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Tin and Its Alloys

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Glossary:

Allotropy: The existence of two or more different forms (allotropes) of the same element that are bonded in a different manner; allotropes are thus different structural modifications of an element.

Grey tin: The low-temperature allotrope of tin having a cubic structure that is stable below about 13°C. Note that the transformation from white tin to grey tin is sluggish and generally does not proceed significantly until the temperature is well below 0°C.

White tin: The high-temperature allotrope of tin having a body centred tetragonal structure that is stable above about 13°C.

X.1 Introduction

X.1.1 Physical properties

The element tin is located in Group VI of the periodic table lying above lead, with which it shares many properties. Tin, like lead, is one of the metals known to antiquity and highly prized for its ability to harden copper, forming bronze. There is evidence that tin was mined in the UK at Cornwall from the early bronze age (2100-1500 BC). Certainly by Roman times tin from the western edge of Europe (mainly Cornwall and Spain) was traded widely throughout the known world. Tin ore resources are not widely distributed and production mainly derives from two forms: (i) hard rock, typified by the Cornish deposits and similar ore bodies in Bolivia and Queensland; and, (ii) alluvial (placer) deposits, typified by the South-East Asian ore field stretching from Indonesia and Malaysia to Thailand.

Tin is allotropic with the normal, metallic (beta) form being body-centred tetragonal above the transformation temperature, which lies at about 13.2°C [1]. The lower temperature allotrope, alpha or “grey” tin, is cubic and forms with a significant volume change that tends to result in disintegration of the material. However, transformation is kinetically sluggish although it can be encouraged by mechanical deformation and delayed, or effectively suppressed to lower temperatures, by impurities such as antimony, lead and bismuth [2]. Grey tin normally appears as nodules of a friable material on the surface of the metallic form and resembles a corrosion product. Thus, the transformation is often not readily distinguishable from corrosion [3]. The transformation mechanism has been studied by high resolution electron microscopy in order to obtain the lattice orientation relationship between the two allotropes [4]. Thus, the (011) plane of grey tin is parallel to the (001) plane of white tin and the [211] direction of grey tin is nearly parallel to the [010] direction of white tin. This evidence supports a model for the alpha to beta transformation that is partly martensitic and partly diffusional.

The use of unalloyed tin is restricted by its low melting point (232°C) and by its low tensile strength (15 MPa). On the other hand, its melting point, and its ability to “wet” other metals (often by formation of intermetallic compounds), facilitates its use as solder (for metal joining) and as a coating (for corrosion protection), while its softness and high ductility make it suitable for cold working and for bearing applications. Given its relatively low melting point, tin recrystallises readily at room temperatures, therefore effects of mechanical working are slight, and arise from differences in grain size and not from effects of work hardening. The production of tin whiskers is also thought to be a consequence of its low melting point and results in the growth of fine threadlike structures, typically about 1-2 µm in diameter, with growth rates of up to millimetres per month under appropriate conditions [5,6].

Given increasing health and safety concerns that puts severe limits on the use of lead in materials there is has been, for some time, a legislative driver for the development of essentially lead-free tin alloys. This has re-introduced problems relating to the formation of grey tin (at lower temperatures) and tin whiskers that were generally absent in lead-containing materials. For example, in the electronic industry, where tin-based solders are now widely used, whisker growth in particular can cause problems such as short-circuiting [7].

X.1.2 Applications

Tin's industrial use is limited by its low strength and very limited solubility for most elements at room temperature [8]. However, tin is essential in a number of alloys where it is a minor constituent (for example in copper-tin bronzes) and also where it is the majority component (for example in pewter). The most important forms in which tin is used are:

1. Tin of more than 99% purity for specialist applications.
2. Tin hardened by additions of 1–2% Cu or Sb.
3. Pewter with 90–95% Sn, 4–8% Sb and 1–2% Cu.
4. Coatings for other metals, which may be pure tin or tin plus a co-deposited species.
5. Soft solders with tin and lead in all proportions.
6. Lead-free soft solders with > 90% Sn and additions of silver, copper, bismuth, indium or zinc.
7. Bearing metals “high tin” and “high lead” with a large range of proportions of tin, antimony, copper and lead; or with tin (5–30%) in aluminium.
8. Diecasting alloys containing 70–80% Sn with antimony, copper and lead, either singly or combined.

The corrosion behaviour of tin and tin alloys, whatever their form, is basically similar, except in the case of solders and bearing metals, where the wide composition range and special duties of the materials give particular issues. The impurities likely to be present in nominally pure tin are unlikely to affect its corrosion resistance, except for minor effects on the rate of oxidation in air. Small aluminium contents, however, may result in a severe intergranular attack by water; the addition of antimony counteracts this effect. Although 0.1% magnesium appears to be tolerable, larger amounts produce effects similar to those of aluminium [2].

Apart from the special uses in solders and bearings metal referred to already, and as coatings, tin and its alloys find employment where advantage can be taken of their physical properties and their fair resistance to tarnish and corrosion in near-neutral environments. Tin has

traditionally been used in many food-grade applications although such applications nowadays increasingly use cheaper materials such as stainless steels and polymers. Tin pipe can be used to condense steam for high-purity distilled water, as a conveyor of beer and soft drinks, especially in coils through cooling media, and, in a larger size, as organ pipes. Some pharmaceutical and food products are packed in tin collapsible tubes and tinfoil coverings are used on cork wads for jar and bottle closures. The tin alloy, pewter, is most valued for the decorative forms into which it is easily worked or cast, but it is also used for drinking vessels and dishes.

X.2. Electrochemistry

X.2.1 Thermodynamics

The Pourbaix diagram for tin, Figure 1, refers only to solutions in which the formation of soluble tin complexes (for example with citric acid) does not occur. Tin is a slightly active metal with its domain of stability below that of the hydrogen equilibrium; in theory it will corrode in acid evolving hydrogen gas. It is more noble than iron and nickel but slightly less noble than lead, although in practise passivity will alter this sequence. Tin shows a wide range of passivity due to the stability of tin (IV) oxide, SnO_2 , which is stable to lower pH than PbO . However, tin will dissolve as Sn^{2+} ions at $\text{pH} < 2$ and as the corresponding (II)- or (IV)-valent oxy-anion species at $\text{pH} > 11$. Note, however, that in regions where, according to the diagram, the dissolution of tin is possible, the rate of corrosion may be very slow. This is because the overpotential for hydrogen evolution on tin is high, particularly in acid solution. Thus, in a range of concentrations of H_2SO_4 [10], the exchange current for the hydrogen evolution reaction was found to be $10^{-11} \text{ A cm}^{-2}$ with a Tafel slope of $0.118 \text{ mV (decade current)}^{-1}$, indicating that a 1-electron transfer reaction was rate controlling. In KOH solutions [11], the exchange current was higher, $3 \times 10^{-6} \text{ A cm}^{-2}$, while the Tafel slope was similar to that in acid, $0.120 \text{ mV (decade current)}^{-1}$. Consequently, in alkaline or moderately acid solutions, free from oxygen or oxidising agents, corrosion of pure tin may be barely detectable, unless the tin is in contact with another metal that has a lower overpotential (higher exchange current density) for hydrogen evolution.

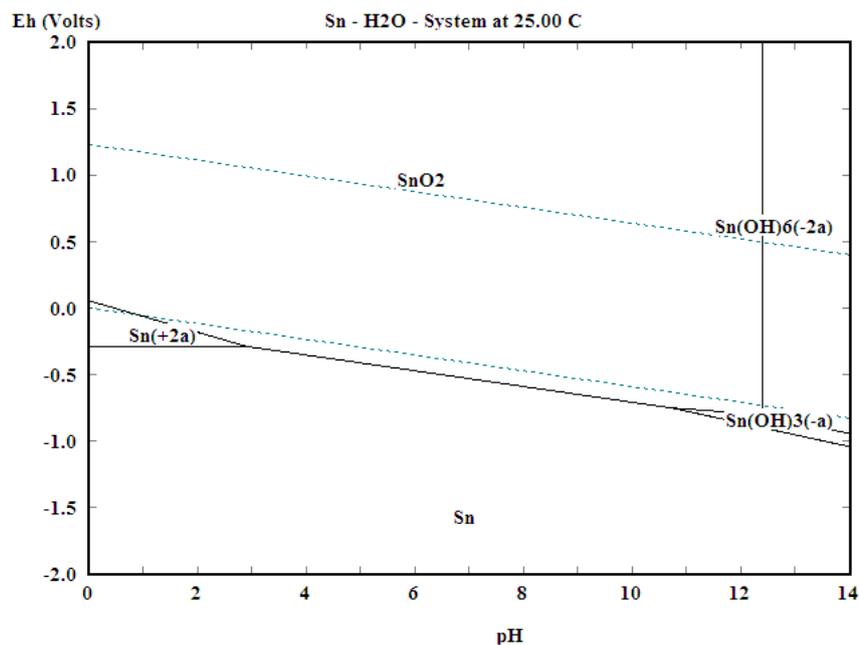


Figure 1: Pourbaix (E-pH) diagram for tin in water at a dissolved concentration of 10^{-5} M tin species [9].

The passivity of tin in the middle pH range (i.e. between about 3 to 10), its solubility in acids or alkalis (modified by the high hydrogen overpotential), and the formation of complex ions (especially with organic acids) are the basis of its general corrosion behaviour. Other properties which have influenced the selection of tin for particular purposes are the low toxicity of tin salts (that permit tin's use in food grade applications) and the absence of catalytic promotion of oxidation processes that may cause changes in oils or other neutral media affecting their quality or producing corrosive acids.

X.2.2 Dissolution

The electrochemistry of tin was extensively reviewed by Stirrup and Hampson in 1977 [12]. As can be seen from the Pourbaix diagram tin shows passivity, by virtue of the formation of Sn(IV) oxide (SnO_2), over an extended pH range from about 3 to above 10. Also, as previously indicated, the dissolution kinetics are kinetically slow, especially in acid, by virtue of a low exchange current density for hydrogen evolution.

At potentials just above its reversible value, tin dissolves under anodic polarisation in acids initially as the stannous ion (Sn^{2+}). In 4-8M sulphuric acid this reaction has a Tafel slope of close to $40 \text{ mV (decade current)}^{-1}$, indicating a two-electron transfer reaction with a probable bisulphate ion intermediate [13]. The stannous ion is unstable in water at most values of pH (except in acid concentrations typically $> 1 \text{ M}$) and at low concentrations is hydrolysed giving a number of species, depending on pH: SnOH^+ , Sn(OH)_2 , Sn(OH)_3^- ; at higher tin concentrations the complex species $\text{Sn}_2(\text{OH})_2^{2+}$ and Sn(OH)_4^{2+} are prevalent [14]. The hydroxide complexes are well known to react with halides to give a number of Sn(II) hydroxy-halide complexes, however, these are only present in solution when the halide concentration is $> 10^{-3} \text{ M}$ and at pH values < 4 . In alkaline conditions, tin initially dissolves as the stannite ion, Sn(OH)_3^- , which is subject to the same speciation as a function of pH as indicated above.

At higher potentials Sn(II) is universally oxidised to Sn(IV) species. There is very little experimental data on this reaction however, Sn(II) to Sn(IV) oxidation was studied in strong sulphuric acid and found to have first order kinetics with respect to the dissolved species; an increase in H^+ ion concentration decreased the reaction rate, while an increase in SO_4^{2-} had the opposite effect.

X.2.3 Passivation

Over the majority of the pH range the passive film is generally assumed to consist of Sn(OH)_4 or SnO_2 however, in view of its very low solubility, data for the speciation of tin (IV) oxides and hydroxides in aqueous environments is very sparse. Indeed, the formation of SnO_2 as the passive film is one of the reasons for the excellent corrosion resistance of tin in non-complexing aqueous environments.

In 4-8M sulphuric acid, passivity is consistent with thin films of stannous oxide (SnO); SnO_2 only formed at significantly more positive potentials [13]. Passive films on tin corroded at the open circuit potentials in 6.7M nitric acid, 5.7M hydrochloric acid and 9M sulphuric acid were analysed by Mössbauer spectroscopy and found to consist of hydrated SnO_2 , $\text{Sn}_4(\text{OH})_6\text{Cl}_2$ and SnSO_4 , respectively [15].

Passive films on tin were studied using infra-red and surface-enhanced Raman spectroscopy [16]. In 0.1M NaOH solution Sn(OH)₄ was found to dominate and further exposure to dry air was found to dehydrate the film to SnO₂ with only a small amount of SnO evident. The passive film on 0.15M NaCl solution (near neutral) was found to consist only of Sn(OH)₄. However, angle-resolved X-ray photoelectron spectroscopy was used to develop a model for the passive film on tin in 0.1M KOH. This found that tin hydroxide was only present in the outer layers of the film. The inner layer consisted of SnO₂ with evidence of SnO adjacent to the metal/oxide interface [17]. This appears to be consistent with results from phosphate buffer solutions (pH 4.3), where Sn(OH)₄ was found along with a reduced species, either Sn(OH)₂ or SnO, at the metal/oxide interface [16]. An electrochemical study of the anodic oxidation of tin was performed in carbonate/bicarbonate buffer solution at pH 8.9. From -0.1V to 1.2V (SCE) tin exhibited an essentially potential independent steady-state passive current, which was found to be independent of flow conditions [18]. The results indicate that the anodic film grows according to the Mott-Cabrera model and is an oxygen ion conductor. Finally, the electrochemical passivation of tin was studied in citric acid buffer at pH 6 [19]. Pre-passivation was found to occur along with Sn(II) and Sn(IV) species while full passivation was associated with Sn(IV) species only. The results indicated that although the initial film formed coincided mainly with Sn(OH)₄, that this transformed at longer times to the more thermodynamically stable SnO₂ species.

In summary, tin is found to passivate in aqueous environments from below pH 1 to above pH 12 forming an oxide film that consists of Sn(OH)₄ or SnO₂. The latter oxide, which is more stable, may form either initially or transforms gradually with time from the hydroxide. It is likely that a thin layer of Sn(II) species is stable at the interface between the passive film and the metal although films consisting predominantly of Sn(II) species are not observed except in high concentrations of reducing acid.

X.3 Corrosion and oxidation

X.3.1 Atmospheric corrosion

X.3.1.1 Oxidation in dry air

Oxidation of tin in dry air is slow; the metal remains bright and interference colours are not developed below about 180°C. On a rolled tin surface heated in air [20,21], the thickness of the oxide grew according to a logarithmic law at temperatures up to about 160°C and according to a parabolic law at higher temperatures, for which the oxide was identified as SnO. For electropolished tin heated in oxygen at pressures of 130 N m⁻² and above, three stages of oxidation were observed at temperatures up to 220°C [22-25]:

1. An initial sigmoid growth curve during nucleation.
2. A logarithmic growth curve when cavities acted as diffusion barriers.
3. Erratic behaviour caused by random film rupture.

The oxide formed was identified as SnO at temperatures down to 75°C. However, a mixture of SnO and SnO₂ is formed in dry air at lower temperatures and, in humid air, at temperatures up to at least 100°C [26]. Electrochemical reduction analysis on tin oxidised in dry air at 125 and 150°C confirmed the presence of SnO with a thin surface layer of SnO₂ [27,28]. Small additions, e.g. 0.1%, of indium, zinc or phosphorus, reduce the rate of oxidation and addition of antimony, thallium or bismuth accelerates it [25].

X.3.1.2 Corrosion in humid air

In the absence of polluting gases or dusts, increasing relative humidity tends to increase the rate of oxidation [29] and may cause the development of interference colours. In an ordinary atmosphere, some corrosion product may be formed over time. However, tin products are not hygroscopic and tin is not attacked at relative humidities below 100% unless the dust falling on the surface is hygroscopic, or impurities in the metal are able to form a hygroscopic product. Indoors, in an unpolluted laboratory atmosphere, a grey film, increasing in weight linearly with time ($4 \text{ mg m}^{-2}\text{d}^{-1}$), is formed, while in sheltered exposure (no rain) outdoors, the corrosion rate declined with time. The reflectivity of the surface is slowly lost if it is left untouched, but may be preserved by regular washing; in one experiment, when the surface was washed at intervals of three weeks, a water wash was adequate for six weeks and although the use of soap was necessary thereafter almost complete preservation of reflectivity was achieved.

The impurities ordinarily present in the atmosphere do not appreciably affect the character of corrosion. No tarnishing effect is exerted by hydrogen sulphide, sulphur dioxide and other acids in low concentrations, including formic, acetic and other organic acids which when evolved from wood or insulating materials are so often destructive to metals other than tin in the confined spaces of electrical equipment or of packages. Chlorides accelerate corrosion and tend to form a white corrosion product containing oxychloride. The presence of some impurities, notably zinc, in the metal may cause tarnishing and loss of brightness in atmospheres containing SO_2 [30]. The corrosion rate of electroplated tin on nickel in the presence of sub-ppm amounts of SO_2 or NO_x on their own did not increase. However, a synergetic effect was found with both pollutants where the corrosion rate was increased significantly.

The atmospheric pollution prevailing in special industrial or laboratory locations may induce more severe corrosion, e.g. the vapours from concentrated hydrochloric or acetic acid will etch tin, and moist sulphur dioxide will produce a sulphide tarnish, as will hydrogen sulphide at temperatures above about 100°C and halogens attack tin readily.

When tin is fully exposed out of doors, corrosion is uniform, and the rate falls only slightly with time. The metal becomes dull and accumulates a compact layer of pale grey product, mainly stannous oxide. Rates observed during exposures in the USA for periods of up to 20 years were $1.3\text{-}1.8 \mu\text{m y}^{-1}$ in industrial atmospheres (i.e. mainly polluted with sulphur dioxide), $1.8\text{-}2.8 \mu\text{m y}^{-1}$ in marine atmospheres (i.e. mainly polluted with sea-salt) and less than $0.5 \mu\text{m y}^{-1}$ in rural atmospheres (i.e. relatively unpolluted) [31].

X.3.1.3 Atmospheric corrosion products

The corrosion of tin in various humid atmospheres has been examined using a number of surface analytical techniques, including X-ray photoelectron spectroscopy (XPS) and auger electron spectroscopy (AES) [26,32,33]. While it is difficult to resolve the oxide from the hydroxide peaks and, hence, to establish their degree of surface hydration, there is general agreement that both SnO and SnO_2 may be present depending on the temperature of exposure.

In atmospheres polluted with > 100 ppm nitrogen dioxide, tin nitrate was reported to form at 30-35% RH [34]. In a mixed atmosphere containing more representative atmospheric conditions (40 ppb H_2S , 350 ppb SO_2 , 500 ppb NO_2 and 3 ppb Cl_2) at 81% RH, only tin oxides were found [35]. An XPS study on the films formed in SO_2 and NO_x found only oxide

species in SO₂ but a mixture of oxides and nitrates with NO_x. No synergy was noted between at ppm concentrations of SO₂ and NO_x at 85% RH [36].

X.3.2 Corrosion in acid

X.3.2.1 Mineral acids

Since the high overvoltage restricts hydrogen evolution, corrosion in organic acids or dilute non-oxidising mineral acids is generally controlled by the rate of supply of oxygen [2,3]. In solutions of acid open to air, with specimens of size 50 x 20 mm completely immersed, corrosion rates were, in a range of 0.1M organic acids, 400–500 g m⁻² d⁻¹ and, in 0.1M hydrochloric or sulphuric acids, 600 g m⁻² d⁻¹. In absence of oxygen, the rates in the two mineral acids were 100–150 g m⁻² d⁻¹, while they were negligible in the organic acids. Phosphoric acid forms a protective layer and, even in the presence of air, the corrosion rate is only about 20 g m⁻² d⁻¹. Nitric acid corrodes tin freely even in the absence of oxygen, however, chromic acid forms a protective film. This film, which contains chromic oxide and tin oxides, will, after withdrawal from the acid, give some degree of protection against mildly corrosive conditions. Thus, hot solutions of chromic acid, alone or mixed with phosphoric acid may be used as passivating media.

X.3.2.2 Organic acids

Tin forms complex ions with many organic acids including those commonly found in fruits (citric, oxalic, malic). This action has important effects on the galvanic behaviour of tin. The normal electrode potential of tin is -0.136 V, but the reduction of stannous ion activity resulting from formation of complexes may depress the corrosion potential to make tin anodic to iron [37].

Attack of tin by oxalic, citric and tartaric acids was found to be under the anodic control of the Sn²⁺ salts in solution in oxygen free conditions [38]. In a study of tin contaminated by up to 1200 ppm Sb, it was demonstrated [39] that the modified surface chemistry catalysed the hydrogen evolution reaction in deaerated citric acid solution. Tin was found to corrode more rapidly in tartaric acid due to the reduction in the hydrogen overpotential; passivation was caused by a film of tin hydroxide or oxide [40].

X.3.3 Corrosion in near-neutral conditions

Pure tin is completely resistant to distilled water, hot or cold. Local corrosion occurs in salt solutions which do not form insoluble compounds with stannous ions (e.g. chloride, bromide, sulphate, nitrate) but is unlikely in solutions giving stable precipitates (e.g. borate, mono-hydrogen phosphate, bicarbonate, iodide) [41]. In all solutions, oxide film growth occurs and the potential of the metal rises. Any local dissolution may not begin for several days but, once it has begun, it will continue, its presence being manifested at first by small black spots and later by small pits. Movement of the solution tends to prevent pitting; stagnation, especially in crevices where the tin touches another solid surface, favours its progress. Contact with a more noble metal such as copper or nickel increases the number and intensity of pits; contact with metals such as aluminium and zinc gives cathodic protection.

As indicated above, the bicarbonate ion inhibits the process, which does not occur, therefore, in many supply waters; attack is most likely in waters which by nature or as a result of treatment have a low bicarbonate content and relatively high chloride, sulphate or nitrate content. The number of points of attack increases with the concentration of aggressive anions and ultimately slow general corrosion may occur.

During exposure of 99.75% tin to sea-water for 4 years, a corrosion rate of 0.0023 mm/y was observed [42]. Corrosion in soil usually produces slow general corrosion with the production of crusts of oxides and basic salts. For example, the production of the significant quantities of the metastable corrosion product romarchite (SnO) is commonly seen when studying pewter corrosion products from marine archaeological sites [43], but is never seen, except transiently or as a thin interfacial phase, in passive films and atmospheric corrosion products.

X.3.4 Corrosion by alkalis

The Pourbaix diagram indicates the possibility of attack by solutions of pH values above about 10.5, but the position of this limit is influenced by temperature, by the constitution of the solution, and by the surface condition of the metal. Corrosion will ensue if the surface oxide is significantly soluble, which will occur increasingly beyond pH 12.

Once corrosion begins, its rate is governed by the oxygen supply and temperature and is not greatly affected by the character of the alkali. Rates of attack for specimens completely immersed in still solutions open to air are about $600 \text{ g m}^{-2} \text{ d}^{-1}$ at 30°C and $1000 \text{ g m}^{-2} \text{ d}^{-1}$ at 70°C . In intermittent immersion such as is experienced in the cleaning of tinned ware by alkaline detergents, however, the rate of corrosion is affected by the nature and concentration of the solution, since these affect the time required for removal of the oxide film at each fresh immersion [44]. Saturated ammonia solutions do not attack tin, possibly because of the negligible oxygen content, but more dilute solutions behave like those of other alkalis of comparable pH. In aerated alkaline conditions, 0.01M to 1M NaOH, corrosion of tin was confirmed to be under cathodic control and additions of other species, apart from chromate, was found to make little difference to the corrosion rate [45]

The removal of oxygen from an alkaline solution, as by the addition of sodium sulphite, can prevent corrosion unless the tin is in contact with another metal, such as steel, from which hydrogen can be evolved. Additions of oxidising agents in small amounts stimulate corrosion but sufficiently large additions produce passivity. Alkaline chromate solutions in the passivating range produce a film containing chromium oxide, which has some protective value [20,46].

X.3.5 Corrosion in foodstuffs

Sulphide solutions, sulphurous acid and some foodstuffs containing organic sulphur compounds, produce stains of sulphide, but the rate of loss of metal is low [2,3]. Milk and milk products are usually without action, although local corrosion has been known to occur in dairy equipment. Beer initially dissolves a trace of tin and this may be sufficient to cause a haze in the liquor, but any corrosion usually slows to an insignificant rate after some time.

In general, near-neutral aqueous products are without action except for possible sulphide staining or, when there are dissolved salts present, some local corrosion. The slight acidity which may develop in solutions of some organic compounds such as formaldehyde or alcohols can be tolerated. Many organic liquids, including oils (essential, animal, vegetable or mineral), alcohols, fatty acids, chlorinated hydrocarbons and aliphatic esters, are without action. The absence of any catalytic action of tin on oxidative changes is helpful in this respect. When, however, mineral acidity can arise, as with the chlorinated hydrocarbons containing water, there may be some corrosion, especially at elevated temperature.

X.3.6 Galvanic corrosion

As indicated from the galvanic series tin is less noble than copper and stainless steels but more noble than most other elements in common use, Table 2. However, tin is usually ineffective as a sacrificial anode due to its very low self-corrosion rate and generally may be safely used in contact with most materials [47]. However, in the presence of species such as citric acid, which can form complex ions, tin will activate with its equilibrium potential moving to more negative values. This effect is important in the corrosion protection of steel cans with tinplate.

Standard reduction potentials (v. SHE)	Practical galvanic series in sea water
$\text{Cu}^{2+} + 2\text{e}^- \Rightarrow \text{Cu}$: +0.34V	graphite
$\text{Pb}^{2+} + 2\text{e}^- \Rightarrow \text{Pb}$: -0.12V	passive stainless steels
$\text{Sn}^{2+} + 2\text{e}^- \Rightarrow \text{Sn}$: -0.14V	copper alloys
$\text{Ni}^{2+} + 2\text{e}^- \Rightarrow \text{Ni}$: -0.25V	tin (and tin-rich solders)
$\text{Fe}^{2+} + 2\text{e}^- \Rightarrow \text{Fe}$: -0.44V	lead (and lead-tin solders)
$\text{Zn}^{2+} + 2\text{e}^- \Rightarrow \text{Zn}$: -0.76V	steel and cast iron
$\text{Al}^{3+} + 3\text{e}^- \Rightarrow \text{Al}$: -1.67V	aluminium
$\text{Mg}^{2+} + 2\text{e}^- \Rightarrow \text{Mg}$: -2.37V	zinc
	magnesium

Table 2: Standard reduction potentials and galvanic series compared with tin

X.4 Applications

X.4.1 Tin coatings

The interested reader is directed to the dedicated section on tin coatings elsewhere in this volume; only brief comments are provided here. Tin coatings may be applied either by hot-dipping from molten metal or by electroplating from either acid or alkaline solutions [2,3] or by metal spraying [48]. Also, tin may be co-deposited during electroplating with a range of other elements such as nickel, cobalt, copper and zinc, all of which give rise to particular properties. Tinplated steel is extremely widely used in the food and beverage canning industry as a container and relies both on the low corrosion rate of tin (can exterior) as well as the common potential reversal to steel in the presence of natural complexing agents (can interior). In practise, due to the cost of tin, it is essential economically to use as thin a layer as possible. Thus, the corrosion protection afforded by the tin is usually supported by internal and external lacquering (organic coating) of the can and it is therefore the organically coated tin that provides the full corrosion protection system for the steel substrate.

The thinnest tin coatings are most efficiently applied by electroplating; where this is likely to give pinholes then surface melt reflowing may be used to improve the performance. Where thicker coatings are required, usually for specialist applications, then for example hot dipping or metal spraying can be used. For example, traditional copper cooking utensils are frequently internally coated with tin to several tens of microns in thickness to prevent the interaction of copper with foods that can lead to the development of taints. The advantage of this process is that when the tin wears off, it can be easily replaced by re-dipping. Hot dipped (and sprayed) coatings take advantage of the formation of tin-iron or tin-copper intermetallic species for excellent adhesion of the coating.

X.4.2 Solders

Alloys of tin with lead and/or a number of other elements comprise a class of jointing materials known as solders. Solders are used for cost-effective and efficient jointing of many materials, most commonly for copper alloys (e.g. heat exchangers) and steels (e.g. cans). Solders are generally characterised by their ability to flow across or “wet” the metal to be jointed; such wetting is usually accomplished by the formation of intermetallic compounds between the solder and the substrate. Thus, tin forms Cu_6Sn_5 and Cu_3Sn with copper alloys [49] and FeSn , Fe_3Sn and FeSn_2 with steel [50]. The mechanical properties of these intermetallic species are critical; thus they provide metallurgical bonding between the jointed materials but must not form brittle phases. Many types of tin-based solders are available, for example: Sn-Pb (traditional solders with compositions from 60/40, 50/50, 40/60 depending on use), Sn-Zn (for jointing aluminium) and Sn-Ag (lead-free solder for general use). In particular, for health reasons, there is an increasing use of low-lead, or lead-free solders, especially for joints in water supply systems and in food canning. These environmental concerns are now involving the electronics industry with a move to lead-free formulations also.

Effective soldering requires a clean surface, free of contamination such as greases, oils and water and removal of the normal air-formed oxide on the material that is to be jointed. Typically this is carried out initially by mechanical abrasion or solvent cleaning with the final removal of the tenacious surface oxide via a “flux”. A flux is, by its nature, corrosive thus careful selection of the flux material is necessary otherwise corrosion in service will be promoted locally [51]. It is, however, possible to select fluxes which are active when hot but give non-corrosive residues when cold, for example, solid organic acids. If it is necessary to use more vigorous materials, such as zinc chloride, any residues must be fully removed. By the nature of their use as jointing material, solders are usually presented to a corrosive environment as a small area within a much larger area of another metal. Thus, if the solder is anodic to the metal it joins, and if the corroding medium has good electrical conductivity, damaging corrosion is possible due to the unfavourable (small anode v. large cathode) anode-to-cathode area ratio.

Traditional lead-tin solders are anodic to copper, but soldered joints in copper pipes have been widely used without trouble for cold supply waters; possibly corrosion is restricted by the deposition of cathodic carbonate scales and the formation of insoluble lead compounds. Hot supply waters tend to be more aggressive but are likely to still give satisfactory service. However, electrolytes of sufficiently high conductivity, such as sea-water, will cause corrosion of soldered joints in copper and copper alloys. In automotive radiators, antifreeze solutions have been alleged to cause corrosion, possibly because materials such as ethylene glycol sometimes detach protective deposits. Sodium nitrite, valuable as a corrosion inhibitor for other metals in a radiator, tends to attack solders, but sodium benzoate is safe and, in addition, protects the soldered joint against the action of nitrites [52].

For environments in which tin is less readily corroded than lead, corrosion resistance of the alloy decreases as the lead content increases; the decrease may, in some circumstances, be sharp at a particular composition. In the more corrosive media, a sharp increase of corrosion rate is observed as the lead content increases beyond 30%. However, in waters with low contents of dissolved salts, the corrosion rate increases slowly with lead content up to about 70% and then rises more steeply. Selective dissolution of tin has been reported to occur in prolonged contact of solders with solutions of anionic surface active agents [53].

In view of the known tendency for lead to be released in supply waters from conventional soldered joints [54], there is an accelerating trend away from the use of lead-containing solders in contact with potable water, which is also being driven by legislation [55]. The effects of galvanic corrosion of one of the substitute alloys (Sn-3Ag) in contact with a number of other metals including copper have therefore been studied [56].

X.4.3 Tin interconnections

Tin-based jointing alloys (solders) are the materials of choice for connections and interconnections in the electronics industry. Traditionally, a eutectic tin-lead (67Sn-33Pb) alloy has been used but the legislative driver for the removal of lead has also affected this sector, which has now effectively moved to encompass the use of lead-free solders. The performance characteristics of electronic connectors is dominated by: (i) local galvanic corrosion between different metals either in contact, or as a coating and influenced by applied direct currents; (ii) by the corrosion of the soldering alloy, which is controlled largely by the presence of residues from various manufacturing and assembly operations; (iii) by fretting forms of corrosion damage induced by repeated making and breaking of electrical contacts and (iv) by the formation of metal whiskers of tin that tend to be produced as a result and applied stress and voltage. All of these phenomena can lead to either to a reduction of performance or to outright failure via a variety of mechanisms [56], the most important of which are increases in the contact resistance with time and short circuit current paths between contacts due to corrosion products, soldering residues (i.e. fluxes) and whiskers of tin.

Many lead-free solders are based on Sn-Ag-Cu formulations with Sn-3.5Ag, Sn-0.7Cu and Sn-3.8Ag-0.7Cu widely in use due to their good mechanical and wetting properties. In 3.5% sodium chloride solution lead-free solders show an improved corrosion resistance compared with Sn-Pb solder, due to lower active currents and lower passive current densities, and that the Sn-Ag material was the most resistant [57]. The contact resistance and fretting corrosion resistance of lead-free solders was measured as a function of time [58]. In this case the contact resistance of the conventional eutectic solder fell more quickly than the lead-free solder however, the fretting corrosion resistance of Sn-Ag materials was generally improved. The lead-free solders performed significantly better than the lead-containing solders after steam aging at 93°C, 100% RH and after mixed flowing gas testing (in 200 ppb NO₂, 10 ppb H₂S, 10 ppb Cl₂) at 30°C and 70% RH.

There is, therefore, good evidence that the general and fretting corrosion behaviour, and consequent contact resistance changes with time, of lead-free solders is at least as good as, and often better than, traditional tin-lead eutectic solders. However, lead-free solders have a greatly increased tendency for the formation of thin filamentary whiskers of tin, which may lead to failure by short-circuit. Tin whisker formation has been known for many years and was originally thought to be driven primarily by electro-migration between two contacts or conductive tracks [59,60]. More recently, however, it has become clear that most whisker growth is a process driven by relief of stresses [61] (i.e. from plating or from contact forces) although electro-migration may play a role in more extreme conditions [62].

X.4.4 Bearing metals

There are several classes of tin-containing bearing alloy for use in lubricating conditions: high-tin alloys (substantially lead-free), bearing alloys containing increasing amounts of lead, and aluminium tin alloys; each class may have minor elements (e.g. antimony, indium) added to promote, for example, intermetallic formation. The corrosion of tin-rich white metal bearings is rare and consequently detailed studies of the phenomenon are not extensive in the

literature. High tin alloys are relatively resistant to corrosion in the organic acids that tend to be formed during the degradation of lubricating fluids and the tin salts that form have anti-oxidant capability. Where corrosion of tin-rich bearings has occurred it is invariably associated with water ingress [63]. For example 500ppm water has been shown to be sufficient to cause corrosion, especially in conjunction with chlorine-based high-pressure additives in the oil [64].

When free access of salt water to a bearing is possible, the tin-lead “Babbitt” alloys are not suitable since they are cathodic to steel shafts. For underwater bearings, alloys with 70% Sn, 1.5% Cu and the balance Zn, are traditionally used; the possible dissolution of zinc gives cathodic protection to the shaft, although the more easily replaced bearing suffers some corrosion.

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