Kirk-Othmer Encyclopedia of Chemical Technology.

LEAD ALLOYS

Lead (qv) is a heavy, soft, bluish gray metal having a low melting point and a high boiling point. The density, coefficient of thermal expansion, malleability, lubricity, and flexibility are high. The tensile and compressive strength, hardness, elastic modulous, elastic limit, creep resistance, and yield strength are quite low. Lead has excellent resistance to corrosion in a wide variety of media, and is easily alloyed with many other metals. Lead alloys, which have low melting points, can be cast into many shapes by using a variety of molding materials and casting processes.

Lead is easily cast and formed. It is one of the oldest known metals, used before 3000 BC. Early civilizations used lead extensively for ornamental and structural uses, and lead pipes used for the transportation of water by the Romans have endured.

About 50% of lead is used as pure lead, lead oxides, or lead chemicals (see Lead compounds); the remainder is used in the form of lead alloys. The principal uses of lead alloys are in lead–acid batteries (qv); for ammunition; cable sheathing; building construction in sheets, pipes, and solders; bearings; gaskets; specialty castings; anodes; fusible alloys; shielding; and weights (see Building materials, survey; Bearing materials; Metal anodes; Solders and brazing alloys).

Lead and its alloys are generally melted, handled, and refined in cast-iron, cast-steel, welded-steel, or spun-steel melting kettles without fear of contamination by iron(qv). Normal melting procedures require no flux cover for lead. Special reactive metal alloys require special alloying elements, fluxes, or covers to prevent dross formation and loss of the alloying elements.

Lead is ductile and malleable, and can be fabricated into various shapes by rolling, extruding, forging, spinning, and hammering. The low tensile strength and very low creep strength of lead make it unsuitable for use without the addition of alloying elements. The principal alloying elements used to strengthen lead are antimony, calcium, tin, copper(qv), tellurium, arsenic, and silver. Minor alloying elements are selenium, sulfur, bismuth, cadmium, indium, aluminum, and strontium.

1. Lead–Antimony Alloys

1.1. Properties

Lead–antimony alloys are the most widely used lead alloys. The lead–antimony phase diagram is shown in Figure 1 (1). Antimony is relatively soluble in molten lead. The lead–antimony system contains a eutectic point at 11.1% antimony and 252°C. The solubility of antimony in solid lead decreases from 3.5 wt % at the eutectic temperature of 252°C to 0.25 wt % at 25°C. The reduced solubility with temperature makes the lead–antimony alloys age hardenable. The grain structure of a typical cast lead–antimony alloy is shown in Figure 2. It consists of a lead matrix (the dark particles in Fig. 2) surrounded by a network of antimony particles (white). These particles provide immediate strength upon casting and also provide high temperature strength. The addition

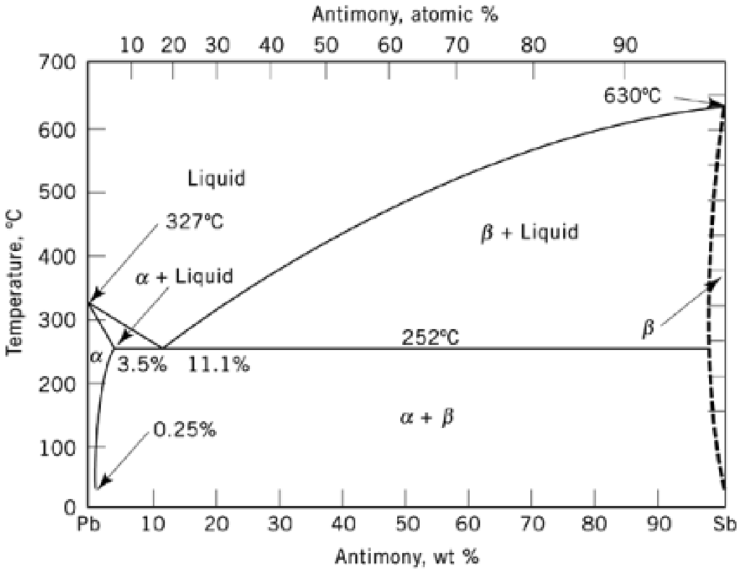

Fig. 1. Lead–antimony phase diagram (1).(Courtesy of McGraw-Hill Book Co., Inc.)

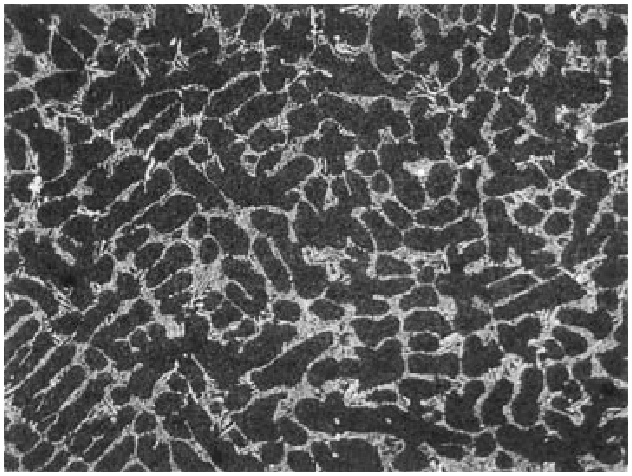

Fig. 2. Grain structure of cast lead–6 wt%antimony alloy showing the dark lead, white antimony eutectic particles at a magnification of $160\times$.

of arsenic dramatically increases the rate of aging and final strength. Addition of tin increases the fluidity and, in combination with copper and arsenic, reduces the rate of oxidation of molten lead–antimony alloys (2).

The mechanical properties of lead–antimony alloys containing arsenic, tin, and copper are shown in Table 1. Most lead–antimony alloys of commercial importance contain 11 wt % or less antimony. High (>5 wt%) antimony alloys are strengthened primarily by the eutectic antimony particles produced during solidification of the alloy. Lower antimony alloys are strengthened by a combination of the eutectic particles and precipitation hardening during aging.

Table 1. Mechanical Properties of Lead–Antimony Alloys[a]

Antimony content, wt %	Yield strength after aging, MPa[b], [c]		Tensile strength, MPa[b]	Elongation, %
11	68.9	74.4	75.9	5
6	55.2	71.0	73.8	8
3	34.0	55.2	65.5	10
2	24.1	37.9	46.9	15
1	13.8	19.3	37.9	20
0	3.5	3.5	11.7	55

[a] After 30 days, unless otherwise noted.
[b] To convert MPa to psi, multiply by 145.
[c] Column on left is after one day.

The decrease in solubility of antimony in lead with decreasing temperature allows the lead–antimony alloys to be precipitation-hardened by proper heat treatment. Differences in the rate of cooling of castings to room temperature can give wide variation in the mechanical properties owing to differences in the amount and type of antimony precipitates produced during cooling. The effects of quenching temperature on the properties of lead–3 wt % antimony alloy aged 1 day are as follows.

Quenching temperature, °C	Tensile strength, MPa (psi)
238	75 (10,875)
230	56 (8,120)
215	38 (5,510)
200	34 (4,930)

1.2. Uses

1.2.1. Lead–Acid Batteries

The primary use for lead–antimony alloys is as electrodes, connectors, and terminals of lead–acid batteries (see Batteries, secondary cells, lead–acid). The lead–antimony alloys, which are strong, creep resistant, and corrosion resistant in sulfuric acid, resist structural changes caused by charge–discharge cycles in the battery. Antimony as an alloying element in the positive electrode grid aids in retaining the active material in the battery and also aids in recharge of the battery when it is deeply discharged. Deep discharge industrial, load-leveling, and motive-power batteries utilize lead alloys containing 5–11 wt % antimony. Large tubular grids use 9–11 wt % antimony.

In lead–acid batteries antimony has one disadvantage. In use, the positive lead grid is oxidized during battery charging. The antimony, oxidized from the positive grid, enters the electrolyte and plates on the negative grid as metallic antimony. The antimony reduces the hydrogen overvoltage at the negative grid causing breakdown of the water in the electrolyte during charging into hydrogen and oxygen, and consumes water in the process. The amount of water loss and subsequent need to add water to the battery decreases as the antimony content of the positive grid decreases (3). Low gassing or maintenance-free batteries have antimony contents of 1.5–2.75 wt %. At this level, the migration of antimony is greatly decreased.

Automobile battery grids employ about 1–3 wt % antimony–lead alloys. Hybrid batteries use low (1.6–2.5 wt %) alloys for the positive grids and nonantimony alloys for the negative grids to give reduced or no water loss. The posts and straps of virtually all lead–acid batteries are made of alloys containing about 3 wt % antimony.

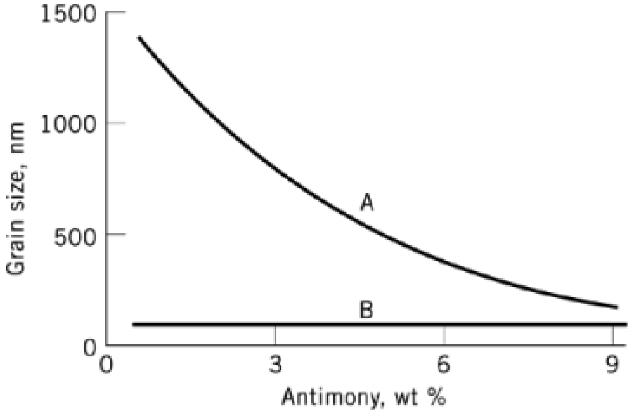

Fig. 3. Grain size as a function of antimony content: A, without grain refiners; B, with addition of selenium (4).(Courtesy of the Electrochemical Society.)

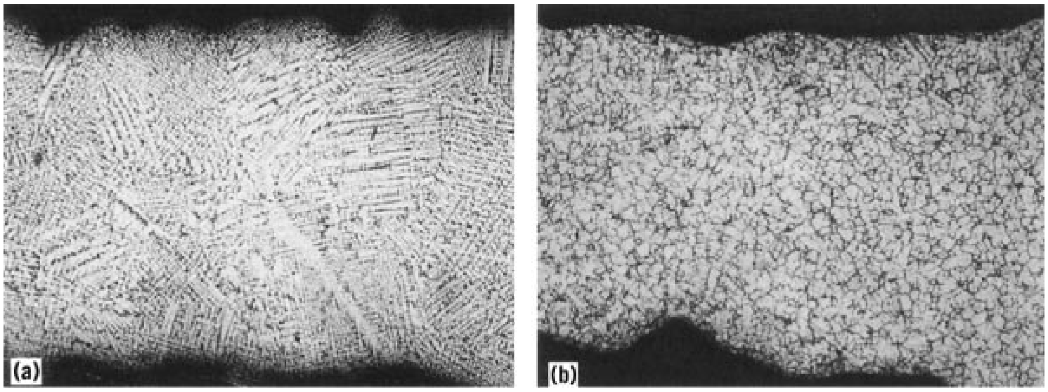

Fig. 4. Grain structure of lead–2 wt%antimony alloy battery grid at a magnification of $_{50\times}$: (**a**) no nucleants; (**b**) containing 0.025 wt%selenium as a grain refiner.

Low antimony alloys decrease water loss when used as positive grids. In alloys having less than 3.5 wt % antimony, however, the increased solidification temperature range and the reduced or negligible amount of eutectic liquid present at the final freezing temperature produces structures highly susceptible to solidification–shrinkage porosity and cracking. The grain size of lead–antimony alloys increases with decreasing antimony content as seen in Figure 3.

As the antimony content of the lead–antimony alloys decreases, the alloys tend to solidify into large, oriented, columnar grains. Figure 4**a** shows the large grains associated with a cast low antimony alloy battery grid. The large grains present areas for preferential mechanical cracking and penetrating corrosion. To prevent the formation of large grains, nucleants are added to lead–antimony alloys. Small amounts of sulfur, copper, or selenium serve as sites for growth of lead crystals during solidification and produce fine, rounded grain structures which are resistant to cracking (2, 4–6).

By using nucleants, fine-grained structures, such as that shown in Figure 4**b,** can be produced in cast alloys independent of the antimony content. The molten metal must be kept at a temperature high enough to assure complete solubility of the nucleants prior to casting the alloy. In the United States primarily copper and sulfur are used as nucleants; in Europe and Asia selenium is used. At very low (1.0–1.6 wt %) antimony contents selenium is used exclusively.

1.2.2. Ammunition

Lead shot is produced by dropping molten lead–antimony alloys containing 0.5–8 wt % antimony through holes in pans into water. The shot alloys contain arsenic in an amount equal to about 20–30 wt % of the antimony content. Arsenic permits the molten drop of lead to become round during freefall. Tin produces elongated shot if present, therefore it is restricted to less than 0.0005 wt %. Shot up to 5.8 mm in diameter is dropped from towers; larger shot must be cast in molds. Lead–antimony (0.5–3.0 wt %) alloys are also used for cast or swaged bullets.

1.2.3. Cable Sheathing

Lead–antimony alloys containing 0.5–1.0 wt % antimony are used to form a barrier sheath in high voltage power cables. Lead–copper and lead–tin–arsenic alloys are also used. Antimony containing alloys are used when higher strength and resistance to vibration is required. British standard BS-801 alloy B contains 0.85 wt % antimony. Lead–antimony alloys having 0.6 wt % or less antimony can be continuously extruded, are impervious to oil and moisture, and remain pliable indefinitely. Lead–antimony (1.0 wt %) is generally used as sleeves for cable splices.

1.2.4. Anodes

Lead–antimony (6–10 wt %) alloys containing 0.5–1.0 wt % arsenic have been used widely as anodes in copper, nickel, and chromium electrowinning and metal plating processes. Lead–antimony anodes have high strength and develop a corrosion-resistant protective layer of lead dioxide during use. Lead–antimony anodes are resistant to passivation when the current is frequently interrupted.

1.2.5. Wrought Lead–Antimony

Most lead–antimony alloys are used in the cast form. Rolling, extruding, or drawing breaks up the as-cast strengthening antimony eutectic particles, thus wrought lead–antimony alloys are weaker and have higher creep rates than cast lead–antimony alloys, but greater strength than lead–copper alloys. These can be easily fabricated into most lead products. Extruded and formed lead–4–6 wt % antimony alloys are used to produce a variety of products for radiation protection. Because of excellent resistance to corrosion by a variety of chemicals, lead–antimony (4–8 wt %) alloys are used for tank linings, pumps (qv), valves, and heating and cooling coils, particularly where sulfuric acid or sulfate solutions are handled at elevated temperature. Arsenic is generally added to increase resistance to creep at elevated temperatures.

1.3. Lead–Antimony–Tin Alloys

Lead–antimony–tin alloys are used for printing, bearings, solders, slush castings, and specialty castings. These alloys have low melting points, high hardness, and excellent high temperature strength and fluidity. Printing alloys generally contain more than 11 wt % antimony and 3–14 wt % tin. The alloys shown in Table 2 have low melting points and high hardness for wear resistance in printing. Replication of mold details is particularly important.

Excellent antifriction properties and good hardness (qv) make lead–antimony–tin alloys suitable for journal bearings. The alloys contain 9–15 wt % antimony and 1–20 wt % tin and may also contain copper and arsenic, which improve compression, fatigue, and creep strength important in bearings. Lead–antimony–tin bearing alloys are listed in ASTM B23-92 (7).

Specialty castings include belt buckles, trophies, casket trim, miniature figures, and hollow-ware. Slush castings are produced by pouring an alloy into a mold, permitting a given thickness to solidify, and pouring out

Table 2. Printing Alloys

	Composition, wt %			Temperature		
Process	Sn	Sb	Pb	Liquidus, C°	Solidus, C°	Brinell hardness
linotype	4	11.5	84.5	243	239	22
electrotype	3	3	94	299	245	14
stereotype	5	14	81	256	240	23
monotype	7	16.5	76.5	275	240	26
foundry type	14	24	62	318	240	32

the remaining liquid to produce a hollow, light, high detail casting. The near-eutectic lead alloy, containing 11 wt % antimony, 1 wt % tin, and 0–0.5 wt % arsenic, has a low melting point which permits silicon rubber molds to be used in spin-casting processes. Lead–antimony–tin alloys for die casting are listed in ASTM B102-93 (7).

Low (2–5 wt %) antimony, low (2–5 wt %) tin lead alloys are used for automobile body solder. Special lead–antimony alloys containing 1–4 wt % antimony are used for wheel-balancing weights, battery cable clamps, collapsible tubes, and highly machined isotope pots.

2. Lead–Calcium Alloys

Lead–calcium alloys are replacing lead–antimony alloys for many applications. Most U.S. original equipment automotive batteries are constructed of lead–calcium grids, whereas most U.S. replacement batteries utilize lead–calcium alloys for the negative grid and lead–antimony alloys for the positive grid. Lead–calcium is used worldwide for standby power, submarine, and specialty sealed batteries. Lead–calcium alloy batteries do not require addition of water and can therefore be sealed. Lead–calcium alloys are used for electrowinning anodes, cable sheathing and sleeving, specialty boat keels, and lead alloy tapes.

2.1. Binary Lead–Calcium Alloys

The lead–calcium phase diagram is shown in Figure 5 (1). The phase diagram is a peritectic having a peritectic temperature of 328.3°C. The maximum solubility of calcium is 0.10 wt % at 328.3°C and rapidly decreases to 0.02 wt % at 200°C and 0.01 wt % at 25°C. The large decrease in solubility with decreasing temperature permits precipitation strengthening of binary lead–calcium alloys by the compound Pb_3Ca. This compound is also formed in molten alloys containing more than 0.07% calcium.

Below 0.10 wt % calcium the alloys solidify into a cellular, dendritic grain structure as seen in Figure 6 (8). Impurities segregate to the intercellular boundaries and are thus accented in the microstructure. Reverse segregation causes some areas of the casting to contain 0.10 wt % calcium regardless of the original calcium content of the melt. Precipitation of calcium occurs by a discontinuous precipitation reaction (8). In this reaction, grain boundaries move through the matrix, the original cast grain is destroyed, and the characteristic serrated grain boundaries of lead–calcium alloys seen in Figure 7 are produced. The calcium content and the rate of grain boundary movement determine the final grain size and shape.

Lead–calcium (0.04%) alloy, used as cable sheaths and sleeves for cable splices, is significantly stronger and has greater creep resistance than lead–copper (0.06 wt %) or lead–antimony (1 wt %). Table 3 compares the mechanical properties of lead–calcium alloy to these alloys and to pure lead. The lead–calcium alloys have outstanding creep and fatigue resistance as well as relatively good ductility. Aging after production may cause a permanent set and difficulty in uncoiling; hence, lead–calcium is used primarily in straight lengths or as sleeves.

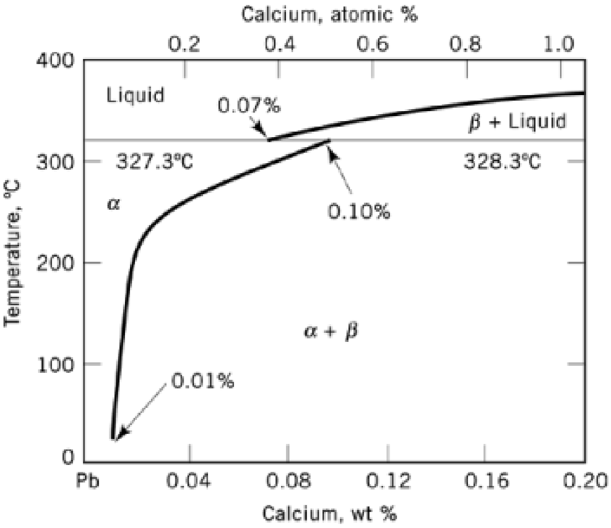

Fig. 5. Lead–calcium phase diagram (1).(Courtesy of McGraw-Hill Book Co., Inc.)

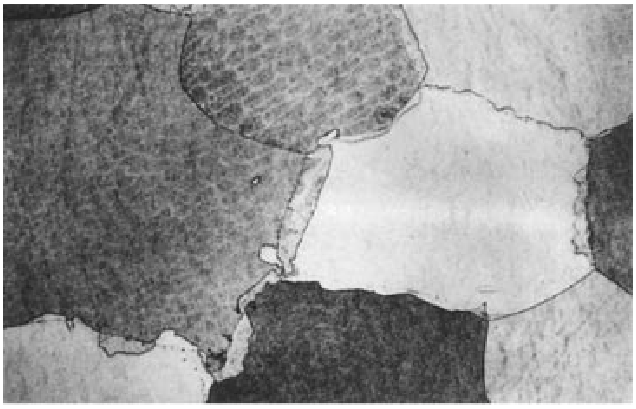

Fig. 6. Large columnar as-cast grain structure of lead–calcium alloys at a magnification of $_{80\times}$.

The main use of binary lead–calcium alloys is for the grids in large, stationary standby power batteries. These batteries use alloys containing 0.03–0.07 wt % calcium. The alloy has sufficient strength for the application, but it is used principally because of its resistance of self-discharge and because it reduces water loss. The grids are large grained and resistant to growth and creep during the long battery life.

2.1.1. Reactivity of Lead–Calcium Alloys

Precise control of the calcium content is required to control the grain structure, corrosion resistance, and mechanical properties of lead–calcium alloys. Calcium reacts readily with air and other elements such as antimony, arsenic, and sulfur to produce oxides or intermetallic compounds (see Calcium and calcium alloys). In these reactions, calcium is lost and suspended solids reduce fluidity and castibility. The very thin grids that are required for automotive batteries are difficult to cast from lead–calcium alloys.

A rapid method to determine the calcium content of lead alloys is a liquid-metal titration using lead–antimony (1%) (9). The end point is indicated by a gray oxide film pattern on the surface of a solidified sample

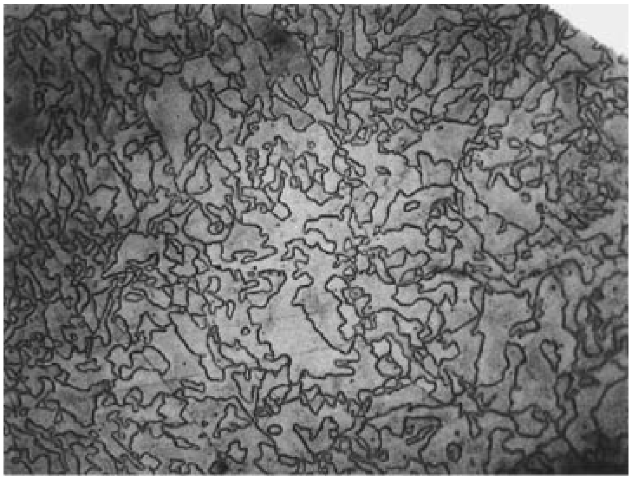

Fig. 7. Grain structure of lead–0.07 wt%calcium alloy aged for seven days showing serrated grain boundaries at a magnification of $320\times$.

Table 3. Mechanical Properties of Pure Lead and Lead Alloys

		Lead alloys		
Property	Pure lead	0.06 wt % Cu	1 wt % Sb	0.04 wt % Ca
tensile strength, MPa[a]	12.2	17.4	20.9	27.9
elongation, %	55	55	35	35
fatigue strength, MPa[a]	2.75	4.90	6.28	9.02

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

of the metal when observed at a 45° angle to a light source. The basis for the titration is the reaction between calcium and antimony. The percentage of calcium in the sample can be calculated from the amount of antimony used. If additional calcium is needed in the alloy, the melt is sweetened with a lead–calcium (1 wt %) master alloy.

2.2. Lead–Calcium–Aluminum Alloys

Lead–calcium alloys can be protected against loss of calcium by addition of aluminum. Aluminum provides a protective oxide skin on molten lead–calcium alloys. Even when scrap is remelted, calcium content is maintained by the presence of 0.02 wt % aluminum. Alloys without aluminum rapidly lose calcium, whereas those that contain 0.03 wt % aluminum exhibit negligible calcium losses, as shown in Figure 8 (10). Even with less than optimum aluminum levels, the rate of oxidation is lower than that of aluminum-free alloys.

Producing lead–calcium–aluminum alloys is difficult. Calcium and aluminum can be added simultaneously to lead using a calcium (73 wt %)–aluminum (27 wt %) master alloy (11) (see Aluminum and aluminum alloys). Using this method, the calcium and aluminum contents can be precisely controlled. Pressed pellets of metallic aluminum and metallic calcium are also used.

Lead alloys containing 0.09–0.15 wt % calcium and 0.015–0.03 wt % aluminum are used for the negative battery grids of virtually all lead–acid batteries in the United States and are also used in Japan, Canada, and Europe. If the molten alloy is held at too low a temperature, the aluminum precipitates from solution, rises to the surface of the molten alloy as finely divided aluminum particles, and enters the dross layer atop the melt.

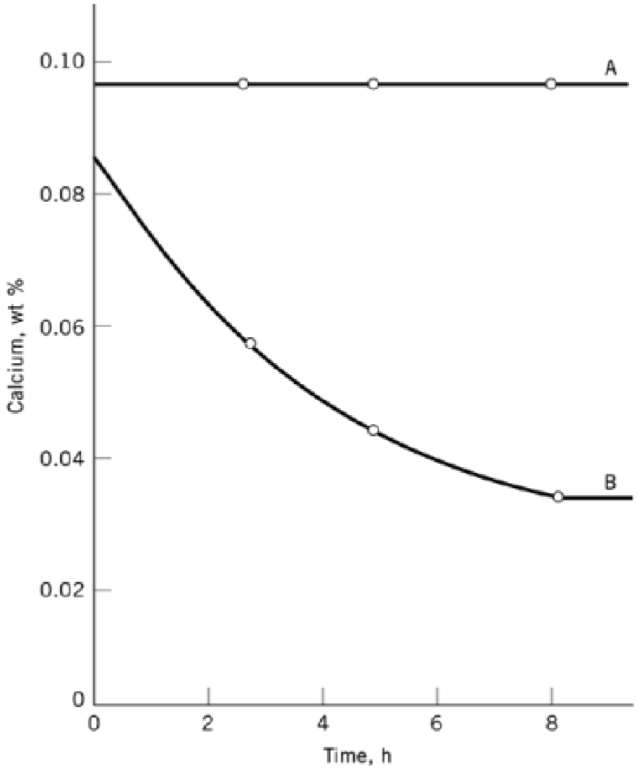

Fig. 8. Effect of aluminum on loss of calcium: A, with 0.03 wt%aluminum; B, without aluminum (10).(Courtesy of the Electrochemical Society.)

2.3. Lead–Calcium–Tin Alloys

Tin additions to lead–calcium and lead–calcium–aluminum alloys enhances the mechanical (8) and electrochemical properties (12). Tin additions reduce the rate of aging compared to lead–calcium binary alloys. The positive grid alloys for maintenance-free lead–calcium batteries contain 0.3–1.2 wt % tin and also aluminum.

Cast lead–calcium–tin alloys usually contain 0.06–0.11 wt % calcium and 0.3 wt % tin. These have excellent fluidity, harden rapidly, have a fine grain structure, and are resistant to corrosion. Table 4 lists the mechanical properties of cast lead–calcium–tin alloys and other alloys.

Table 4. Mechanical Properties of Cast Lead Alloys

	Lead alloy components, wt %						
Property	Cu 0.06	Ca 0.06	Ca 0.04, Sn 0.50	Ca 0.08, Sn 0.30	Ca 0.08, Sn 0.50	Ca 0.08, Sn 1.0	Sb 6.0
tensile strength, MPa[a]	17.4	34.8	41.8	46.0	48.8	59.7	59.2
yield strength, MPa[a]	9.0	24.3	27.9	34.8	38.2	46.0	55.8
elongation, %	55	30	15	20	15	15	15
time to failure,[b] h		10	30	50	100	450	>10, 000

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

[b] At 20.9 MPa.

Wrought lead–calcium–tin alloys contain more tin, have higher mechanical strength, exhibit greater stability, and are more creep resistant than the cast alloys. Rolled lead–calcium–tin alloy strip is used to produce automotive battery grids in a continuous process (13). Table 5 lists the mechanical properties of rolled lead–calcium–tin alloys, compared with lead–copper and rolled lead–antimony (6 wt %) alloys.

Table 5. Mechanical Properties of Rolled Lead Alloys

	Lead alloy components, wt %					
Property	Cu 0.06	Ca 0.06	Ca 0.04, Sn 0.50	Ca 0.065, Sn 0.70	Ca 0.06, Sn 1.30	Sb 6.0
tensile strength, MPa[a]	17.4	32.8	48.8	62.8	69.6	30.6
yield strength, MPa[a]	9.0	25.1	46.0	59.2	66.2	19.5
elongation, %	55	35	15	10	10	35
time to failure,[b] h		7	850	3,000	>10,000	1.5

[a] To convert MPa to psi, multiply by 145.
[b] At 20.9 MPa.

2.3.1. Lead Anodes

A principal use for lead–calcium–tin alloys is lead anodes for electrowinning. The lead–calcium anodes form a hard, adherent lead dioxide layer during use, resist corrosion, and greatly reduce lead contamination of the cathode. Anodes produced from cast lead–calcium (0.03–0.09 wt %) alloys have a tendency to warp owing to low mechanical strength and casting defects.

Wrought lead–calcium–tin anodes have replaced many cast lead–calcium anodes (14). Superior mechanical properties, uniform grain structure, low corrosion rates, and lack of casting defects result in increased life for wrought lead–calcium–tin anodes compared to other lead alloy anodes.

3. Lead–Copper Alloys

The lead–copper phase diagram (1) is shown in Figure 9. Copper is an alloying element as well as an impurity in lead. The lead–copper system has a eutectic point at 0.06% copper and 326°C. In lead refining, the copper content can thus be reduced to about 0.08% merely by cooling. Further refining requires chemical treatment. The solubility of copper in lead decreases to about 0.005% at 0°C.

High copper–lead alloys generally contain 60–70% copper. The mechanical properties of sand-cast copper–lead alloys are shown in Table 5. The high copper alloys are difficult to cast and are susceptible to extensive segregation. Cast lead–copper (60–70 wt %) alloys are used as bearing and bushings for high temperature service (see HIGH TEMPERATURE ALLOYS). More recently, the cast alloys have been replaced by sintered copper powder products infiltrated with lead to produce more uniform distribution of the lead.

Only lead alloys containing copper below 0.08% have practical applications. Lead sheet, pipe, cable sheathing, wire, and fabricated products are produced from lead–copper alloys having copper contents near the eutectic composition. Lead–copper alloys in the range 0.03–0.08 wt % copper are covered by many specifications: ASTM B29-92 (7), QQL 171 (United States), BS 334, HP2 Type 11 (Canada), DIN 1719 (Germany), and AS 1812 (Australia).

Lead–copper alloys are specified because of superior mechanical properties, creep resistance, corrosion resistance, and high temperature stability compared to pure lead. The mechanical properties of lead–copper alloys are compared to pure lead, and to lead–antimony and lead–calcium alloys in Tables 4 and 5.

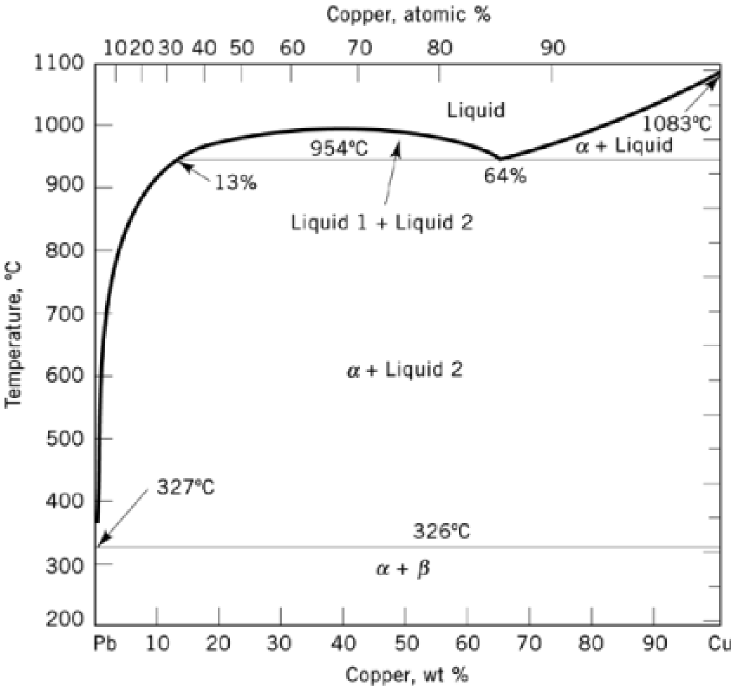

Fig. 9. Lead–copper system (1).(Courtesy of McGraw-Hill Book Co., Inc.)

Lead–copper alloys are the primary material used in the continuous extrusion of cable coverings for the electrical power cable industry in the United States. Other alloys, containing tin and arsenic as well as copper, have also been developed for cable sheathing in the United States to provide higher fatigue strength.

Extruded or rolled lead–copper alloys contain a uniform dispersion of copper particles in a lead matrix. Because the solid solubility of copper in lead is very low, copper particles in the matrix remain stable up to near the melting point of lead, maintaining uniform grain size even at elevated temperature.

Copper-containing lead alloys undergo less corrosion in sulfuric acid or sulfate solutions than pure lead or other lead alloys. The uniformly dispersed copper particles give rise to local cells in which lead forms the anode and copper forms the cathode. Through this anodic corrosion of the lead, an insoluble film of lead sulfate forms on the surface of the lead, passivating it and preventing further corrosion. The film, if damaged, rapidly reforms.

Lead–copper alloys are also used as tank linings, tubes for acid mist precipitators, steam heating pipes for sulfuric acid or chromate plating baths, and flashing and sheeting (see Tanks and pressure vessels).

4. Lead–Silver Alloys

Silver readily forms alloys with lead. Lead is often used as a base metal solvent for silver recovery processes. The lead–silver system is a simple eutectic having the eutectic point at 2.5 wt % silver and 304°C. The solid solubility of silver in lead is 0.10 wt % at 304°C, dropping to less than 0.02 wt % at 20°C.

Lead–silver alloys show significant age hardening when quenched from elevated temperature. Because of the pronounced hardening which occurs using small amounts of silver, the content of silver as an impurity in pure lead is restricted to less than 0.0025 wt % in most specifications. Small additions of silver to lead produces high resistance to recrystallization and grain growth.

The principal uses for lead–silver alloys are as anodes and high temperature solders. Only lead–silver alloys containing less than 6 wt % silver are used commercially. Lead alloys containing 0.75–1.25 wt % silver are used as insoluble anodes in the electrowinning of zinc and manganese. Some zinc refineries have reduced the silver content of the anodes to as low as 0.25 wt %. Lead–calcium–silver anodes are also used for zinc electrowinning. Silver promotes the formation of very hard, dense, electrically conducting layers of lead dioxide on the surface of the anode.

Silver reduces the oxygen evolution potential at the anode, which reduces the rate of corrosion and decreases lead contamination of the cathode. Lead–antimony–silver alloy anodes are used for the production of thin copper foil for use in electronics. Lead–silver (2 wt %), lead–silver (1 wt %)–tin (1 wt %), and lead–antimony (6 wt %)–silver (1–2 wt %) alloys are used as anodes in cathodic protection of steel pipes and structures in fresh, brackish, or seawater. The lead dioxide layer is not only conductive, but also resists decomposition in chloride environments. Silver-free alloys rapidly become passivated and scale badly in seawater. Silver is also added to the positive grids of lead–acid batteries in small amounts (0.005–0.05 wt %) to reduce the rate of corrosion.

Lead–silver alloys are used extensively as soft solders; these contain 1–6 wt % silver. Lead–silver solders have a narrower freezing range and higher melting point (304°C) than conventional solders. Solders containing 2.5 wt % silver or less are used either as binary alloys or combined with 0.5–2 wt % tin. Lead–silver solders have excellent corrosion resistance. The composition of lead–silver solders is listed in ASTM B32-93 (solder alloys) (7).

5. Lead–Tellurium Alloys

Tellurium is often used in lead alloys when high mechanical strength at minimal alloy content is required. It is used for pipes and sheets, shielding for nuclear reactors (qv), and cable sheathing. Lead alloys containing 0.035–0.10 wt % tellurium generally also contain copper in amounts of 0.03–0.08 wt %. The U.S. Federal Specifications QQL-201F and ASTM B749-91 (7) cover the use of wrought lead–tellurium alloys. Lead–tellurium alloys for cable sheathing are specified by German DIN 17 640.

Cold-rolled alloys of lead with 0.06 wt % tellurium often attain ultimate tensile strengths of 25–30 MPa (3625–5350 psi). High mechanical strength, excellent creep resistance, and low levels of alloying elements have made lead–tellurium alloys the primary material for nuclear shielding for small reactors such as those aboard submarines. The alloy is self-supporting and does not generate secondary radiation.

Wrought or extruded lead–tellurium (0.035–0.10 wt %) alloys produce extremely fine grains. The binary alloy is, however, susceptible to recrystallization. The addition of copper or silver reduces grain growth and retains the fine grain size. Because tellurium is a poison for sealed lead–acid batteries, the tellurium content of lead and lead alloys used for such purposes is usually restricted to less than 1 ppm.

6. Lead–Tin Alloys

Lead alloys with tin in all proportions, providing a series of alloys that have wide application in many industries. The phase diagram in Figure 10 shows a eutectic composition of 61.9 wt % Sn–39.1 wt % Pb melting at 183°C (1). The solid solution of tin in lead decreases from 19.0 wt % at 183°C to 1.9 wt % at 20°C, and the solubility of lead in tin ranges from 2.5 wt % at 183°C to <0.3 wt% at 20°C.

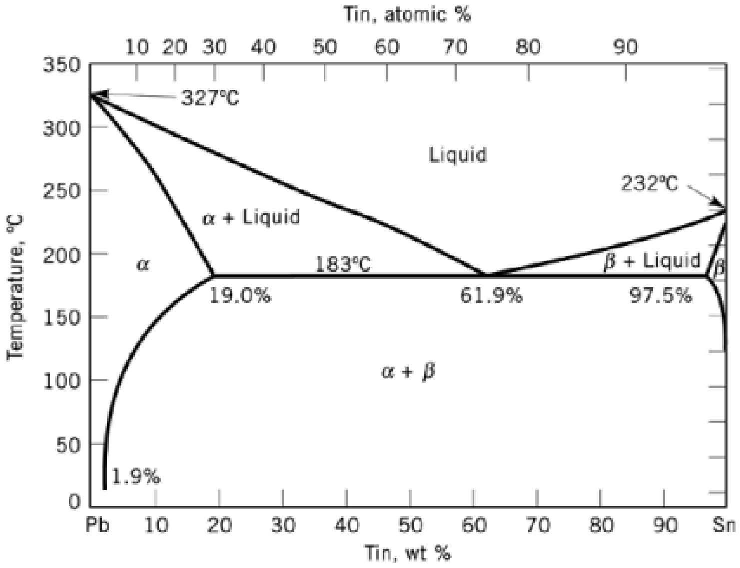

Fig. 10. Lead–tin system (1).(Courtesy of McGraw-Hill Book Co., Inc.)

7. Solders

The principal use of lead–tin alloys is as solders for sealing and joining metals. Solders range in composition from 20 to 98 wt % lead, the remainder being tin. Lead–tin (2 wt %) solder is used to seal the side seams of steel (tin) cans. Additions of 0.5 wt % silver to the alloy significantly improves the creep strength which is essential in pressurized cans. Pre-tinned cans allow the use of low tin solder. High speed manufacturing of cans requires an alloy having a very narrow freezing range.

Lead–tin alloys containing 40–50 wt % tin are used for general-purpose soldering. Low melting lead–tin solder having 63 wt % tin is used for electronic soldering, particularly for printed circuit boards. Lead alloys having 15–30 wt % tin are used for soldering automobile radiators and other types of heat exchangers. A lead alloy containing 2.5 wt % tin and 0.5 wt % silver is used when high temperature fatigue and creep strengths are required, for example, in soldered connections in heat exchangers. Solders having 35–40 wt % tin have a wide plastic range and are used for wiping lead joints. Sometimes 0.5–2.0 wt % antimony is added to improve mechanical properties. Antimony contents of 0.2–0.5 wt % prevent brittle phase transformations at low temperature. Lead–tin solder alloys are listed in ASTM B32-93 (7).

7.1. Corrosion Protection

Lead–tin alloys are used for corrosion-resistant coatings on steel and copper (see Metallic coatings). Terne steel is steel sheet coated with a lead alloy containing 15–20 wt % tin. This alloy contains sufficient tin to alloy with the surface of the steel. Terne sheets are produced flat or coiled, carrying different coating weights. These coated sheets are used for radio and television chassis, roofs, fuel tanks, air filters, oil filters, gaskets, metal furniture, gutters, and downspouts. Terne steel has good corrosion resistance, draws well, is relatively cheap, and offers a good base for painting.

A similar coating, containing 4 wt % tin, is applied to copper sheet and is used primarily for building flashings. Other lead–tin alloys, usually with 50 wt % tin, are applied as coatings to steel and copper electronic components for corrosion protection, appearance, and ease of soldering. Lead–tin alloys can be built up easily to any desired thickness by electroplating (qv) from a fluoborate solution. Electroplated coatings are not recommended for corrosion protection because these tend to be porous (see ELECTRONICS, COATINGS).

Tin is also used as an alloying element in lead–antimony alloys to improve fluidity and to prevent drossing, in lead–calcium alloys to improve mechanical properties and enhance electrochemical performance, in lead–arsenic alloys to maintain a stable composition, and as an additive to low melting alloys.

Lead–tin (1.8–2.5 wt %) is used both as a cable sheathing alloy (BS 801 alloy A and DIN 17640) and as a battery connector alloy in sealed lead–calcium–tin batteries (15). Tin is generally added to lead–arsenic cable alloys in small amounts. The arsenic alloys have excellent creep resistance and mechanical properties, but are unstable and lose arsenic readily by oxidation. The addition of small amounts of tin (0.10–0.20 wt %) eliminates arsenic loss. Lead alloys having 0.4 wt % tin and 0.15 % cadmium, which are used for cable sheathing, do not age harden, show excellent corrosion and creep resistance, and are very ductile.

8. Other Alloys

8.1. Low Melting Alloys

Lead alloys having large amounts of bismuth, tin, cadmium, and indium that melt at relatively low (10–183°C) temperatures are known as fusible or low melting alloys. The specifications of many of these alloys are listed in ASTM B774-87 (7).

These alloys are used as fuses, sprinkler system alloys, foundry pattern alloys, molds, dies, punches, cores, and mandrels where the low melting alloy is often melted out of a mold. The alloys are also used as solders, for the replication of human body parts (see Prosthetic devices), and as filler for tube bending. Lead–indium alloys are often used to join metals to glass.

9. Reactive Lead Alloys

Strontium–lead alloys behave similarly to lead–calcium alloys in terms of mechanical properties and performance. Lead–strontium (0.08–0.20 wt %) alloys, also containing aluminum, have been used as battery grid alloys. These have excellent fluidity, harden rapidly, and have excellent resistance to corrosion. However, these alloys over-age rapidly, resulting in significant loss of mechanical strength within several days. The addition of 1 wt % or more of tin is required to resist over-aging. The high cost of lead–strontium alloys compared to lead–calcium alloys has restricted usage. Lead–strontium–tin alloys are used as anodes for copper electrowinning.

Lead–lithium and lead–lithium–tin alloys have been proposed as alloys for lead–acid battery grids because of very rapid aging and very high mechanical properties. These alloys are, however, susceptible to grain boundary corrosion. Lead–lithium alloys containing strontium, barium, and calcium have been used for bearings. The high melting point and the retention of mechanical properties and stability at high temperatures make these alloys particularly attractive for bearings. The addition of aluminum to prevent oxidation permits casting at high temperatures without oxidation.

10. Occupational Health and Safety

Because of the toxicity of lead, special care must be taken when working with lead alloys. Lead and its inorganic compounds are neurotoxins which may produce peripheral neuropathy. For an overview of the effects of lead exposure, see Occupational Exposure to Lead, Appendix A (29 CRF 1910.1025) (see Lead compounds, industrial toxicology).

Most lead alloys are first melted during processing. The melting or fusing of lead alloys may generate lead oxides, drosses, or fumes which can present a health hazard. The principal routes for absorption of lead metal are inhalation and ingestion. Inhalation can be avoided by use of ventilators and respirators where the exposure is above the permissible exposure limit (PEL) or the threshold limit value (TLV) specified by OSHA (United States) or other local, municipal, or federal regulations. These limits vary considerably by industry and country but generally consist of a PEL of ca $50 - 200\ \mu\text{g/m}^3$ of lead in air, and lead levels of $50 - 80\ \mu\text{g/dL}$ in whole blood.

Coveralls or other full-body clothing should be worn when working with lead alloys and properly laundered after use. Hard hats, safety glasses, safety boots, and other safety equipment should be worn as appropriate for the industrial environment where the lead alloys are used. Hands, face, neck, and arms should be washed before eating or smoking.

Lead–antimony or lead–arsenic alloys must not be mixed with lead–calcium (aluminum) alloys in the molten state. Addition of lead–calcium–aluminum alloys to lead–antimony alloys results in reaction of calcium or aluminum with the antimony and arsenic to form arsenides and antimonides. The dross containing the arsenides and antimonides floats to the surface of the molten lead alloy and may generate poisonous arsine or stibine if it becomes wet. Care must be taken to prevent mixing of calcium and antimony alloys and to ensure proper handling of drosses.

If the temperature of a molten lead–calcium (tin)–aluminum alloy is not kept sufficiently high, finely divided aluminum particles may precipitate and float to the top of the melt. These may become mixed with oxides of lead in the dross. The finely divided aluminum particles can react violently with the oxides in the dross if ignited. Ignition can occur if attempts are made to melt or burn the dross away from areas of buildup with a torch. The oxides in the dross can supply oxygen for the combustion of aluminum once ignited.

Despite the benefits of lead and lead alloys, the use of these materials is declining rapidly, owing primarily to environmental health and safety factors. For many years, lead alloys were the materials of choice for many corrosive environments, but are now being replaced by stainless steel, plastics, and exotic metals. The toxic nature of lead requires special precautions and handling not necessary with other materials. These requirements have reduced the usage of lead alloys.

11. Other Uses for Lead Alloys

11.1. Antifriction

Lead has excellent antifriction properties which make it a good base element in bearings. When combined with other metals such as antimony, tin, copper, calcium, or aluminum, it provides excellent antifriction properties with the other metal providing strength. Powdered lead has extensive use as antiseize material for oilfield and mining industries because the lead does not adhere to the mating surfaces and prevents galling (see Mineral recovery and processing; Petroleum).

11.2. Sound Attenuation

The high density and low strength of lead makes it an excellent barrier material for reducing the transmission of noise from adjacent areas . The excellent sound attenuation properties of lead have been used by combining powdered lead with plastics and fibers to produce curtain walls or lead-bearing composites. In most of these applications, lead is alloyed with a small amount of copper.

11.3. Radiation Shielding

Because of the relatively high (11.35 g/cm^3) density of lead, it is used extensively for shielding of x-rays and gamma-rays in the form of sheets, shot, brick, or special castings. Lead sheet is most commonly used for lining x-ray rooms. The flat sheet lead is bonded to the supporting wall panels and the seams are covered with additional lead to prevent radiation leakage.

Lead bricks are generally used as temporary shields for radiation sources at nuclear power stations, research institutes, hospitals, and fuel reprocessing plants. Flat, rectangular bricks require a double layer with staggered seams whereas the interlocking bricks require only one course. Lead shot can be poured into inaccessible areas like a liquid.

Lead-loaded plastics containing up to 90 wt % lead are used in x-ray protection as aprons and temporary shields in medical and industrial applications. Leaded glass is used to attenuate radiation where viewing the ongoing process is required. Steel-jacketed containers filled with lead or special lead containers are used to transfer, ship, and store fuel rods, radioactive sources, and nuclear waste. Lead is generally used where space is limited.

12. Corrosion Resistance

Lead and many of its alloys exhibit excellent corrosion resistance owing to the rapid formation of a passive, impermeable, insoluble protective film when the lead is exposed to the corrosive solution (see Corrosion and corrosion control).

Lead shows excellent resistance to phosphoric and sulfuric acid in almost all concentrations and at elevated temperatures, as well as to sulfide, sulfite, and sulfate solutions. The corrosion film is insoluble lead sulfate which rapidly reforms if it is damaged. Lead is also resistant to chlorides, fluorides, and bromates at low concentrations and low temperatures. However, because lead is soluble in nitric and acetic acids, it is not resistant to these acids.

Because the corrosion resistance of lead and lead alloys is associated with the formation of the protective corrosion film, removal of the film in any way causes rapid attack. Thus the velocity of a solution passing over a surface can lead to significantly increased attack, particularly if the solution contains suspended particulate material. Lead is also attacked rapidly in the presence of high velocity deionized water. The lack of dissolved minerals in such water prevents the formation of an insoluble protective film. In most solutions, lead and lead alloys are resistant to galvanic corrosion because of the formation of a nonconductive corrosion film. In contact with more noble metals, however, lead can undergo galvanic attack which is accelerated by stray electrical currents.

The excellent corrosion-resistant lead dioxide, PbO_2, film formed on anodes and lead–acid battery positive grids in sulfuric acid has enabled lead insoluble anodes and lead–acid batteries to maintain the dominant positions in their respective fields.

13. Economic Aspects

Worldwide lead consumption was about 4.2 million in 1993. About 50% was produced from mined ore and 50% was produced from recycled lead-bearing products, primarily from used lead–acid batteries. In the United States, about 1.4 million t of lead was consumed in 1993; about 80% of the lead consumed was for the production of lead–acid batteries. Worldwide about 50% of the lead consumed is used for lead–acid batteries. In the United States, about 97% of the lead used in lead–acid batteries is recycled, making lead the most recycled of any metal in the world (see Recycling, nonferrous metals). The lead usage throughout the world is about 50% pure lead, primarily for active materials of lead–acid batteries, gasoline additives, pigments, and glasses and glazes. The remaining material is consumed in the form of lead alloys.

The principal manufacturers of lead and lead alloys in North America are Tonolli, NOVA, Cominco, and Noranda in Canada; Doe Run, ASARCO, RSR Corp., Exide, Schuylkill, Sanders, GNB, and East Penn in the United States; and Penoles in Mexico. In Europe, the principal manufacturers are Union Meniere in Belgium; Metallgellschaft in Germany; Metalleurop in Germany–France; Brittania Refined Metals and H. J. Enthoven in the U.K.; Nuova SAMIM in Italy; and Boliden in Sweden. In Asia and Australia the principals are MIM and Pasminco in Australia; Mitsui, Mitsubishi, and Toho Zinc in Japan; and Korea Zinc in Korea.

The worldwide price for lead is determined daily by trading on the London Metal Exchange (LME). During the past several years, lead and lead alloy prices have been depressed by excess stocks in LME warehouses. These stocks of lead have come from the former Eastern Bloc countries, primarily from government stockpiles but also as exports to generate foreign exchange. LME average lead price for the year 1987 was \$0.59/kg and for the years 1988 through 1992, \$0.65, \$0.67, \$0.81, \$0.56, and \$0.54/kg, respectively. Prices for lead alloys generally reflect the additional cost of the metals used to produce the lead alloys above the cost of lead.

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