-):

$$M^0 = M^+ + e^- \qquad (1)$$

The metal ion, M^+, is lost into the water medium; hence, this is the material loss that characterizes the usual concept of "corrosion." A reduction half-reaction must also take place. That reaction takes place to the water. The reduction reaction for water takes the form:

$$H_2O + e^- = 1/2H_2(g) + OH^- \qquad (2)$$

The electron released from M^0 when it became M^+ is taken by the water molecule which then converts to hydrogen gas ($H_2(g)$) plus a hydroxide (OH^-) molecule. The presence of

the OH^- causes the water to become slightly alkaline (pH>7). The half-reactions are combined into a total reaction for the overall corrosion process which is shown below:

$$M^0 + H_2O = 1/2H_2(g) + \{M^+ + OH^-\} \quad (3)$$

The M^+ and OH^- are indicated as having "combined" with one-another as represented by their enclosure in the brackets { }. In reality, there are three pathways into which that combination can culminate[6]. For example, the M^+ and OH^- may bond directly, forming a metal-hydroxide of stoichiometry, $M(OH)_n$. Or, the metal and oxygen in the OH^- combine to create a metal-oxide compound, MO_n. Both the hydroxide and oxide formations would then appear as corrosion products on the metal surface. The third route is that the metal and oxygen combine as in the oxide case, but still retain a charged state and so, would be lost as ions in the water.

Clearly, these reactions become much more complex when the water contains other ionic species. Those ions may come from salts such as NaCl in sea water . Acids (HCl, HNO_3, etc.) and alkaline materials (NaOH, KOH, etc.) realize their activity from ions such as H^+, Cl^-, or OH^-. In the case of solder joints, ions may be present in the flux residues that remain after the soldering operation has been completed. In the presence of water, including water vapor in high humidity conditions, these ions will once again become active and can pose a corrosion concern to the solder joint. Chemical used to remove flux residues may also contain corrosive ions and thus, must be completely removed from the structure in order to prevent corrosion of the solder joint during service. Atmospheric gases such as CO_2 and O_2, when dissolved in the water, will significantly impact corrosion of the metal. The corrosion process can cause metal loss as the atoms are converted to ions and are then lost "permanently" into the electrolyte. Or, the metal ion may remain with the substrate in the form of a corrosion by-product such as a hydroxide compound or a metal oxide. As noted previously, it cannot be assumed that the corrosion by-product has the same structural properties as the underlying material.

How can one determine whether the corrosion process will actually occur? This is done with the use of the *galvanic series*. The galvanic series provides a ranking of corrosion potential for various materials under a particular corrosive environment (or electrolyte). The series illustrates only the thermodynamic "go, no-go" potential for corrosion; it does not indicate corrosion rates. Also, the series are determined under the premise that the materials have a nascent oxide on them; the corrosion potential of a material is very sensitive to oxide stoichiometry and thickness. Shown in Fig. 2 is the galvanic series for a number of metals and alloys in seawater[7]. Galvanic series are also available

for more specialized cases such as specifically Al alloys in 3.5% NaCl solutions[8]. Referring to Fig. 2, the more "noble" materials (going to the right in the diagram) have a lesser tendency towards corrosion when immersed in seawater; the more "active" materials (going to the left in the diagram) have a relatively greater tendency to corrode in this environment. It is observed that Al alloys stand a much greater likelihood of corroding in seawater when compared to Ni-Cr-Mo Alloy C. It is interesting to note that 50Sn-50Pb solder, 100Sn, 100Pb, and Cu all have similar corrosion potentials; they occupy positions at about the middle of the group, showing a relatively satisfactory resistance to attack in seawater conditions.

Galvanic-assisted corrosion.

The second category is that of *galvanic-assisted* or simply, *galvanic corrosion.* Galvanic corrosion is an acceleration of atmospheric corrosion on a metal or alloy due to its contact with anther metal or alloy. Of course, there is still the requirement for the presence of an atmosphere or other environment that is capable of supporting the corrosion process. As well, galvanic corrosion can result in any one or more of the aforementioned corrosion mechanisms: uniform corrosion, pitting corrosion, crevice corrosion, and intergranular corrosion. Galvanic corrosion is of particular concern to the service life of solder joints because solder joints are, by their nature, comprised of two or more dissimilar metals contacting one-another.

In order to gain a utilitarian understanding of galvanic corrosion, it is important that, first, the engineer understand the fundamentals of galvanic corrosion as they apply to the *idealized* or textbook situation. Then, the added complexities of surface oxides/contamination and real-world environments (electrolyte compositions, temperature, etc.) and how they significantly limit the application of those idealized fundaments are then considered.

The idealized view of galvanic corrosion can be found in nearly all textbooks on introductory chemistry or chemical engineering. Shown in Fig. 3 is a schematic diagram illustrating the textbook description of galvanic corrosion. Two metals, M_1^0 and M_2^0, are connected to one-another through a conductive wire. The metals are immersed into each of two electrolytes. Those electrolytes contain ions of the same metals M_1^0 and M_2^0 that have been immersed into them; they are designated M_1^+ and M_2^+, respectively. It will be assumed for the discussion that metal M_1^0 forms the *cathode* . At the cathode, the *reduction half-reaction* takes place in which the M_1^+ ions in the electrolyte are converted to neutral metal ions (M_1^0) and deposited onto the electrode surface. The M_1^+ ions have their charge removed (or "reduced" to zero) by receiving electrons, e^-, from the M_1^0 surface:

$$M_1^+ + e^- = M_1^0 \quad (4)$$

The M_1^0 electrode receives electrons come from the other metal electrode (M_2^0). That electrode is the *anode* at which the *oxidation half-reaction* takes place. There, the neutral metal atoms, M_2^0, on the electrode surface are converted to ions, M_2^+, plus an electron, e^-:

$$M_2^0 = e^- + M_2^+ \quad (5)$$

The M_2^+ ions are lost from the electrode and enter the electrolyte. The electron that is created is then transferred to the cathode to support the reduction half-reaction there. *The process by which ions are lost from the anode by dissolution into the electrolyte, represents the material loss that is traditionally associated with corrosion activity.*

It is noted in Fig. 3 that a *salt bridge* connects the two electrolytic baths. The salt bridge allows ionic species to travel between the two half-reaction cells in order to balance the movement of electrons from that anode to the cathode. Allowing a continuous movement of ions prevents a charge build-up (polarization) within either cell that would quickly shut down the needed electron flow and the corrosion process. The salt bridge, which is required in fundamental laboratory experiments, represents one of the discrepancies between textbook discussions on galvanic corrosion versus real-world situations - solder joints or otherwise. Nevertheless, it is still instructive to continue with the current analysis.

When given two metals, M_1^0 or M_2^0, it is necessary to determine which one will spontaneously corrode as the anode and which will be the cathode. This determination is illustrated with the following example. Like the generalized case of atmospheric corrosion, spontaneous galvanic corrosion is also based upon a thermodynamic "go, no-go" determination. That determination uses data provided in the *Table of Standard Reduction Potentials (SRP)* (Table 1)[9].[2] Each metal is represented by a reversible equation ;*reduction half-reactions* are read in the left-to-right direction and the *oxidation half-reactions* would be read in the right-to-left direction. For example, in the case of lithium (Li), the reduction reaction has an SRP value, E^0, of -3.05V. However, the reverse

[2] A word of caution: corrosion is a very old field of study. As a consequence, previously used nomenclature and conventions are often mixed with the newer formats that have been adopted by many standards organizations. The sign in front of a number is just as important as the magnitude of the number. Unfortunately, sign conventions may differ between sources. Therefore, the engineer is advised to carefully examine data between different sources prior to computing the corrosion potential.

(oxidation) reaction would have a potential of +3.05V. (The potentials are "standard" because they are referenced against the *standard hydrogen electrode* which has been accepted to have a potential value of $E^0 = 0.00$ volts.) In a spontaneous, galvanic corrosion condition, one of the two metals provides the reduction half-reaction while the other metal experiences the reverse, or oxidizing half-reaction. The combination of reduction and oxidation "half-reactions" describes the total, galvanic corrosion reaction in that bi-metal couple.

Note: The SRP reactions and SRP values were determined for the *pure* metals (that are placed into very controlled, 1Molar, ionic solutions) and referenced to the standard hydrogen electrode. The presence of an oxide film on the metal surfaces will significantly alter the reduction/oxidation potential values. Therefore, the textbook computation for galvanic corrosion based upon SRP values represents a second discrepancy between the fundamental discussions and the real-world circumstances. The SRP potentials are determined for pristine metals and generally do not account for metal oxides nor electrolytes typically found in actual applications.

A specific example will illustrate the use of Table 1. This example will assess a metal couple between Al and Cu. The SRP half-reactions and their respective potentials (E^o) from Table 1 are:

$$Al^{3+} + 3\,e^- \leftrightarrow Al \qquad E^o = -1.67V$$
$$Cu^{1+} + e^- \leftrightarrow Cu \qquad E^o = +0.52V$$

Next, the total corrosion process is determined by combining the two half-reactions. But, since corrosion requires one reaction to be a reduction, and the other to be an oxidation reaction, one of the two reactions must be reversed into its "oxidation" counterpart. Similarly, the sign of E^o for the oxidation half-reaction will have to be reversed. The Cu reaction will be so chosen (the choice will be of no consequence as will be demonstrated):

$$Cu = Cu^{1+} + e^- \qquad E^o = -0.52V$$

Before the *reduction half-reaction for Al* is added to the *oxidation half-reaction of Cu.*, it is necessary to conserve electrical charge. That is, the number of electrons (e^-) on the left-hand side of the reduction reaction must equal the number of e^- appearing on the right-hand side of the oxidation half-reaction. Therefore, the Cu half-reaction for oxidation must be multiplied by 3. *However, the SRP value E^o remains the same; the value is not multiplied by 3; only the half-equation is altered to reflect the charge balance.* Now, the two half-

reactions are added together and the number of electrons will cancel out. Likewise, the SRP's are added together, retaining their respective sign convention. The total reaction is referred to as the *reduction-oxidation, or "redox" reaction*:

$$Al^{3+} + 3Cu = Al + 3Cu^{+} \quad E^{o} = -2.19V$$

The negative sign indicates that this reaction, as shown in the direction of left-to-right above, is not spontaneous (i.e., it signifies the "no-go" thermodynamic criterion). On the other hand, the reversed reaction, which is read right-to-left, has a value of E^{o} equal to +2.19V.

$$Al + 3Cu^{+} = Al^{3+} + 3Cu \quad E^{o} = +2.19V$$

The latter reaction, in which Al would be oxidized and thus, experience material loss, and Cu would be reduced, is spontaneous because E^{o} would have a positive sign. And it is the spontaneous reaction that will reflect the potential corrosion of the Al/Cu metal couple in the presence of an electrolyte. This example was selected because, in fact, it represents one of those cases in which, qualitatively, the theoretical calculation describes the real situation. That is, Al and Cu should not be soldered together for use in a corrosive medium; the Al member will quickly begin to corrode (oxidation half-reaction). However, the real-world redox reaction is not likely to have the magnitude of E^{o} be 2.19 V; that value will be altered by the oxides that are present on the part surfaces as well as the character and strength of the electrolyte.

As a second example, the corrosion potential of a joint formed between Sn-Pb solder and Cu is examined. Here, Sn will be used to represent the solder "metal." since the reduction potential for Pb is nearly identical to that of Sn (Table 1). The SRP values and half-reactions are listed below:

$$0.5Sn^{2+} + e^{-} = 0.5Sn \qquad E^{o} = -0.14V$$
$$Cu^{+} + e^{-} = Cu \qquad E^{o} = +0.52V$$

The total reaction that represents the *spontaneous* process is:

$$Cu^{+} + 0.5Sn = Cu + 0.5Sn^{2+} \quad E^{o} = +0.66V$$

Therefore, from these fundamental computations, it would be expected that the solder would be the corroding member in a Cu/Sn-Pb solder joint. However, this is rarely the case, as is further evidenced by the galvanic series for sea water corrosion in Fig. 3. Tin, Pb, and Sn-Pb solders tend to be more noble that Cu simply because of the tenacious oxides (particularly Pb) that grow on their surfaces.

In the above discussion, there were three factors that cause these simply calculations to be, at best, only a first-order approximation of galvanic corrosion in actual metal couples such as solder joints (Fig. 3). (1) There are very few circumstances in which the electrolyte contains ions of the respective electrode (anode and cathode) species. Moreover, even a vague concept of the salt bridge is not realistic in an actual situation. (2) The second factor that tends to invalidate corrosion predictions based upon the potentials listed in Table 1 is *metal oxidation.* The composition and thickness of surface oxides on metals will dramatically alter their electrochemical potential. Moreover, the properties of the oxides that form under specific environments will differ and thus, so will the structures' corrosion behavior. (3) The cathodic (reduction) reaction rarely occurs to one of the metal members. That is because there is actual a third member present in the corrosion system - *water.* In nearly all cases, the cathodic reaction involves H_2O or the O_2 dissolved in it. The reduction reaction for H_2O was presented in equation (2). When sufficient O_2 is dissolved in the water, the following cathodic reaction may also be observed:

$$O_2 + 2H_2O + 4e^- = 4\,OH^- \qquad (6)$$

Irrespective of whether equations (2) or (6) are active, it is important to note that the cathodic reaction does not normally occur to one of the metal members. Of course, that is not to say that the cathodic reduction of H_2O or O_2 will not occur *on* the surface of one of the metals.

The best approach to determining corrosion behavior in a metal (galvanic) couple (solder joint) is to refer to a galvanic series chart such as shown in Fig. 2. First, it is accepted that the cathodic reaction will most likely involve H_2O or other electrolyte that may be present. Between two metals present in the joint, the more "active" metal in the galvanic series will be the anode and corrode by providing the oxidation half-reaction As the difference in potential between the two metals increases, the more likely it will become that the more-active member will preferentially corrode. However, that difference in corrosion activities in the chart does not provide an indication of the rate of corrosion by the anodic material; those rate kinetics are determined primarily by details of the solder joint materials (composition, oxide layer properties, etc.) and the environment (electrolyte concentrations,

time, temperature, etc.). Similarly, the preference of one corrosion mechanism, such as pitting, over another mechanism, such as general corrosion, will also depend upon these details. As noted previously, a separate chart would be required for each different electrolyte that may be of interest.

It is also important to note that the above concepts of galvanic-assisted corrosion by dissimilar materials in contact with one-another can be extended to the microstructural level, as well. For example, many solders are actually composites of several phases. In the presence of an electrolyte, one phase may be more active than the other and therefore, preferentially corrode as the anode in the couple. The selective loss of the anodic phase is often refereed to as *leaching*. In the case of the traditional Sn-Pb solders, the Sn-rich phase would be slightly more active than the Pb-rich phase according to the standard potentials in Table 1. However, because both materials form relatively tenacious oxides, that difference in potentials is significantly reduced. In fact, preferential leaching of Sn is most often encountered in metallographic sample preparation techniques that use relatively strong acids.

Voltage-assisted corrosion

Some applications entail metal structures that are subjected to electrical voltages. Under such circumstances, the corrosion process may be affected by that voltage. The voltage actually alters the "natural" corrosion (charge) potential between the cathode and anode material half-reactions. This situation is termed voltage-assisted corrosion. Voltage-assisted corrosion can affect atmospheric corrosion as well as galvanic (assisted) corrosion processes. Illustrated in Fig. 5a is the case in which two strips of the same material are simply immersed into an electrolyte (e.g., water) with no applied voltage. The two strips would corrode to the same extent, via the same mechanism (e.g., pitting) because they have equal corrosion potentials. However, when a voltage (potential) is placed between the two strips (Fig. 5b), the strip on the negative terminal receives electrons and would thus establish a reduction reaction as the cathode. Conversely, the oxidation reaction would take place on the other strip as the voltage source removes electrons from it. That strip becomes the anode and is where corrosion (metal loss) would occur. Accelerated corrosion at the anode may manifest itself as an actual increase in the rate of material loss or by-product formation, or it may result in a change in the observe corrosion mechanism, such as a switch from pitting to general corrosion.

Of course, voltage-assisted corrosion can be superimposed on a galvanic corrosion situation. However, the effect of the applied voltage depends upon the magnitude of that voltage; the selection of materials to receive the "+" and "-" terminals of the DC source; and

the difference in the ("natural") corrosion potentials between the two materials. The applied voltage can be used to alter the relative corrosion potential between the two metal members, even to the point of switching the anode (corrosion) from one to the other material.

An important consequence that is often observed with voltage-assisted corrosion is *electromigration*[10, 11]. This phenomenon is illustrated in Fig. 6. Two metal pads, having the same composition, are located on top of an insulating material. Each of the two pads are connected to the respective terminals of a DC voltage supply. An electrolyte is deposited across the two pads The metal strip which is connected to the positive terminal, forms the cathode and supports the reduction half-reaction. The pad connected to the negative terminal forms the anode and provides the oxidation reaction. Metal ions are created at the surface of the anode pad as the corrosion by-produce. Those ions can then travel through the electrolyte and reach the cathode. There, the ions are reduced to neutral atoms and will build up on the pad surface. The transfer of metal from the anode to the cathode under the applied voltage is the process of electromigration. The accumulation of anodic material will continue until either the anode material has been completely consumed or the material build-up from the cathode, forming a ligament that reaches the anode and causes a short circuit.

The conductive ligament formed by electromigration is typically short-lived. The path is vaporized by Joule heating almost immediately upon passage of a current. The vaporization of the corrosion product often erases evidence of its existence, thereby hindering failure analysis determinations. This phenomenon has most often been observed in circuit board electronics applications. The momentary short-circuit can damage sensitive electronic components, or cause intermittent failures of electronic circuitry as the paths are created and destroyed. Nevertheless, electromigration can scale up as a function of applied voltage and electrolyte strength, becoming a concern for larger structural members subjected to higher electrical voltages (e.g., power distribution facilities). Electromigration is sometimes the source of persistent "grounding problems" in both small- and large-scale electrical circuitry.

Stress corrosion and corrosion fatigue cracking

Finally, it should be noted that corrosion processes can be accelerated by *applied stresses* on a solder joint. The imposition of mechanical loads on the structure, and in particular, tensile stresses, may cause the solder or base material(s) to have an increased sensitivity to corrosion processes. This phenomenon is termed *stress corrosion cracking (failure)* in the case of static loads, or in the case of cyclic, fatigue loads, it is called *corrosion fatigue failure*[12,13]. At this time, the author is not aware of any extensive

studies that have examined either cracking phenomenon in solder materials or solder joint structures. The additional variable of mechanical loading can complicate the task of predicting corrosion activity in the solder joint. Unfortunately, experimental data that describes stress corrosion or corrosion fatigue cracking are not readily available, forcing the design engineer to rely on in-house laboratory experiments or field monitoring of actual assemblies. *The impact of mechanical loads (either service stresses or residual stresses) has been found to be significant in other metals and alloy, and thus, should receive consideration in the course of designing and/or testing a solder joint that will be placed in an environment having both corrosive media and mechanical loads.*

Corrosion mitigation

Several approaches can be taken to prevent unwanted corrosion activity in solder joints. One means of limiting atmospheric, galvanic-assisted, or voltage-assisted corrosion processes is to remove or isolate the joint area from the corrosion medium. In a specialized case for solder joints, this approach begins at the product manufacturing step by the complete removal of flux or other processing residues (e.g., caustic cleaning solutions) from the part. Although these residues may be relatively benign in the a dried state, the presence of water vapor or liquid can quickly make them corrosive to the joint structure. Under the more general precept of atmospheric or environmental corrosion, it is not possible to remove the damaging conditions. Therefore, preventing exposure to those environments requires the use of barrier coatings or finishes. Coatings may be organic, such as conformal layers, paints and varnishes[14,15]. It is important that the organic layer have suitable adhesion to the solder joint area. Such adhesion may be significantly degraded by the presence of residues from fluxes or cleaning agents. The use of organic coatings must also be weighed against the potential need for reworking the joint. When repair or rework procedures are performed, all traces of the coating must first be removed from around the joint before desoldering and resoldering activities are allowed to take place.

Coatings may also be inorganic. Inorganic coatings are generally deposited *metal* finishes such as provided by electroplating and electroless processes. Also, thermal spray coatings can provide an inorganic barrier layer having a variety of traditional and custom material composition to meet the particular application. In the case of deposited metal coatings, it is desirable that the finish forms a tenacious oxide that is, itself, resistant to chemical attack or breakdown. Nickel, Cu, Zn (galvanizing processes), and even Sn can serve in this regard. Noble metal finishes such as Au, Pt, and Ag may be a cost-effective option. Chromium and Cd coatings have a long history of providing excellent corrosion

protection for soldered structures; however, today, concerns regarding the environmental hazards of these heavy metals and their plating processes have significantly limited their availability within the industry.

Besides acting as a physical barrier between the metal and environment, metal coatings can also offer corrosion protection by allowing themselves to corrode preferentially with respect to the solder joint materials. The coating is then said to be a *sacrificial layer* or *sacrificial anode* because it "sacrifices" itself to preserve the base metal or solder. Referring to the galvanic series for sea water in Fig. 2, a sacrificial material would be one that is more active that either the Sn-Pb solder (50-50 is exemplified) or Cu. The bottom of chart indicates that Al, Cd or Zn coatings would provide viable candidates. It can also be inferred from the position of the low-carbon steels and cast irons that Fe would also provide anodic protection.

Solder joints attaching Al or Al alloy base materials to one-another, using Sn-based solders can pose a particular corrosion concern for almost any service application. In this case, a multi-coating technique has been shown to provide added corrosion resistance[16]. First, a Cu or Ni layer is deposited on the Al or Al alloy surface (with a prior "zincate" activation strike) to establish a solderable surface. The solder joint is then completed. Next, a Zn or Cd coating is deposited over the entire structure, including the solder joint. The Zn and Cd coatings serve two functions. First of all, they have tenacious surface oxides to act as a barrier against potentially corrosive service environments. Secondly, although not sacrificial to Al, the Zn or Cd coatings are sacrificial to the underlying Ni or Cu layers. Therefore, should the physical barrier provided by the Zn or Cd coating be breached, the Zn or Cd will preferentially corrode as opposed to the Ni or Cu layer (and the Sn-based solder). The Ni or Cu finish will remain intact so as to provide a second barrier layer for protecting the underlying Al or Al alloy base material.

Whether the coating is an organic material or electrodeposited metal, it is important to verify that the part is completely covered, and that the finish has the proper thickness, *everywhere*. As the coating becomes thinner, the likelihood of ever-present pinholes in the finish can expose the substrate surface to the corrosive environment. Such a breach of the coating thickness can lead to severe, localized corrosion as illustrated schematically in Fig. 7. In some cases, the corrosion damage often progresses under the coating with little or no indication until after a major catastrophic failure has occurred.

In the specific case of galvanic corrosion, besides isolating the metal surfaces from the electrolyte, the "galvanic" corrosion potential may also be reduced through the choice of materials comprising the joint. Unfortunately, other criteria such as mechanical function, solderability for cost-effective manufacturing, or cosmetic appearance have a priority when

it comes to choosing the base materials and filler metal that will comprise the solder joint. Materials choices based upon corrosion criteria are only considered when damaging environments are explicitly present, such as chemical processing or salt water conditions. The design engineer can obtain an initial indication the corrosion potential between metal components in a solder joint by consulting a galvanic series chart (Fig. 2) for the particular environmental conditions. Should the galvanic series confirm that a thermodynamic potential exists for corrosion activity between two or more of alloys, then a search should be made to locate any available corrosion *rate* data that is pertinent to the specific service conditions. An absence of such data may necessitate an experimental program (laboratory or field study) in order to obtain the important corrosion rate kinetics.

Voltage-assisted corrosion and electromigration can be reduced or eliminated by generally two approaches. As previously discussed, the solder joint can be isolated from the environment as a first measure, generally through the use of organic coatings. Inorganic (metallic) coatings can only be used when it they are not likely to cause an electrical short circuit. Changing the materials used in the solder joint may provide a second option. For example, Ag has been found to be particularly susceptible to electromigration under an applied voltage[11]. Silver-based alloys are often used as contact materials and electroplated Ag coatings are widely used in electrical connections; Ag is suited for these electrical applications due to its low resistance. In addition, Ag coatings offer good protection against atmospheric corrosion. However, it should be noted that past studies on the electromigration behavior of Ag have pertained to only the elemental metal (e.g., wrought material and platings) or Ag coatings. There is no evidence that Ag-containing solders are prone to electromigration[10]. Nevertheless, a material change-out from Ag to a less susceptible material provides one course-of-action towards eliminating this particular consequence of voltage-assisted corrosion situation.

Finally, in the event that mechanical loads have been observed to accelerate atmospheric or galvanic corrosion processes in the solder joint, then isolation of the solder joint from the corrosive media through the use of coatings becomes the first recourse. Unfortunately, in the case of conduit that is transporting the corrosive material, the application of coatings or metal finishes may not be possible. Under those circumstances, it is necessary to select a different filler metal (or base metal) that is less susceptible to corrosion activity. Reducing or eliminating the mechanical load may not always be a viable approach towards mitigating stress-assisted corrosion mechanisms. However, changing the loading conditions at the joint structure may be realized by altering the local geometry. For example, the more problematic tensile stress can be eliminated in favor of more benign shear stresses by simple changing from a butt (tensile) joint to a lap (shear) joint.

Summary

Corrosion is an important consideration in the design of a solder joint. In the case of conduit, corrosion must be addressed with respect to both the (outside) service environment as well as the nature of the medium being transported within the pipe or tube structure. Solder joints can be susceptible to atmospheric corrosion, galvanic-assisted corrosion, voltage-assisted corrosion, stress corrosion cracking, and corrosion fatigue cracking. Galvanic corrosion is of particular concern, given the fact that solder joints are comprised of different metals or alloys in contact with one-another. Each of these corrosion processes can be manifested in one or more of the following corrosion mechanisms: uniform corrosion, pitting, crevice corrosion, and intergranular (interphase) corrosion. The (thermodynamic) potential for corrosion to take place in a particular environment requires the availability of the galvanic series for those conditions, and which includes the metals or alloys in question. However, these series cannot provide the necessary kinetics data that determine material loss under the specified service conditions. The latter information requires the availability of laboratory test or field evaluation data provided through the existing literature or obtained by in-house testing.

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Figures

Fig. 1 Corrosion activity in a solder joint between 96.5Sn-3.5Ag solder and Cu base materials.

Fig. 2 Galvanic series for several metals and alloys in sea water. *(used with permission of ASM International)*

Fig. 3 Schematic diagram illustrating the textbook description of galvanic corrosion.

Fig. 4 The configuration of a solder joint as a potential galvanic, corrosion cell.

Fig. 5 (a) Two metals of the same composition are immersed into an electrolyte. Both exhibit similar corrosion behaviors (e.g., mechanisms, rates, etc.). (b) When a voltage is applied between the two metal members, the strip connected to the negative terminal will provide the oxidation half reaction and corrode.

Fig. 6 The process of electromigration between two metal under an applied electrical potential.

Fig. 7 Schematic diagram of corrosion process caused by the breach in a protective finish.

Tables

Table 1 Standard Reduction Potentials of Selected Metals. *(used with permission of J Wiley and Sons).*

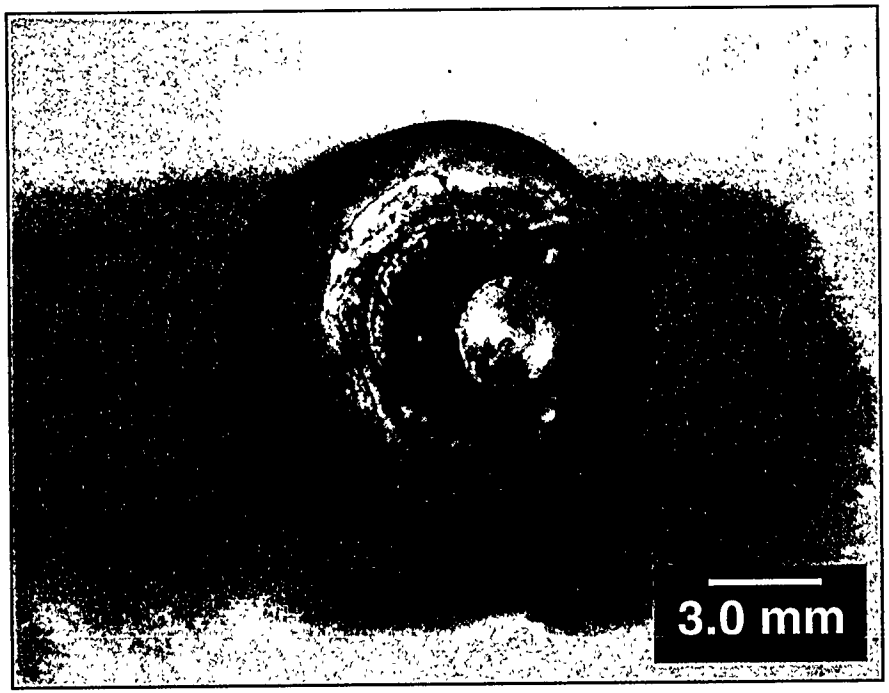


Fig. 1a

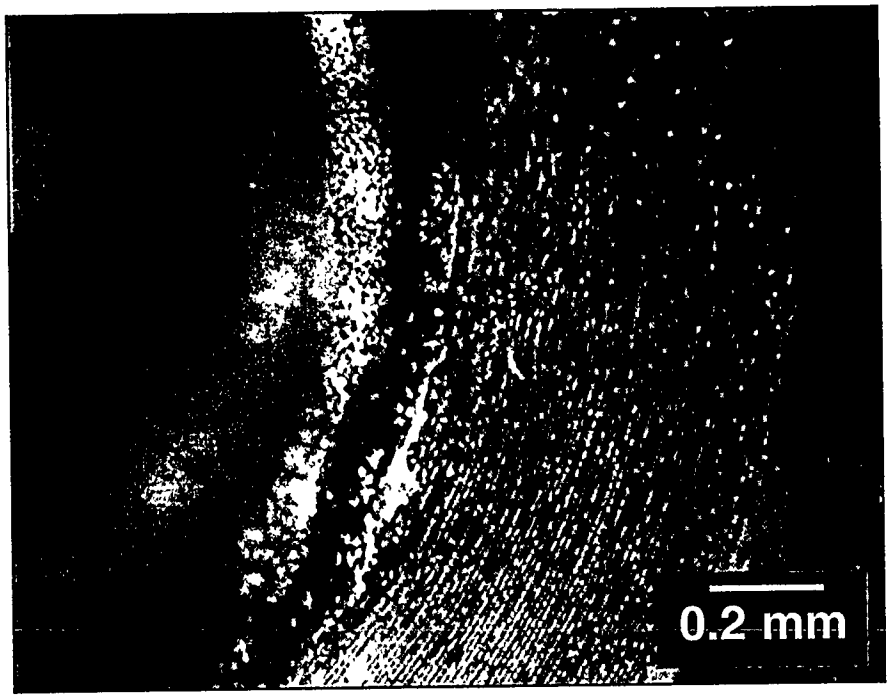


Fig. 1b

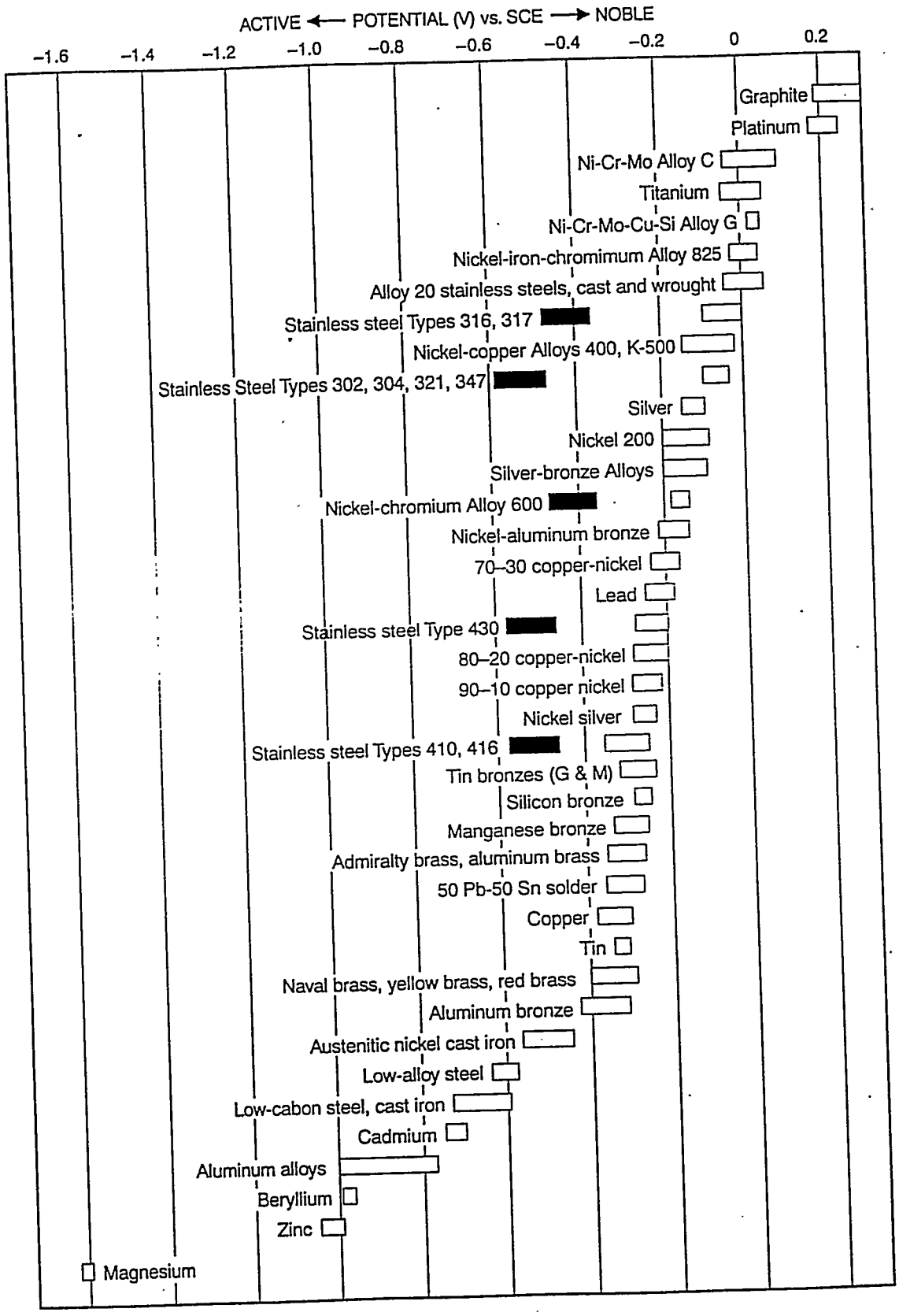

ACTIVE ← POTENTIAL (V) vs. SCE → NOBLE
−1.6
−1.4
−1.2
−1.0
−0.8
−0.6
−0.4
−0.2
0
0.2
Graphite
Platinum
Ni-Cr-Mo Alloy C
Titanium
Ni-Cr-Mo-Cu-Si Alloy G
Nickel-iron-chromimum Alloy 825
Alloy 20 stainless steels, cast and wrought
Stainless steel Types 316, 317
Nickel-copper Alloys 400, K-500
Stainless Steel Types 302, 304, 321, 347
Silver
Nickel 200
Silver-bronze Alloys
Nickel-chromium Alloy 600
Nickel-aluminum bronze
70–30 copper-nickel
Lead
Stainless steel Type 430
80–20 copper-nickel
90–10 copper nickel
Nickel silver
Stainless steel Types 410, 416
Tin bronzes (G & M)
Silicon bronze
Manganese bronze
Admiralty brass, aluminum brass
50 Pb-50 Sn solder
Copper
Tin
Naval brass, yellow brass, red brass
Aluminum bronze
Austenitic nickel cast iron
Low-alloy steel
Low-cabon steel, cast iron
Cadmium
Aluminum alloys
Beryllium
Zinc
Magnesium

FIG. 2

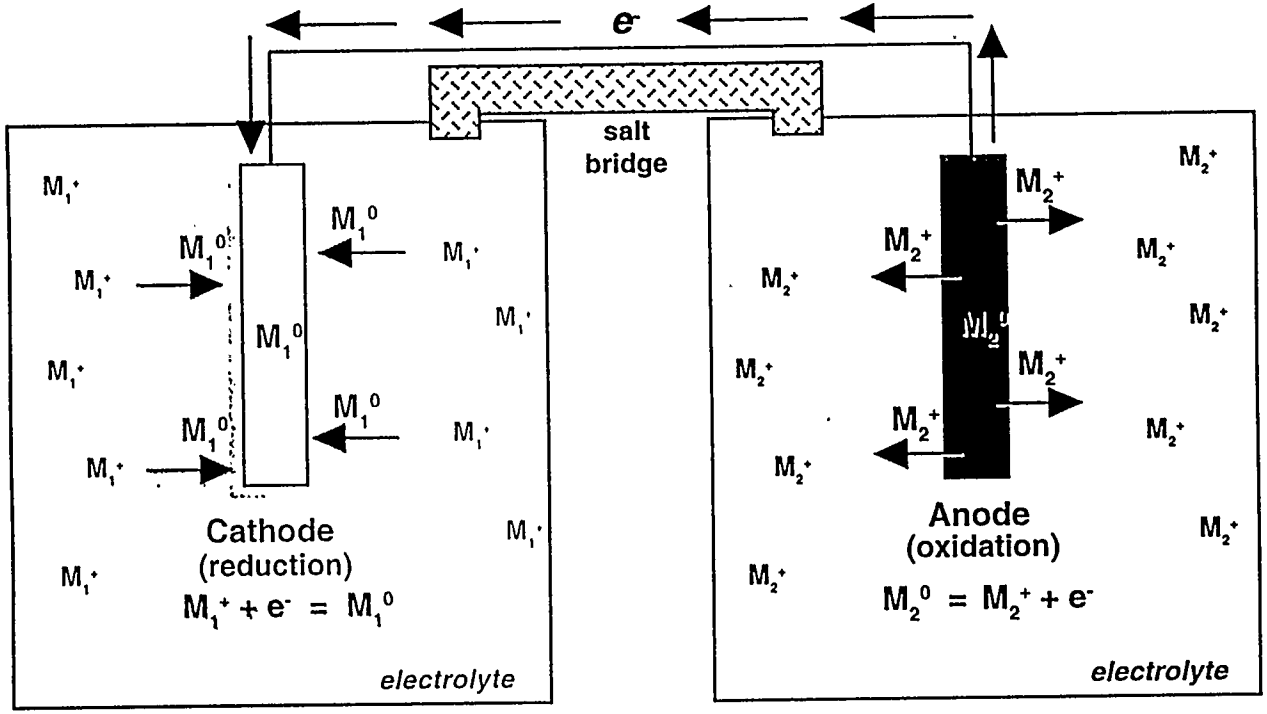
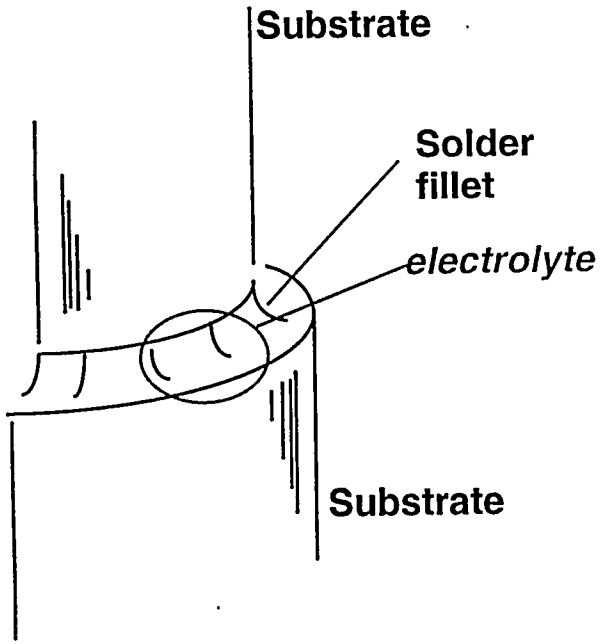

e-
salt bridge
Cathode
(reduction)
M1+ + e- = M10
electrolyte
Anode
(oxidation)
M20 = M2+ + e-
electrolyte

Fig. 3



Solder Joint

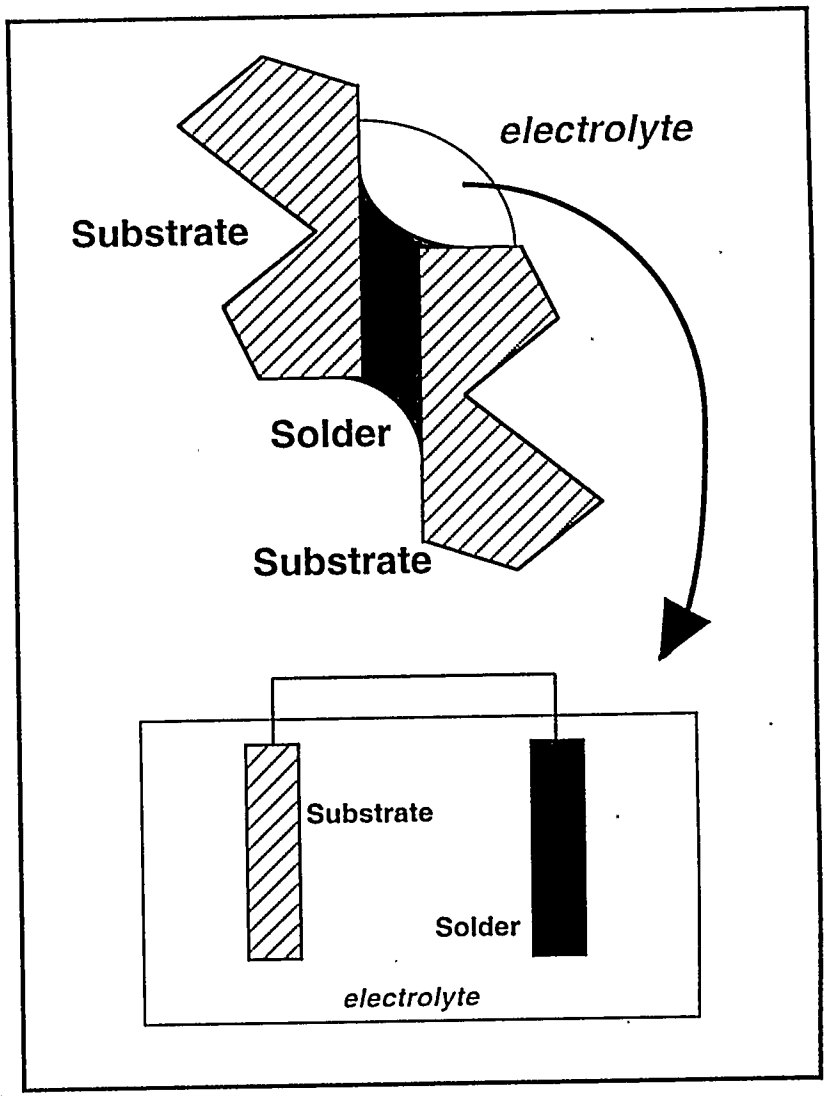
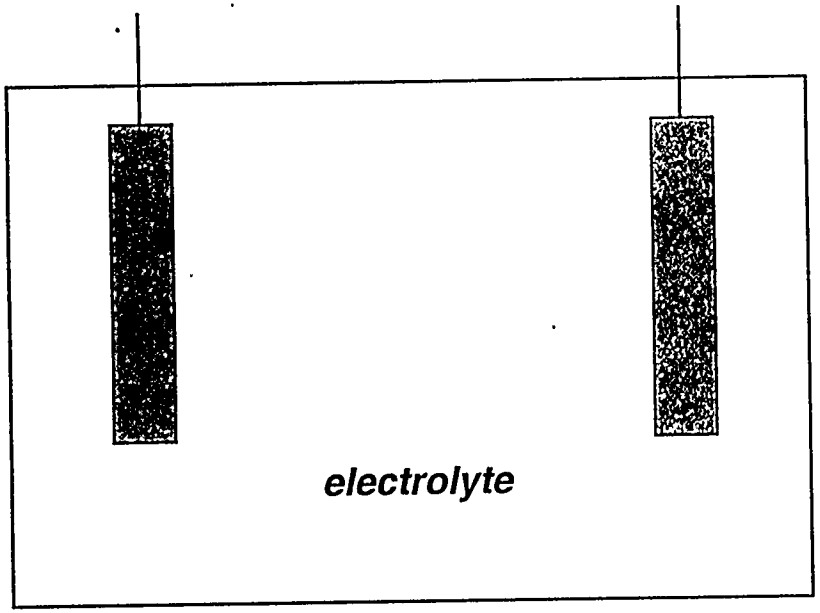
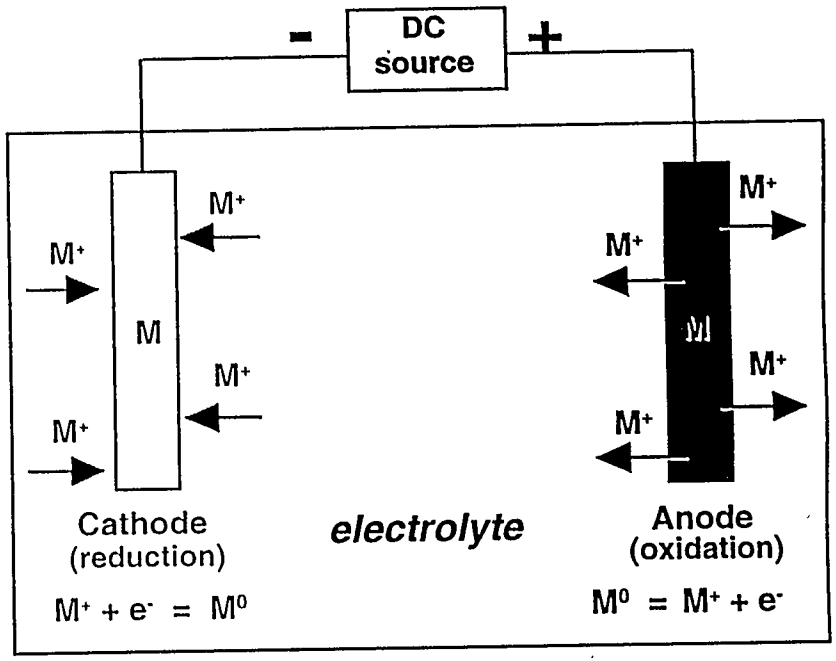


Fig. 4


electrolyte

(a)


-
DC source
+
M⁺
M⁺
M
M⁺
M⁺
M⁺
M⁺
M
M⁺
M⁺
Cathode
(reduction)
M⁺ + e⁻ = M⁰
electrolyte
Anode
(oxidation)
M⁰ = M⁺ + e⁻

(b)

Fig. 5

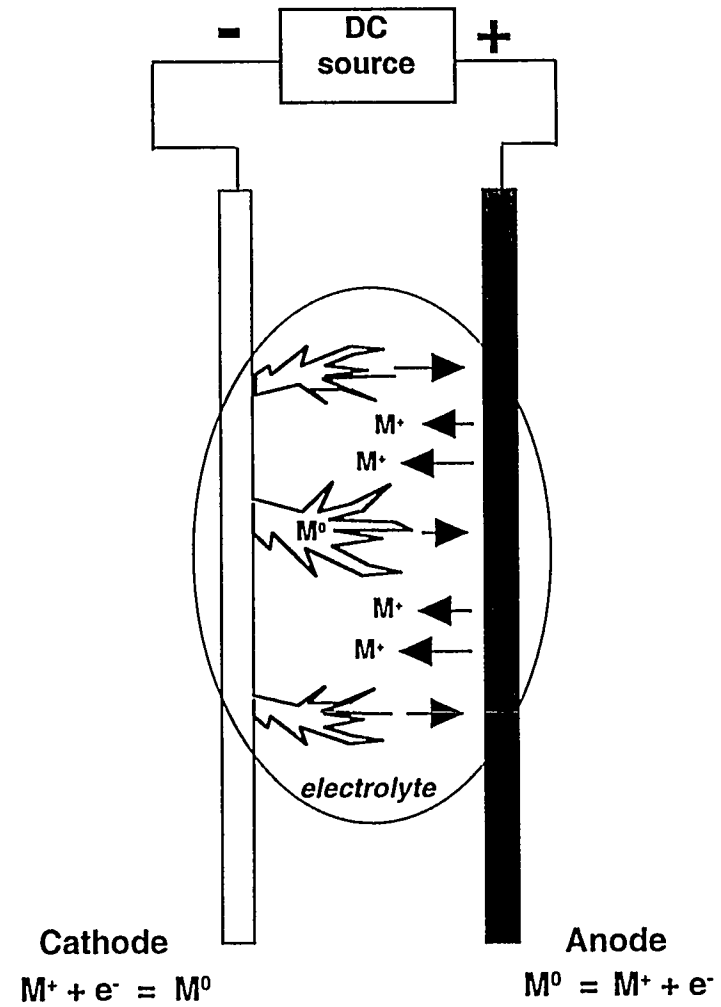


Fig. 6

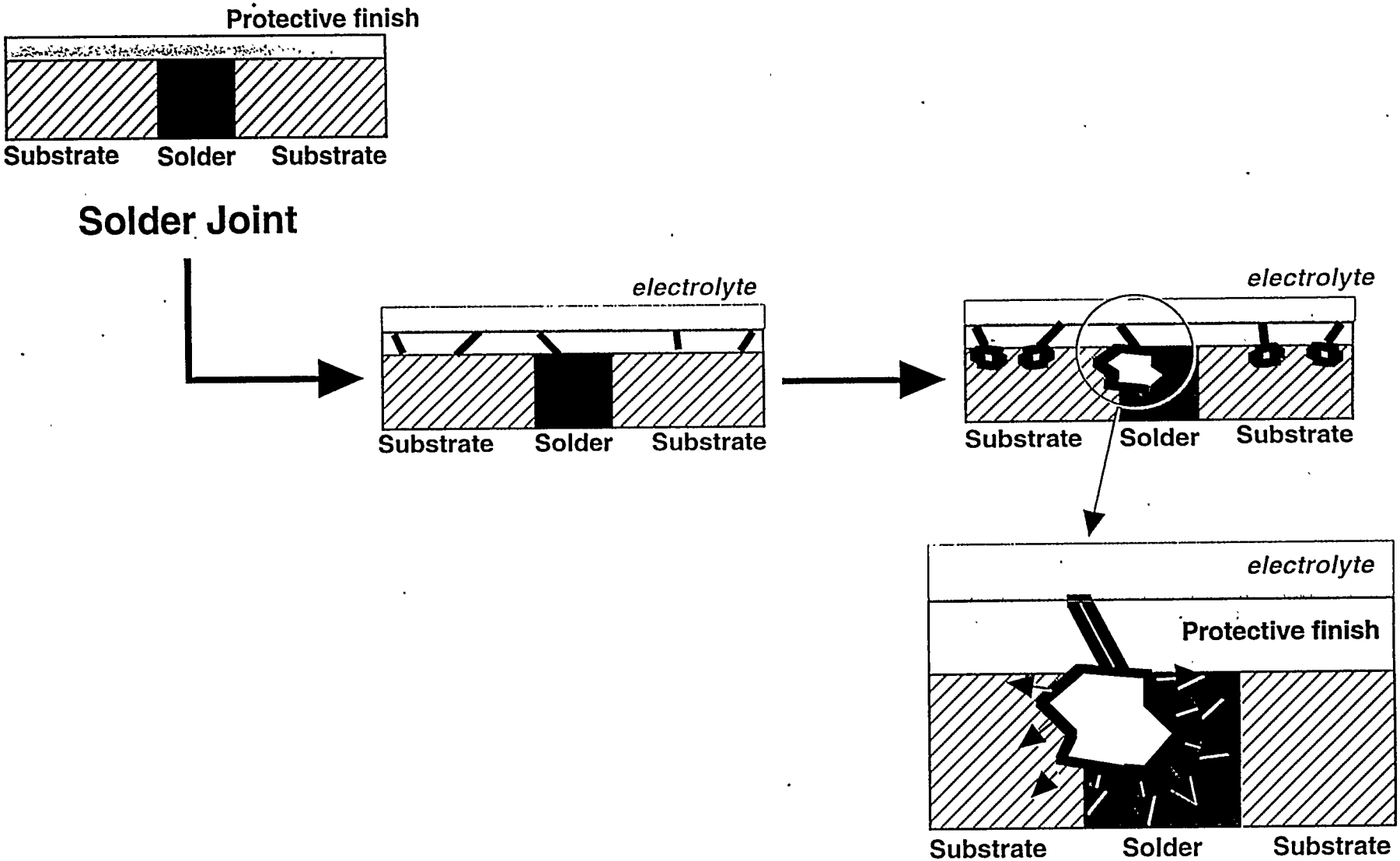

Protective finish
Substrate
Solder
Substrate
Solder Joint
electrolyte
Substrate
Solder
Substrate
electrolyte
Substrate
Solder
Substrate
electrolyte
Protective finish
Substrate
Solder
Substrate

Fig. 7

Table 10
Standard Reduction Potentials at 25°C

Half-Reaction	$\mathcal{E}°$ (volts)
$Li^+ + e^- \rightarrow Li$	–3.05
$K^+ + e^- \rightarrow K$	–2.92
$Ba^{2+} + e^- \rightarrow Ba$	–2.90
$Ca^{2+} + 2e^- \rightarrow Ca$	–2.76
$Na^+ + e^- \rightarrow Na$	–2.71
$Mg^{2+} + 2e^- \rightarrow Mg$	–2.38
$Al^{3+} + 3e^- \rightarrow Al$	–1.67
$Mn^{2+} + 2e^- \rightarrow Mn$	–1.03
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	–0.83
$Zn^{2+} 2e^- \rightarrow Zn$	–0.76
$Cr^{3+} + \rightarrow Cr$	–0.74
$Fe^{2+} + 2e^- \rightarrow Fe$	–0.44
$Cd^{2+} + 2e \rightarrow Cd$	~~–0.45~~ –0.40 ✓
$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	–0.36
$Ni^{2+} + 2e^- \rightarrow Ni$	–0.25
$Sn^{2+} + 2e^- \rightarrow Sn$	–0.14
$Pb^{2+} 2e^- \rightarrow Pb$	–0.13
$Fe^{3+} + 3e^- \rightarrow Fe$	–0.04
$2H^+ + 2e^- \rightarrow H_2$	0.00
$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27
$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Cu^+ + e^- \rightarrow Cu$	0.52
$I_2\ (aq) + 2e^- \rightarrow 2I^-$	0.54
$Fe^{3+}\ e^- \rightarrow Fe^{2+}$	0.77
$Ag^+ + e^- \rightarrow Ag$	0.80
$Br_2(aq) + 2e^- \rightarrow 2Br^-$	1.09
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23
$MnO_2 + 4H^+ + 2e^- \rightarrow 2Cr^3 + 7H_2O$	1.28
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33
$Cl_2(g) + 2e^- \rightarrow 2Cl^-$	1.36
$2ClO_3^- + 12H^+ 10e^- \rightarrow Cl_2 + 6H_2O$	1.47
$8H^+ + MnO_4^- + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.49
$Au^{3+} + 3e^- \rightarrow Au + 1.5$	1.50 ✓
$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78
$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$	2.00
$F_2 + 2e^- \rightarrow 2F^-$	2.87

Table 1