

A review of Corrosion and environmental effects on electronics

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Abstract

Electronic industry uses a number of metallic materials in various forms. Also new materials and technology are introduced all the time for increased performance. In recent years, corrosion of electronic systems has been a significant issue. Multiplicity of materials used is one reason limiting the corrosion reliability. However, the reduced spacing between components on a printed circuit board (PCB) due to miniaturization of device is another factor that has made easy for interaction of components in corrosive environments. Presently the knowledge on corrosion issues of electronics is very limited. This paper reviews briefly the materials used in electronic systems, factors influencing corrosion, types of corrosion observed in electronics, and testing methods.

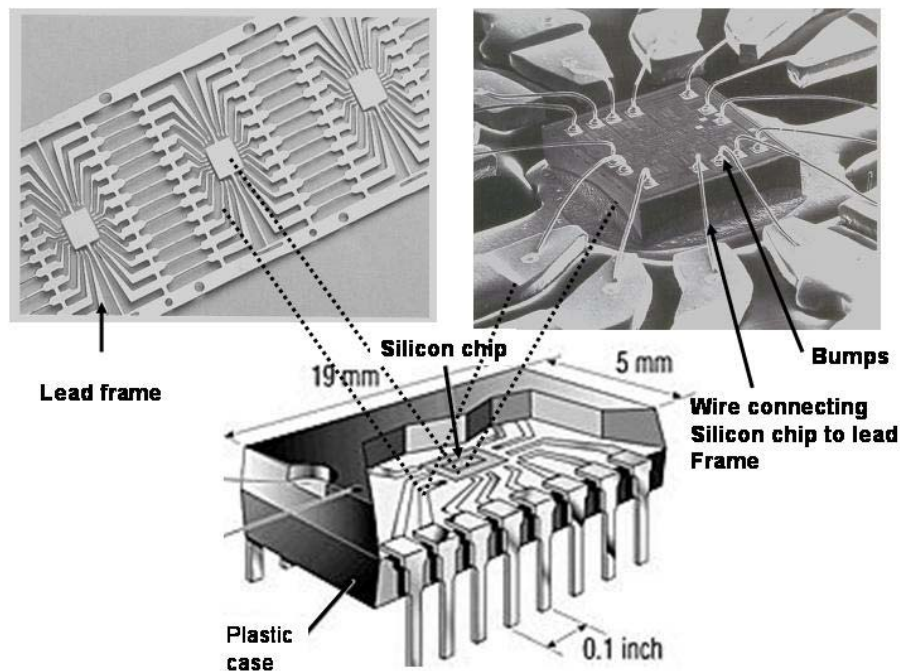
Introduction

Presently electronic devices are used under service conditions that were never thought off few years back. Simultaneously, increased use of electronics has also increased the demand for reliability. The demand for miniaturization, multiplicity of materials used, effect of process residues together with unpredictable user environment has opened up serious corrosion problems. The consumer electronics is one sector where the user environment is highly variable. Overall size of electronic equipment has also been decreasing presently at a faster rate. The size of the ICs has been decreased by a factor of 10 over the last couple of years, which means that the spacing between the IC components is ~ 200 nm. For components on a PCB, the spacing is around 5 microns, while in mid-90's it was 100 microns. The reduction in size and distance between components makes the system more susceptible to corrosion problems. To generate a fault in the conducting path of such constructions, a material loss of the order of picograms (10^{-12}) is sufficient [1]. Therefore, even a small environmental impact can cause huge damages if the components are not well protected. When the device is in use, the large voltage gradients between points on a PCB will accelerate the corrosion problems dramatically. However, the impact of voltage gradient on PCB corrosion is often overlooked with respect to damage in electronic circuits.

Present review discuss briefly about important electronic components and parts, materials used in them, and various corrosion issues related to materials combinations and design. A brief discussion on the effect of various parameters and testing methods are also included.

Materials in electronic systems

From the viewpoint of a corrosion specialist, corrosion in electronics is not a surprise due to the multiplicity of materials used simultaneously with several other factors conducive for corrosion. As the materials used are many and component designs are complicated, it is beneficial for the non-electronic reader to have knowledge on these prior to the discussion on corrosion issues. A detailed discussion on every component is beyond the scope of this view,



0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99

Different methods are used for bonding the wire to the lead frames. These are: Ultrasonic bonding (U/S), thermo sonic bonding (T/S) and thermo compression bonding (T/C). Further, there are two ways of joining the wire to silicon chip. One process is called ball bonding and the other wedge bonding.

Figure 2 shows a ball bonding of gold wire to aluminium PVD coating on silicon chip. The picture also shows how the material is compressed out of the interface area. Ball bonding is possible with a lot of different materials Au/Au, Au/Ni, Au/Ag, Al/Al, and Cu/Al to name a few. Only few corrosion cases have been reported on Ball bonded parts, although the possibility of galvanic corrosion is over looked. However, there are other problems related to intermetallic phase formation and Kirkendall effect at the interface.

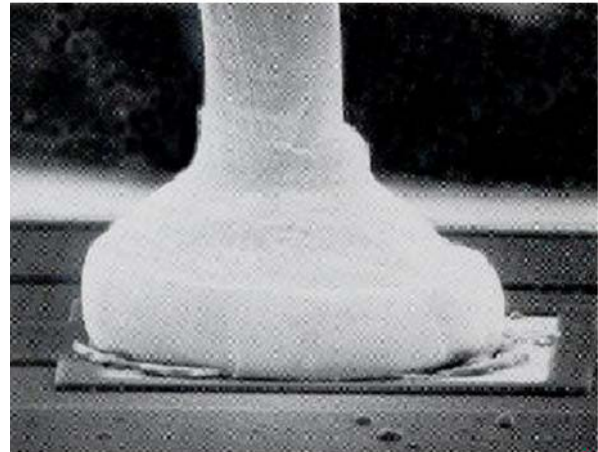


Figure 2. Picture of a ball bonded gold wire to aluminium on an IC circuit

Printed Circuit Board (PCB):

PCB is a macro-electronic structure compared to an IC, where a number of electronic parts are integrated (including ICs) on a fibreglass epoxy polymer with interconnecting lines as shown in Figure 3c. Typical PCB consists of copper connecting path integrated in a fibreglass reinforced epoxy polymer (Figure 3a). The PCB can be made of a series of layered structure (from double to multi layer) with each layer consisting of interconnecting lines (Figure 3b). The line in each layer is connected to the lines on top and bottom through blind holes, which is plated. The connection paths are made solderable with a Sn-Pb coating, which also act as an etch-resist in the manufacturing process. Recent processes for PCB wiring use ENIG-process (Electroless Nickel-Gold). The ENIG consists of a few micron thick Ni-P (EL Ni) coating on the base copper on PCB, followed by a thin gold layer on EL Ni [3]. Thickness of the gold layer varies from 50 – 100 nm. The reason for using the ENIG process in the first place is to produce a PCB with good solderability. However later, the good connecting property of the gold has also been used for connectors by using a thin layer of gold coatings. Some type of PCBs use “thick-film” connecting paths either in combination with copper on PCB or just in uncomplicated printed and hardened film made with application of a silver paste. Figure 3c shows the PCB with various components mounted on them. If water layer is present, many of the components can get connected to each other, which is easier with reduction in spacing between them.

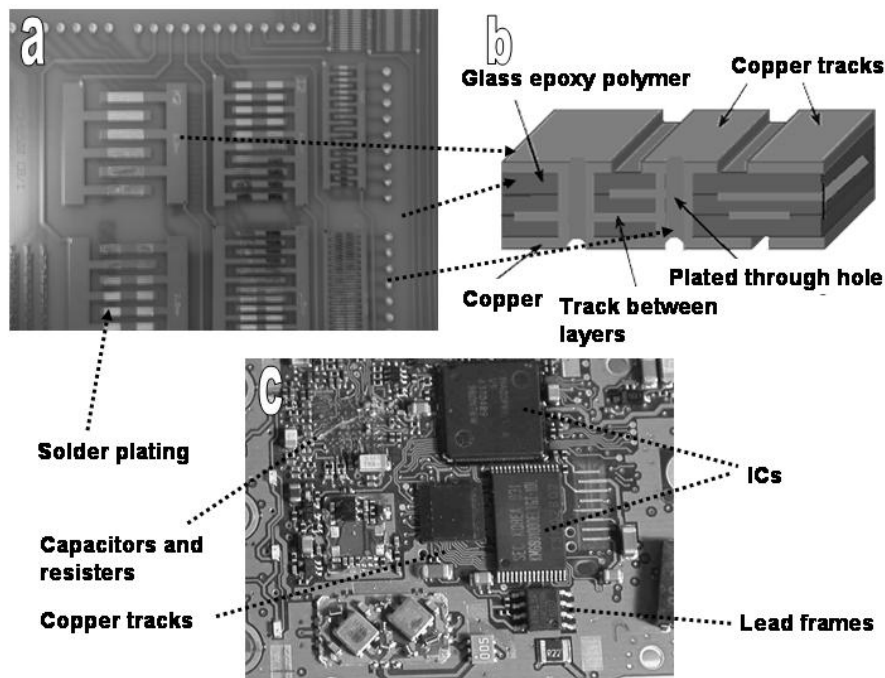


Figure 3. Description of a PCB: (a) PCB with connecting lines, (b) schematic of the cross section of a PCB, and (c) PCB with component mounted on it.

Electronic connectors:

There is a large spectrum of materials used for electronic connectors. Figure 4 shows one type connection interface used for PCBs with gold layer on the top. The classical materials used for low-voltage electronics are the copper and copper alloys, which are electroplated with a noble metal such as gold. Table 1 shows some of the material combinations used for electronic connectors.

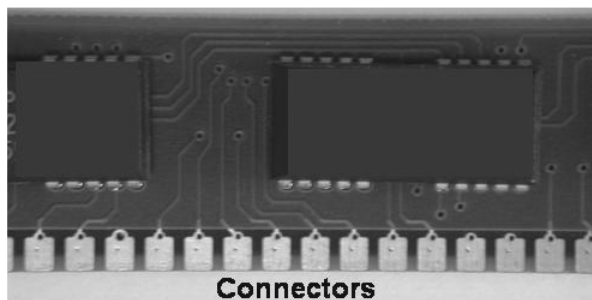


Figure 4. Electronic connecting part on a PCB

Table 1: Materials used for electronic connectors

Basic Materials	CuSn6 CuBe2 CuNi10Sn2 X12CrNi 177
Connection Surface	Hard gold Palladium + hard gold-flash Palladium/nickel + hard gold-flash

Use of palladium and palladium-nickel alloys is however decreasing due to the high cost of palladium. Gold or palladium coating is needed to prevent nickel diffusion.

Today electronic connectors are mainly manufactured with reel to reel plating, which is an effective and cheap process so that it is possible to make selective deposition of the noble metal exactly at the area of contact. It is also possible to make coating with varying thickness

having a thick layer at the connecting area to withstand greater wear. Electronic connectors made of graphite are often used in the “thick-film” techniques.

Computer hard disk:

Inside of a computer hard disk drive consists of several components as shown in Figure 5. The round disc platter is the magnetic recording media for hard disc. The platter is usually made of aluminium electroplated with nickel, and an over layer of 50 nm thick magnetically active cobalt alloy using PVD. Over the magnetic cobalt layer there is a thin layer of carbon, which is also coated using PVD. The arm like device that extends over the disc platter is known as the head arm, and is the device that reads the information out of the disc platter. The head arm is attached to the head actuator, which controls the head arm. Not shown is the chassis which encases and holds all the hard disk drive components.

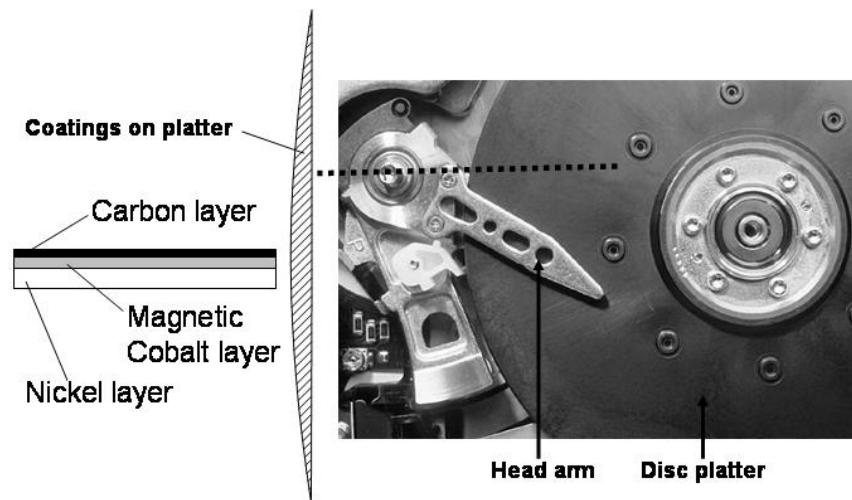


Figure 5. Computer hard disk with description of components [4].

Electronic encapsulation materials:

The materials generally used for electronic packaging are metallic or polymeric materials. For electronic packaging, the material should have good conductivity in order to get good Electro Magnetic Interference (EMI) shielding. Therefore, if polymers are used, it is often necessary to coat the surface with a good metallic material to increase the shielding capability. For this purpose a thick layer of copper/nickel or aluminium coating is usually employed. The copper/nickel coating is usually made by electroplating, while the aluminium coating is made by PVD process. Rarely silver is used in some applications because of the high EMI shielding capability. The common metallic materials used for electronic structural parts are galvanized / chromated steel, but recently light metals such as magnesium is increasingly used for electronic packaging. Magnesium casing have been largely used for laptops and cell phones because its ability to die-cast thin complicated structures having desired strength and weight. A part made of magnesium with similar EMI shielding capability as steel weigh much less, so that lighter structures can be produced with magnesium. From the corrosion point of view,

few properties of the encapsulation materials are extremely important other than corrosion and environmental degradation of the material itself. These are the water permeability, wettability of the surface, and probably the heat transfer.

Lead free solder systems

A new set of lead free solder systems are emerging as replacement for lead solders due to potential health hazards of lead. European lead free legislation calls for total withdrawal of lead solders by 2008 [5]. Therefore, electronic industries are on a transition path to lead free solders. The candidate alloy components involve Sn as the base element, Ag, Bi, Cu, and Zn as the major alloying elements, and some other minor additions such as In and Sb. However, based on the market developments, it appears that the ternary system Sn-Ag-Cu emerges as the primary choice for replacement. Alloys within the composition range Sn-[3.4-4.1] Ag-[0.45-0.9] Cu are generally recommended.

However, presently very little is known about the metallurgy and corrosion aspects of lead free solder systems. All lead free compositions consist of Sn as the base element with Ag and Cu. Although Sn itself is corrosion resistant, addition Cu and Ag could decrease the resistance. Copper and silver are two elements that have high migration susceptibility, and there are few reports [6,7] suggesting that Sn-Cu-Ag systems are susceptible to electrolytic migration. More research is needed on all aspects of lead free solder systems prior to their implementation, so that the lead free technology could be used more efficiently in electronic systems.

Causes of corrosion in electronic systems

As indicated before, the materials and miniaturization has significantly contributed to the corrosion of electronic systems. However, there are several other environment related factors that could accelerate the corrosion process, which needs to be controlled in order to reduce the corrosion effects in electronics systems.

Among the environmental issues, a significant problem is the residues found on the PCBs. Following classification can be made for residues, which will be useful for further discussions:

- Process related residues
- Service related residues

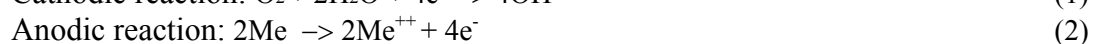
Process related residues are the contamination on the surface due to the remains of the chemicals used for the manufacturing process. This could be the left over of original chemicals or decomposed fractions of a compound formed during the production cycle. These are the fluxing agents, etching medium, plating bath residues, or additives from the polymeric materials. Although the solder fluxes are designed to give (especially the no-clean variety)

essentially no residue after the soldering process, depending on the temperature cycles and applications, small amount of original compound or decomposed products could remain on the surface. In practice, tiny fractions of these chemicals are enough to accelerate the corrosion process. A study reported [8] on the effect of no-clean flux on electrolytic migration found that fluxes like RF800 and TN/4A are problem free for PCBs or hybrid circuits, while SL65 and LP-11AC varieties are only suitable for PCBs. Use of SL65 and LP-11AC for hybrid circuit applications resulted in Ag dendrites due to electrolytic migration.

The service related residues are the residues introduced during exposure to service environments. They can be aggressive ions like chlorides, SO₂(g), NO₂(g), or other types of chemically aggressive ions. Presence of such substances triggers corrosion to a large extent under humid conditions. The dust particle is another issue, which can act as a moisture trapping agent. Formation of water layer is easy on a dusted surface compared to the clean one. Therefore, corrosion is possible even at relatively low humidity such as 50-70%. If the surface of the electronic components is not contaminated, corrosion will not be a large issue. However, in practise significant levels of contamination could be detected on printed circuit boards and components.

Water layer or a tiny water drop-let sitting on the surface of a PCB can generate micro-galvanic cell by electrically connecting the two metallic parts. Within the micro-galvanic cell, cathodic reaction takes place on the noble electrode (eg. graphite, gold, silver, copper or negatively charged part under applied potential), while the anodic reaction occurs on the active electrode by metal dissolution. However, due to the large ohmic drop experienced in the thin film solution, anodic reaction often takes place on a close by cathodic part. It is important to notice that the electrical charge is transported by electrons in the metallic material and by ions in the liquid. The transfer of charge from metal surface (electronic conductor) to solution (ionic conductor) interface occurs by an electrochemical reaction namely oxidation or reduction.

From the mechanistic viewpoint, corrosion of electronics is similar to the atmospheric corrosion. Under humid conditions, the condensed water layer at the surface of a PCB generates conducting path (electrolyte) for corrosion. It is like a tiny corrosion cell with adjacent components on a PCB acting as electrodes. The cathode reaction will be the reduction of oxygen by the diffusion of oxygen from the atmosphere through the thin layer of water to the electrode surface. And the anodic reaction is the dissolution of metal subjected to corrosion.



One problem with atmospheric corrosion is that the conditions can change with time. This could be either due to a change in the weather conditions, local environment, conditions

related to the equipment etc. Therefore, in general the rate of corrosion is determined by the following factors:

- Wet/dry cycle – the time of which the surface is wet or dry,
- Composition of the moisture,
- Temperature.

Thermodynamics of corrosion:

Thermodynamic principles, especially the Pourbaix diagrams [9] will be a useful tool to predict corrosion problems in electronics in terms of the use materials, environment, and applied voltage for operating the device. As a first approximation, using Pourbaix diagrams, one could predict the behaviour when different materials are coupled or same materials with different potential gradients on a PCB are connected by an environment. Presently, computer programmes are available for constructing Pourbaix diagram for any metals/alloys within an environment of choice. As an example, Figure 6 shows the Pourbaix diagram for gold in chloride solutions constructed using the standard Outokumpu HSC Chemistry 4.0 software. Contrary to the normal perception of gold as a stable material, Figure 6 shows that the gold can corrode over a range of potentials and pH in chloride solution forming AuCl_3 . The potential values corresponds to the stability of AuCl_3 could be easily achieved in many electronics systems clearly predicting the vulnerability.

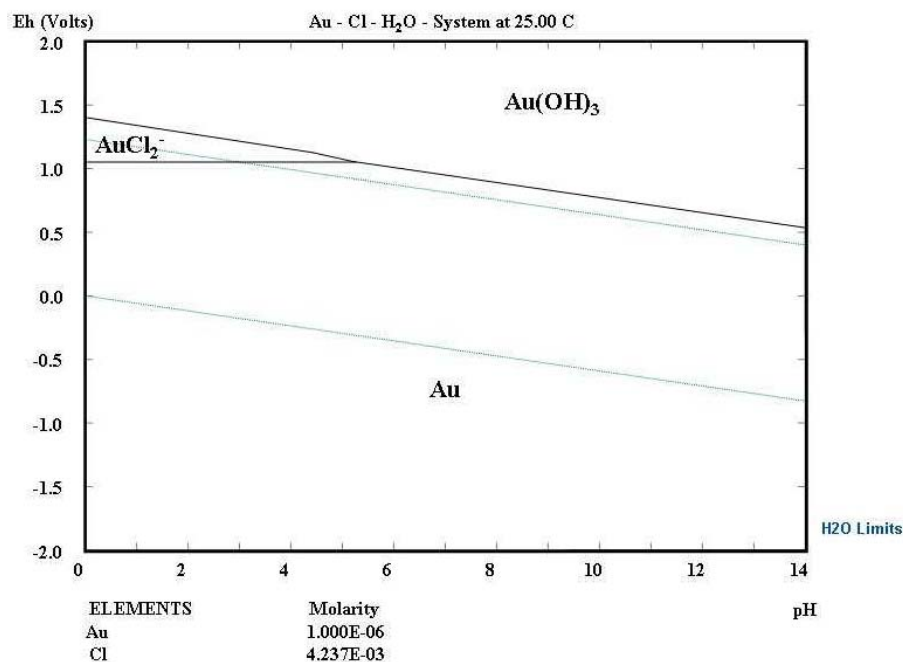


Figure 6. Pourbaix diagram for gold constructed using Outokumpu HSC Chemistry 4.0 software in 250 mg/l chloride solution

Major forms of corrosion observed in electronic systems

Electronic systems could experience various types of corrosion, although the underlying mechanism in all cases is electrochemical in nature. A detailed discussion on every form of

corrosion is not possible here, however following are the most prominent corrosion problems found for electronic systems.

Gas phase corrosion:

Presence of low levels of hydrogen sulphide could create severe problems in electronics. The most susceptible material to H_2S in the electronic system is silver due to the formation of silver sulphide crystals. Figure 7 shows the damage to the silver-palladium thick film due to its exposure to H_2S . The problem is well known in environments even with low concentrations of H_2S (under 50ppb), which is below the detection limit of H_2S by smell.

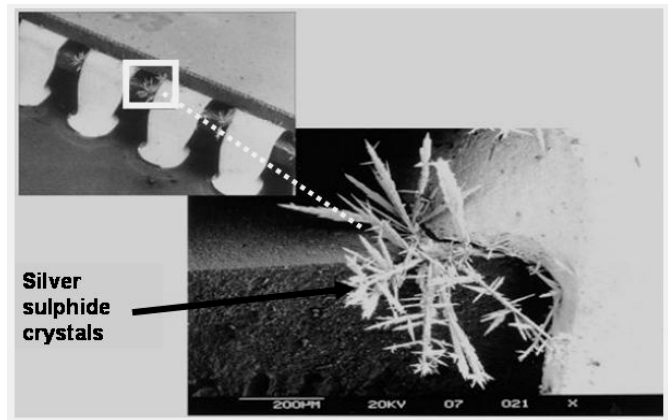


Figure 7. Formation of silver sulphide on a silver-palladium film on exposure to H_2S [10].

Anodic corrosion and electrolytic metal migration:

Electrolytic migration is a typical form of corrosion found on electronic systems. In general terms, it is similar to the stray current corrosion usually observed in equipments exposed to high magnetic or electric field. In an electronic system, electrolytic migration occurs due to the presence of a potential gradient between two conductors connected by a thin layer of solution. For example two solder points on a PCB connected by a thin layer of liquid water. The metal ions dissolve from the positive electrode (anode) and migrate towards the oppositely charged negative electrode (cathode) and deposit there. However, whether a specific metal ion deposit on the cathode or not depends on the stability of the ion in aqueous solution. Therefore, only few metals are susceptible to electrolytic migration, while others just precipitate as hydroxides or other compounds. A typical example of non-migrating metal used in electronics is aluminium. In humid environment with chlorides, aluminium dissolves and forms hydroxide (or hydroxy chlorides) instead of migrating to the cathode regions. On the other hand metals like Cu, Ag, Sn, Pb etc. migrate upon dissolution and deposit at the cathode at least over a range of potentials and pH predicted by the Pourbaix diagram [9] where particular ions are stable.

Electrolytic metal migration is a very common form of corrosion observed for electronic systems attributed to the presence of susceptible metals such as Pb, Sn, Cu, Au, Ag etc. Due to electrolytic migration, dendrites grow from cathode to anode filling the gap finally leading to electric short and system failure. Figure 8a shows a typical example of the dendrite formation between silver coatings on a PCB due to electrolytic metal migration. Figure 8b

shows another example where the copper lines are involved, however, only pitting could be seen as the potential and pH window of exposure is in the passive region. Similar behaviour could be observed for the corrosion of aluminium connecting lines on an IC chip.

In the future, it is felt that electrochemical migration will become one of the most severe problems in electronic soldering for the following two reasons. One arises from the narrow conductor spacing due to miniaturization. At constant voltage, the electric field between the conductors rises inversely with the conductor spacing, and electrochemical migration is known to be enhanced under high electric fields [11,12]. The second reason is based upon the changes in the micro-soldering process. Soldering in inert gas atmospheres using low residue fluxes and the so called no-clean fluxes that require no cleaning step have become popular. But the reliability of assembled boards after long time use, especially the corrosion stability has not been established yet. This change in the cleaning and soldering processes provides a higher chance for corrosion and ECM.

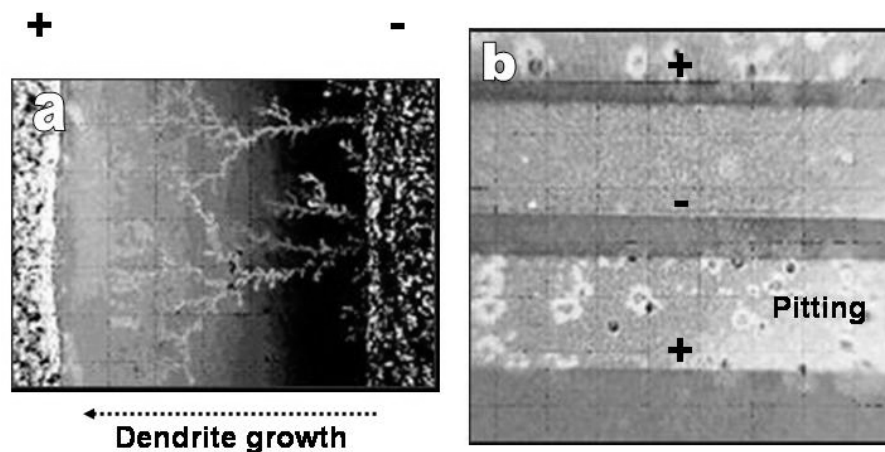


Figure 8. Corrosion problems due to electric field between conducting lines on a PCB: (a) silver dendrite formation due to migration and (b) pitting between copper conducting lines [13].

Cathodic corrosion:

Some metals used for electronic systems are soluble in acidic and alkaline environments over a wide range of potentials and pH. For example, the Pourbaix diagram [9] for Al and Zn shows solubility in acidic and alkaline environments above the equilibrium dissolution potential, which itself is a function of pH in the alkaline range. In a micro-galvanic cell, at the cathode oxygen reduction takes place as per equation (1), which produce OH^- ions. Production of OH^- ions at the cathode surface shifts the pH to alkaline values causing the metals like aluminium to dissolve.

Therefore, although in principle the metals should be cathodically protected, due to the change in pH a new dynamic equilibrium is created at the cathode surface at which certain

metals could dissolve. Among the metallic materials used for electronic applications, aluminium conducting paths for IC chips are susceptible to this type of corrosion. A schematic of the corrosion process is shown Figure 9.

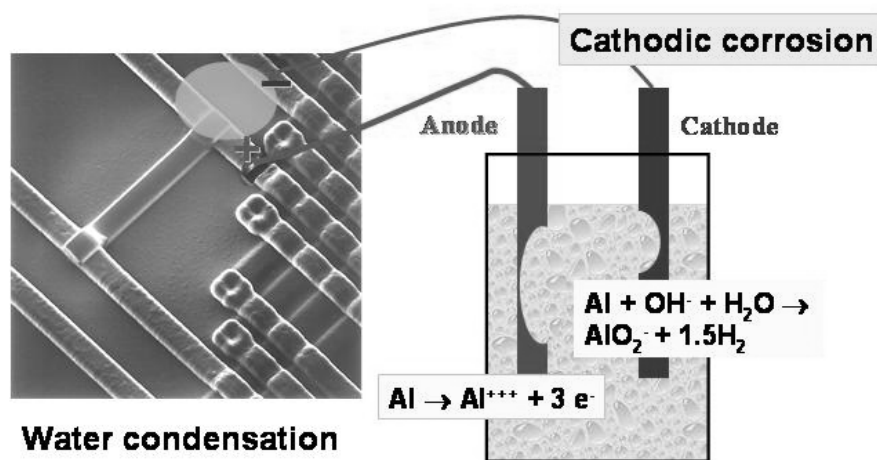


Figure 9. Schematic of the possible cathodic corrosion problem for aluminium conducting lines on ICs.

The phenomenon is known for IC3 circuits where the electrical field between the conducting paths is big. The problem is probably also observed where aluminium tread is used for drilling. The cathodic corrosion is also detrimental to the reliability of ICs if it occurs in combination with another problem called “pop corning effect”. The “pop corning effect” is due to the ingression of moisture during the soldering process causing de-bonding and cracking.

Galvanic corrosion:

This type of corrosion is attributed to the use of materials with widely varied electrochemical properties. In electronic systems, galvanic corrosion manifest in many ways and considered as dreadful for connectors and switches. For connectors and switches, the corrosion products formed by the galvanic corrosion induce high resistance in the circuit. Usually the connectors are made of multi-layer metallic coatings as described before. The metallic layers have distinctly different electrochemical properties. A typical example is the ENIG parts on the PCB. Figure 10 shows a mobile phone key-pad made by the ENIG process and corrosion due to galvanic coupling between layers. As shown Figure 10, the immersion gold (IM Au) layer is porous that exposes part of the EL Ni layer. The large difference in electrochemical potential between EL Ni and IM Au cause corrosion of EL Ni (see solid arrows in Figure 10d), while the Au layer acts as powerful cathode. As the corrosion proceeds, pitting of EL Ni layer exposes Cu at deep pit areas (see dotted arrows in Figure 10d). Even in the absence of porosity on the top coating, the gap between metallic component and resist edge can be point where all the metallic layers get exposed to the solution. Palladium has been introduced as a substitute for gold, but Pd has faster cathodic reaction kinetics than gold. Therefore, use of Pd can enhance the galvanic corrosion problems.

The bonding process ICs use different metals that can generate galvanic corrosion problems if moisture ingress occurs due to any damage in the encapsulation material. Often a gold/aluminium bonding is used for IC chips – a combination seldom safe from the corrosion point of view due to the large difference in electrochemical potentials. The lead frame is also coated with solderable coatings, which are generally noble than the base material. Therefore, any mechanical defects in the coating can cause corrosion problems.

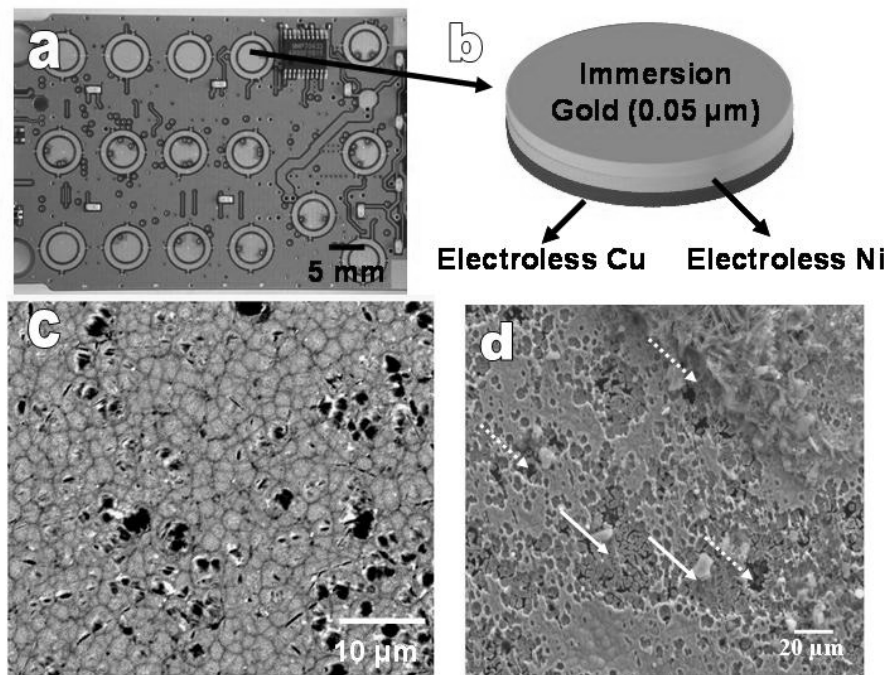


Figure 10. Cell phone key-pad system and galvanic corrosion: (a) key-pad, (b) schematic of the layers on key-pad, (c) microstructure of the gold layer, and (d) corrosion of the key-pad in chloride solutions.

Carbon or graphite is often considered as inert and stable. Graphite is used in thick film, which is applied directly to the copper substrate to achieve a good connection for touch connectors. It has been found that the graphite parts have low anodic and cathodic reaction kinetics [14]. Therefore, at least from the corrosion point of view, graphite is a material that could replace gold.

Galvanic corrosion problems in hard disk:

Although the hard disk assembly consists of many materials (Figure 5), no major corrosion damage has been reported. There has been a report [13] on the corrosion damage caused by the amorphous graphite layer (30 nm thick) on the top. The corrosion problem is due to the coupling between graphite and magnetic material cobalt (50 nm thick), which is responsible for data storage. Corrosion of such a thin layer is obviously a significant issue that can cause multiple problems to the functioning of hard disks. A hard disk typically rotates at a speed of about 4000 rpm and the “reading / writing head” is only 50 nm away from the rotating disc.

Therefore, high planarity of the surface is most important.

Fretting corrosion:

The most reliable material for electronic switches is gold. However, gold is expensive so from time to time electronic industries have been trying to use tin coated copper switches. The tin coated copper surface is solderable as well. The most important problem with electronic switches and contacts is the relative motion between contacting parts due to small amplitude vibration. The vibratory motion can be relatively low (10-200 micron) and caused by floor vibration, thermal stresses etc. The relative movement of the contacting part due to vibration destroy oxide film on the contacting surface. The new surface generated reacts with the environment to form a new film, which will be destroyed during the subsequent movements. In this way, a large number of oxide debris will be produced, which will affect the electrical properties by increasing contact resistance. This results in current spikes and damage to the electronic device.

Due to fretting corrosion, the switches in an oscillating movement (10 cycles/min) have experienced an increase in connection resistivity from 1 milliohm to 1 ohm within 20 min [15]. It is obvious that the use of gold, which is not producing an oxide layer, as the connection material could solve this problem except for the cost. Another way of solving the problem is to have a good design for switches and contacts for ensuring mechanical stability.

Stray current corrosion:

Stray currents can occur if the conductors are placed in a high electric or magnetic fields. Presence of stray currents over the PCB surface can generate corrosion problems. The example in Figure 11 shows severe corrosion damage (see arrow) to a module of the micro waver for 24 GHz, which is built in a control equipment used in situations where water condensation is possible [10]. The module is manufactured using an aluminium-silicon die-cast alloy followed by a passivation process using chromate. After few hours of use, severe corrosion was noticed on the surface.



Figure 11. Stray current corrosion of a micro wave module for 24 GHz used in a control equipment.

The reason for the corrosion is that the micro waves are inducing severe turbulent flow on the surface of aluminium. If this occurs in combination with a wet surface (due to condensed

water), there will be large eddy currents in the fluid film. The rate of corrosion depends upon the local resistivity of the electrolyte.

Testing methods for electronics

Corrosion testing:

One major difficulty for corrosion testing of electronic components is that the measurement needs to be carried out at tiny areas with sizes ranging from few mm to μm . The corrosion group in IPL, Technical University of Denmark built microelectrochemical systems suitable for this purpose. A popular idea involves the use of a pipette connected to a system to control the solution flow at the tip. Through addition of reference and counter electrodes, the pipette system becomes a microscopic electrochemical cell, which can then be used with high precision to determine the electrochemical characteristics of a small region of interest. The resolution of the technique is determined by the size of the pipette tip. The microelectrochemical systems in our laboratory have resolution ranging from $\sim 1\text{ mm} - 10\text{ }\mu\text{m}$. The set up has also been used in combination with high resolution video microscope for in-situ visualization of corrosion.

Figure 12 shows a picture of the microelectrochemical set up with a tip resolution 1 mm. Microelectrochemical set up consists of an electrochemical head containing the solution, counter and reference electrodes, which is attached to the carousel of an optical microscope. The cell is connected to a pipette, which makes contact with a local region of the working electrode (in this case the PCB used for investigation). The lateral resolution of the technique is determined by the dimensions of the pipette tip.

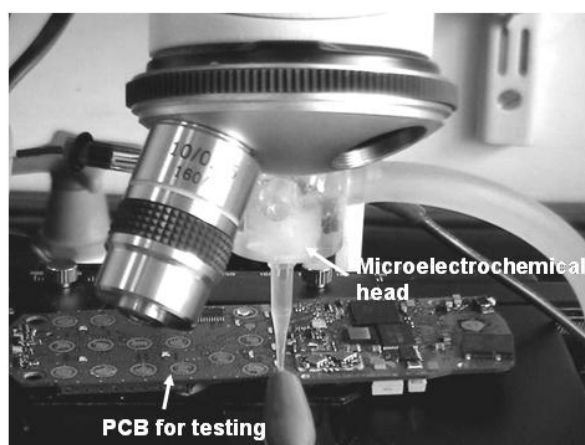


Figure 12. Microelectrochemical set up.

Localized extraction system for residues:

Cleanliness of the PCB surface is most important in reducing the corrosion problems. Therefore, identifying and quantifying residues on a PCB surface is extremely important. Localized pockets of contamination are not identified when analyzing whole board areas using standard extraction techniques. The most effective way for residue detection is to have a system for localized extraction. The extracted residues can then be analyzed by standard techniques like ion chromatography.

Systems capable of extracting residues from localized areas (0.1 in²) are now available. The tool called C3 (Critical Cleanliness Control), developed by Foresite, USA as an automated, faster, localized extraction and cleanliness for the production floor [16]. The samples extracted using C3 can be used in conjunction with ion chromatography, FTIR or SEM/EDX to identify the type and level of residue that created a corrosive event on the test electrode.

Summary

Several materials are used in electronic industry and new materials are emerging all the time. However, the materials combinations together with demand for miniaturization and large spread in user environment have introduced significant corrosion problems. Presence of process and service related residues on the electronic component is an important factor in dictating the corrosion problem, hence cleanliness place a big role in corrosion control. New testing methods and standards have to be developed, although the localised detection methods such as microelectrochemical technique and localised residue analysing systems are very much useful.

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