TIN AND TIN ALLOYS

1. Introduction

Tin [7440-31-5] is one of the world's most ancient metals. When and where it was discovered is uncertain, but evidence points to tin being used in 3200–3500 BC. Ancient bronze weapons and tools found in Ur contained 10–15 wt % tin. In 79 AD, Pliny described an alloy of tin and lead now commonly called solder (see Solders and brazing alloys). The Romans used tinned copper vessels, but tinned iron vessels did not appear until the fourteenth century in Bohemia. Tinned sheet for metal containers and tole (painted) ware made its appearance in England and Saxony about the middle of the seventeenth century. Although tinplate was not manufactured in the United States until the early nineteenth century, production increased rapidly and soon outstripped that in all other countries (1).

In most cases, tin is used on or in a manufactured material in small amounts, much out of proportion to the purpose it serves. Nevertheless, tin in some form has been associated with the economic and cultural growth of civilization. Food preservation and canning developed rapidly with the invention of tin-coated steel; transportation and high speed machinery became a reality with the invention of tin-base bearing metals; the casting of type metal was an important advance in printing technology; bronze alloys became weapons, tools, and architectural objects; tin alloys are used in organ pipes and bells; and telecommunications and electronic equipment depend upon the tin–lead soldered joint. In modern technology, new uses of tin include the plating of protective coatings, nuclear energy, plastics and other polymers, agriculture, biochemistry, electronic packaging, and glassmaking.

2. Occurrence

Of the nine different tin-bearing minerals found in the earth's crust, only cassiterite [1317-45-9], SnO_2, is of importance. Over 80% of the world's tin ore occurs in low grade alluvial or eluvial placer deposits where the tin content of the ore can be as low as 0.015%. Complex tin sulfide minerals such as stannite [12019-29-3], $Cu_2S{\cdot}FeS{\cdot}SnS_2$; teallite [12294-02-9], $PbSnS_2$; cylinderite [59858-98-9], $PbSn_4FeSb_2S_{14}$; and canfieldite [12250-27-0], Ag_8SnS_6, are found in the lode deposits of Bolivia and Cornwall associated with cassiterite and granitic rock. In the lode mines, the ores often contain 0.8–1 wt % of tin metal. No workable tin deposits have been found in the United States.

Table 1 gives world production, reserves, and reserve base data (2).

Tin-mining methods depend on the character of the deposit. Primary deposits are embedded in underground granitic rock and recovery methods are complex. The more important secondary deposits are in the form of an alluvial mud in the stream beds and placers and the recovery is simpler than lode mining. Cassiterite is recovered from alluvial deposits by dredging, hydraulicking where a head of water permits it, jets and gravel pumps on level ground, or open-pit mining.

Gravel-pump mining is widely used in southeast Asia and probably accounts for 40% of the world's tin production. Powerful jets of water are directed onto the mine face to break down the tin-bearing soil, which is allowed to collect in a sump. A gravel pump in the sump elevates the watery mud to a wooden trough termed a palong in the trade. The palong has a gentle slope and as the ore flows down the slope, the tin oxide particles, which are 2.5 times heavier than sand, are trapped behind wooden slats or riffles. Periodically, the preliminary concentrates are collected and transferred to the dressing shed for final concentration. Hydraulicking and open-pit mining methods also involve gravity separation with water in palongs (see Minerals recovery and processing).

Dredging is mining with a floating dredge on an artificial pond in a placer. Chain buckets or suction cutters, digging at depths of 46 m, transfer the tin-bearing mud to revolving screens, hydrocyclons, jigs, shaking tables, classifiers, and similar equipment. The sand and dirt are removed in these preliminary roughing steps. The mineral is further beneficiated in dressing sheds on shore with modern techniques such as flotation (qv), heavy-media separation, and electrostatic, magnetic, and spiral separators for the removal of associated minerals (see Separation, magnetic). Final concentrates ready for direct smelting contain 70–77 wt % tin, which is almost pure cassiterite.

Underground-lode deposits in Bolivia are located at very high altitudes, 4000–5000 m above sea level, whereas the lode deposits in Cornwall are ca 430 m below sea level. Access to the lodes is by shaft sinking or by adits, ie, passages driven into the side of a mountain, depending on the terrain. The ore is broken from the working face by blasting and drilling. Further crushing and grinding above-ground is necessary to produce the finely divided ore capable of being concentrated by the various gravity-concentration methods and mechanical separations commonly used for alluvial deposits.

Tin concentrates from the lode deposits are 40–60 wt % tin and must be further upgraded before smelting. Roasting the ore removes sulfur and arsenic; the sulfides of iron, copper, bismuth, and zinc are converted to oxides and lead sulfide is oxidized to sulfate. When the concentrates contain considerable quantities of sulfides, the impurities are sometimes removed by a chloridizing roast, followed by leaching. Advances in froth-flotation methods offer another alternative for the removal of unwanted sulfide minerals. When the concentrates are roasted with 1–5 wt % salt, NaCl, in an oxidizing atmosphere, sodium sulfate and the chlorides of the metals are formed without attack on the tin oxide. Many chlorides are volatile; bismuth, lead, arsenic, antimony, and silver may be partially removed in the form of fume; leaching with water removes the remaining chlorides which are readily soluble (see Tin compounds).

3. Physical Properties

Physical, mechanical, and thermal constants of tin are shown in Table 2.

Although the pure metal has a silvery-white color, in the cast condition it may have a yellowish tinge caused by a thin film of protective oxide on the surface. When highly polished, it has high light reflectivity. It retains its brightness well during exposure, both outdoors and indoors.

The melting point (232°C) is low compared with those of the common structural metals, whereas the boiling point (2625°C) exceeds that of most metals except tungsten and the platinum group. Loss by volatilization during melting and alloying with other metals is insignificant. Tin is a soft, pliable metal easily adaptable to cold working by rolling, extrusion, and spinning. It readily forms alloys with other metals, imparting hardness and strength. Only small quantities of some metals can be dissolved in pure liquid tin near its melting point. Intermetallic compounds are freely formed, particularly with metals of high melting point, and some of these compounds are of metallurgical importance. Copper, nickel, silver, and gold are appreciably soluble in liquid tin. A small amount of tin oxide dispersed in tin has a hardening effect.

Molten tin wets and adheres readily to clean iron, steel, copper, and copper-base alloys, and the coating is bright. It provides protection against oxidation of the coated metal and aids in subsequent fabrication because it is ductile and solderable. Tin coatings can be applied to most metals by electrodeposition (see Electroplating).

Tin exists in two allotropic forms: white tin (β) and gray tin (α). White tin, the form which is most familiar, crystallizes in the body-centered tetragonal system. Gray tin has a diamond cubic structure and may be formed when very high purity tin is exposed to temperatures well below zero. The allotropic transformation is retarded if the tin contains small amounts of bismuth, antimony, or lead. The spontaneous appearance of gray tin is a rare occurrence because the initiation of transformation requires, in some cases, years of exposure at -40°C. Inoculation with α-tin particles accelerates the transformation.

4. Chemical Properties

Tin, at wt 118.69, falls between germanium and lead in Group IV A of the periodic table. It has ten naturally occurring isotopes, which, in order of abundance, are 120, 118, 116, 119, 117, 124, 122, 112, 114, and 115.

Tin is amphoteric and reacts with strong acids and strong bases, but is relatively resistant to nearly neutral solutions. Distilled water has no effect on tin. Oxygen greatly accelerates corrosion in aqueous solutions. In the absence of oxygen, the high over-potential of tin (0.75 V) causes a film of hydrogen to be retained on the surface which retards acid attack. The metal is normally covered with a thin protective oxide film which thickens with increasing temperature.

A reversal of potential of the tin–iron couple occurs when tin-coated steel (tin-plate) is in contact with acid solutions in the absence of air. The tin coating acts as an anode; it is the tin that is slowly attacked and not the steel. This unique property is the keystone of the canning industry because dissolved iron affects the flavor and appearance of the product. Thus, the presence of tin protects the appearance and flavor of the product.

Tin does not react directly with nitrogen, hydrogen, carbon dioxide, or gaseous ammonia. Sulfur dioxide, when moist, attacks tin. Chlorine, bromine, and iodine readily react with tin; with fluorine, the action is slow at room temperature. The halogen acids attack tin, particularly when hot and concentrated. Hot sulfuric acid dissolves tin, especially in the presence of oxidizers. Although cold nitric acid attacks tin only slowly, hot concentrated nitric acid converts it to an insoluble hydrated stannic oxide. Sulfurous, chlorosulfuric, and pyrosulfuric acids react rapidly with tin. Phosphoric acid dissolves tin less readily than the other mineral acids. Organic acids such as lactic, citric, tartaric, and oxalic attack tin slowly in the presence of air or oxidizing substances.

Dilute solutions of ammonium hydroxide and sodium carbonate have little effect on tin, but strong alkaline solutions of sodium or potassium hydroxide, cold and dilute, dissolve tin to form stannates.

Neutral aqueous salt solutions react slowly with tin when oxygen is present but oxidizing salt solutions, such as potassium peroxysulfate, ferric chloride and sulfate, and aluminum and stannic chlorides dissolve tin. Nonaqueous organic solvents, lubricating oils, and gasoline have little effect.

5. Processing

5.1. Smelting.

Although the metallurgy of tin is comparatively simple, several complicating factors must be dealt with in tin smelting: The temperature necessary for the reduction of tin dioxide with carbon is high enough to reduce the oxides of other metals which may be present. Thus, reduced iron forms troublesome, high melting compounds with tin, the so-called hard head of the tin smelter. Tin at smelting temperatures is more fluid than mercury at room temperature. It escapes into the most minute openings and soaks into porous refractories. Furthermore, tin reacts with either acid or basic linings, and the slags produced contain appreciable quantities of tin and silica and must be retreated.

Because of the high tin content of the slag, a primary smelting is used to effect a first separation, followed by a second stage to process the slag and hardhead from the first smelting plus refinery drosses.

In primary smelting, carbon (in the form of coal or fuel oil) is the reducing agent. During heat-up, carbon monoxide is formed by reaction with carbon dioxide of the furnace atmosphere. The carbon monoxide reacts with the solid cassiterite particles to produce tin and carbon dioxide:

$$2CO + SnO_2 \longrightarrow Sn + 2CO_2 \qquad (1)$$

As the temperature rises, silica (which is present in nearly all concentrates) also reacts with cassiterite under reducing conditions to give stannous silicate:

$$SnO_2 + CO + SiO_2 \longrightarrow SnSiO_3 + CO_2 \qquad (2)$$

Iron, also present in all concentrates, reacts with silica to form ferrous silicate:

$$Fe_2O_3 + CO + 2SiO_2 \longrightarrow 2FeSiO_3 + CO_2 \qquad (3)$$

The silicates formed in reactions 2 and 3 fuse with the added fluxes to form a liquid slag at which point carbon monoxide loses its effectiveness as a reducing agent. Unreacted carbon from the fuel then becomes the predominant reductant in reducing both stannous silicate to tin and ferrous silicate to iron. The metallic iron, in turn, reduces tin from stannous silicate:

$$SnSiO_3 + Fe \rightleftharpoons FeSiO_3 + Sn \qquad (4)$$

This is the equilibrium established at the end of each smelting cycle. By this time, a considerable proportion of the tin produced in the heat-up stages has been drained from the furnace and only the metal remaining in the furnace at the final tapping time comes into equilibrium with the slag (4).

Primary smelting can be carried out in a reverberatory, rotary, or electric furnace. The choice depends more on economic circumstances than on technical considerations (4). Thus, in the Far East, reverberatory furnaces fired with anthracite coal as the reductant were and still are widely used. Indonesia and Singapore use slow-speed rotary furnaces. Both Malaysia and Thailand have added new electric-furnace smelting capacity in order to improve smelting efficiencies. Reverberatory and rotary furnaces are also used in Indonesia. On the other hand, the smelters in Central Africa, including those in Zaire and Rwanda as well as those in South Africa, which are far away from coal sources, use electric furnaces because of the availability of electric power.

The development of satisfactory processes for the fuming of tin slags has been one of the greatest contributions to tin smelting in recent years. This work, stimulated by the need for better metal recoveries, relies on the formation and volatilization of tin as SnO_2 in a type of blast furnace (5). The process requires the addition of pyrites (FeS_2) to the tin-rich slag where it reacts to produce $FeSiO_3$ and SnS. The tin sulfide vapor oxidizes to SnO_2 and is carried out in the furnace exhaust gases where it is collected and recycled.

Fuming is also an alternative to roasting in the processing of low grade concentrates (5–25 wt % tin). This procedure yields a tin oxide dust, free of iron, which is again fed back to a conventional smelting furnace.

5.2. Refining. The crude tin obtained from slags and by smelting ore concentrates is refined by further heat treatment or sometimes electrolytic processes.

The conventional heat-treatment refining includes liquidation or sweating and boiling, or tossing.

In liquidation, tin is heated on the sloping hearth of a small reverberatory furnace to just above its melting point. The tin runs into a so-called poling kettle, and metals that melt sufficiently higher than tin remain in the dross. Most of the iron is removed in this manner. Lead and bismuth remain, but arsenic, antimony, and copper are partly removed as dross.

In the final refining step, the molten tin is agitated in the poling kettles with steam, compressed air, or poles of green wood which produce steam. This process is referred to as boiling. The remaining traces of impurities form a scum which is removed and recirculated through the smelting cycle. The pure tin is cast in iron molds in the form of 45-kg ingots. Purity is guaranteed to exceed 99.8%.

Iron, copper, arsenic, and antimony can be readily removed by the above pyrometallurgical processes or variations of these (4). However, for the removal of large quantities of lead or bismuth, either separately or together, conventional electrolysis or a newly developed vacuum-refining process is used.

Electrolytic refining is more efficient in regard to both the purity of the product and the ratio of tin to impurities in by-products. However, a large stock of the crude-tin anodes is tied up in the cells, requiring a high capital investment for equipment. An electrolytic plant working with an acid stannous salt at ca 108 A/m^2 requires ca 25 metric tons of working anodes for every ton of refined tin produced per day. Because of these high costs, fire refining should be used as much as possible. The by-products containing high lead, bismuth, and other metal impurities can then be treated in a modest electrolytic plant (6).

An electrorefining plant may operate with either an acid or an alkaline bath. The acid bath contains stannous sulfate, cresolsulfonic or phenolsulfonic acids (to retard the oxidation of the stannous tin in the solution), and free sulfuric acid with β-naphthol and glue as addition agents to prevent tree-like deposits on the cathode which may short-circuit the cells. The concentration of these addition agents must be carefully controlled. The acid electrolyte operates at room temperature with a current density of ca 86–108 A/m^2, cell voltage of 0.3 V, and an efficiency of 85%. Anodes (95 wt % tin) have a life of 21 d, whereas the cathode sheets have a life of 7 d. Anode slimes may be a problem if the lead content of the anodes is high; the anodes are removed at frequent intervals and scrubbed with revolving brushes to remove the slime (7).

The alkaline bath contains potassium or sodium stannate and free alkali and operates without addition agents. The solution must, however, be heated to 82°C. Stannous tin must be absent because it passivates the anodes. The tin dissolves as stannate, $SnO^{2-}{}_3$, but only if the anodes are initially coated with a film of yellow-green hydrated oxide, $SnO_2{\cdot}2H_2O$. This so-called filming is accomplished by passing a high current through the anode after insertion in the cell; the current density is reduced to normal once the film is formed. Slow insertion of the anode with the current turned on gives the same result. The advantages of the alkaline electrolyte are ease of operation and the capability of using a lower grade of anode. The disadvantages are that the solution must be heated and that the current-carrying species is Sn^{4+}, giving an electrochemical equivalent half that of the acid electrolyte. At equilibrium, the lead plumbite is almost completely precipitated as hydroxide in the slime, but some antimony remains in solution. The spent anode is returned to the fire-refining process for recovery of lead, antimony, etc. The plated cathode sheets, weighing ca 90 kg, are melted in a holding pot and cast into ingots. Part of the metal from the holding pots is used to form the starter cathode sheets weighing ca 7.2 kg each.

5.3. Secondary Tin. In 2004, >about 9000 metric tons of tin were recovered in the United States from scrap (2). Sources include bronze rejects and used parts, solder in the form of dross or sweepings, dross from tinning pots, sludges from tinning lines, babbitt from discarded bearings, type-metal scrap, and clean tinplate clippings from container manufacturers. High purity tin is recovered by detinning clean tinplate (see Recycling).

Alloy scrap containing tin is handled by secondary smelters as part of their production of primary metals and alloys; lead refineries accept solder, tin drosses, babbitt, and type metal. This type of scrap is remelted, impurities such as iron, copper, antimony, and zinc are removed, and the scrap is returned to the market as binary or ternary alloy. The dross obtained by cleaning up the scrap metal is returned to the primary refining process.

6. Economic Aspects

Tin has not been mined in the United States since 1993. In 2003, consumption of primary tin declined 3%, however demand is expected to slowly rise in the next few years at the rate of 1%/yr. The rate could increase if new applications, especially lead-free solders find acceptance. World tin reserves appear to be adequate. The United States must depend on imports and recycling to meet its demands (8).

Table 3 gives economic data for the United States (2).

Tin Technology, Uxbridge, UK, reports that for the world market, annual consumption in 2004 was estimated to rise to 300,000 t for the first time. Asia accounts for one half of world use and consumption rose by 10% in 2003 over use in 2002. China accounts for most of the worldwide use of tin and it use is expected to rise as manufacturing activity has been transferred to China from other parts of the world. Tin consumption in Japan has risen due largely to a switch to lead-free soldering. Lead-free solders will have a positive impact on the world market for tin (9).

7. Specifications and Analytical Methods

The ASTM Classification of Pig Tin B 339 lists three grades as shown in Tables 4 and 5 (10).

In the field, cassiterite ore is usually recognized by its high density (7.04 g/cm^3), low solubility in acid and alkaline solutions, and extreme hardness. Tin in solution is detected by the white precipitate formed with mercuric chloride. Stannous tin in solution gives a red precipitate with toluene-3,4-dithiol.

The tin content of ores, concentrates, ingot metal, and other products is determined by fire assay, fusion method, and volumetric wet analysis.

In a fire-assay method used at the smelters, a weighed quantity of concentrate is mixed with sodium cyanide in a clay or porcelain crucible and heated in a muffle furnace at red heat for 20–25 min. The tin oxide is reduced to metal, which is cleaned and weighed. Preliminary digestion of the concentrate with hydrochloric and nitric acids to remove impurities normally precedes the sodium cyanide fusion.

Tin ores and concentrates can be brought into solution by fusing at red heat in a nickel crucible with sodium carbonate and sodium peroxide, leaching in water, acidifying with hydrochloric acid, and digesting with nickel sheet. The solution is cooled in carbon dioxide, and titrated with a standard potassium iodate–iodide solution using starch as an indicator.

The determination of tin in metals containing over 75 wt % tin (eg, ingot tin) requires a special procedure (11). A 5-g sample is dissolved in hydrochloric acid, reduced with nickel, and cooled in CO_2. A calculated weight of pure potassium iodate (dried at 100°C) and an excess of potassium iodide (1:3) are dissolved in water and added to the reduced solution to oxidize 96–98 wt % of the stannous chloride present. The reaction is completed by titration with 0.1 *N* KIO_3–KI solution to a blue color using starch as the indicator.

Several ASTM methods are available for the determination of tin in tin-containing alloys such as solder, babbitt, and bronze (12).

The purity of commercial tin is under strict control at the smelters. Photometric, chemical, atomic absorption, fluorimetric, and spectrographic methods are available for the determination of impurities (11).

8. Health and Safety Factors

Tests have shown that considerable quantities of tin can be consumed without any effect on the human system. Small amounts of tin are present in most liquid canned products; the permitted limit of tin content in foods is 300 mg/kg in the United States and 250 ppm in the UK, which far exceed the amount in canned products of good quality (13) (see also Tin compounds).

9. Uses

The major uses for tin in 2004 were as follows: cans and containers, 27%; electrical, 23% construction, 10%; transportation, 10%; other, 30%.

Tin is used in various industrial applications as cast and wrought forms obtained by rolling, drawing, extrusion, atomizing, and casting; tinplate, ie, low carbon steel sheet or strip rolled to 0.15–0.25 mm thick and thinly coated with pure tin; tin coatings and tin alloy coatings applied to fabricated articles (as opposed to sheet or strip) of steel, cast iron, copper, copper-base alloys, and aluminum; tin alloys; and tin compounds.

9.1. Cast and Wrought Forms. Thousands of tons of tin ingots are cast into anodes for plating processes. Tin foil is used for electrical condensers, bottle-cap liners, gun charges, and wrappings for food. Tin wire is used for fuses and safety plugs. Extruded tin pipe and tin-lined brass pipe are the first choice for conveying distilled water and carbonated beverages. Sheet tin is used to line storage tanks for distilled water. Tin powder is used in powder metallurgy, the largest use going to tin powder mixtures with copper to form bronze parts. It is also used for coating paper and for solder pastes. In the float-glass process, adopted by all leading plate-glass manufacturers, the molten glass is allowed to float and solidify on the surface of a pool of molten tin which provides an ideally flat surface. The endless glass ribbon has a surface so smooth that costly grinding and polishing are unnecessary.

9.2. Tinplate. The development of tinplate was associated with the need for a reliable packaging material for preserving foods. It comprises in one inexpensive material the strength and formability of steel and the corrosion resistance, solderability, absence of toxicity, and good appearance of tin. The tin coating is applied by electroplating in a continuous process or by passing cut sheet through a bath of molten tin. In the United States, tinplate is now made mainly by the electrolytic process with less than 1% of production from hot-tinning machines.

The electrolytic process is flexible and capable of applying tin coatings from 250 nm to 2.5 μm on each face. A thick coating can be applied to one side of the sheet and a thinner coating to the other (differential tinplate) providing a cost savings to the can manufacturer if less protection is needed on the outside of the can. The thinner coatings usually require a baked enamel coating over the tin, except when packaging dry foods and nonfood products.

In addition to the packaging of foods and beverages in regular containers, a large quantity of tinplate is used in the form of aerosol containers for cosmetics, paint, insecticides, polishes, and other products. Decorative trays, lithographed boxes, and containers of unusual shape are additional outlets for tinplate.

A tinplate container has an energy advantage over some of the competitive container materials, as shown in Table 6. By virtue of its magnetic properties, tinplated material is more readily separated by other forms of industrial or domestic waste.

9.3. Tin Coatings.

The coating may be applied by hot-dipping the fabricated article in liquid tin, by electroplating using either acid or alkaline electrolytes, and by immersion tinning (see below). The hot-tinned coating is bright. Electrodeposited coatings are normally dull as plated, but may be flow-brightened by heating momentarily to the melting point by induction or in hot air or oil. Proprietary bright tin-plating processes have been developed and are in commercial use. These incorporate long-chain organic molecules as brightening and leveling agents in a stannous sulfate electrolyte. An anti-tarnish coating has been reported (15).

The coating thickness may range from 0.0025 to 0.05 mm, depending on the type of protection required. Pure tin coatings are used on food-processing equipment, milk cans, kitchen implements, electronic and electrical components, fasteners, steel and copper wire, pins, automotive bearings, and pistons.

For articles that require only a very thin film of tin, seldom exceeding 0.8 μm immersion tin coatings are applied. The process is based on chemical displacement by immersion in a solution of tin salts. A autocatalytic tin-deposition process was developed (16).

9.4. Catalysts.

Researchers at the University of Wisconsin have developed a nickel–tin–aluminum catalyst that would replace precious platinum in a process for extracting hydrogen gas from plants. The relatively low temperature process was said to be environmentally sustainable and greenhouse-gas neutral. The nickel–tin combination reacts with biomass-derived oxygenated hydrocarbons to produce hydrogen and carbon dioxide without producing large amounts of unwanted methane. The new catalyst offers the opportunity to make the transition from fossil fuel-based economy to one based on renewable resources (17).

10. Tin Alloys

10.1. Alloy Coatings.

Tin-alloy coatings provide harder, brighter, and more corrosion-resistant coatings than tin alone. Tin–copper electrodeposited coatings (12 wt % tin) have the appearance of 24-carat gold and provide a bronze finish for furniture hardware, trophies, and ornaments (see Coatings). They also provide a stop-off coating (resist) for nitriding.

Tin–lead coatings (10–60 wt % tin) can be applied by hot-dipping or electrode position to steel and copper fabricated articles and sheet. A special product is terne plate used for roofing and flashings, automobile fuel tanks and fittings, air filters, mufflers, and general uses such as covers, lids, drawers, cabinets, consoles for instruments, and for radio and television equipment. Terne plate is low carbon steel, coated by a hot-dip process with an alloy of tin and lead, commonly about 7–25 wt % tin, remainder lead. Electroplating is another possibility.

Because of the ease with which they can be soldered, electroplated tin–lead coatings of near eutectic composition (62 wt % tin) are extensively used in the electronics industry for coating printed circuit boards and electrical connectors, lead wires, capacitor and condenser cases, and chassis.

Tin–nickel electrodeposited coatings (65 wt % tin) provide a bright decorative finish with a corrosion resistance that exceeds that of nickel and copper–nickel–chromium coatings. A new and expanding use for tin–nickel is for printed circuit boards. Such coatings deposited on the copper-clad boards are etch-resistant and provide protection for the conducting path. The well-established decorative and functional uses are for watch parts, drawing instruments, scientific apparatus, refrigeration equipment, musical instruments, and handbag frames.

Tin–zinc coatings (75 wt % tin) have application as a solderable coating for radio, television, and electronic components. They also provide galvanic protection for steel in contact with aluminum.

A ternary tin–copper–lead coating, 2 Cu–8 Sn–90 Pb, is a standard overplate for steel-backed copper–lead automotive bearings.

Tin–cadmium coatings are particularly resistant to marine atmospheres and have applications in the aviation industry.

10.2. Alloy Solder.

Tin and lead combine easily to form a group of alloys known generally as soft solders. The joining of metals with tin-containing solders can be attributed to several properties. Their low melting point allows simple equipment to be used for melting and joining, the alloys are unsurpassed in wetting and adhering to clean metal surfaces and flowing into small spaces, and they are relatively cheap. The tin–lead solders have no serious competitors in the field of low temperature joining (see Solders and brazing alloys).

Tin is the important constituent in solders because it is the element that wets the base metal, such as copper and steel, by alloying with it. Solders are used mainly in auto radiators, air conditioners, heat exchangers, plumbing and sheet-metal joining, container seaming, electrical connections in radio and television, generating equipment, telephone wiring, electronic equipment and computers, and aerospace equipment (see Table 7). Lead-free solder alloys, where the tin is alloyed individually with antimony, silver, gold, zinc, or indium, are available for special joining applications where properties such as high strength, absence of toxicity, and special corrosion resistance are required.

Oki Electric Company has announced that it has jointly developed a heating technology for lead-free soldering called Component Temperature Control Reflow Technology. This technology will enable manufacturers to automate soldering for low heat tolerance electronic components using a lead-free solder that has a higher melting temperature than lead solders. Tin is the dominant material in conventional solders and is the dominant component in all lead free solders (18). Researchers are continuing to search for advanced and sustainable lead-free solders that include tin as a substitute component (19,20).

One major project in research is the next Generation Environment-Friendly Soldering Technology (EFSOT) initiative (21).

Low melting or fusible alloys (mp, 20–176°C) may be loosely described as solders and are employed for sealing and joining materials which may be damaged in ordinary soldering practice. They have applications in automatic safety devices, foundry patterns, electroforming, tube bending, tempering baths, molds for plastics, and denture models. Fusible alloys, mostly eutectic alloys, are usually two-, three-, four-, or even five-component mixtures of bismuth, tin, lead, cadmium, indium, and gallium.

10.3. Bronze. Copper–tin alloys, with or without other modifying elements, are classed under the general name of bronzes. They can be wrought, sand-cast, or continuously cast into shapes. Binary tin–copper alloys are difficult to cast because they are prone to gassing, which can be alleviated by additions of phosphorus and zinc. The phosphor bronzes (5–10 wt % tin) are preferred because they have superior elastic properties, excellent resistance to alternating stress and corrosion fatigue and to corrosive attack by the atmosphere and water, and superior bearing properties. So-called gun metals containing 1–6 wt % zinc and 5–10 wt % tin are gas-free, pressure-tight alloys used for valves and fittings for water and steam lines. These alloy types may be further modified with lead to improve machinability and, in the case of the phosphor bronzes, to obtain a more conformable bearing alloy. The 85 Cu–5 Sn–5 Zn–5 Pb alloy is a popular composition. Bronzes are especially applicable to marine and railway engineering pumps, valves and pipe fittings, bearings and bushings, gears and springs, and ship propellers. Included in special bronze alloys is bell metal, known for its excellent tonal quality, containing 20 wt % tin, and statuary bronze (see Copper alloys).

10.4. Bearing Metals. Metals used for casting or lining bearing shells are classed as white bearing alloys, but are known commercially as babbitt (see Bearing materials). The term white metal was used by Isaac Babbitt in 1839 in his description of tin-base bearing metals supported by a stronger shell. Although white metal is a general term for many white-colored alloys of relatively low melting point, the white-metal product mentioned in Table 4 is made from pewter, britannia, or jeweler's metal (alloys containing ca 90–95 wt % tin, 1–8 wt % antimony and 0.5–3 wt % copper).

The term babbitt includes high tin alloys (substantially lead-free) containing >80 wt % tin, and high lead alloys containing ≥ 70 wt % lead and ≤ 12 wt % tin. Both have the characteristic structure of hard compounds in a soft matrix, and although they contain the same or similar types of compounds, they differ in composition and properties of the matrix.

The common high tin babbitts are all based upon the tin–antimony–copper system. Compositions and properties of the more widely used tin-base bearing alloys are given in Table 8. Antimony up to 8.0% strengthens the bearing alloy matrix by dissolving in the tin. Above 8.0%, hard particles of tin–antimony compound (SnSb) are formed which tend to float. Additions of copper secure a uniform distribution of these hard particles in a soft but rigid bearing matrix.

The lead-base babbitts are based upon the lead–antimony–tin system, and, like the tin-base, have a structure of hard crystals in a relatively soft matrix. The lead-base alloys are, however, more prone to segregation, have a lower thermal conductivity than the tin-base babbitts, and are employed generally as an inexpensive substitute for the tin-base alloys. Properly lined, however, they function satisfactorily as bearings under moderate conditions of load and speed.

Both types of babbitt are easily cast and can be bonded rigidly to cast iron, steel, and bronze backings. They perform satisfactorily when lubricated against a soft steel shaft, and occasional corrosion problems with lead babbitt can be corrected by increasing the tin content or shifting to high tin babbitt.

Babbitt alloys are suitable for hundreds of types of installations involving the movement of machinery, eg, the main, crankshaft, connecting rod big end, camshaft, and journal bearings associated with marine propulsion, railroad and automotive transportation, compressors, motors, generators, blowers, fans, rolling-mill equipment, etc.

The field of bearing metals also includes bronze and aluminum alloys. The aluminum–tin alloys have fatigue properties comparable with white-metal alloys at ordinary temperatures but at the temperatures encountered in automobile engines (up to 250°C) they are much stronger. An aluminum–tin alloy containing 6.5 wt % Sn, 1 wt % Cu, and 1 wt % Ni is used in applications such as bushings and solid bearings in aircraft landing gear assemblies subject to shock loads of 48 MPa (ca 7000 psi), as tracks for vertical boring mills, and as floating bearings in gas-turbine engines, diesel locomotive and tractor engines, and cold-rolling mills. A modification of this alloy contains also 2.5 wt % silicon. Increasing the tin content of 20 wt % gives a good compromise between fatigue strength and softness, and such steel-backed aluminum–tin alloys are used for connecting rod and main bearings for passenger cars, automatic transmission bushings, camshaft bearings, and thrust washers.

10.5. Pewter. Modern pewter may have a composition of 90–95 wt % tin, 1–8 wt % antimony, and 0.5–3 wt % copper. Lead should be avoided by contemporary craftsman because it causes the metal surface to blacken with age. Pewter metal can be compressed, bent, spun, and formed into any shape, as well as being easily cast. A wide variety of consumer articles are available from domestic and foreign manufacturers. Reproductions of pewter objects from colonial times, some cast from the original molds, are popular.

10.6. Type Metals. The printing trade still requires some amounts of lead-based alloys containing 10–25 wt % antimony and 3–13 wt % tin. By varying the tin and antimony content, type suitable for each printing process can be obtained. Linotype machines demand a fluid and mobile metal with a short freezing range. Casting stereotype plates requires cool metal and a hot box with progressive solidification from the bottom up. Monotype, with the higher percentages of tin and antimony, provides a type with a fine face and superior wear resistance. Foundry type is extra hard-wearing and has extra long life, which reduces the need for recasting for duplicating jobs.

10.7. Alloyed Iron. Tin-alloyed flake and nodular cast irons are widely used throughout the world. As little as 0.1% tin when added to flake and spheroidal graphite cast irons in the pouring ladle gives the iron a structure that is completely pearlitic. Tin-inoculated iron has a uniformity of hardness, improved machinability, wear resistance, and better retention of shape on heating. Where pearlitic and heat-resistant cast irons are required, such as for engine blocks, transmissions, and automotive parts, tin additions may provide a suitable material.

10.8. Special Alloys. Alloys of tin with the rarer metals, such as niobium, titanium, and zirconium, have been developed. The single-phase alloy Nb_3Sn [12035-04-0] has the highest transition temperature of any known superconductor (18 K) and appears to keep its superconductivity in magnetic fields up to at least 17 T (170 kG). Niobium–tin ribbon, therefore, is of practical importance for the construction of high field superconducting solenoid magnets.

Tin is an important addition to titanium. As a nominal addition (2–4% Sn), tin is a solid-state strengthener, retards interstitial diffusion, and promotes plasticity and free-scaling. Some of the more widely used commercial alloys include 92.5 Ti–5 Al–2.5 Sn, 86 Ti–6 Al–6 V–2 Sn, and 86 Ti–6 Al–2 Sn–4 Zn–2 Mo.

Because of its low neutron absorption, zirconium is an attractive structural material and fuel cladding for nuclear power reactors, but it has low strength and highly variable corrosion behavior. However, Zircalloy-2, with a nominal composition of 1.5 wt % tin, 0.12 wt % iron, 0.05 wt % nickel, 0.10 wt % chromium, and the remainder zirconium, can be used in all nuclear power reactors that employ pressurized water as coolant and moderator (see Nuclear reactors).

Dental amalgams, mainly silver–tin–mercury alloys, have been used as fillings for many years (see Dental materials). The most common alloy contains 12 wt % tin.

10.9. Other Uses. The production of finished shapes from iron powder by compacting and sintering utilizes about 100,000 t of iron powder annually; copper powder (2–10 wt %) is normally added as a sintering aid. Addition of 2% tin powder or equal amounts of tin and copper powder considerably lowers the sintering temperature and time of sintering at a cost saving. The tin addition also improves dimensional control. Iron powder plus 10 wt % powdered lead–tin metal is pressed and sintered to make pistons for use in automotive hydraulic brake cylinders.

The electronics and aerospace industries have for a number of years used gold-plated printed circuit boards and component leads where highest reliability is desired. Problems in the use of gold coatings have plagued the industry and the trend is toward the substitution of tin–lead or tin coatings for the gold coatings. Tin–nickel coatings with a thin flash of tin or gold are also used as a substitute for heavy gold coatings (see Electrical connectors).

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Table 1. **World Mine Production, Reserves, and Reserves Base; $\times 10^3$ t**[a,b]

	Mine production		Reserves	Reserve base
	2003	2004[c]		
United States	0	0	20	40
Australia	6.5	1.2	110	300
Bolivia	15	16.9	450	900
Brazil	14.2	14	540	2,500
China	50	100	1,700	3,500
Indonesia	70	70	800	900
Malaysia	3.4	3.5	1,000	1,200
Peru	38	40.2	710	1,000
Portugal	1	0.5	70	80
Russia	2	2.5	300	350
Thailand	0.8	0.8	170	200
Vietnam	4.6	na	na	na
other countries	1	1	180	200
World total (rounded)	*207*	*250*	*6,100*	*11,000*

[a] Ref. 2.

[b] na = not available.

[c] Estimated.

Table 2. **Physical Properties of Tin**[a]

Property	Value
mp, °C	231.9
bp, °C	2625
sp gr	
a-form (gray tin)	5.77
b-form (white tin)	7.29
liquid at mp	6.97
transformation temp $\beta \rightleftarrows \alpha$, °C	13.2
vapor pressure, Pa[b]	
at 1000 K	986×10^{-6}
1300 K	1.1
1500 K	22.6
2000 K	4.08×10^{3}
2550 K	91×10^{3}
surface tension, at mp, mN/m (= dyn/cm)	544
viscosity, at mp, mPa(= cP)	1.85
specific heat, at 20°C, J/(kg·K)[c]	222
latent heat of fusion, kJ/(g·atom)[c]	7.08
thermal conductivity, at 20°C, W/(nK)	65
coefficient of linear expansion, $\times 10^{-6}$	
at 0°C	19.9
100°C	23.8
shrinkage on solidification, %	2.8
resistivity of white tin, μΩm	
at 0°C	11.0
100°C	15.5
200°C	20.0
mp (solid)	22.0
mp (liquid)	45.0
volume conductivity, % IACS	15
Brinell hardness, 10 kg, 5 mm, 180 s	15
at 20°C	3.9
220°C	0.7
tensile strength, as cast, MPa[d]	
at 15°C	14.5
200°C	4.5
−40°C	20.0
−120°C	87.5
latent heat of vaporization, kJ/mol[c]	296.4

[a] Ref. 3.
[b] To convert Pa to mm Hg, multiply by 0.0075.
[c] To convert J to cal, divide by 4.184.
[d] To convert MPa to psi, multiply by 145.

Table 3. **U. S. Economic Data for Tin**[a,b]

Category	2000	2001	2002	2003	2004[c]
production:					
secondary (old scrap)	6,560	6,700	6,760	5,420	6,000
secondary (new scrap)	9,140	7,200	3,790	2,460	3,000
imports for consumption, refined tin	44,900	37,500	42,200	37,100	40,000
exports, refined tin	6,640	4,350	2,940	3,690	4,600
shipments from Government stockpile excesses	12,000	12,000	8,960	8,880	9,000
consumption, reported:					
primary	38,100	34,200	34,000	32,900	33,000
secondary	8,940	7,630	5,830	4,490	5,000
consumption, apparent	57,200	48,300	55,700	48,700	50,400
price, average, cents per pound:					
New York market	255	211	195	232	412
New York composite	370	315	292	340	643
London	246	203	184	222	422
Kuala Lumpur	244	201	184	222	386
stocks, consumer and dealer, yearend	10,400	9,620	8,910	7,950	8,000
net import reliance[d] as a percentage of apparent consumption	88	86	88	89	88

[a] Ref. 2.

[b] Data in metric tons unless otherwise noted.

[c] Estimated.

[d] Imports−exports + adjustments for Government and stock changes.

Table 4. **Classification of Pig Tin**[a]

ASTM designation	Tin, %[b,c]	General applications
ultrapure	99.95	analytical standards and research, pharmaceuticals, fine chemicals
A standard	99.85	collapsible tubes, unalloyed (block) tin products, electrotinning, tin-alloyed cast iron, high grade solders
grade A tinplate	99.85	food containers, foil

[a] Ref. 10.

[b] A more complete description of these grades is given in the full ASTM Standard B339-93.

[c] Percent shown is minimum.

Table 5. **Chemical Composition and Impurity Contents of Tin**

Element[a]	Composition, wt % Grade A	Grade A for the manufacture of tinplate	Ultra pure grade
tin	99.85[b]	99.85[b]	99.95[b]
antimony	0.04	0.04	0.005
arsenic	0.05	0.05	0.005
bismuth	0.030	0.030	0.015
cadmium	0.001	0.001	0.001
copper	0.04	0.04	0.005
iron	0.010	0.010	0.010
lead	0.05	0.020	0.001
nickel + cobalt	0.01	0.01	0.010
sulfur	0.01	0.01	0.010
zinc	0.005	0.005	0.005
silver	0.01	0.01	0.010
other impurities[c]		0.010	0.010

[a] Value is maximum unless otherwise noted.

[b] Value is minimum.

[c] Maximum per impurity not listed above.

Table 6. **Energy Consumption in Container Manufacturing**[a]

Container type	Energy consumed in producing raw material, GJ/t[b]	Number of containers per ton	Energy consumed per container, kJ[b]
tinplate can	49	16,500	3,010
aluminum can	395	44,500	8,660
bimetallic can	77	18,400	4,210
glass bottle			
returnable	54.8	2,000	27,540
nonreturnable	54.8	4,000	13,770

[a] Ref. 14.

[b] To convert J to Btu, divide by 1054.

Table 7. **Solders and Their Uses**

Alloy content, wt %	Melting range, °C	Typical tensile strength of cast solder, MPa[a]	Uses
		General engineering	
60 Sn, 40 Pb	183–188	53	electronics and instruments
50 Sn, 50 Pb	183–212	45	sheet-metal work and light engineering
40 Sn, 60 Pb	183–234	43	general engineering and capillary fittings
30 Sn, 70 Pb	183–255	43	plumbers' solder, cable joining, automobile radiators
20 Sn, 80 Pb	183–276	42	automobile radiators
40 Sn, 57.8 Pb, 2.2 Sb	185–227	51	similar to 40 Sn, 60 Pb solder
		Special purpose	
2 Sn, 98 Pb	315–322	28	tinplate can side seams
10 Sn, 90 Pb	267–301	37	cryogenics
5 Sn, 93.5 Pb, 1.5 Ag	296–301	39	
62 Sn, 36 Pb, 2 Ag	178	43	creep resistance
95 Sn, 5 Sb	236–243	40	
95 Sn, 5 Ag	221–225	59	
98 Sn, 2 Ag	221–235	26	food and beverage containers
100 Sn	232	14	
52 Sn, 30 Pb, 18 Cd	145	43	low melting solder
80 Sn, 20 Zn	200–265	70	soldering aluminum

[a] To convert MPa to psi, multiply by 145.

Table 8. **Composition and Properties of ASTM B 23 Bearing Alloys**[a]

		Compressive strength, MPa[b]		
Alloy no.	Nominal composition, wt %	Yield[c]	Ultimate[d]	Brinell hardness[e]
1	91 Sn, 4.5 Sb, 4.5 Cu	30	89	17.0
2	89 Sn, 7.5 Sb, 3.5 Cu	42	103	24.5
3	84 Sn, 8 Sb, 8 Cu	46	121	27.0
4	75 Sn, 12 Sb, 10 Pb, 3 Cu	38	111	24.5
5	65 Sn, 15 Sb, 18 Pb, 2 Cu	35	104	22.5

[a] Ref. 22.

[b] To convert MPa to psi, multiply by 145.

[c] Determined at a total deformation of 0.125% reduction in gauge length.

[d] Determined from unit load required to produce a 25% deformation of specimen length.

[e] Average of three values using a 10 mm ball and applying a 500-kg load for 30 s.