ALUMINUM AND ALUMINUM ALLOYS

1. Introduction

Aluminum [7429-90-5], Al, is a silver-white metallic element in group III of the periodic table having an electronic configuration of $1s^22s^22p^63s^23p^1$. Aluminum exhibits a valence of +3 in all compounds except for a few high temperature gaseous species in which the aluminum may be monovalent or divalent. Aluminum is the most abundant metallic element on the surfaces of the earth and moon, comprising 8.8% by weight (6.6 atomic %) of the earth's crust. However, it is rarely found free in nature. Nearly all rocks, particularly igneous rocks, contain aluminum as aluminosilicate minerals.

Although impure metallic aluminum was isolated in 1824 by reducing aluminum chloride [7446-70-0], AlCl₃, using potassium amalgam, Wöhler, who produced higher purity aluminum by a similar method in 1827 and determined its properties, is often given the credit for the discovery. The metal remained a laboratory curiosity until 1854 when the method of preparation was improved, using sodium as a reductant, and commercial quantities of relatively pure aluminum were produced. The present industrial production method was developed independently in 1886 by both Paul-Louis Héroult in France and Charles Martin Hall in Oberlin, Ohio.

Aluminum reflects radiant energy throughout the spectrum. It is odorless, tasteless, nontoxic, and nonmagnetic. Because of its many desirable physical, chemical, and metallurgical properties, aluminum is the most widely used non-ferrous metal. The utility of the metal is enhanced by the formation of a stable adherent oxide surface that resists corrosion. Because of high electrical conductivity and lightness, aluminum is used extensively in electrical transmission lines. High purity aluminum is soft and lacks strength but its alloys, containing small amounts of other elements, have high strength-to-weight ratios. Alloys of aluminum are readily formable by many metalworking processes; they can be joined, cast, or machined and accept a wide variety of finishes. Aluminum, having a density about one-third that of ferrous alloys, is used in transportation and structural applications where weight saving is important.

2. Physical Properties

The properties of aluminum vary significantly according to purity and alloying (1). Physical properties for aluminum of a minimum of 99.99% purity are summarized in Table 1. Although a number of radioactive isotopes have been artificially produced (see RADIOISOTOPES), naturally occurring aluminum consists of a single stable isotope, ²⁷Al, having a cross section for thermal neutrons of 0.215×10^{-28} m². This low cross section and the short half-life of the radioactive product from neutron irradiation make aluminum an attractive material for use within nuclear reactors. Aluminum crystallizes in the face-centered cubic system having a unit cell of 0.40496 nm at 20°C. The unit cell contains four atoms and has a coordination number of 12. The distance of closest approach of atoms is 0.2863 nm. The effects of temperature on the density of aluminum are shown in Table 2. The change in density at the solid–liquid transformation corresponds to a volume increase of ca 6.5%. The heat capacities of solid and liquid aluminum are shown in Table 3. Other thermodynamic data are available in reference 3.

The linear expansion of a luminum over several temperature ranges can be calculated from equations $1{-}3$

$$L_t(-200 \text{ to } 0^\circ \text{C}) = L_0 \left[1 + \text{C} (21.57t + 0.00443t^2 - 0.000124t^3) 10^{-6}
ight]$$
(1)

$$L_t(-60 \text{ to } 100^{\circ}\text{C}) = L_0 \left[1 + \text{C} \left(22.17t + 0.012t^2 \right) 10^{-6} \right]$$
(2)

$$L_t(0 \text{ to } 500^{\circ}\text{C}) = L_0 \left[1 + \text{C} \left(22.34t + 0.00997t^2 \right) 10^{-6} \right]$$
(3)

where $L_0 = \text{length at } 0^{\circ}\text{C}$, $L_t = \text{length at temperature } t$, and C = alloy constant, which is unity for pure aluminum. The thermal conductivity of aluminum at

Property Value atomic number 13atomic weight 26.9815 density at 25°C, kg/m³ 2698 melting point, °C 660.2boiling point, °C 2494 thermal conductivity at $25^{\circ}C$, W/m · K) 234.3latent heat of fusion, J/g^{a} 395 latent heat of vaporization at bp $\Delta H_{\rm v}$, kJ/g^a 10,777 65% IACS^b electrical conductivity electrical resistivity at 20°C, $\Omega{\cdot}m$ 2.6548×10^{-8} temperature coefficient of electrical resistivity, $\Omega \cdot m / {}^{\circ}C$ 0.0043 electrochemical equivalent, mg/°C 0.0932 electrode potential, V -1.66magnetic susceptibility, g⁻¹ 0.6276×10^{-6} Young's modulus, MPa^c 65,000 tensile strength, MPa^c 50

Table 1. Physical Properties of Aluminum

^a To convert J to cal, divide by 4.184.

^b International Annealed Copper Standard.

^c To convert MPa to psi, multiply by 145.

Density, kg/m ³
2698
2680^a
2660^a
2620^a
2550^a
2368
2357
2345
2332
2319
2304

Table 2. Density of 99.996% Aluminum

 a Calculated from density at $25^\circ\mathrm{C}$ and volume expansion at elevated temperatures.

^b Ref. 2.

various temperatures is shown in Table 4. The thermal and electrical conductivities are related by

$$K = 2.1 \ \lambda T \cdot 10^{-6} + 12.55 \tag{4}$$

where K = thermal conductivity in W/m · K), $\lambda =$ electrical conductivity in S/m (or reciprocal Ω m), and T = temperature K. The electrical resistivity of aluminum of 99.996% purity is $2.6548 \times 10^{-8} \ \Omega \cdot$ m at 20°C and the temperature coefficient of electrical resistivity is 0.0043 Ω °C. The effects of temperature on electrical resistivity for solid and liquid aluminum are shown in Table 5. Aluminum becomes superconductive at temperatures near absolute zero and has a

Toble 0. Heat Canadity of Aluminum^a

Table 3. Heat Capacity of Aluminum [®]					
Temperature, K	Heat capacity, $\mathbf{J}/(\mathbf{kg}\cdot\mathbf{K})^{b}$				
Crystalline solid					
0	0.00				
100	481.7				
200	790.8				
298	897.2				
300	898.7				
400	955.6				
500	994.8				
600	1033.5				
700	1078.5				
800	1132.7				
900	1197.4				
Liquid					
1000 and higher	1273.5				

 a Ref.3.

^b To convert J to cal, divide by 4.184.

282 **ALUMINUM AND ALUMINUM ALLOYS**

	Thermal conductivi			
Temperature, K	$99.996\%\mathrm{Al}^a$	$99.95\%\mathrm{Al}^b$		
4	3150.6			
6	4196.6			
8	5196.5			
10	5995.7			
15	6794.8			
20	5497.8			
50	949.8			
100	301.2			
150	244.7			
200	234.3			
300	234.3			
298		225.1		
523		203.3		
723		189.9		
923		186.2		
1013		59.8^c		
1173		75.3^c		

Table 4. Thermal Conductivity of Aluminum

Ref.4.

 b Ref.5.

^c Liquid aluminum.

transition temperature of 1.187 K. Resistivity at very low temperatures is strongly increased by impurities.

2.1. Optical Properties. The index of refraction and extinction coefficient of vacuum-deposited aluminum films have been reported (8,9) as have the total reflectance at various wavelengths and emissivity at various temperatures

Temperature, °C	Resistivity, $\Omega \cdot \mathbf{m} imes 10^{-8}$
$Solid^a$	
0	2.42
100	3.50
200	4.63
300	5.81
400	7.05
500	8.36
600	9.77
650	10.56
$Liquid^b$	
660	24.20
700	24.75
800	26.25
1000	29.20
1200	32.15

Table 5. Electrical Designitivity of Alumiu

^b Ref. 7.

	Solubility ^a , m	$ m L~H_2/100~g~Al$		
Temperature, $^{\circ}\mathrm{C}$	Reference 11	Reference 12		
Solid				
400	0.004	0.003		
500	0.01	0.01		
600	0.025	0.03		
660	0.04	0.05		
Liquid				
660	0.69	0.46		
700	0.91	0.63		
800	1.68	1.23		
850	2.18	1.66		

Table 6. Solubility of Hydrogen in Aluminum

 a Values at 20°C and 202.3 kPa (14.7 psi); pressure of hydrogen over sample is 101.3 kPa (1 atm).

(10). Emissivity increases significantly as the thickness of the oxide film on aluminum increases and can be 70-80% for oxide films of 100 nm.

2.2. Solution Potential. The standard electrode potential of aluminum $(Al \rightarrow Al^{3+} + 3e)$ is -1.66 V on the standard hydrogen scale and -1.99 V on the 0.1 N calomel scale at 25°C. In the electromotive force series this places aluminum cathodic to magnesium and anodic to zinc, cadmium, iron, nickel, and copper. Aluminum electrode potentials are irreversible in aqueous solutions and vary significantly with pH. Potentials measured in highly basic solutions are anodic to those measured in acid solutions.

2.3. Surface Tension and Viscosity. The surface tension of molten aluminum, determined by the method of maximum bubble pressure, is 0.86 ± 0.2 N/m (860 dyn/cm) in the range of $700-750^{\circ}$ C. The viscosity of 99.996% aluminum at these same temperatures is 1 - 1.2 mPa · s(= cP).

2.4. Aluminum and Hydrogen. Hydrogen is the only gas known to be appreciably soluble in solid or molten aluminum. Hydrogen can be introduced into liquid aluminum from reaction with moisture present in the furnace atmosphere or the refractories, or with moisture entrapped in the oxide film of the solid aluminum before melting. The solubility of hydrogen in molten and solid aluminum is shown in Table 6.

3. Chemical Properties

3.1. Reactions with Elements and Inorganic Compounds. Aluminum reacts with oxygen O_2 , having a heat of reaction of -1675.7 kJ/mol (-400.5 kcal/mol) Al₂O₃ produced.

$$2 \operatorname{Al} + 3/2 \operatorname{O}_2 \longrightarrow \operatorname{Al}_2 \operatorname{O}_3 \tag{5}$$

In dry air at room temperature this reaction is self-limiting, producing a highly impervious film of oxide ca 5 nm in thickness. The film provides both stability at

ambient temperature and resistance to corrosion by seawater and other aqueous and chemical solutions. Thicker oxide films are formed at elevated temperatures and other conditions of exposure. Molten aluminum is also protected by an oxide film and oxidation of the liquid proceeds very slowly in the absence of agitation.

At high temperatures, aluminum reduces many oxygen-containing compounds, particularly metal oxides. These reactions, of the type shown in equation 6, are used in the manufacture of certain metals and alloys, as well as in the thermite welding process.

$$3 \text{ MO} + 2 \text{ Al} \longrightarrow \text{Al}_2\text{O}_3 + 3 \text{ M}$$
 (6)

Molten aluminum reacts violently with water and the molten metal should not be allowed to touch damp tools or containers. In finely divided powder form, aluminum also reacts with boiling water to form hydrogen and aluminum hydroxide [21645-51-2]; this reaction proceeds slowly in cold water.

Aluminum does not combine directly with hydrogen, but it does react with nitrogen sulfur and carbon in oxygen-free atmospheres at high temperatures. To form aluminum carbide [1299-86-1], Al_4C_3 , temperatures above 1000°C are required. Aluminum nitride [24304-00-5], AlN, is produced by arcing high purity aluminum electrodes in a nitrogen atmosphere. Aluminum sulfide [1302-81-4], Al_2S_3 , and aluminum phosphide [20859-73-8], AlP, result from reaction at high temperatures with sulfur and phosphorus respectively.

Very high purity aluminum, resistant to attack by most acids, is used in the storage of nitric acid, concentrated sulfuric acid, organic acids, and other chemical reagents. Aluminum is, however, dissolved by aqua regia. Because of its amphoteric nature, aluminum is attacked rapidly by solutions of alkali hydroxides evolving hydrogen and forming soluble aluminates. Aluminum reacts vigorously with fluorine chlorine, bromine, and iodine to form trihalides, and with chlorinated hydrocarbons in the presence of water. It also reacts to form a volatile aluminum chloride when heated in a current of dry oxygen-free chlorine or hydrogen chloride. Gaseous monohalides can be formed by passing the trihalides over aluminum at temperatures above $800^{\circ}C$

$$AlX_3 + 2 Al \longrightarrow 3 AlX$$
 (7)

Aluminum hydroxide and aluminum chloride do not ionize appreciably in solution but behave in some respects as covalent compounds. The aluminum ion has a coordination number of six and in solution binds six molecules of water existing as $[Al(H_2O)_6]^{3+}$. On addition of a base, substitution of the hydroxyl ion for the water molecule proceeds until the normal hydroxide results and precipitation is observed. Dehydration is essentially complete at pH 7.

Aluminum is attacked by salts of more noble metals. In particular, aluminum and its alloys should not be used in contact with mercury or mercury compounds.

3.2. Reaction with Organic Compounds. Aluminum is not attacked by saturated or unsaturated, aliphatic or aromatic hydrocarbons. Halogenated derivatives of hydrocarbons do not generally react with aluminum except in the presence of water, which leads to the formation of halogen acids. The chemical

stability of aluminum in the presence of alcohols is very good and stability is excellent in the presence of aldehydes, ketones, and quinones.

Organic compounds that form with aluminum other than through a direct metal-to-carbon bond include the metallo-organics, represented as AI-X-R where X may be oxygen, nitrogen, or sulfur, and R is a suitable organic radical. The alcoholates or alkoxides are compounds of this type where R is an alcohol (see ALKOXIDES, METAL). Compounds having an aluminum-to-carbon bond include polymers that may be linear or cross-linked. They are best described as vinyl, divinyl, and trivinyl aluminum halides that polymerize rapidly to compounds the structures of which are not completely understood. Aluminum alkyls are also aluminum-carbon bond compounds. These are not polymeric but are viewed as being bridge compounds of varying complexity. Alkylaluminum compounds are used as catalysts in the preparation of oriented crystalline polyolefins leading to the production of elastomers that are essentially identical in structure to natural rubber (see ELASTOMERS, SYNTHETIC).

4. Manufacture and Processing

4.1. Raw Materials. Aluminum, the third most abundant element in the earth's crust, is usually combined with silicon and oxygen in rock. When aluminum silicate minerals are subjected to tropical weathering, aluminum hydroxide may be formed. Rock that contains high concentrations of aluminum hydroxide minerals is called bauxite [1318-16-7]. Although bauxite is, with rare exception, the starting material for the production of aluminum, the industry generally refers to metallurgical grade alumina [1344-28-1], Al_2O_3 , extracted from bauxite by the Bayer Process (see ALUMINUM COMPOUNDS), as the ore. Aluminum is obtained by electrolysis of this purified ore. The specification of metallurgical alumina is given in Table 7.

4.2. Cryolite. Cryolite [15096-52-3], Na₃AlF₆, is the primary constituent of the Hall-Héroult cell electrolyte. High purity, natural cryolite is found in Greenland, but its rarity and cost have caused the aluminum industry to substitute synthetic cryolite. The latter is produced by the reaction of hydrofluoric acid HF, with sodium aluminate [1302-42-7], NaAlO₂, from the Bayer process

$$6 \text{ HF} + 3 \text{ NaAlO}_2 \longrightarrow \text{Na}_3 \text{AlF}_6 + 3 \text{ H}_2 \text{O} + \text{Al}_2 \text{O}_3$$
(8)

Gaseous hydrofluoric acid is generally made by the reaction of acid-grade fluorspar CaF₂, with sulfuric acid (see Fluorine compounds, inorganic)

$$CaF_2 + H_2SO_4 \longrightarrow 2 HF + CaSO_4$$
 (9)

No cryolite is actually needed once the smelting process is in operation because cryolite is produced in the reduction cells by neutralizing the Na₂O brought into the cell as an impurity in the alumina using aluminum fluoride.

$$4 \operatorname{AlF}_3 + 3 \operatorname{Na}_2 O \longrightarrow 2 \operatorname{Na}_3 \operatorname{AlF}_6 + \operatorname{Al}_2 O_3 \tag{10}$$

	Influencing operations ^a Major Minor			Specifications	
Item			Normal range	Typical	Desirable
particle size, µm	Р	Ca	10-200	>10% >150% 10% 44	> 2% > 150% = 2%20
chemical composition	_	~			
Na_2O	P	Ca	0.3 - 0.7%	0.5%	0.35%
Fe_2O_3	D	Cl	0.01-0.04%	0.03%	0.015%
SiO_2	D		0.01 - 0.03%	0.025%	0.020%
CaO	D,Cl		0.02-0.08%	0.06%	0.030%
TiO_2			0.002-0.005%	0.005%	0.002
CuO			0.001-0.01%	0.01%	
K_2O			0.000 - 0.05%	0.005%	
MgO				0.002%	
P_2O_5				0.001%	
NiO Cr. O				0.005%	
$\mathrm{Cr}_2\mathrm{O}_3 \ \mathrm{LOI}^b$			0.3 - 1.5%	0.002%	
total water			0.3 - 1.5% 1.5 - 4.0%	3.5%	
surface area, m ² /g			20-100	60	80
α -Al ₂ O ₃	Ca		5-90%	40%	10%
attrition index	P,Ca		4-15	4070	8
crystallite size, μm	P P		10-200		20
angle of repose, deg	Ca		30 - 45		35
bulk density, kg/m ³	Cu		00 10		00
loose			800-1100		
packed			950 - 1300		

Table 7. Properties of Metallurgical Grade Alumina

 a Designations are as follows: Ca = calcination, Cl = clarification, D = digestion, and P = precipitation.

 \hat{b} LOI = loss on ignition.

Thus operating cells need aluminum fluoride [7784-18-1], AlF_3 , rather than cryolite. Much aluminum fluoride is produced in a fluidized bed by the reaction of hydrofluoric acid gas and activated alumina made by partially calcining the alumina hydrate from the Bayer process

$$Al_2O_3 \cdot XH_2O + 6 HF \longrightarrow 2 AlF_3 + (X+3) H_2O(g)$$
 (11)

Aluminum fluoride is also made by the reaction of fluosilicic acid H_2SiF_6 , a byproduct from phosphoric acid production (see Phosphoric ACID AND THE PHOS-PHATES), and aluminum hydroxide from the Bayer process.

$$H_2SiF_6 + 2 Al(OH)_3 \longrightarrow 2 AlF_3(aq) + SiO_{2(s)} + 4 H_2O$$
(12)

The AlF_3 solution is filtered, AlF_3 precipitated by heating, flash dried, and calcined.

The equivalent of 3-4 kg of F per metric ton of aluminum produced is adsorbed from the bath into the cell lining over the lining's life (3-10 yr). The

recoverable fluoride, 70–75%, requires an expensive recovery plant justified largely on an ecological basis. The most common method of recovery treats the crushed lining using dilute NaOH to dissolve the cryolite and other fluorides. The solution is filtered and the NaF:AlF₃ mol ratio adjusted to 3:1 whereupon-Na₃AlF₆ is precipitated by neutralizing the NaOH using CO₂.

Fluoride Availability. The aluminum industry in the United States uses about 15 kg of fluoride ion per metric ton aluminum, 10–25% of which is lost. The remainder, consisting of cryolite generated in reduction cells and of bath in scrap cell linings, is stored for future use. New fluoride for the aluminum industry comes largely from fluorspar, the world reserves of which are widespread and abundant (see FLUORINE COMPOUNDS, INORGANIC). Fluoride is also recovered from phosphate rock, generally as fluosilicic acid, in producing phosphoric acid. Mexico, the world's largest producer of fluorspar, supplies over 20% of the world's demand and 75% of U.S. usage. The aluminum industry uses about 21% of the fluoride consumed in the United States. Improved emission control (see EXHAUST CONTROL, INDUSTRIAL) and recycling of fluorides continue to reduce the fluoride requirements of the aluminum industry.

4.3. Electrolysis of Alumina. Since the discovery of the process by Hall and Héroult, nearly all aluminum has been produced by electrolysis of alumina dissolved in a molten cryolite based bath. The aluminum is deposited molten on a carbon cathode, which serves also as the melt container. Simultaneously, oxygen is deposited on and consumes the cell's carbon carbon anode(s) (13). Pure cryolite melts at 1012°C, but alumina and additives, namely 4–8% calcium fluoride CaF₂, 5–13% aluminum fluoride, 0–7% lithium fluoride LiF, and 0–5% magnesium fluoride, MgF₂, lower the melting point, allowing operation at 920–980°C. The system Na₃AlF₆–Al₂O₃ (Fig. 1) has a eutectic at 10.5 wt % Al₂O₃ at 960°C (14). Figure 2 gives liquidus temperatures in the system Na₃AlF₆–AlF₃–Al₂O₃

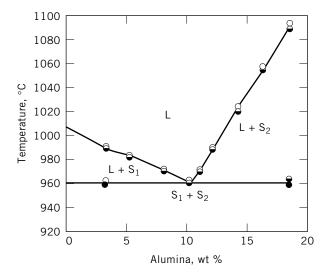


Fig. 1. Cryolite–alumina phase diagram from 0 to 18.5% alumina. L, liquid; S_1 , cryolite; S_2 , corundum; \bigcirc , liquid; \bigcirc , liquid and solid; \bigcirc , solid (14).

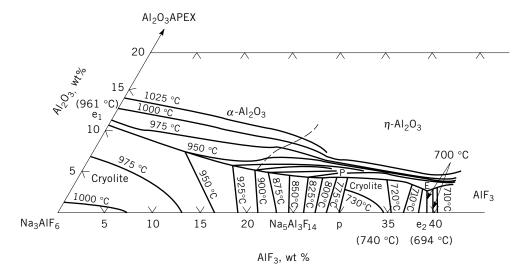


Fig. 2. The system $Na_3AlF_6-AlF_3-Al_2O_3$: P, ternary peritectic point (28.3% $AlF_3-4.4\%Al_2O_3-67.3\%Na_3AlF_6$, 723°C); E, ternary eutectic point (37.3% $AlF_3-3.2\%Al_2O_3-59.5\%Na_3AlF_6$, 684°C); p, binary peritectic point; e, e₁, binary points (15).

(15). Equations for the liquidus temperature and alumina solubility have also been worked out for the $Na_3AlF_3-LiF-CaF_2-AlF_3-Al_2O_3$ system (16). Joule heat from the flow of electric current is more than adequate to maintain the melt temperature.

Although the mechanism of electrolysis is still imperfectly understood, most investigators (17) agree that cryolite ionizes as

$$Na_{3}AlF_{6} \longrightarrow 3 Na^{+} + AlF_{6}^{3-}$$
(13)

$$\mathrm{AlF}_6^{3-} \rightleftharpoons \mathrm{AlF}_4^- + 2 \mathrm{F}^- \tag{14}$$

Alumina dissolves at low concentrations by forming oxyfluoride ions having a 2:1 ratio of aluminum to oxygen $(Al_2OF_{2n}^{4-2n})$,

$$Al_2O_3 + 4 AlF_6^{3-} \longrightarrow 3 Al_2OF_6^{2-} + 6 F^-$$
 (15)

for example, at higher alumina concentrations, oxyfluoride ions with a 1:1 ratio of aluminum to oxygen $(Al_2O_2F_{2n}^{2-2n})$ are formed (18)

$$2 \text{ Al}_2 O_3 + 2 \text{ Al} F_6^{3-} \longrightarrow 3 \text{ Al}_2 O_2 F_4^{2-} \tag{16}$$

Cells are generally operated using 1.5-6 wt % Al_2O_3 in the electrolyte. Saturation ranges between 6-12% Al_2O_3 depending upon composition and temperature.

Ion transport measurements indicate that Na^+ ions carry most of the current, yet aluminum is deposited. A charge transfer probably occurs at the cathode interface and hexafluoroaluminate ions are discharged, forming aluminum and F^- ions to neutralize the charge of the current carrying Na^+

$$12 \operatorname{Na}^{+} + 4 \operatorname{AlF}_{6}^{3-} + 12 e^{-} \longrightarrow 12 (\operatorname{Na}^{+} + \operatorname{F}^{-}) + 4 \operatorname{Al} + 12 \operatorname{F}^{-}$$
(17)

Oxyfluoride ions are discharged at the anode, forming carbon dioxide and aluminum fluoride. The first oxygen can be removed more readily from $Al_2O_2F_4^{2-}$ than either the second or the oxygen from $Al_2OF_6^{2-}$

$$2 \operatorname{Al}_2 \operatorname{O}_2 F_4^{2-} + C \longrightarrow \operatorname{CO}_2 + 2 \operatorname{Al}_2 \operatorname{OF}_4 + 4 e^-$$
(18)

$$Al_2OF_4 + Al_2OF_6^{2-} \rightleftharpoons Al_2O_2F_4^{2-} + 2AlF_3$$
(19)

Combining alumina dissolution, equation 16, and the anode and cathode reactions, equations 17–19, gives the overall reaction

$$2 \operatorname{Al}_2 \operatorname{O}_3 + 3 \operatorname{C} \longrightarrow 4 \operatorname{Al} + 3 \operatorname{CO}_2 \tag{20}$$

According to Faraday's law, one Faraday ($26.80 \text{ A} \cdot \text{h}$) should deposit one gram equivalent (8.994 g) of aluminum. In practice only 85-95% of this amount is obtained. Loss of Faraday efficiency is caused mainly by reduced species (Al, Na, or AlF) dissolving or dispersing in the electrolyte (bath) at the cathode and being transported toward the anode where these species are reoxidized by carbon dioxide forming carbon monoxide and metal oxide, which then dissolves in the electrolyte. Certain bath additives, particularly aluminum fluoride, lower the content of reduced species in the electrolyte and thereby improve current efficiency.

Equipment. A modern alumina smelting cell consists of a rectangular steel shell typically $9 - 16 \text{ m} \times 3 - 4 \text{ m} \times 1 - 1.3 \text{ m}$. It is lined with refractory insulation that surrounds an inner lining of baked carbon (see CARBON-ARTIFICIAL GRAPHITE). Few materials other than carbon are able to withstand the combined corrosive action of molten fluorides and molten aluminum. Thermal insulation is adjusted to provide sufficient heat loss to freeze a protective coating of electrolyte on the inner walls but not on the bottom, which must remain substantially bare for electrical contact to the molten aluminum cathode. Steel (collector) bars are joined to the carbon cathode at the bottom to conduct electric current from the cell. Current enters the cell either through prebaked carbon anodes (Fig. 3) or through a continuous self-baking Soderberg anode (Fig. 4).

Prebaked anodes are produced by molding petroleum coke and coal tar pitch binder into blocks typically 70 cm \times 125 cm \times 50 cm, and baking to 1000–1200°C. Petroleum coke is used because of its low impurity (ash) content. The more noble impurities, such as iron and silicon, deposit in the aluminum whereas less noble ones such as calcium and magnesium, accumulate as fluorides in the bath. Coal-based coke could be used, but extensive and expensive prepurification would be required. Steel stubs seated in the anode using cast iron support the anodes (via anode rods) in the electrolyte and conduct electric current into the anodes (Fig. 3). Electrical resistivity of prebaked anodes ranges from 5 – 6 $\Omega \cdot$ m; anode current density ranges from 0.65 to 1.3 A/cm².

A Soderberg anode is formed continuously from a paste of petroleum coke and coal tar pitch added to the top of a rectangular steel casing typically $6-8 \text{ m} \times 2 \text{ m} \times 1 \text{ m}$ (Fig. 4). While passing through the casing, the paste bakes forming carbon to replace the anode being consumed. The baked portion extends past the casing and into the molten electrolyte. Electric current enters

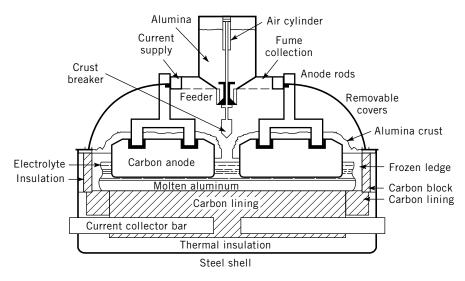


Fig. 3. Aluminum electrolyzing cell with prebaked anode.

the anode through vertical or sloping steel spikes (also called pins). Periodically, the lowest spikes are reset to a higher level. Resistivity of Soderberg anodes is about 30% higher than prebaked anodes. Current density is lower, ranging from 0.65 to 0.9 A/cm².

Molten aluminum is removed from the cells by siphoning, generally daily, into a crucible. Normally the metal is 99.6–99.9% pure. The principal impurities

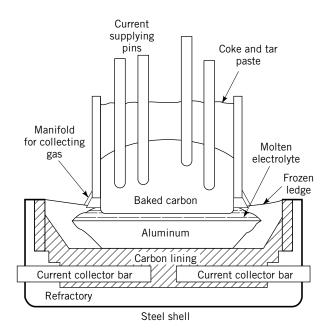


Fig. 4. Aluminum electrolyzing cell with Soderberg anode.

			Total energy			
Operation	$\begin{array}{c} \text{Thermal,} \\ \text{MJ}^{b} \end{array}$	Electric, kW · h	Fossil and hydro, MJ^b	If all fossil, MJ^b		
mining and refining smelting mill processing	$30,000 \\ 19,000^c \\ 19,000$	480 15,000 1,830	$35,200 \\ 146,400 \\ 33,700$	$35,200 \\ 182,500 \\ 38,900$		
Total	68,000	17,310	215,300	256,600		

Table 8. Energy Consumption Per Metric Ton of Aluminum Produced^a

^aValues are approximate. Actual energy consumption depends upon the particular plant, alloy produced, and product formed. ^b To convert MJ to Mcal, divide by 4.184.

^c Includes forming, baking, and fuel value of anodes.

are Fe, Si, Ti, V, and Mn, and come largely from the anode, but also from the alumina.

4.4. Energy Considerations. Table 8 gives a breakdown of the energy required to produce aluminum. Note that smelting consumes about 65% of the required energy. In the United States most of this energy comes from fossil fuels. In other parts of the world, hydropower is a significant source of power for melting aluminum.

Some steps in aluminum production are quite energy efficient. Bayer plants make extensive use of heat exchangers to recover heat from material leaving high temperature operations for use in lower temperature operations (see HEAT EXCHANGE TECHNOLOGY). Fluid-bed calciners reduce energy consumption by 30%over the older rotary kiln calciners of alumina. On the other hand, melting and holding furnaces are only about 30% efficient in use of energy. Efficiency has been increased by improved firing practice and in some cases further improved by using heat from stack gases to preheat incoming air.

Furnaces used to bake anodes for prebake cells use the cooling anodes to preheat combustion air. Hot combustion gases from the baking zone are used to preheat incoming anodes. Using these techniques, about 4.2 MJ/kg (1004 kcal/kg) of anode carbon or only 2520 MJ/t $(6.03 \times 10^5 \text{ kcal/t})$ of aluminum is required to produce anodes.

Alternating current is converted to direct current (dc) for the smelting cells by silicon rectifiers. High conversion efficiency (over 99%) and minimum capital costs are achieved when the rectified voltage is 600-900 V dc. Because aluminum smelting cells operate at 4.5-5.0 V, 130 or more cells are connected in series, forming what the industry calls a potline, which may operate at 50-360 kA.

The individual components of smelting-cell voltage and energy are shown in Figure 5. The electrical energy required to decompose alumina $E_1 = 2.233$ V in a cryolite bath 65% saturated with alumina is given by

$$E_1 = \left(-\Delta G_1/nF\right) - \left(RT/nF\right)\ln a(\mathrm{Al}_2\mathrm{O}_3) \tag{21}$$

where ΔG_1 , the free energy of formation of α -alumina [12252-63-0], is -1280.02 kJ/mol(-305.93 kcal/mol), (although the feed to the cell is largely

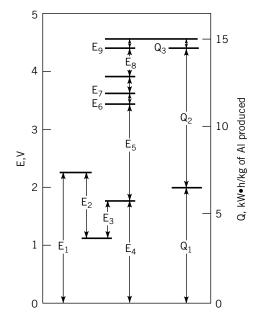


Fig. 5. Energy requirements of the Hall-Héroult cell (25-27). E_1 , decomposition of alumina; E_2 , depolarization by carbon; E_3 , anode overvoltage; E_4 , counter electromotive force; E_5 , bath voltage drop; E_6 , bath bubble voltage; E_7 , anode voltage drop; E_8 , cathode voltage drop; E_9 , external voltage drop; Q_1 , enthalpy to produce aluminum; Q_2 , cell heat losses; Q_3 bus heat loss.

 γ -Al₂O₃, α -Al₂O₃ is the phase in equilibrium with the bath); R is the gas constant (8.314 J/(mol · K)); T is bath temperature (1245 K); n = 6 electrons transferred; F is the Faraday constant (96.491 kJ/g · equiv); and a(Al₂O₃) is the activity of alumina; a is 0.3 at 65% saturation. Oxygen deposition on the anode is depolarized by carbon, subtracting $E_2 = 1.026$ V given by

$$E_2 = (-\Delta G_2/nF) - (RT/\ln F)\ln K \tag{22}$$

where ΔG_2 is the free energy of formation of carbon dioxide and *K* the oxygen plus carbon reaction equilibrium constant. There is an anode overvoltage slightly over 0.5 V given by

$$E_3 = (RT/\alpha nF)\ln\left(i/i_o\right) \tag{23}$$

where *i* is current density, n = 2 electrons per oxygen, and i_o and α are experimental constants typically 50 A/m² and 0.52, respectively. Cathode overvoltage is minimal. Combining E_1 , E_2 , and E_3 gives E_4 the counter electromotive force (CEMF) of the cell of about 1.73 V. Linear extrapolation of cell volts vs current to zero current gives an apparent CEMF about 0.1 V lower because of the change in overvoltage with current. Below 2% alumina concentration, overvoltage becomes significant, the CEMF rises and fluoride is codeposited with oxygen. This causes the bath no longer to wet the anode and a gas envelope to form

around it. In order for the current to arc across this poorly conductive layer the voltage must rise (>30 V) and this high voltage, called anode effect, generates some carbon tetrafluoride gas [75-73-0], CF_4 , wastes power, and may overheat the cell. Anode effects can be minimized or eliminated by careful control of alumina additions.

$$E_5 = IL/KA \tag{24}$$

Bath voltage E_5 is about 1.7 V, where *I* is current, *L* the anode-to-cathode spacing (4–5 cm), *K* the electrical conductivity of the bath, 2.0–2.4 $(\Omega \cdot m)^{-1}$), and *A* the effective bath area. Anode gas bubbles raise the bath's apparent resistivity, increasing its voltage about 0.17 V as indicated by E_6 . Anode voltage E_7 represents the potential drop through the anode, its connecting stub, and the contact between them. It ranges from 0.25 to 0.3 V using prebake anodes and 0.45–0.55 V using Soderberg anodes. Cathode voltage E_8 includes the voltage loss in the lining, collector bars, and the contact between the two. It ranges from 0.35 to 0.55 V. There are also voltage losses in external conductors in the range 0.1–0.2 V, E_9 , that do not contribute heat to the cell.

The right side of Figure 5, depicting heat, shows where the electrical power, in volts, is expended. The two scales correspond at 90% current efficiency. Reduction of alumina consumes carbon producing aluminum, carbon dioxide, and carbon monoxide. Assuming a typical CO:CO₂ ratio of 0.265, the energy (enthalpy) Q_1 required to reduce alumina (γ -Al₂O₃) using carbon at 970°C is 6.419 kW · h/kg of aluminum. Q_1 (19) includes the energy required to heat the alumina and carbon. The free energy (ΔG) part of the enthalpy (ΔH) required for this reduction is supplied by voltage, $E_1 - E_2$. The heat Q_2 that must be dissipated is 8.12 kW · h/kg aluminum. Heating external to this cell is Q_3 , ca 0.53 kW · h/kg aluminum. Dividing the productive energy Q_1 by the total electrical energy input $Q_1 + Q_2 + Q_3$ gives an electrical power efficiency of 42.6% for this typical cell.

Carbon consumption also represents energy consumption. Carbon reacting stoichiometrically with alumina to produce aluminum and carbon dioxide would require 0.33 kg carbon per kg aluminum; however, about 0.43 kg carbon per kg aluminum is consumed in the system, making the efficiency of carbon consumption 77%. Both carbon and electrical power can be saved by lowering bath temperature, but decreased alumina solubility and freezing limit this option. Bath additives allow temperature lowering but they also lower alumina solubility. Increasing aluminum fluoride concentration improves current efficiency but also increases the emission of fluoride fumes into the atmosphere. Power can be saved by lowering cell voltage, but when this is accomplished by lowering the anode-cathode spacing, current efficiency is lowered, often nullifying the power saving. Considerable voltage is lost in the anode and cathode. Soderberg cell efficiency has been increased through improved anode material and design, better insulation of the cathode, and automatic alumina feed systems. It is difficult to obtain large gains in prebaked anode cells because they already have higher power efficiency. However, use of cements that improve the electrical contact to the carbon cathode block and substituting semigraphitic carbon for carbon can save 2–5% of electric power.

Energy Conservation. The U.S. Department of Energy (DOE) has sponsored research on inert anodes and refractory hard metal (RHM) composite cathodes. Success in these developments could significantly lower the energy required to reduce alumina. Inert anodes would eliminate the consumption of anode carbon and allow improved sealing of the cell for reduced heat loss and reduced fluoride emission. RHM cathodes would be wetted with a thin film of aluminum which would drain to a sump and provide stable cathodic surface rather than the present aluminum pool that sloshes about owing to electrohydrodynamic effects. The stable cathode should improve current efficiency and also allow closer interelectrode spacing for reduced power consumption.

A patent describes the use of ceramic inert anodes for electrolytic production of high purity aluminum (20). The most promising route to reduced energy requirement, however, is through recycling of scrap aluminum. Recycling scrap requires less than 5% of the energy required to produce new metal. The recycling rate for aluminum beverage cans in the United States has typically been in the 62-67% range for the decade of the 1990's. Where possible, these recycling approaches should be extended to other aluminum scrap (see RECYCLING).

Comparisons of production energies per metric ton for different metals strongly prejudice the case against light metals. A fairer comparison is energy per unit volume, which more closely approximates the basis for substituting metals. Additionally, the lower energy requirement of recycled metal is often not considered. The energy savings in the application of light metals frequently exceeds the energy for their production. In fact, saving gasoline by substituting aluminum for ferrous materials in automobiles may be one of the nation's lowest cost options for extending fuel supplies (21). One of the goals of the Partnership for a New Generation of Vehicles is the development of family car prototype that will get nearly three times the corporate average fuel economy federal regulation requirement of 27.5 mi/gal (22). At least 10% of the electrical energy generated in the U.S. is lost through heating of transmission and distribution lines. Larger aluminum conductors often give lower lifetime costs (cost of energy lost plus investment costs) and would save energy. Other energy-saving applications include aluminum storm doors and windows, aluminum-pigmented heat-reflecting paints, and aluminum heat exchangers.

4.5. Alternative Processes for Aluminum Production. In spite of its industrial dominance, the Hall-Héroult process has several inherent disadvantages. The most serious is the large capital investment required resulting from: the multiplicity of units (250–1000 cells in a typical plant), the cost of the Bayer alumina-purification plant, and the cost of the carbon–anode plant (or paste plant for Soderberg anodes). Additionally, Hall-Héroult cells require expensive electrical power rather than thermal energy, most producing countries must import alumina or bauxite, and petroleum coke for anodes is in limited supply.

Aluminum can be produced by metallothermic, carbothermic, or electrolytic reduction processes. The earliest commercial process for producing aluminum (1855–1893) was sodiothermic reduction of aluminum halides. Once the Hall-Héroult process became commercial, however, sodiothermic reduction was not competitive.

Most attempts at direct carbothermic reduction of alumina have been electrically heated. Low yields of aluminum have been obtained owing to the formation of solid aluminum carbide and aluminum suboxide [12004-36-3], Al₂O, and aluminum vapors that react with carbon monoxide as they leave the furnace (23). However, yields approaching 100% at high energy efficiency can be obtained by staging the reactions as shown below and recovering the volatiles, the backreaction products, and the heat on incoming reactants (24):

$$2 \operatorname{Al}_2 O_3 + 9 \operatorname{C} \longrightarrow \operatorname{Al}_4 C_3 + 6 \operatorname{CO} \left(\operatorname{at} 1930 - 2030^{\circ} \operatorname{C} \right)$$
(25)

$$Al_4C_3 + Al_2O_3 \longrightarrow 6 Al + 3 CO (at 2030 - 2130^{\circ}C)$$
 (26)

Vaporization and carbide formation can be reduced, however, by adding to the electric furnace a metal (or metal oxide that is subsequently reduced to the metal), such as iron, silicon, copper, or tin to alloy with the aluminum produced and lower its vapor pressure. However this may require a separate purification step to remove the other metal. The greater volume of gas passing through the charge in an aluminum blast furnace generally causes very low yields. Nevertheless, a 33% Al, 42% Fe, 21% Si, 4% others alloy has been successfully produced in a pilot oxygen blast furnace at moderately high yield (25). It is then necessary to extract the aluminum from the alloy in a separate operation. Extraction of pure aluminum from the molten alloy has been accomplished electrolytically by the three-layer process. Attempts have also been made to electro-refine the solid alloy using a low melting chloride electrolyte. Neither method has proved to be economic.

Selective solution of the aluminum from the alloy using a volatile metal, such as mercury, lead, bismuth, cadmium, magnesium, or zinc, has been investigated. After extracting the aluminum from the original alloy into the volatile metal, the volatile metal is distilled, leaving pure aluminum. Neither electrolysis nor volatile metal extraction can extract aluminum from iron aluminide [12004-62-5], FeAl₃, titanium aluminide [12004-78-3], TiAl₃, or Al₄C₃.

A third technique employs monovalent aluminum. By bringing vapors of aluminum fluoride or aluminum chloride into contact with carbothermically reduced aluminum alloy at 1000–1400°C, the following reaction occurs

$$AlX_3(g) + 2 Al(alloy) \longrightarrow 3 AlX(g)$$
 (27)

The monohalide vapors are conveyed to a slightly cooler zone $(700-800^{\circ}C)$ where the reaction reverses, resulting in the condensation of pure aluminum. The monochloride process was carried to the demonstration plant stage but was abandoned because of corrosion problems (26).

A fourth alloy separation technique is fractional crystallization. If silica is co-reduced with alumina, nearly pure silicon and an aluminum silicon eutectic can be obtained by fractional crystallization. Tin can be removed to low levels in aluminum by fractional crystallization and a carbothermic reduction process using tin to alloy the aluminum produced, followed by fractional crystallization and sodium treatment to obtain pure aluminum, has been developed (27). This method looked very promising in the laboratory, but has not been tested on an industrial scale.

The vapor pressure of aluminum can be lowered by alloying it with aluminum carbide: over 40% aluminum carbide is soluble in aluminum at 2200°C (25). Thus an alloy of aluminum and aluminum carbide was produced at 2400°C by controlling the stoichiometry of the charge (28). When the alloy was tapped from the furnace and allowed to cool slowly, the aluminum carbide crystallized in an open lattice and the interstices filled with pure aluminum. The aluminum was removed by leaching with molten chlorides or by vacuum distillation of the aluminum from the alloy. The aluminum carbide residue was recycled to the arc furnace. This process has been further improved (29), going to three stages to decarbonize the aluminum—two in the hearth and one in an external holding furnace. A liquid aluminum and a slag which was recycled were obtained. The process gave good yields and produced aluminum at less than 11 kW · h/kg, but was not developed past the pilot stage.

In 1976 the first section of a new smelting process that required 30% less electric power than the best Hall-Héroult cells came on stream. In this process, alumina, carbon, and chlorine reacted to produce aluminum chloride and carbon dioxide. The aluminum chloride was electrolyzed in bipolar electrode cells to produce aluminum and chlorine and the chlorine was recycled to make more aluminum chloride. After six years of operation, the plant was shut down for economic reasons: repair and maintenance were excessive. The process was designed to use heavy fuel oil (bunker C) as the source of carbon. The chemical reactors never reached design capacity. Increasing their size or number would have been too expensive. The chemical reactor produced a trace of polychlorinated biphenyl which, rather than being destroyed in the cell, continued to accumulate within the system. Its removal and decomposition to environmentally safe products was expensive.

4.6. High Purity Aluminum. The Hall-Héroult process cannot ensure aluminum purity higher than 99.9%. Techniques such as electrolytic refining and fractional crystallization are required to produce metal of higher purity. Development of an electrolytic refining process was begun in 1901 and made workable by 1919. The Hoopes process is based upon the use of a cell containing three liquid layers, as depicted in Figure 6. Aluminum is electrochemically transported from the bottom alloy layer (anode) through an intermediate electrolyte

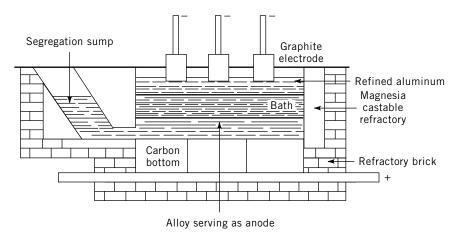


Fig. 6. Cell for the electrolytic refining of aluminum.

Characteristic	Hoopes	Pechiney	AIAG Neuhausen
	Cathode layer		
Al purity	99.98%	99.99 + %	99.99 + %
density, g/mL	2.29	2.30	2.30
	Electrolyte		
composition, %	C C		
NaF	25 - 30	17	18
AlF_3	30 - 38	23	48
CaF_2			16
BaF_2	30 - 38		18
$BaCl_2$		60	
Al_2O_3	0.5 - 7.0		
density, g/mL	2.5	2.7	2.6
resistivity, $\Omega \cdot \mathbf{cm}$	0.3	0.75 - 0.85	1.1
	Anode layer		
composition, %			
Al	75	67	70
Cu	25	33	30
density, g/cm ³	2.8	3.14	3.05
	Operating characteristi	c	
cell amperage, A	20,000	25,000	14,000
voltage, V	5 - 7	6.9	5.5 - 5.3
current density, A/cm ²	0.95	0.40	0.36
current efficiency, %	90 - 98	96 - 98	92 - 95
operating temperature, $^\circ\mathrm{C}$	950 - 1000	750	740

Table 9. Electrolytic Purification Processes^a

^a Refs. 14 and 31.

layer to the high purity top layer (cathode). The bottom phase consists of impure aluminum plus an alloying agent (usually copper) to increase the density above that of the fused salt electrolyte. The composition of the electrolyte is selected to have a density less than the alloy layer but greater than pure aluminum. Electrical connection is made to the alloy through carbon or graphite blocks and graphite is used for the cathode connection. Aluminum is purified because metals more noble than aluminum are not oxidized and remain in the anodic layer. Metals less noble than aluminum are oxidized at the anode, but not reduced at the cathode. Hence impurities accumulate as chlorides or fluorides in the electrolyte.

This process used an all-fluoride electrolyte, a portion of which was frozen on the carbon sidewalls to prevent short circuiting through the walls. One version of the cell operated at 20,000 A and $950-1000^{\circ}$ C. The highest purity aluminum produced was 99.98%. A summary of the cell characteristics is given in Table 9.

In 1932 the Pechiney Company in France perfected an electrolyte that consists of a chloride-fluoride mixture (Table 9) and melts at 720°C. This allowed low temperature operation (750°C) and the use of a nonconducting magnesia brick lining. Purities as high as 99.995% have been reported. In 1937 the Société Suisse de l'Aluminum Industrie (AIAG) at Neuhausen patented a low melting (720°C) all-fluoride electrolyte. This electrolyte also allows low temperature operation and the use of a magnesia brick lining. Operating characteristics are similar to the Pechiney process (Table 9).

An important design feature of modern purification cells is the segregation sump pictured in Figure 6 (30). It is normally operated at least 30° C cooler than the main cell and serves as the charging port of the cell. As impurities concentrate on the bottom layer, saturation is reached and crystals preferentially form in the cooler sump where they can be removed. This procedure greatly extends the operating life of the cell and allows use of the process to recover certain types of scrap (31), as well as purifying smelting-grade aluminum. Electrolytic purification, using either of the low melting electrolytes, is a principal source of commercially produced high purity aluminum.

Fractional crystallization processes are also used commercially to produce high purity metal from lower grade aluminum. These processes rely on the fact that most impurities preferentially concentrate either in the liquid or the solid as aluminum freezes, eg, zone melting (see ZONE REFINING) (32) where a molten zone is moved along an aluminum bar. Impurities that lower the melting point of aluminum, such as silicon and iron, concentrate in one end of the bar while impurities that raise the melting point, such as titanium and vanadium, concentrate in the other end. After several passes the ends are removed leaving the middle region as the high purity product.

In one process (33) high purity crystals are formed by cooling a molten aluminum surface using air. After the furnace is nearly filled with crystals, the remaining liquid is drained and the crystals remelted to yield the high purity product. Starting with 99.9% smelting-grade metal, aluminum of purity higher than 99.995% has been produced by fractional crystallization.

	Produc	ction	Year end capacity		
Country	2000	2001^c	2000	2001^{c}	
United States	3,668	2,600	4,270	4,280	
Australia	1,770	1,800	1,770	1,770	
Brazil	1,280	1,200	1,260	1,260	
Canada	2,370	2,500	2,370	2,550	
China	2,550	2,700	2,640	2,640	
France	441	450	450	450	
Norway	1,030	1,000	1,020	1,020	
Russia	3,240	3,200	3,200	3,200	
South Africa	671	680	676	676	
Venezuela	570	570	640	640	
other countries	6,440	6,680	7,500	7,670	
World total (rounded)	24,000	23,400	25,800	26,200	

Table 10. World Smelter Production and Capacity^{*a,b*}

^a Ref. 34.

^b Data in thousand metric tons of metal.

^c Estimated.

Vol. 2

5. Production

World smelter production and capacity are given in Table 10 (34). Primary U.S. production by company is listed in Table 11 (35).

In 2000, U.S. production of aluminum was 3.7×10^6 t. U.S. metal recovered from new and old scrap decreased by 7% to 3.45×10^6 t.

The tremendous growth of aluminum production as compared to other metals is shown in Table 12 (36).

6. Economic Aspects

Aluminum prices have historically been more stable than other nonferrous metals. Beginning in the 1970s, however, aluminum prices have fluctuated as shown in Table 13 (31). These fluctuations reflect increased energy costs as well as increased costs of raw materials. Improvements in production processes as well as a rebalancing of demand and supply are expected to stabilize aluminum prices in the future.

U.S. imports for consumption decreased in 2000 compared to those in 1999 reversing a trend starting in 1997. Total exports increased 7% in 2000. Canada remains the largest shipper to the United States. Exports from the U.S. are listed in Table 14 and imports to the U.S. are listed in Table 15 (35).

7. Analysis

Aluminum is best detected qualitatively by optical emission spectroscopy. Solids can be vaporized directly in a d-c arc and solutions can be dried on a carbon electrode. Alternatively, aluminum can be detected by plasma emission spectroscopy using an inductively coupled argon plasma or a d-c plasma. Atomic absorption using an aluminum hollow cathode lamp is also an unambiguous and sensitive qualitative method for determining aluminum.

Quantitative aluminum determinations in aluminum and aluminum base alloys is rarely done. The aluminum content is generally inferred as the balance after determining alloying additions and tramp elements. When aluminum is present as an alloying component in alternative alloy systems it is commonly determined by some form of spectroscopy (qv): spark source emission, x-ray fluorescence, plasma emission (both inductively coupled and d-c plasmas), or atomic absorption using a nitrous oxide acetylene flame.

The predominant method for the analysis of aluminum-base alloys is spark source emission spectroscopy. Solid metal samples are sparked directly, simultaneously eroding the metal surface, vaporizing the metal, and exciting the atomic vapor to emit light in proportion to the amount of material present. Standard spark emission analytical techniques are described in ASTM E101, E607, E1251 and E716 (37). A wide variety of well-characterized solid reference materials are available from major aluminum producers for instrument calibration.

	(thous	nd capacity and metric tons)			
Company	1999	2000	2000 ownership		
Alcan Aluminum Corp.:					
Sebree, KY	186	186	Alcan Aluminium Ltd., 100%		
Alcoa Inc.: ^b					
Alcoa, TN	210	210	Alcoa Inc., 100%		
Badin, NC	115	115	Do.		
Evansville, IN (Warrick)	300	300	Do.		
Femdale, WA (Intalco)	272	272	Alcoa Inc., 61%; Mitsui & Co. Ltd., 32%; YKK Corp., 7%		
Frederick, MD (Eastalco)	174	174	Do.		
Longview, WA^d	204	204	Alcoa Inc., 100%		
$Massena, NY^d$	123	123	Do.		
Massena, NY	125	125	Do.		
Mount Holly, SC	215^c	215	Alcoa Inc., 50.3%; Century Aluminum Co., 49.7%.		
Rockdale, TX	315	315	Alcoa Inc., 100%		
Troutdale, OR^{d}	121	121	Do.		
Wenatchee, WA	220	220	Do.		
Total	$2,390^{c}$	2,390			
Century Aluminum Co.:					
Ravenswood, WV	168^c	168	Century Aluminum Co., 100%		
Columbia Falls Aluminum Co.:	1.00	1.00	Classes A.C. 100%		
Columbia Falls, MT	168	168	Glencore AG, 100%		
Goldendale Aluminum Co.:	100	100	Clansons AC 100%		
Goldendale, WA	168	168	Glencore AG, 100%		
Goldendale, WA	168	168	Private interest, 60%; employees, 40%		
Kaiser Aluminum & Chemical Corp.:	200	200			
Mead, WA (Spokane)	200	200	MAXXAM Inc., 100%		
Tacoma, WA	73	73	Do.		
Total	273	273			
NSA:	225	005			
Hawesville, KY	237	237	Southwire Co., 100%		
Noranda Aluminum Inc.:	2220	222			
New Madrid, MO	222^c	222	Noranda Mines Ltd., 100%		
Northwest Aluminum Corp.:	00	00	Drivete interests 1000		
The Dalles, OR	82	82	Private interests, 100%		
Ormet Primary Aluminum Corp.:	055	057	O		
Hannibal, OH	255	257	Ormet Corp., 100%		
Vanalco Inc.:	110	110	Variales Inc. 100%		
Vancouver, WA Grand total	116	116	Vanalco Inc., 100%		
Grunu totat	4,270	4,270			

Table 11.	Primary	Annual	Aluminum	Production	Capacity	in the	United	States,
by Comp	any ^a							

^a Data are reounded to no more the significant digits; may not add to totals shown. ^b Individual plant capacities are U.S. Geological Survey estimates based on company reported total. ^c Revised.

^d Alcoa and Reynolds in June 2000.

Year	Al^b	Cu^c	Mg^d	Pb^d	Zn		
1900	5.7	449	0.01	877	479		
1950	1,516	2,791	21	1,752	1,985		
1960	4,732	4,631	93	2,436	3,019		
1970	9,780	6,885	223	3,660	5,022		
1980	16,043	7,984	317	5,456	6,115		
1990	18,174	9,668	368	5,699	7,086		
1999	23,074	11,337	393	6,120	8,406		

Table 12. Growth of Aluminum Production Compared to Other Metals, ×10³t/yr^a

^a Ref. 36.

^bAl - primary production only. ^cCu - smelter production only. ^dMg, Pb - include both primary and secondary.

Year	Price, \$/kg
1966	0.540
1967	0.551
1968	0.564
1969	0.599
1970	0.633
1971	0.639
1972	0.583
1973	0.559
1974	0.752
1975	0.877
1976	0.977
1977	1.132
1978	1.170
1979	1.309
1980	1.534
1981	1.676
1982	1.676
1983	1.712
1984	1.786
1985	1.786
1986	1.232
1987	1.594
1988	2.427
1989	1.937
1990	1.631
1991	1.311
1992	1.267
1993	1.175
1994	1.569
1995	1.893
1996	1.571
1997	1.699
1998	1.443
1999	1.448
2000	1.64
2001	1.54

Table 13. Aluminum^a Price Averages from 1966 to 2001^a

^a From Ref. 35, Pure, 99.5%, ingot aluminum at New York.

302 ALUMINUM AND ALUMINUM ALLOYS

	Total,	1999	Total, 2000		
Country or territory	Quantity (metric tons)	Value (thousands, \$)	Quantity (metric tons)	Value (thousands, \$)	
Azerbaijan	1	3			
Brazil	60,300	173,000	32,900	99,800	
Canada	795,000	1,560,000	854,000	1,740,000	
France	7,220	31,500	7,350	32,800	
Germany	7,340	39,400	6,900	38,100	
Hong Kong	29,400	49,900	33,000	49,900	
Italy	2,710	12,900	2,110	12,100	
Japan	117,000	241,000	81,900	184,000	
Korea, Republic of	46,800	84,600	58,200	127,000	
Mexico	306,000	670,000	321,000	768,000	
Netherlands	2.150	7,700	3,940	14,500	
Philippines	847	2,620	1,080	4,020	
Russia	14	158	258	1,250	
Saudi Arabia	8,210	22,500	8,380	20,300	
Singapore	3,250	15,500	3,390	17,300	
Slovakia	9	54	11	35	
Slovenia	58	140	(3/)	4	
South Africa	328	1,940	118	1,210	
Taiwan	42,900	64,800	40,900	66,000	
Thailand	4,100	14,700	8,700	27,400	
Ukraine	(3/)	4	1	25	
United Kingdom	18,100	78,800	26,900	104,000	
Venezuela	18,100	40,700	17,300	40,500	
other	175,000	418,000	248,000	532,000	
Total	1,640,000	3,530,000	1,760,000	3,880,000	

Table 14	U.S.	Exports	of	Aluminum,	b١	/ Country ^a
	0.0.	Exports	U 1	Alaminani,	~ >)	

^{*a*} Source: U.S. Census Bureau.

In addition to the spark emission methods, quantitative analysis directly on solids can be accomplished using x-ray fluorescence, or, after sample dissolution, accurate analyses can be made using plasma emission or atomic absorption spectroscopy (38).

8. Environmental Considerations

Fluoride emission from aluminum smelting cells has long been an area of great concern (39). One source of fluoride evolution is melt entrained in the gas generated at the anodes. Additionally, sodium tetrafluoroaluminate [13821-15-3], NaAlF₄, has a significant vapor pressure, 190–330 Pa (1.4–2.5 mm Hg), over the melt. The melt vapor pressure increases as melt temperature and aluminum fluoride concentration increase, but decreases as alumina, calcium fluoride, and sodium fluoride concentration increase. Both entrained liquid and NaAlF₄ gas solidify to form fluoride particulates. Moisture entering the melt adsorbed on alumina, and from the hydrogen content of the anodes, results in hydrolysis of AlF₃ in the melt forming hydrogen fluoride (HF) gas. Historically, treatment consisted of passing the exhausted gases through electrostatic precipitators to remove

	Tota	al, 1999	Total, 2000		
	Quantity	Value	Quantity	Value	
Country	(metric tons)	(thousands, \$)	(metric tons)	(thousands, \$)	
Argentina	27,700	\$39,700	61,700	105,000	
Australia	63,000	94,000	25,800	45,100	
Bahrain	49,200	80,700	44,100	82,500	
Belgium	4,260	12,600	3,810	11,800	
Brazil	91,500	115,000	85,500	136,000	
Canada	2,210,000	3,460,000	2,150,000	3,780,000	
Croatia	273	933	163	547	
Czech Republic	714	1,890	328	1,070	
France	23,900	68,900	22,700	61,300	
Germany	46,500	161,000	49,100	176,000	
Italy	5,670	12,900	3,220	11,000	
Japan	24,800	82,000	22,500	82,700	
Korea, Republic of	21,400	42,300	13,900	35,200	
Mexico	106,000	151,000	102,000	171,000	
Netherlands	15,400	25,600	6,930	16,300	
Norway	5,030	9,240	7,110	14,000	
Panama	7,420	10,400	8,690	13,800	
Russia	831,000	1,100,000	837,000	1,280,000	
Slovakia	204	218	257	282	
Slovenia	4,000	11,800	4,350	14,000	
South Africa	22,500	34,500	47,900	90,600	
Spain	5,600	10,200	905	2,470	
Tajikistan	17,200	20,600		,	
Ukraine	32,200	36,900	17,000	19,800	
United Arab Emirates	21,000	28,300	58,300	101,000	
United Kingdom	45,500	91,300	26,300	75,200	
Venezuela	169,000	236,000	165,000	236,000	
Other	151,000	258,000	148,000	293,000	
Total	4,000,000	6,200,000	3,910,000	6,860,000	

Table 15. U.S. Imports for Consumption of Aluminum, by Country^a

^a Ref. 35

particulates, followed by wet scrubbers to remove HF. This technique has largely been replaced by highly (over 99%) efficient dry scrubbers that catch particulates and adsorb HF on alumina (40) that is subsequently fed to the cells. Hence, nearly all the fluoride evolved is fed back into the cell. A monolayer of HF is chemisorbed in the Al_2O_3 and converted to AlF_3 on heating when the alumina is fed to the cell. HF in excess of the monolayer is desorbed and becomes a rapidly increasing circulating load in the system if the alumina used does not have adequate surface area. A surface area of 45 m²/g chemisorbs 1.35% HF and is generally adequate.

Hydrocarbon fumes evolved during anode baking are generally disposed of by burning. Additional fuel is required to support combustion because the hydrocarbon concentration is low. In some plants these products are now absorbed in a fluid bed of alumina for burning in a concentrated form. This treatment also catches the fluoride evolved during anode baking. Handling of alumina and coke presents dusting problems. Hoods and exhaust systems collect the dust, which is then separated from the exhaust air either by cyclones, electrostatic precipitators, filter bags, or a combination of these methods, and recycled to the process (see AIR POLLUTION CONTROL METHODS).

Chlorine fluxing of aluminum to remove hydrogen and undesirable metallic impurities has largely been supplanted by fumeless fluxing procedures, which generally employ a low vapor pressure melt of alkali chlorides containing a small amount of aluminum chloride as the active ingredient.

The linings of aluminum reduction cells must be replaced periodically. These spent linings represent the largest volume of waste associated with the smelting process. Because they contain fluorides and cyanide, they must be either stored under roof or buried in landfills lined with impervious materials to prevent leaching and contamination of the environment. The large volumes involved make these procedures costly and research is being directed toward destroying the cyanide and recovering valuable components from the lining. Some potential uses for recoverables are as a flux in the steel industry, in making rock wool, as supplemented fuel for cement manufacture, and as fuel in fluidizedbed boilers.

Table 10. nepresentative duides and neg	guiatory Standarus
Standards	$\begin{array}{c} Concentration \\ (mg/m^3) \end{array}$
United States	
ACGIH TLV TWA	
metal dust, as Ai	10
pyropowder, as Ai	5
welding fume, as Ai	5
OSHA PEL	
total dust	15
respirable dust	5
welding fumes, pyropowders, as Ai	5
NIOSH REL	
total dust, as Ai	10
respirable dust	5
pyropowders, welding fumes, as Ai	5
UK, metal, as Ai	10
10-min STEL	20
Germany, as metal, fine dust	6
Sweden, total dust	10
respirable	4
Australia, for metal	10
welding fumes, pyropowder	5

Table 16. Representative Guides and Regulatory Standards^{*a,b*}

^a Ref. 42.

 $^{^{}b}$ ACGIH = The American Conference of Governmental Industrial Hygienists. NIOSH = National Institute of Occupational Safety and Health. OSHA = Occupational Safety and Health Agency. PEL = Permissible exposure level. REL = Relative exposure level. STEL = Short-term exposure limit. TLV = Threshold limit values. TWA = Time weighted average.

9. Recycling

Aluminum recovered in 2001 from purchased scrap was about 3.2×10^6 t, of which 60% came from new (manufacturing) scrap and 40% from old scrap (discarded aluminum products). Aluminum recovered from old scap was equivalent to approximately 20% apparent consumption (35).

According to figures released by the Aluminum Association Inc, the Can Manufacturer's Institute, and the Institute of Scrap Recycling Industries, 62.6×10^9 used beverage containers were recycled in the United States in 2000. The recycling rate was 62.1% in 2000, a decrease from 62.5% in 1999. However, 2000 was the twelfth consecutive year that aluminum can recycling rate was greater than 60%. According to the organizations, aluminum beverage cans produced in the United State in 2000 had an average of 51% postconsumer recycled content, the highest percentage of all packaging materials (41).

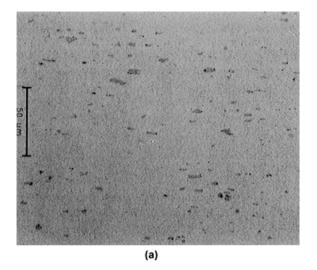
10. Health and Safety Factors

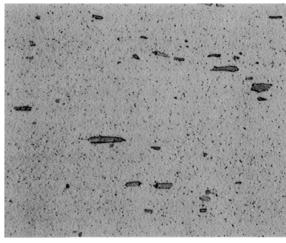
Table 16 lists some representative guides and regulatory standards presently extant for aluminum metal dusts or powders (42). The major difference in the U.S. standards is the discordance between the higher OSHA PEL as compared with ACGIH and NIOSH. The lower recommendations of the latter two organizations are based on their adherence to a generic standard recommended for all dusts not otherwise classified (NOC).

11. Aluminum Alloys

Aluminum obtained by electrolysis of cryolite baths contains iron [7439-89-6] and silicon [7440-21-3] as impurities. Iron content may vary from 0.05 to 0.4% and silicon from 0.05 to 0.1% depending on the raw materials and the age and condition of the reduction cell. Primary aluminum metal also contains small, usually not to exceed 0.05% in total, amounts of many other elements. Some of these trace impurities are Cu, Mn, Ni, Zn, V, Na, Ti, Mg, and Ga, most of which are present in quantities substantially below 100 ppm.

Many of the properties of aluminum alloy products depend on metallurgical structure which is controlled both by the chemical composition and by processing (43). In addition to features such as voids, inclusions, grains, subgrains, dislocations, and vacancies which are present in virtually all metallic products, the structure of aluminum alloys is characterized by three types of intermetallic particles. Aluminum metallurgists refer to these as constituent particles, dispersoid particles, and precipitate particles. Constituent particles are formed during solidification generally as a byproduct of a divorced eutectic reaction and range in size in the final product from about 1-20 micrometers, Figure 7a. These negatively affect toughness of high strength alloy products. Dispersoids and precipitates both form by a solid-state reaction. The particles known as dispersoids characteristically form during thermal treatment of an ingot by precipitation of solid solution which exceeds maximum solid solubility because of nonequilibrium





(b)

Fig. 7. Alloy 3004 sheet. (a) $Al_6(Fe, Mn)$ and $Al_{12}(Fe, Mn)$ Si constituent particles. Magnification is \times 500. (b) Etched to reveal the $Al_6(Fe, Mn)$ and $Al_{12}(Fe, Mn)$ dispersoids. Magnification is \times 1000.

conditions during ingot solidification. Dispersoids, about 10-200 nm in the largest dimension, are present in most aluminum alloy products. See Figures 7**b** and 8. Their primary function is to control grain size, grain orientation (texture), and degree of recrystallization. Particles classified as precipitates from during heat treatment of the final mill product by precipitation from a supersaturated solid solution that does not exceed the maximum equilibrium solid solubility. In the final product, their size may range from disks a few atoms thick by a few nm in diameter up to needlelike or platelike particles which may exceed 1 micrometer

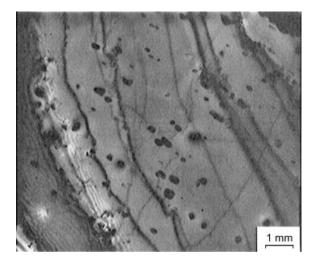


Fig. 8. Transmission electron micrograph showing the Al_{12} (Fe, Mn)₃Si and Al_6 (Fe, Mn) dispersoid particles in alloy 3004 sheet.

in the largest dimension (Fig. 9). Precipitates may confer high strength. The nature of the constituent, dispersoid, and precipitate particles depends strongly on the phase diagrams of the particular alloy.

11.1. Binary Alloys. Aluminum-rich binary phase diagrams show three types of reaction between liquid alloy, aluminum solid solution, and other

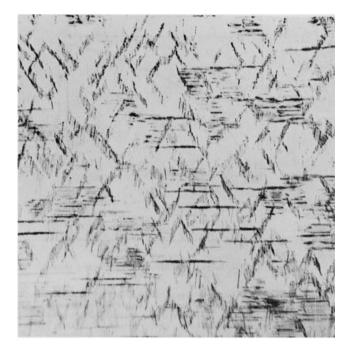


Fig. 9. Transmission electron micrograph at 40,000 magnification showing S'-phase precipitates in Al-Cu-Mg alloy sheet aged 12 h at 100° C.

41.36		Reaction		Solubility of M $\%$	
Al–M system	Туре	Temperature, $^{\circ}C$	Solid	Liquid	Other phase
Al–Si Al–Cr Al–Pb	eutectic peritectic monotectic	$577 \\ 651 \\ 326.8$	$\begin{array}{c} 1.65\\ 0.77\end{array}$	$\begin{array}{c} 12.60\\ 0.41\end{array}$	Si CrAl ₇ Pb

Table 17. Phase Transformations in Binary Aluminum Alloys

phases: eutectic, peritectic, and monotectic. Table 17 gives representative data for reactions in the systems Al-M. Diagrams are shown in figures 10–19. Compilations of phase diagrams may be found in reference (44).

Al-Fe. TheAl-Fe system (Fig. 10), is important because virtually all commercial aluminum alloys contain some iron [7439-89-6], Fe. The system has a eutectic at 1.9% Fe, but solid solubility of only 0.05% Fe. Consider an alloy containing 0.3% Fe. During solidification, most of the Fe remains in the liquid phase until a eutectic of solid solution plus Al₃Fe constituent particles freezes. Alternatively, constituents of the metastable Al₆Fe phase [12005-28-6] may form during solidification. These transform to equilibrium Al₃Fe by heating

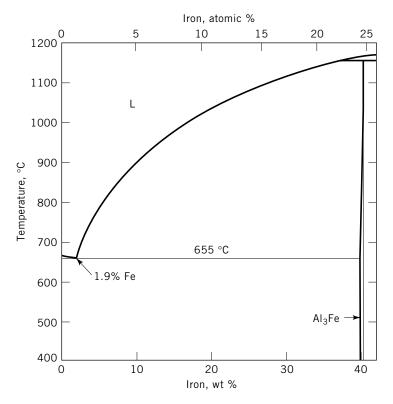


Fig. 10. Al-Fe phase diagram, where L is liquid. Drawing by J. Murray.

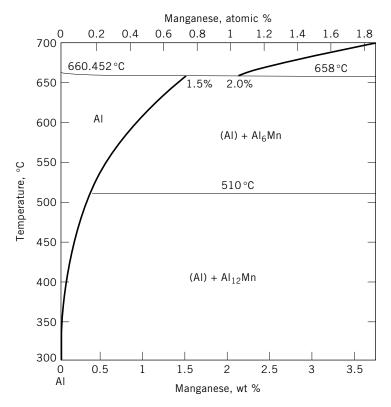


Fig. 11. Al–Mn phase diagram, where L is liquid. Drawing by J. Murray.

above 500°C. If the solidification rate is rapid enough, more than 0.05% Fe remains in supersaturated solid solution. This excess amount can precipitate as Al_3Fe dispersoids during subsequent thermal treatment. In more complex alloys, such as Al-Fe-Si, Al-Fe-Mn, and Al-Cu-Fe, most of the iron is contained in constituent particles formed by eutectic decomposition. In all cases the maximum solid solubility of iron in aluminum is 0.05% or less.

Al-Mn. The Al-Mn system (Fig. 11), the basis for the oldest yet most widely used aluminum alloys, is characterized by a eutectic at 1.95% Mn and 658° C. Maximum solid solubility is 1.76% manganese, Mn, and the intermetallic phase in aluminum-rich alloys is Al₆Mn [12043-69-5]. The Al₁₂Mn phase [12446-45-6] is difficult to nucleate in binary Al-Mn alloys, but Al₁₂(Mn,Cr) forms readily in the Al-Mn-Cr ternary alloy. Most of the manganese added to commercial alloys is usually retained in supersaturated solution in the ingot. Commercial alloys based on the Al-Mn system always contain some iron and silicon, and in the presence of these elements manganese precipitates as dispersoids which may be Al₆(Fe,Mn) or Al₁₂(Fe,Mn)₃Si. The dispersoid particles provide a modicum of dispersion strengthening, increase the degree of strain hardening, refine the recrystallized grain structure and influence its crystallographic orientation, and minimize strain localization during plastic deformation.

Al–Cu. Many structural aluminum alloys contain significant amounts of copper Cu. There is a eutectic in the Al–Cu system at 33.2% Cu and 548° C, but

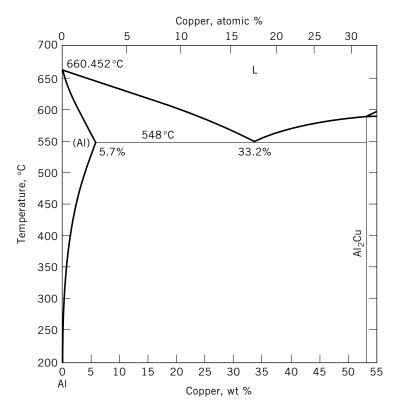


Fig. 12. Al-Cu phase diagram, where L is liquid. Drawing by J. Murray.

the important feature (Fig. 12) is the maximum solubility of 5.7% Cu at 548°C which decreases drastically at lower temperatures. This decreasing solubility with decreasing temperature is necessary for the phenomenon known as age hardening or precipitation strengthening. Consider an alloy containing 4% Cu. During solidification, it separates into a solid solution of copper in aluminum and a liquid containing copper in aluminum until a temperature of 548°C is reached. Then, the remaining liquid freezes as a solid solution of 5.7% Cu in Al plus a eutectic of this solid solution and Al₂Cu constituent particles. The alloy product may be subsequently heated in the solid-state above about 425°C to dissolve the Al₂Cu constituents (solution heat treatment). Rapid cooling to room temperature (quenching) retains the Cu in supersaturated solution. This unstable solution decomposes at room temperature (natural aging) by the formation of clusters of Cu atoms (G-P or Guinier-Preston zones) on preferred crystallographic planes. The G-P zones strengthen the alloy product by resisting the passage of dislocations. Heating to 100-200°C (artificial aging or elevated temperature precipitation treatment) provides enough energy for the formation of metastable forms of Al₂Cu precipitates (θ' or θ'') which provide even more strengthening. Thermal treatment at 250° C and higher (annealing) converts the metastable precipitates to the equilibrium Al₂Cu precipitates (θ), and the product softens.

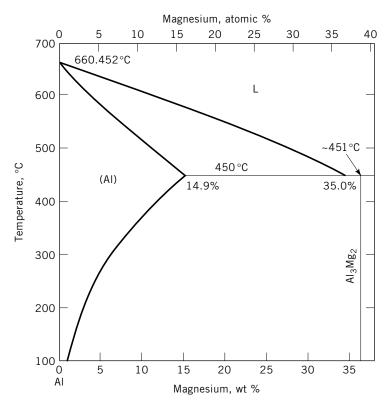


Fig. 13. Al–Mg phase diagram, where L is liquid. Drawing by J. Murray.

Al-Mg. Almost every commercial structural aluminum alloy contains magnesium as an alloying element. The Al-Mg system (Fig. 13) has a eutectic at 35% magnesium Mg, and 451°C. Maximum solid solubility is 14.9% Mg, and solubility decreases to about 0.8% Mg at room temperature. Despite this decreased solubility, precipitation strengthening by the mestable β' -phase precursor to the equilibrium β -phase Al₃Mg₂ precipitates is observed only at very high magnesium levels. Commercial alloy products based on the Al-Mg system are strengthened by the effect of the magnesium in solid solution (solid solution hardening). Strength is enhanced by cold-working the products (strain-hardening). Strength levels are not as high as in most precipitation strengthened alloys, but the products have good ductility and corrosion resistance.

AI-Si. Al-Si alloys (Fig. 14) possess high fluidity and castability and are consequently used for weld wire, brazing, and as casting alloys. The range of silicon [7440-21-3], Si, is about 5 to 20% in commercial casting alloys. This system has a eutectic at 12.6% Si and 577°C; maximum solid solubility of Si is 1.65%. The constituent which forms during eutectic decomposition is essentially pure Si. Hypereutectic alloys are used for engine blocks because the hard Si particles are wear-resistant. The Si particles, which form during solidification, are coarse and acicular. Micro additions of sodium [7440-23-5], Na, antimony [7440-36-0], Sb, and strontium [7440-24-6], Sr, modify the faceted structure of primary silicon

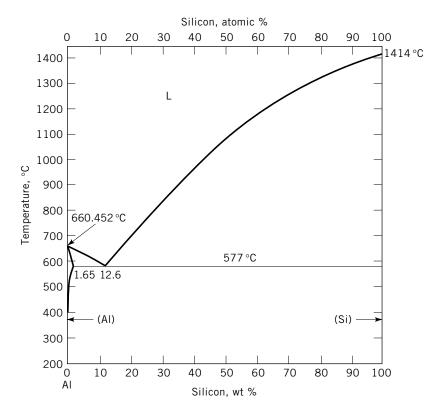


Fig. 14. Al–Si phase diagram, where L is liquid. Drawing by J. Murray.

particles in hypereutectic alloys to spherulitic and the flake structure of eutectic silicon to a finer fibrous morphology.

Al-Li. Alloys containing about two to three percent lithium Li, (Fig. 15) received much attention in the 1980s because of their low density and high elastic modulus. Each weight percent of lithium in aluminum alloys decreases density by about three percent and increases elastic modulus by about six percent. The system is characterized by a eutectic reaction at 8.1% Li at 579°C. The maximum solid solubility is 4.7% Li. The strengthening precipitate in binary Al-Li alloys is metastable Al₃Li [12359-85-2], δ' , having the cubic L1₂ crystal structure, and the equilibrium precipitate is complex cubic Al-Li [12042-37-4], δ . The nature of the phase relationships involving δ' has been the subject of much discussion. Portions of the metastable phase boundaries have not yet been agreed upon.

Al–Cr. Although no commercial alloys are based on this system, chromium, Cr, is an ingredient of several complex and commercially significant alloys (Fig. 16). The Cr is added for control of grain structure. The Al–Cr system has a peritectic portion at 661°C where solid solubility is 0.7% Cr and liquid solubility is 0.4% Cr. Freezing of binary alloys containing >0.4% Cr produces coarse primary crystals (metallic inclusions) of Al₇Cr [12005-37-7] which may adversely affect mechanical properties. In complex alloys, the liquid solubility can be reduced such that formation of primary Al₇Cr crystals may occur at significantly lower Cr contents.

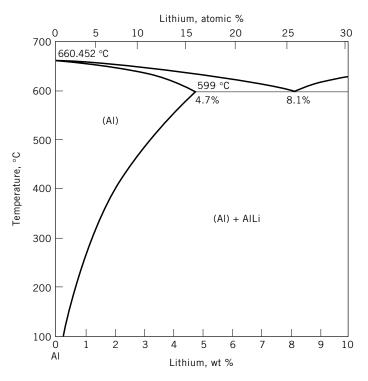


Fig. 15. Al-Li phase diagram. Drawing by J. Murray.

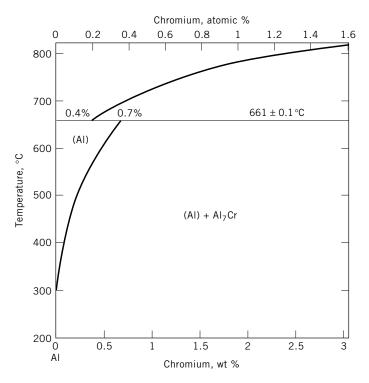


Fig. 16. Al-Cr phase diagram. Drawing by J. Murray.

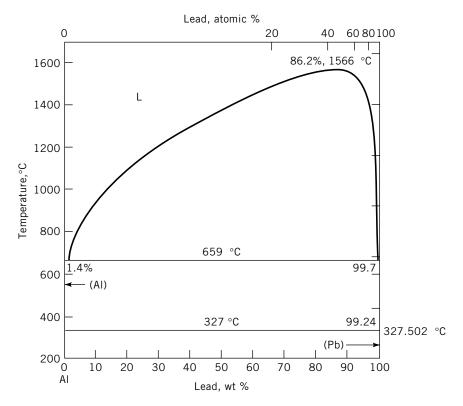


Fig. 17. Al–Pb phase diagram, where L is liquid. Drawing by J. Murray.

Al–Pb. Both lead Pb, and bismuth, Bi, which form similar systems (Fig. 17), are added to aluminum alloys to promote machinability by providing particles to act as chip breakers. The Al–Pb system has a monotectic reaction in which Al-rich liquid freezes partially to solid aluminum plus a Pb-rich liquid. This Pb-rich liquid does not freeze until the temperature has fallen to the eutectic temperature of 327° C. Solid solubility of lead in aluminum is negligible; the products contain small spherical particles of lead which melt if they are heated above 327° C.

AI-Zn. Aluminum-rich binary alloys (Fig. 18) are not age hardenable to any commercial significance, and zinc, Zn, additions do not significantly increase the ability of aluminum to strain harden. Al–Zn alloys find commercial use as sacrificial claddings on high strength aircraft sheet or as sacrificial components in heat exchangers.

AI-Zr. This system (Fig. 19) has a peritectic reaction at 660.8°C at which solubility is 0.28% zirconium Zr, solid and 0.11% Zr liquid. The equilibrium phase on the aluminum-rich end of the phase diagram is tetragonal Al₃Zr [12004-83-0], β . Coarse primary particles of β -phase have a tendency to form during solidification when the zirconium content is much above 0.12%. A metastable form of Al₃Zr having a cubic L1₂ structure, β' , is formed when supersaturated

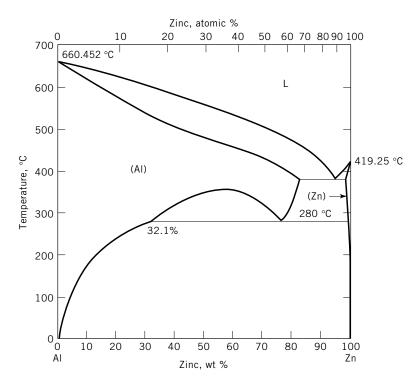


Fig. 18. Al–Zn phase diagram, where L is liquid. Drawing by J. Murray.

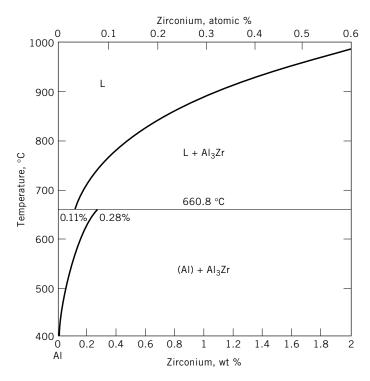


Fig. 19. Al-Zr phase diagram, where L is liquid. Drawing by J. Murray.

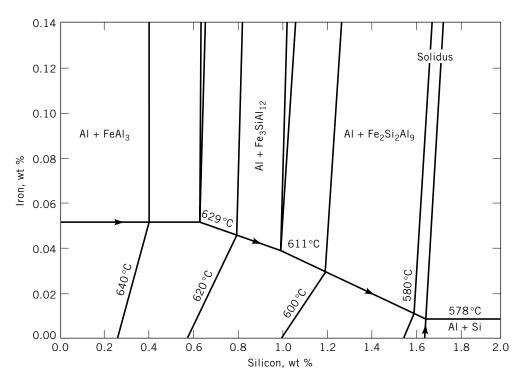


Fig. 20. Solidus for aluminum-rich Al-Fe-Si alloys.

zirconium precipitates as a dispersoid. Although this phase is nonequilibrium, it is extremely resistant to transformation to the equilibrium β -phase.

11.2. Ternary Alloys. Almost all commercial alloys are of ternary or higher complexity. Alloy type is defined by the nature of the principal alloying additions, and phase reactions in several classes of alloys can be described by reference to ternary phase diagrams. Minor alloying additions may have a powerful influence on properties of the product because of the influence on the morphology and distribution of constituents, dispersoids, and precipitates. Phase diagrams, which represent equilibrium, may not be indicative of these effects.

AI-Fe-Si. Iron and silicon, present in primary aluminum, may also be added to produce enriched alloys for specific purposes. The equilibrium phase fields in the AI-Fe-Si system are shown in Figure 20 and Table 18. The intermetallic phases have a limited range of composition when in equilibrium with

Designation	Formula	CAS Registry Number	Fe, %	Si, %
$\begin{array}{c} \alpha\text{-}(Al\text{-}Fe\text{-}Si) \\ \beta\text{-}(Al\text{-}Fe\text{-}Si) \end{array}$	$egin{array}{lll} Al_3Fe \ Al_{12}Fe_3Si \ Al_9Fe_2Si_2 \ Si \end{array}$	$\begin{matrix} [12004-62-5] \\ [12397-58-9] \\ [12397-57-8] \\ [7440-21-3] \end{matrix}$	41 32 27 negligible	$\begin{array}{c} {\rm negligible} \\ 5.5 \\ 14 \\ {\sim}100 \end{array}$

Table 18. Intermetallic Phases in Al-Mg-Zn Alloys

the aluminum solid solution. The amount of iron in solid solution in the matrix is small, so almost all of the iron is in the intermetallic compounds. At low silicon contents the iron is present as Al_3Fe except for about 0.01% Fe in solid solution. As silicon content increases, the ternary intermetallic compound $Al_{12}Fe_3Si$, α -(Al-Fe-Si), appears. At higher silicon contents $Al_9Fe_2Si_2$, β -(Al-Fe-Si), appears in which a higher amount of silicon is combined with iron. The positions of the phase fields move to lower silicon content with decreasing temperature.

The phases present in products can differ from those predicted from equilibrium diagrams. Nonequilibrium metastable phases form at solidification rates experienced in commercial ingots. Because of the low rate of diffusion of iron in aluminum, equilibrium conditions can only be established by long heat treatments and are very slowly approached at temperatures below about 550°C. Small additions of other elements, particularly manganese, can also modify the phase relations.

AI-Mg-Si. An important class of commercial alloys is based on the Al-Mg-Si system because of its precipitation hardening capabilities and good corrosion resistance. The precipitation hardening results from precipitation of a meta-stable precursor of magnesium silicide Mg₂Si, from solid solution. The phase relations are as shown in Figure 21. At low magnesium contents the alloys may contain silicon as a second phase. As magnesium increases, the ternary phase field Al-Mg₂Si-Si is entered, and at higher magnesium contents the phase field Al-Mg₂Si. The solubility of Mg₂Si decreases at higher magnesium contents. Heat treatment at high temperatures can put as much as 1.8%

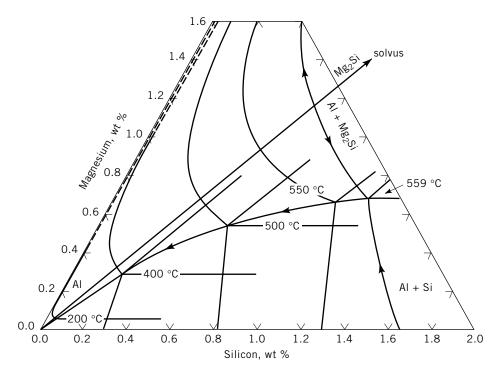


Fig. 21. Solvus for aluminum-rich Al-Mg-Si alloys.

318 ALUMINUM AND ALUMINUM ALLOYS

 Mg_2Si into solid solution, and cooling at a sufficient rate can retain it therein. The cooling rate required depends on the amount of Mg_2Si dissolved. Compositions that have magnesium and silicon in the exact ratio to form Mg_2Si are not widely employed commercially, because alloys containing silicon in excess of that required to form Mg_2Si develop higher strength. Silicon, however, has a tendency to precipitate on grain boundaries. Consequently, excess-silicon alloy products must be quenched at a higher rate to prevent brittle intergranular fracture.

Al-Mg-Mn. The basis for the alloys used as bodies, ends, and tabs of the cans used for beer and carbonated beverages is the Al-Mg-Mn alloy system. It is also used in other applications that require excellent weldability and corrosion resistance. These alloys have the unique ability to be highly strain hardened yet retain a high degree of ductility. Some of the manganese combines with the iron to form Al₆(Fe,Mn) or Al₁₂(Fe,Mn)₃Si constituent particles during solidification, but most remains in supersaturated solid solution until it precipitates as Al₆(Fe,Mn) or Al₁₂(Fe,Mn)₃Si dispersoids during ingot thermal treatment. No ternary Al-Mg-Mn phases are present in commercial alloys; mechanical properties reflect the enhanced strain hardening characteristics of the matrix with magnesium in solution and the effects of the Mn-bearing dispersoids in stabilizing the deformation substructure.

Most alloys contain no more than 5% Mg and because of the slow precipitation kinetics of Al_3Mg_2 at these levels, the magnesium is easily retained in solution during processing. Natural aging is insignificant at these low magnesium levels, but with levels of 4% Mg or more, small amounts of β may precipitate at grain boundaries after long times, and this may cause susceptibility to intergranular corrosion. Special thermal treatments (tempers) have been developed to prevent this.

Al-Cu-Mg. The first precipitation hardenable alloy was an Al-Cu-Mg alloy. There is a ternary eutectic at 508°C, and there are nine binary and five ternary intermetallic phases. For aluminum-rich alloys, only four phases are encountered in addition to the aluminum solid solution (Table 19). Several commercial alloys are based on the age hardening characteristics of the metastable precursors of θ or S-phase, principally θ' or S'. Hardening by T- and β -phases is not very effective. Alloys of greatest age hardenability have compositions near the Cu:Mg ratio of the S-phase. Additions of about 0.12% Mg to alloys containing as much as 6% Cu, however, significantly increase strength by refining the θ' precipitate.

Solid-state reactions in these alloys can be understood with reference to Figures 22 and 23. Heat-treatable Al–Cu–Mg alloys are solution treated above the solvus temperatures for S-phase or θ -phase and quenched. At age hardening

Designation	Formula	CAS Registry Number	Cu, %	Mg, %
θ	Al ₂ Cu	[12004-15-8]	54	negligible
\mathbf{S}	Al_2CuMg	[12004-18-1]	46	$1\overline{7}$
Т	Al_6CuMg_4	[12253-80-7]	25	28
β	Al_3Mg_2	[12004-68-1]	negligible	38

Table 19. Intermetallic Phases in AI-Cu-Mg Alloys

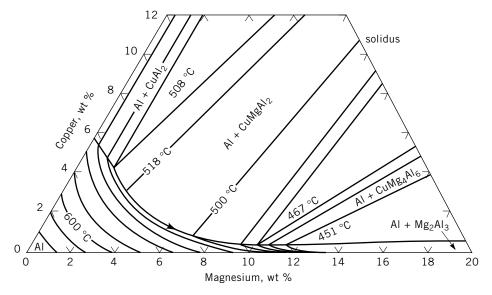


Fig. 22. Solidus for aluminum-rich Al-Cu-Mg alloys.

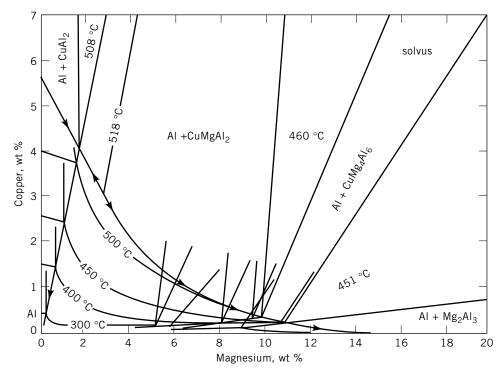


Fig. 23. Solvus for aluminum-rich Al-Cu-Mg alloys.

Designation	Formula	CAS Registry Number	Mg, %	Zn, %
$\begin{array}{c} \mathbf{M} \text{ or } \mathbf{\eta} \\ \mathbf{T} \\ \boldsymbol{\beta} \end{array}$	$\begin{array}{c} MgZn_2\\ Al_2Mg_3Zn_3\\ Al_3Mg_2 \end{array}$	$egin{array}{c} [12032-47-2] \ [12004-33-0] \ [12004-68-1] \end{array}$	$17 \\ 30-20 \\ 38$	79 25–70 negligible

Table 20. Intermetallic Phases in Al-Mg-Zn Alloys

temperatures the solvus curves are at very low copper and magnesium contents, and appreciable supersaturation is achieved. As magnesium increases above the ratio in S-phase the amount of this phase that can be formed decreases, so the amount of age hardening decreases. The excess magnesium contributes to solid solution strengthening. Excess copper is restricted by the solubility of θ -phase. The precursors to both θ - and S-phases are heterogeneously nucleated during elevated temperature precipitation heat treatments. Cold-working after quenching and prior to artificial aging increases the density of dislocations that nucleate precipitation, thus refining the precipitate structure and increasing strength.

Al-Mg-Zn. Although neither aluminum-rich binary Al-Zn nor Al-Mg alloys are precipitation hardenable, the ternary system is a source of alloys strengthened in this manner. The intermetallic phases encountered in aluminum-rich alloys are shown in Table 20. Alloy compositions are selected for precipitation of an M- or η -phase precursor because T-phase is less effective as a strengthener. Commercially important alloys always contain more zinc than magnesium to provide attractive combinations of strength, extrudability, and

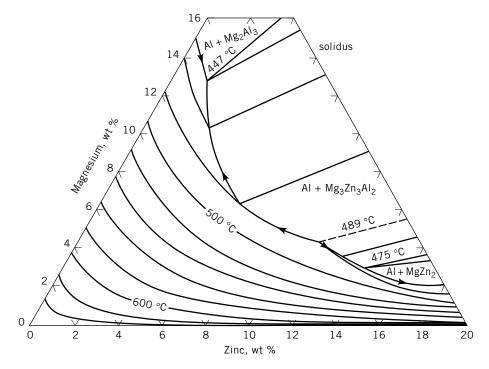


Fig. 24. Solidus for aluminum-rich Al–Zn–Mg alloys.

weldability. As a generality, resistance to stress-corrosion cracking increases as the Zn:Mg ratio increases.

The Al-Mg-Zn solidus in Figure 24 illustrates the high solid solubility of both magnesium and zinc. Melting temperatures of the eutectics are lower than in the Al-Mg-Si and Al-Cu-Mg systems. Solid-state reactions can be understood with reference to Figure 25. Substantial amounts of magnesium and zinc can be dissolved well below melting temperatures, and appreciable supersaturation and age hardening can be achieved.

Al-Cu-Li. Although the addition of Cu to Al-Li alloys increases density, the boost in strength more than offsets the density increase so that Al-Cu-Li alloy products develop higher specific strengths (strength/density) than do binary Al-Li alloy products. Furthermore, the fracture toughness and corrosion resistance of products manufactured from Al-Cu-Li alloys are higher than these properties in binary Al-Li alloy products. The phases in equilibrium at $327-350^{\circ}C$ are presented in Figure 26 (45). Designations for equilibrium and metastable phases in Al-Cu-Li alloys and their crystal structures are presented in Table 21 in order of increasing lithium content of the phase. The strengthening precipitates in most Al-Cu-Li alloys that have commercial significance are δ' and T₁. The T₂-phase decreases toughness when it precipitates on grain boundaries.

Al-Li-Mg. In aluminum-rich alloys the ternary phase, T, sometimes designated as Al₂LiMg, is encountered in addition to AlLi (δ), Al₃Mg₂ (β), and Al₁₂Mg₁₇ [12254-22-7] (γ), Figure 27. Assessment of the composition of the

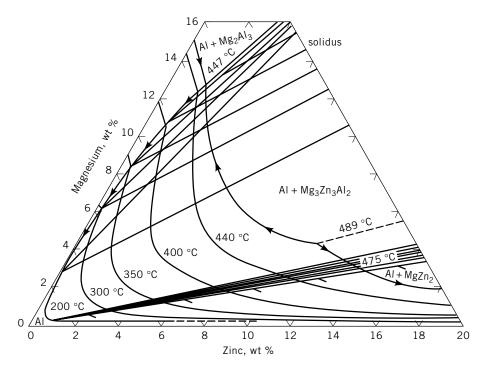


Fig. 25. Solvus for aluminum-rich Al–Zn–Mg alloys.

Vol. 2

Designation	Formula	Crystal structure
θ	Al ₂ Cu	tetragonal
θ'	Al–Cu	tetragonal
θ''	Al–Cu	tetragonal
Ω	Al–Cu	tetragonal
T_B	Al ₆ Cu ₄ Li	CaF_2
T_1	Al_2CuLi	hexagonal
R	$Al_5 CuLi_3$	Im3
T_2	Al ₆ CuLi ₃	icosohedral
T_2	Al ₆ CuLi ₃	rhombohedral
δ	Al_3Li	$L1_2$
δ	AlLi	$\overline{B32}$

Table 21. Equilibrium and Metastable Phases in AI-Cu-Li Alloys

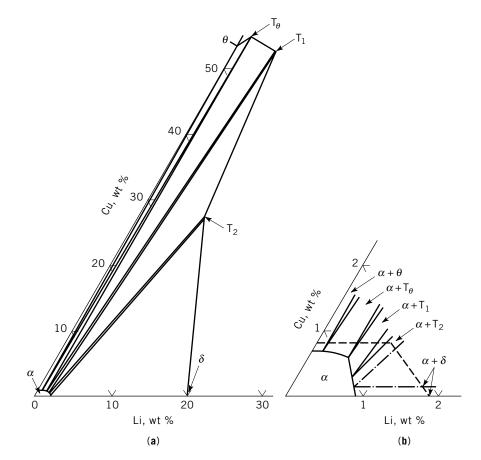


Fig. 26. Isothermal section of Al–Cu–Li system at 350° C (adapted from ref.46); (a), isothermal section; (b), limits of solid solubility for α -phase. Solid lines correspond to proposed limits for 327° C (47); dashed lines correspond to 350° C section.



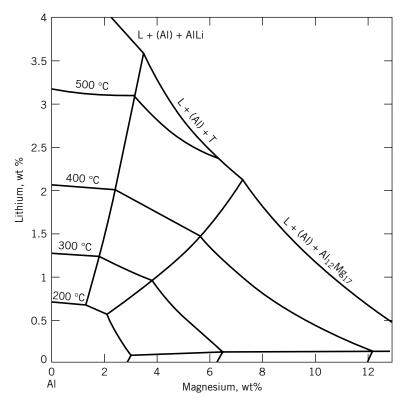


Fig. 27. Projection of solvus surface of Al–Li–Mg system, where L is liquid and T is temperature.

T-phase indicates that it contains 15.5 atomic % Mg and 32 atomic % Li. The high solubility of magnesium is unaffected by lithium, and no metastable phase in addition to Al₃Li (δ') is formed. Alloys in this system are solid solution strengthened by magnesium and age harden by precipitation of δ' .

11.3. Quaternary and Higher Alloys. Further additions to commercial aluminum alloys usually are made either to modify the metastable strengthening precipitates or to produce dispersoids.

Modifications to Precipitates. Silicon is sometimes added to Al-Cu-Mg alloys to help nucleate S' precipitates without the need for cold work prior to the elevated temperature aging treatments. Additions of elements such as tin cadmium, and indium I, to Al-Cu alloys serve a similar purpose for θ' precipitates. Copper is often added to Al-Mg-Si alloys in the range of about 0.25% to 1.0% Cu to modify the metastable precursor to Mg₂Si. The copper additions provide a substantial strength increase. When the copper addition is high, the quaternary Al₄CuMg₅Si₄ Q-phase must be considered and dissolved during solution heat treatment.

The highest strength aluminum alloy products are based on the Al–Cu– Mg–Zn system and all are strengthened by precursors to the η -phase. Copper and aluminum can substitute for zinc in MgZn₂, so η -phase may be represented as Mg (Al,Cu,Zn). No quaternary phases are a factor in aluminum-rich Al–Cu–Mg–Zn

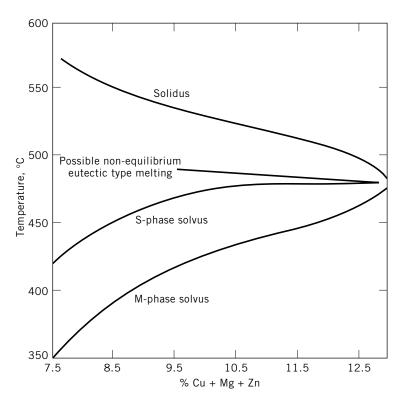


Fig. 28. Isopleth in Al-Cu-Mg-Zn system where the appropriate ratio is Cu:Mg:Zn = 1 : 1.4 : 3.3. Courtesy of E. DaPos.

alloys, but Al₂CuMg, S-phase, may be present in higher solute alloys. The isopleth in Figure 28 for alloys in the ratio of 1.6% Cu, 2.5% Mg, and 5.6% Zn illustrates that the S-phase solvus is always higher than that for η -phase for such alloys. The addition of copper to Al-Mg-Zn alloys above about 0.25% Cu increases strength and reduces the weldability and resistance to general corrosion of products, whereas additions above about 1.5% Cu significantly increase strength and resistance to stress-corrosion cracking.

Several of the Al–Li alloys developed in the 1980s contain both magnesium and copper. No quaternary Al–Cu–Li–Mg phase has been found in the alloys. The S'-phase in addition to δ' and T₁ provides precipitation hardening.

When combined with magnesium, silver has found commercial use as an alloying element in several aluminum alloys for specialized applications. It was added to an Al–Cu–Mg–Zn forging alloy to increase the resistance to stress-corrosion cracking and to an Al–Cu–Mg casting alloy to increase strength. In the late 1980s, combined Ag and Mg additions were shown to increase strength of an Al–Cu alloy (48). Additions of lithium to this basic composition further increased strength (49). The effect of the combined usage of Ag and Mg was attributed to promoting the precipitation of a phase designated Ω that was believed to contain Mg and Ag atoms, but has recently been identified in a binary Al–Cu alloy (50).

Dispersoid Formers. The three elements commonly added to precipitation hardenable alloys to form dispersoids are manganese, chromium, and zirconium. The amounts customarily used (0.5% Mn, 0.2% Cr, and 0.1% Zr) remain in supersaturated solid solution during ingot casting and precipitate as dispersoids during thermal treatment of the ingot. These dispersoids serve to minimize recrystallization during solution heat treatment of products such as plate, forgings, and extrusions which are hot-worked, and to maintain a fine recrystallized grain size in sheet and tubing which is cold-worked.

The manganese in commercial Al–Cu–Mg alloys precipitates as $Al_{20}Cu_2$ Mn_3 [12355-72-5] dispersoid particles. These dispersoids also help strengthen the products because, during quenching, they promote the formation of dislocations that serve as sites for heterogeneous nucleation during artificial aging. The chromium in commercial Al–Cu–Mg–Zn alloys precipitates as $Al_{12}Mg_2Cr$ dispersoids. These particles are more effective than $Al_{20}Cu_2Mn_3$ dispersoids in controlling recrystallization and in providing fine grain size in cold-worked products. They do not contribute to age hardening, but serve to nucleate η -phase particles heterogeneously during a slow quench, decreasing the strength of slowly quenched products because the solute is unavailable for controlled precipitation during artificial aging treatments. The zirconium in commercial Al–Cu–Mg–Zn,

Aluminum Association	Casting	A	Alloying elements, $\%$			
designation	$process^a$	Si	Cu	Mg	$Others^{b}$	Applications
208.0	S	3.0	4.0			general purpose
213.0	Р	2.0	7.0			cylinder heads, timing gears
242.0	S,P		4.0	1.5	2.0 Ni	cylinder heads, pistons
295.0	\mathbf{S}	1.1	4.5			general purpose
B295.0	Р	2.5	4.5			general purpose
308.0	Р	5.5	4.5			general purpose
319.0	S,P	6.0	3.5			engine parts, piano plates
A332.0	P	12.0	1.0	1.0	2.5 Ni	pistons, sheaves
F332.0	Р	9.5	3.0	1.0		pistons, elevated temperatures
333.0	Р	9.0	3.5	0.3		engine parts, meter housings
355.0	S,P	5.0	1.3	0.5		general: high strength, pressure tightness
356.0	S,P	7.0		0.3		intricate castings: good strength, ductility
360.0	D	9.5		0.5	2.0 Fe max	marine parts, general purpose
380.0	D	8.5	3.5			general purpose
A413.0	D	12.0				large intricate parts
443.0	D	5.3			2.0 Fe max	carburetors, fittings, cooking utensils
B443.0	S,P	5.3			0.8 Fe max	general purpose
514.0	Ś			4.0		hardware, tire molds, cooking utensils
520.0	S			10.0		aircraft fittings
A712.0	\mathbf{S}		0.5	0.7	$6.5\mathrm{Zn}$	general purpose

Table 22. Compositions of Aluminum Foundry Alloys

^a S, sand cast; P, permanent mold cast; D, pressure die cast.

^bAluminum and impurities constitute remainder.

Vol. 2

Al–Cu–Li, and Al–Cu–Mg alloys precipitates as metastable Al₃Zr, β' , dispersoids. Products which contain β' -phase dispersoids are not as quench sensitive as those which contain Al₁₂Mg₂Cr. Alloys in the Al–Mg–Si system may contain either manganese, chromium, or zirconium. Some Al–Mg–Zn alloys contain both chromium and manganese, and at least one contains all three dispersoid forming elements.

11.4. Foundry Alloys and Their Characteristics. Unalloyed aluminum does not have either mechanical properties or casting characteristics suitable for general foundry use yet both can be greatly improved by the addition of other elements. The most common addition is silicon which enhances fluidity, increases resistance to hot-cracking, and improves pressure tightness. Because binary Al–Si alloys have relatively low strengths and ductility, other elements such as copper and magnesium are added to obtain higher strengths through heat treatment. The compositions of representative foundry alloys are shown in Table 22, and typical mechanical properties are presented in Table 23.

The alloys are identified by a series of three-digit numbers where the first digit indicates the alloy group as shown. The aluminum is at least 99% pure.

Alloy and temper	Tensile strength, MPa ^a	Yield strength, MPa ^a	Elongation, %	Brinell hardness
Sand castings				
208.0-F	145	95	2.5	55
242.0 - T21	185	125	1	70
242.0 - T77	205	160	2	75
295.0 - T4	220	110	9	60
295.0 - T6	250	165	5	75
319.0 - F	185	125	2	70
319.0 - T6	250	165	2	80
355.0 - T6	240	170	3	80
256.0 - T6	225	165	3	70
B443.0-F	130	55	8	40
514.0 - F	170	85	9	50
520.0 - T4	330	180	16	75
A712.0–T5	240	170	5	75
Permanent mold castings				
242.0-T61	325	290	0.5	110
308.0 - F	195	110	2	70
319.0 - F	235	130	2.5	85
319.0 - T6	275	185	3	95
F332.0-T5	250	195	1	105
355.0 - T6	290	185	4	90
356.0 - T6	260	185	5	80
B443.0-F	160	60	10	45
Die castings				
360.0	305	170	3	75
380.0	315	160	3	80
A413.0	290	130	3	80
443.0	225	95	9	50

Table 23. Mechanical Properties of Aluminum Foundry Alloys

^{*a*} To convert MPa to psi, multiply by 145.

Vol. 2			ALUMINU	JM ANI	D ALUM	INUM AI	LLOYS	327
First digit	1	2	3	4	5	7	8	9
Element	Al	Cu	Si–Cu–Mg	\mathbf{Si}	Mg	Zn	Zn	Other

In addition to these elements, foundry alloys may contain a small amount of titanium, for grain refinement, as well as small additions of manganese, chromium, or nickel. A high strength Al–Cu–Mg alloy for aircraft use contains silver for added strength by modifying the precipitate phase. Alloys intended for pressure die casting may have high iron contents to resist welding to the dies. Lower grades of the same alloys may be used in sand casting and permanent mold castings with some benefits to mechanical properties. Castings are produced in an F temper (as-cast) and a T temper (heat treated) where higher strengths or other special characteristics are desired.

Die castings produced in a cavity which has been evacuated contain significantly less porosity and hence, are more ductile. Such castings were produced on an experimental basis in the 1980s. This process can product some parts which compete with either forged or sheet metal components.

11.5. Wrought Alloys and Their Characteristics. Alloys for the production of wrought products are selected for fabricability as well as their physical, chemical, and mechanical properties. Usually, these alloys are less highly alloyed than those for foundry use and contain less iron and silicon. A series of alloys based on the eutectic Al-Fe-Si composition, however, has been developed to provide good combinations of strength and formability in thin sheet products. The compositions of some of the more common alloys are shown in Table 24. The alloys are identified by four-digit numbers, where the value of the first digit identifies the alloy type and principal alloying addition. The aluminum is at least 99% pure.

First digit	1	2	3	4	5	6	7	8
Element	Al	Cu	Mn	\mathbf{Si}	Mg	Mg+Si	Zn	Other

In addition to these principal alloying elements, which provide solid solution strengthening and/or precipitation strengthening, wrought alloys may contain small amounts of titanium and boron [7440-42-8], B, for control of ingot grain size, and ancillary additions of chromium, manganese, and zirconium to provide dispersoids. All commercial alloys also contain iron and silicon.

Mechanical properties of wrought aluminum alloy mill products depend on temper as well as on chemical composition. The letter O following the alloy designation indicates a final annealing operation to achieve lowest strength and highest ductility. The letter H indicates that the product is in a strain-hardened condition or temper as a result of cold rolling, drawing, or other types of working. The first digit following the H indicates whether the product received some thermal treatment after cold working; the second digit implies property level. The letter T signifies a heat treatment to obtain solute precipitation and

			All	oy elem	ents, %				
Aluminum Association designation	Si	Fe	Cu	Mn	Mg	Cr	Zn	$Others^{a}$	Applications
1100			0.12					$1.0 \mathrm{Si} + \mathrm{Fe} \mathrm{max}$	cooking utensils, heat exchanger
1350								0.5 max	electrical conductor
2014	0.8		4.4	0.8	0.5				aircraft structures, and forced wheels
2024			4.4	0.6	1.5				aircraft structures,
2195			4.0		0.6			1.1 Li,	aerospace structure, welded
								0.12 Zr,	
								$0.4~\mathrm{Ag}$	
2219			6.3	0.3				0.1 V,	aerospace structures, welded
								0.18 Zr,	
								0.06 Ti	
2519			5.9	0.3	0.2			$0.1{ m V},0.18{ m Zr}$	armor and aerospace structures, welded
3003			0.12	1.1					general purpose, cooking utensils
3104			0.15	1.0	1.1				general purpose, can body sheet
3105				0.6	0.5				building products, bottle caps (sheet)
5052					2.5	0.25			general purpose sheet
5083				0.7	4.4	0.15			pressure vessels, marine applications
5182				0.35	4.5				can lids, automotive sheet
5657			~ ~ ~		0.8				bright trim and lighting sheet
6022	1.0		0.05		0.55				automotive body sheet
6111	0.8		0.70	0 5	0.7				automotive body sheet
6013	0.8		0.8	0.5	1.0	0.00			tubing and aerospace structures, welded
6061	0.6		0.25		1.0	0.20			general purpose, structures, forged truck wheels
$\begin{array}{c} 6063 \\ 6201 \end{array}$	$\begin{array}{c} 0.4 \\ 0.7 \end{array}$				0.7				general purpose, building products (extrusions) electrical conductor
7005	0.7			0.45	0.8	0 1 9	4 5	0.14 Zr	
7005			1.6	0.40	$\begin{array}{c} 1.4 \\ 2.5 \end{array}$	$0.13 \\ 0.25$	$\begin{array}{c} 4.5\\ 5.6\end{array}$	0.14 ZF	truck and, railroad cars (extrusions) aircraft structures
7075 7150			$1.0 \\ 2.2$		$\frac{2.5}{2.3}$	0.20	5.6 6.4	0.12 Zr	aerospace structures
8079	0.2	1.0	4.4		2.0		0.4	0.14 21	packaging and household foil
8079	0.2 0.7	0.8							packaging foil, formed containers
0011	0.1	0.0							packaging ton, tor med containers

 Table 24. Typical Compositions of Wrought Aluminum Alloys (Major Alloying Elements Only)

^{*a*} Aluminum and impurities constitute remainder.

hardening. The numbers following the T further define the condition of the product by indicating the type of thermal or working operation employed in producing the material.

Mechanical properties also depend on product form and test direction because the manufacturing operations used to produce the mill products may significantly affect the final crystallographic texture and extent of mechanical fibering. For example, the longitudinal yield strength of alloy 7075–T6 rod produced by axisymmetric extrusion may be as much as 140 MPa (20,000 psi) higher than that of 7075–T6 sheet. The typical long-transverse mechanical properties of some wrought aluminum alloys in the form of sheet or plate are presented in Table 25.

12. Thermal Treatment of Alloys

Aluminum alloys are subjected during manufacture to a variety of thermal treatments that range from heating to assist fabrication, to heating for control of final properties. Although the natural oxide film on aluminum provides good protection against surface oxidation and deterioration during such treatments, controlled atmospheres are sometimes employed for products requiring minimum surface oxide such as foil and sheet for reflectors. The atmosphere may be nitrogen or burned producer gas that is dried prior to use in the furnace. The introduction of sulfur compounds into furnace atmospheres should be avoided because in the presence of moisture sulfur compounds tend to break down the protective aluminum oxide film permitting further oxidation to occur. Nascent hydrogen is a product of such a reaction and may diffuse into the metal, forming voids or blisters, especially in the high strength Al-Cu-Mg or Al-Cu-Mg-Zn alloys. Such problems can be minimized by using low dew point atmospheres, eliminating sulfur compounds, and paying careful attention to recommended times and temperatures of heat treatment. Additional protection can be obtained by adding small quantities of boron trifluoride BF₃, or one of several fluoroborate compounds to the furnace atmospheres. These fluorides tend to form protective films that resist breakdown by moisture and sulfur compounds.

12.1. Homogenization. Ingots are usually preheated prior to rolling, forging, or extrusion to increase workability. The process is commonly referred to as homogenization because chemical segregation of the major alloying elements that are completely soluble in the solid-state is reduced. In addition, however, supersaturation of elements such as manganese, chromium, and zirconium is relieved during the preheat operation, so these elements become more segregated when they precipitate as dispersoids. Also during the homogenization treatment, metastable compounds may transform into the more stable equilibrium form. Incipient melting is usually avoided during preheating, but homogenization treatments are often close to eutectic or solidus temperatures, so care must be taken.

12.2. Annealing. The resistance to further deformation of aluminum alloy products at elevated temperatures reaches a steady value after a modest strain when the rate of formation of fresh dislocations is balanced by the rate

330 ALUMINUM AND ALUMINUM ALLOYS

Alloy and temper	Tensile strength, MPa^a	Yield strength, MPa ^a	Elongation,%	Brinell hardness	$egin{array}{c} { m Elastic} \ { m modulus,} \ { m MPa}^a imes 10^3 \end{array}$
1100-0	90	35	35	23	69
1100-H14	125	115	9	32	69
1100-H18	165	150	5	44	69
1350 - O	85	30	-		69
1350–H19	185	165			69
2014–T6	485	415	13	135	73
2024 - T3	485	345	18	120	73
2024–T81	485	450	7	125	73
2021 101 2195-T8	585	545	8	120	10
2100 - 10 2219 - T62	415	290	10	110	73
2219–102 2219–T81	455	$\frac{250}{350}$	10	123	73
2519–181 2519–T87	500	450	10	120	72
3003–O	110	40	30	28	69
3003–H14	150	145	8	40	69
3003–H14	200	145	4	55	69
3003-1110 3004-0	180	70	20^{4}	$\frac{55}{45}$	69
3004–0 3004–H34	240	200	20 9	45 63	69 69
	$\frac{240}{285}$		9 5	63 77	69 69
3004–H38		250	3 24	11	
3105 - 0	115	55			69 60
3105-H25	180	160	8	47	69 70
5052-O	195	90	25	47	70
5052-H34	260	215	10	68	70
5052-H38	290	255	7	77	70
5083–O	290	145	22	65	71
5083-	315	225	16	82	71
H321					
5182–O	270	130	23	64	71
5654 - H25	185	145	9		69
6013 - T6	395	350	11		69
6022 - T4	230	120	28		68
6061 - O	125	55	25	30	69
6061 - T4	240	145	22	65	69
6061 - T6	310	275	12	95	69
6063 - T6	240	215	12	73	69
6111 - T4	265	130	25		69
7005 - T53	395	345	15	105	70
7075 - T6	570	505	11	150	72
7075 - T76	525	450	11		72
7075 - T73	505	415	11		72
7150 - T77	600	565	10		71
8011-O	45	95	20		

Table 25. Long Transverse Properties of Wrought Aluminum Alloy Products

^{*a*} To convert MPa to psi, multiply by 145.

of annihilation. This process is known as dynamic recovery. During deformation processing by hot rolling, the metal temperature has a tendency to decrease. When this happens the rate of dynamic recovery decreases, so the resistance to further deformation increases because the dislocation density increases. In the rolling of sheet to thicknesses below about 4 mm, the final 25 to 50% reduction is usually done cold to provide close dimensional control. In-process

annealing is employed to decrease the dislocation density thereby increasing the plasticity of the hot-rolled metal prior to cold rolling. This thermal process also modifies the crystallographic texture, a very important consideration in producing products requiring control of anisotropy. During cold rolling, the dislocation density progressively increases with increasing strain, so for the thinnest sheet or foil, more than one in-process anneal may be employed. The temperatures employed for annealing are usually in the range of 350–400°C.

Annealing is also employed as a final mill operation to produce a material having high formability for subsequent customer shaping or forming operations. For precipitation hardenable alloys, the cooling rate must be controlled so that the equilibrium phases precipitate as coarse, nonstrengthening particles. Some tempers of strain-hardenable alloy products are produced by partial annealing or recovery treatments to provide attractive combinations of strength and formability. Highly cold-worked products are heated for combinations of time and temperature sufficient to provide enough energy to rearrange and eliminate some of the dislocations introduced during cold working but insufficient to allow the product to recrystallize by the motion of high angle grain boundaries.

12.3. Solution Heat Treatment. Solution heat treatment is the first stage of a series of operations to achieve precipitation hardening. The product is heated to a high temperature to dissolve as many soluble particles as practicable. Times for adequate dissolution depend on the size of the particles to be dissolved. Thick castings generally require many hours because the particles are a combination of products of eutectic decomposition and of precipitates which form and coarsen during the slow cool of the casting. Thin sheet may require less than a minute provided that the process was controlled so that the precipitate particles did not coarsen during fabrication. Heating is usually performed in an electrical resistance furnace, but molten salt is used for higher heating rates to produce fine grain size in sheet. Much sheet is solution heat treated in a continuous web, fed from a coil into a horizontal furnace.

12.4. Quenching. After solution treatment, the product is generally cooled to room temperature at such a rate to retain essentially all of the solute in solution. The central portions of thicker products cannot be cooled at a sufficient rate to prevent extensive precipitation in some alloys. Moreover, some forgings and castings are deliberately cooled slowly to minimize distortion and residual stress produced by differential cooling in different portions of the products. Cold water, either by immersion or by sprays, is the most commonly used cooling medium. Hot water or a solution of a polymer in cold water is used when the highest rates are not desired. Dilute Al-Mg-Si and Al-Mg-Zn extrusions can be effectively solution heat treated by the extrusion process; therefore, they may be quenched at the extrusion press by either air or water.

12.5. Precipitation Heat Treatment. The supersaturated solution produced by the quench from the solution temperature is unstable, and the alloys tend to approach equilibrium by precipitation of solute. Because the activation energies required to form equilibrium precipitate phases are higher than those to form metastable phases, the solid solution decomposes to form G-P zones at room temperature (natural aging). Metastable precursors to the equilibrium phases are formed at the temperatures employed for commercial precipitation heat treatments (artificial aging).

		Alloy 6061		Alloy 2024			
Aging time	Tensile strength, MPa ^a	Yield strength, MPa ^a	$\begin{array}{c} {\rm Elongation,} \\ \% \end{array}$	Tensile strength, MPa ^a	Yield strength, MPa ^a	Elongation, %	
5 min	165	55	28	365	155	23	
$30\mathrm{min}$	170	60	28	370	170	23	
1 h	175	65	28	385	195	23	
$2\mathrm{h}$	185	70	27	415	225	23	
4 h	195	80	27	440	265	23	
8 h	205	90	26	455	275	23	
1 day	220	105	25	460	285	22	
1 wk	235	125	24	465	290	22	
1 mo	250	130	24	470	290	21	
$1{ m yr}$	260	140	23	470	290	21	

Table 26. Age Hardening of Aluminum Alloys 6061 and 2024 at Room Temperature after Heat Treatment and Quench

^a To convert MPa to psi, multiply by 145.

Natural Aging (Room Temperature Precipitation Heat Treatments) Certain alloys are capable of developing commercially useful properties when the products are allowed to age at room temperature. In general, the properties of 2xxx alloy products stabilize after about a week, and those of 6xxx alloy products attain about 90% of their peak properties after the same time period (Table 26). Products of these alloys are referred to as being in the T4 temper after about one week natural aging. For several Al–Cu–Mg alloys, cold working a few percent before natural aging is complete significantly increases strength relative to material in a T4 temper. The T3 temper designation is used to describe such products. In contrast to the behavior of 2xxx and 6xxx alloy products, properties of 7xxx alloy products continue to change at a logarithmic rate for decades. Consequently, naturally aged 7xxx alloy products are not used for

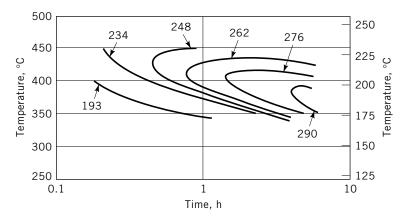


Fig. 29. Effects of time and temperature of precipitation treatments on yield strength of alloy 2036–T4 sheet. Numbers represent strength in MPa. To convert MPa to psi, multiply by 145.

commercial applications. The W temper designation accompanied by a time is used to describe 7xxx alloy products in naturally aged conditions.

Artificial Aging (Elevated Temperature Precipitation Heat Treatments). Most precipitation hardenable alloy products are heated at slightly elevated temperatures after solution treatment and quenching to accelerate age hardening. Effects of time and temperature on yield strength of alloy 2036 sheet are illustrated in Figure 29 (51). The T6 temper is generally used to designate material aged by the practice which produces the highest practicable strength. When cold work prior to artificial aging produces a significant positive effect on strength, the T8 temper designation is employed for material worked and aged to the highest practicable strength. Multistep aging treatments are sometimes employed to produce T7 tempers which enhance the combination of strength and resistance to exfoliation and stress-corrosion cracking of 7xxx alloy products.

13. Shaping and Fabricating of Alloys

Aluminum alloys are commercially available in a wide variety of cast forms and in wrought mill products produced by rolling, extrusion, drawing, or forging. The mill products may be further shaped by a variety of metal working and forming processes and assembled by conventional joining procedures into more complex components and structures.

13.1. Melting and Casting. For energy savings and economy, some aluminum is alloyed and cast into ingot at smelting plants. Alloy ingot is then shipped to fabricating plants for conversion into mill products such as plate, forgings, extrusions, and tubing. Considerable scrap is generated in such mill operations, and plants remelt the scrap and cast ingots to salvage the metal. In remelting aluminum for the production of new ingot, selected mill scrap and purchased scrap are combined with sufficient pure metal and additions in the form of alloys rich in the alloying elements. Melting temperatures are in the range of $700-750^{\circ}$ C; casting temperatures vary with alloy but typically are about 50° C above the temperature of initial solidification.

In remelting for the production of ingot, dross is formed in substantial quantities and is collected by skimming. Dross may consist of up to 5% of the melt where clean mill scrap is used but is much higher for operations using painted foil or post-consumer scrap. The primary components of dross are aluminum oxide and entrained aluminum plus small amounts of magnesium oxide, aluminum carbide, nitride, and extraneous matter. Such dross is generally treated in rotary furnaces using fluxes of sodium chloride and potassium chloride to recover the metal values.

Scrap that is unsuitable for recycling into products by the primary aluminum producers is used in the secondary aluminum industry for castings that have modest property requirements. Oxide formation and dross buildup are encountered in the secondary aluminum industry, and fluxes are employed to assist in the collection of dross and removal of inclusions and gas. Such fluxes are usually mixtures of sodium and potassium chlorides. Fumes and residues from these fluxes and treatment of dross are problems of environmental and economic importance, and efforts are made to reclaim both flux and metal values in the dross.

Concern for the environment has prompted legislation which encourages recycling (qv) of aluminum beverage containers. Billions of used beverage containers are returned every year to the primary aluminum companies (about 62% of the aluminum cans produced in 2000 were recycled), and technology has been developed to remelt this thin scrap metal with acceptable loss from oxidation. The use of recycled metal has obviated the need for additional smelting capacity, thus saving energy and minimizing cost increases of aluminum products.

After remelting and skimming, the molten metal is treated to remove dissolved hydrogen (the only gas soluble in aluminum), inclusions, and undesirable trace elements such as sodium. Generally this is accomplished by bubbling chlorine or a mixture of chlorine and nitrogen through the molten metal by means of graphite tubes. In large-scale modern operations use is made of in-line filtering and fluxing systems between the holding furnace and the casting station. Choice between deep-bed filters having a counter flow of inert gas and disposable foam ceramic filters depends on quality and economic considerations (52). In-line processes are more efficient than furnace fluxing, and their use reduces hydrogen, inclusion content, and undesirable trace elements to very low levels without significant fume generation and air pollution.

Solidification of molten aluminum containing equilibrium volumes of hydrogen (Table 6) can result in significant porosity because of the greatly reduced solubility of hydrogen in solid aluminum. Commercial filtering and fluxing practices reduce hydrogen contents of the molten metal to an operating level where this is usually not a problem. Hydrogen contents of between about 0.06 and 0.2 ppm are usually obtained in the final product depending on the alloy. The solid solubility of hydrogen is considerably higher in Al–Li alloys, hence they can tolerate more hydrogen without inducing porosity (52).

Most ingot for fabrication into rolled products, forgings, or extrusions is produced by the direct chill (DC) process or a modification. The process employs a short mold having a moveable bottom. During casting the bottom of the mold is moved downward through a spray of water that cools the mold and chills the ingot. Ingot length is limited only by the supply of metal and the depth of the casting pit. Rectangular cross-section ingot for rolling flat products is typically 40 to 60 cm thick and may be as much as 120 cm in width. Ingot having a round cross section is routinely cast in diameters to 90 cm.

Since the early 1980s, electromagnetic (EM) casting, where an electromagnetic field is used to contain the molten metal during casting, has been gaining increased acceptance (53). Because the EM process provides the closest approach to continuous heat removal, the surface defects associated with the DC processes are largely eliminated.

Some aluminum alloys are cast as strip or rod for fabrication into sheet, foil, or wire by introducing the molten metal directly between rolls or between moving plates or steel bands that form the desired shape. Casting operations of this type have the advantage of eliminating capital investment in large break-down mills and extrusion presses. The more rapid solidification also reduces the constituent size and increases the amount of supersaturated solute. The process is limited to 1xxx, 3xxx, and certain 8xxx alloys which have a small freezing range. **13.2. Fabrication.** After the preheat or homogenization step, the ingots may be fabricated directly. Often, however, the preheated ingots are reheated in a separate operation before the first metal working operation. Bulk deformation temperatures usually range from about 350 to 500°C.

Rectangular ingots are generally broken down using a four-high reversing mill. Some gauges may be rolled to completion on a reversing mill, but thinner plate gauges are usually transferred to a series of rolling mills for fabricating to final gauge. Thicker sheet gauges, above about 5 mm, are generally hot-rolled to flat sheet on such a continuous hot line. Thinner gauges are usually coiled at an intermediate gauge as they exit the continuous hot line, annealed, then cold-rolled about 25% or more to final gauge. Sheet may be annealed and cold-rolled to foil. Thin sheet wider than the equipment used for continuous solution heat treatment must be produced by a batch process as flat sheet.

In extrusion, a heated length of ingot (billet) is forced under pressure to flow from a container through a die opening to form an elongated shape or tube. In the direct extrusion process the metal is pushed through the die. In the indirect extrusion process the die is forced into the metal. Productivity is higher using the indirect process because friction of the billet with the container walls is eliminated. The surface layers of the ingot used for the indirect process must be machined (scalped) because the surface of the billet becomes the surface of the extruded product in this process. Extrusion can economically produce many shapes, including hollows, that would be difficult or expensive to produce by alternative fabricating processes. Extruded rod or tube is frequently employed as stock in the production of drawn wire or tubing. Extrusion is sometimes used to produce starting billet for forging.

Forgings are produced by pressing or hammering ingots or billets either into simple shapes on flat dies or into complex shapes in cavity dies. Several sets of dies may be employed in arriving at the final shape. Equipment varies from simple drop hammers and mechanical presses to large hydraulic presses.

Most aluminum mill products are used in the manufacture of more complex shapes. This can be accomplished by conventional metal removal techniques and by common fabricating and joining procedures. The latter include welding, brazing, soldering, and adhesive bonding, as well as mechanical methods of joining. Methods of fabricating include bending, deep drawing, stamping, stretch forming, impact extrusion, ironing, and swaging. The bodies of two-piece carbonated beverage cans, the largest market for aluminum sheet, are produced at high rates (about 200–300 per minute per bodymaker) by stamping a disk, drawing the disk into a cup, ironing to elongate the cup into a can, shearing to trim the can, and swaging to provide the neck.

Intricate shapes which once had to be made by joining a large number of parts are made by a process known as superplastic forming. In this process, aluminum alloy sheet that has been processed to develop an extremely fine grain size (typically about 10 micrometers in diameter) is slowly deformed either into a female die or over a male die. For those components that require metal removal, techniques include shearing, grinding, and a variety of common machining procedures. Aluminum is also being successfully processed using high speed machining techniques that employ ceramic tools and special equipment.

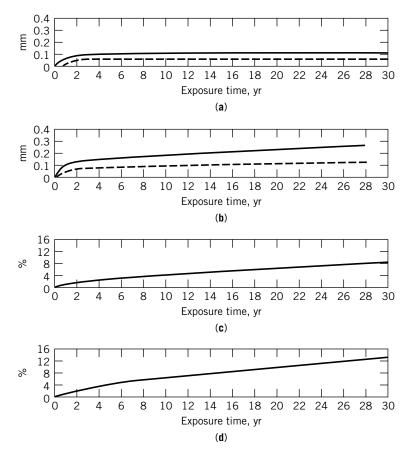


Fig. 30. Weathering of wrought aluminum alloys 1100, 3003, and 3004: (a) and (b), — maximum and --- average depth of pitting-type corrosion; (c) and (d), loss in tensile strength; in industrial (a and c) and seacoast (b and d) environments.

14. Corrosion

Aluminum and aluminum alloys are employed in many applications because of the ability to resist corrosion. Corrosion resistance is attributable to the tightly adherent, protective oxide film present on the surface of the products. This film is 5–10 nm thick when formed in air; if disrupted it begins to form immediately in most environments. The weathering characteristics of several common aluminum alloy sheet products used for architectural applications are shown in Figure 30. The loss in strength as a result of atmospheric weathering and corrosion is small, and the rate decreases with time. The amount of corrosion that occurs is a function of the alloy as well as the severity of the corrosive environment. Wrought alloys of the Al, Al–Mn, Al–Mg, and Al–Mg–Si types have excellent corrosion resistance in most weathering exposures including industrial and seacoast atmospheres. Alloys based on additions of copper, or copper, magnesium, and zinc, have significantly lower resistance to corrosion.

337

Solution	Potential, V^a
Al_3Mg_2	-1.24
$Al + 4 MgZn_2$	-1.07
$Al + 4 Zn^b$	-1.05
$MgZn_2$	-1.05
Al_2CuMg	-1.00
$Al + 1 Zn^b$	-0.96
$\mathrm{Al} + 7~\mathrm{Mg}^b$	-0.89
${ m Al}+5~{ m Mg}^b$	-0.87
Al_6Mn	-0.85
99.95 Al	-0.85
$Al + 1 Mg_2Si$	-0.83
$al + 1 Si^{b}$	-0.81
$\mathrm{Al} + 2\mathrm{Cu}^b$	-0.75
Al_2Cu	-0.73
$AI + 4 Cu^b$	-0.69
Al_3Fe	-0.56
Al ₃ Ni	-0.52
Si	-0.26

Table 27. Electrode Potentials of Aluminum SolidSolutions and Intermetallic Particles

 a 0.1 N calomel scale, measured in an aqueous solution of 53 g/L NaCl + 3 g/L H_2O_2 at 25 °C.

^b Solid solution.

Atmospheric corrosion is electrochemical in nature and depends on the flow of current between anodic and cathodic areas. The resulting attack is generally localized to particular features of the metallurgical structure. Features that contribute to differences in potential include the intermetallic particles and the electrode potentials of the matrix. The electrode potentials of some solid solutions and intermetallic particles are shown in Table 27. Iron and silicon impurities in commercially pure aluminum form intermetallic constituent particles that are cathodic to aluminum. Because the oxide film over these constituents may be weak, they can promote electrochemical attack of the surrounding aluminum matrix. The superior resistance to corrosion of high purity aluminum is attributed to the small number of these constituents.

Intermetallic particles formed by interaction of aluminum and alloying elements such as copper, magnesium, lithium, and zinc also have electrode potentials that differ from those of aluminum or the solid solutions in which they exist. If such particles are finely divided and uniformly distributed, their effect on corrosion is minimal. During quenching or aging treatments, however, precipitates may localize at grain boundaries, and render them susceptible to intergranular exfoliation corrosion or stress-corrosion cracking (SCC). In the 1960s, a series of tempers was developed for commercial Al-Cu-Mg-Zn alloys which modify the precipitate structure so that the products are highly resistant to these phenomena (54) even in the short-transverse direction. These tempers are designated T73, highly resistant to both SCC and exfoliation corrosion; T76, resistant to exfoliation corrosion and more resistant to SCC than products in T6 tempers, and T74, corrosion characteristics intermediate to T73 and T76. Because the strength of products in these T7 tempers was as much as 20% less than that possible using the T6 temper, in the late 1980s a process was developed that provided T6 strength and T76 corrosion characteristics (52). The process was first commercialized on alloy 7150 in and later alloy 7055 as the T77 temper. These materials have been specified for upper wing skins and other aircraft structure that is dominated by compressive loading.

The resistance to corrosion of some alloy sheet is improved by cladding the sheet with a thin layer of aluminum or aluminum alloy that is anodic to the base alloy. These anodic layers are typically 5-10% of the sheet thickness. Under corrosive conditions, the cladding provides electrochemical protection to the core at cut edges, abrasions, and fastener holes by corroding preferentially. Aircraft skin sheet is an example of such a clad product.

Aluminum alloys are used widely for processing, handling, and storing a variety of chemicals. Aluminum generally has a high resistance to corrosion by chemical solutions in the pH range of 4.5–8.5 because the protective oxide film is relatively stable within this range. In strongly acidic or alkaline solutions, the film is less stable and resistance to corrosion is impaired. Dry inorganic salts are usually not corrosive to aluminum. Organic acids and alcohols can be handled in aluminum equipment if a trace of water is present to maintain the oxide film.

15. Finishes for Aluminum

Finishes for aluminum products can be both decorative and useful. Processes in use include anodic oxidation, chemical conversion coating, electrochemical graining, electroplating (qv), thin film deposition, porcelain enameling, organic coating, and painting. Some alloys respond better than others to such treatments.

Anodic oxidation is an electrochemical process in which the oxide film is increased in thickness by making the product the anode in a cell containing a suitable electrolyte and an inert cathode (see Electrochemical processing). Sulfuric acid solutions are widely employed as electrolytes for anodizing; they produce clear oxide coatings on pure aluminum and high purity Al-Mg and Al-Mg-Si alloys. As the purity of the metal decreases, iron and silicon and other impurities and their reaction products form in the oxide film and decrease its transparency. This imparts a gray appearance to the finish. Sheet for reflectors and for automotive and appliance trim is made from high purity alloys to obtain maximum brightness and specularity. Oxide thickness generally does not exceed 0.01 mm for such products. Colored oxide films are produced by anodizing in mixed acid electrolytes the principal components of which are organic sulfonic acids and a small amount of sulfuric acid. Colors range from pale yellow to dark bronze and black. The color results from modification of the oxide and inclusion of intermetallic particles, metal, and reaction products in the oxide. Such coatings are widely employed in architectural applications for aluminum and are usually 0.02–0.03 mm thick.

Thin, porous anodic films provide an excellent base for paint (qv) coatings (qv), as do certain chemical and mechanical treatments. These are employed to disrupt the natural oxide film on aluminum and eliminate contaminants that

would interfere with wetting of the surface by organic coatings. Chemical conversion coatings convert a portion of the base alloy to one of the components of a chemical film which is then integral with the metal surface. Carbonate, chromate, and phosphate films are produced in this manner and have excellent adhesion qualities. Chemically produced metallic coatings (qv) are also used extensively to provide a base for organic coatings. The zinc immersion coating is the most widely employed of the chemical displacement films.

Zinc, tin, and nickel immersion coatings are used as a base for electroplating. Anodizing and mechanical roughening treatments are also employed. Good surface preparation is required for good adherence of electrodeposits, which can be of any commonly electroplated metal. Electroplating conditions and solutions are the same as those for steel and other metals (see METAL SURFACE TREATMENTS). Deposition of thin films of oxides or other ceramics by vapor deposition or other means is beginning to be commercially applied to aluminum products (see FILM DEPOSITION TECHNIQUES).

Porcelain enameling requires the use of frits and melting temperatures of 550°C or below. Enamels are applied over chemical conversion coatings that are compatible with the frit. Alloy selection is important to obtain good spall resistance. Alloys 1100, 3003, and 6061 are employed most extensively among wrought products and alloy 356 for castings.

16. Uses

Transportation accounted for 35% of U.S. consumption in 2001, packaging, 25% building 15%, consumer durables, 8% electrical, 7%, and other, 10% (34). Table 28 gives data on U.S. shipments by market.

16.1. Containers and Packaging. Aluminum packages exploit the barrier properties of aluminum (impervious to light and gas transmission) and corrosion resistance of selected alloys. By the end of 1999, the steel beverage can had been virtually eliminated from the market in the United States. Worldwide approximately 180 billion aluminum cans are produced each year, with more than 1/2 of that consumption in North America. The two-piece aluminum can has been continuously improved to reduce metal content and maintain performance and reliability in the demanding beer and soft drink market. Alloys 3004 (can body) and 5182 (can lid) have also been optimized to improve can making efficiency with thinner sheet. Aluminum convenience food cans for items

Table 28. U.S. Shipments of Aluminum by Market, × 10 ^{5 a}										
market	1975	1980	1985	1990	1995	1999				
building and construction	1,019	1,189	1,375	1,208	1,215	1,468				
transportation	775	1,012	1,383	1,454	2,608	3,601				
containers and packa- ging	914	1,512	1,865	2,165	2,308	2,316				
consumer durables	342	398	484	509	621	760				
electrical	552	633	632	595	630	739				

Table 29	110	Shipments	of	Aluminum	by	Markat	v 1∩ ³ a
Table 28.	0.5.	Snipments	ΟΤ	Aluminum	pv	Market.	× 10

^a Aluminum Statical Review, 1980–1999

such as meat, pudding and fish are also produced in large quantities. Other aluminum rigid containers are the aerosol can, produced from an impact extrusion process and formed containers for frozen foods, pie plates, and baked goods.

Aluminum foil continues to be an important portion of the packaging business. Foil may be produced as household wrap ("Reynolds Wrap") or used in a laminate with paper or plastic for packaging of cereal, frozen foods or pharmaceutical products.

16.2. Building and Construction. Despite the growth of other markets for aluminum products, the worldwide building and construction industry continues to consume vast quantities of aluminum in a wide variety of applications. Good resistance to weather, adequate strength, light weight, and the ability to accept a wide range of finishes are advantages for aluminum in these applications. Alloys such as 3003, 3004, and 3105 produced as sheet are used for residential siding, gutters, industrial and farm roofing, and siding. Alloy 6063 and 6060 extrusions are typically used for both structural and decorative door and window frame structures. Aluminum wire and rod are used to fabricate nails, screen wire, and many types of fasteners. Anodized and/or painted panels of many colors and textures are used for building panels and store fronts.

16.3. Transportation. Aluminum serves the worldwide transportation market for aerospace, automotive and truck, railroad, and marine transportation. Aluminum's low density, moderate cost, high damage tolerance, and wide range of product forms and tempers in comparison to other materials makes it ideal for most types of vehicles where life cycle costs are an issue.

Aerospace. The high strength/weight ratio and relatively moderate cost of aluminum alloys still make them attractive for aircraft construction. The heat treatable 2xxx and 7xxx alloys are used bor both supporting structure and skins for wings, fuselages and other components of military and commercial airplanes. Weldable alloys are used for construction of large fuel tanks for the Space Shuttle. The choice of alloy, temper, and final product depend upon the mechanical properties required for the initial design and the expected service conditions over the life of the aircraft. Static strength and fracture toughness, corrosion resistance, and response to cyclic (fatigue) loads and corrosion are all considered in selecting the appropriate aluminum product for the application.

Ground Transportation. Aluminum's biggest growth has been in the use of cast components (engines, wheels, cylinder heads) for cars and trucks. Side panels of aluminum sheet and floors made from extrusions help to save weight in the truck trailer market. The use of aluminum in the typical family vehicle grew from 75 kg in 1991 to more than 11 kg in 2000 (56). New alloys with higher strength after paint baking and improved formability have made significant inroads into the sheet metal applications such as hoods and deck lids of automobiles. Brazed heat exchangers are replacing copper radiators in large quantities for automotive applications. Aluminum radiators and other heat exchangers may be produced in a variety of ways, but typically use a special clad brazing sheet and formed aluminum foil (fin stock). On the high end of the market, high performance luxury and sports vehicles have been produced which exploit the advantages of various aluminum product forms: sheet extrusions, and castings. When designed and joined properly the weight savings and performance of these all aluminum vehicles are truly impressive. Most important, however, is

the experience gained in producing these vehicles that will be put to use in higher volume models in future years.

Railroad and Marine. Aluminum continues to be designed into new railroad vehicles either for hauling commodities such as coal or high performance cars for passenger trains. The design and construction of new high speed "fast ferries" for use in the Pacific regions have raised the demand for higher performance welded 5xxx aluminum sheet and plate structures. Large 5xxx plates up to 200 mm thick are used for the construction of LNG (Liquefied Natural Gas) tanker ships. Aluminum canoes, pleasure craft, and deck houses for naval vehicles also employ significant amounts of aluminum sheet, plate, and extrusions.

Other. Aluminum is used in the home as cooking utensils (the first commercial use of aluminum), refrigerators, air conditioners, satellite dishes, appliances, insect screening, and hardware. It is also for toys, sporting equipment, lawn furniture, lawn mowers, and portable tools. In many of these applications, anodized or colored coatings are employed for decorative purposes.

Aluminum is an excellent conductor of electricity, having a volume conductivity 62% of that of copper. Because of the difference in densities of the two metals, an aluminum conductor weighs only half as much as a copper conductor of equal current carrying capacity. Because of its lightness, aluminum has been used extensively for overhead transmission lines. Both standed aluminum conductors and steel core stranded conductors are employed. Alloys include conductor grades 1350 and 6201 along with newer compositions. Aluminum is also used as cable sheathing, replacing the neutral in three-phase systems. Aluminum is used in insulated cable, for bus bars, and for transformer windings, magnet wire, building wire, and 99.99% aluminum is used to connect integrated circuits. An aluminum-air fuel cell has exhibited a high energy output, which results from the characteristic energy density of aluminum. These cells can be used in electric vehicles, emergency power sources, and portable electronic devices (57).

Aluminum has many applications in the chemical and petrochemical industries such as for piping and tanks in alloys 1100, 3003, 6061, 6063, and the Al-Mg alloys. Aluminum is chosen for its resistance to corrosion by the chemicals involved as well as for its mechanical properties, light weight, and thermal conductivity. Aluminum is also used in the storage and packaging of chemicals. Applications range from large Al-Mg alloy tanks for the storage of ammonium nitrate and liquefied natural gas to collapsible tubes for dispensing pharmaceuticals and toiletries. The absence of any harmful reaction with the microorganisms involved in the manufacture of pharmaceuticals is obviously important in this application of aluminum.

BIBLIOGRAPHY

"Aluminum and Aluminum Alloys" in *ECT* 1st ed., Vol. 1, pp. 591–623, by J. D. Edwards and F. Keller, Aluminum Research Laboratories, Aluminum Company of America; in *ECT* 2nd ed., Vol. 1, pp. 929–990, by P. Vachet, Cie de Produits Chimiques et Électrométallurgiques, Péchiney; in *ECT* 3rd ed., Vol. 2, pp. 129–188, by W. A. Anderson and W. E. Haupin, Aluminum Company of America; in *ECT* 4th ed., Vol. 2, pp. 184–251 by James T. Stally and Warren Haupin, Aluminum Company of America; "Aluminum and Aluminum Alloys" in *ECT* (online), posting date: December 4, 2000, by James T. Stally and Warren Haupin, Aluminum Company of America.

CITED PUBLICATIONS

- J. Hatch, ed., Aluminum: Properties and Physical Metallurgy, American Society for Metals, Metals Park, Ohio, 1984.
- 2. E. Gebhardt, M. Becker, and A. Dorner, Z. Metallkd. 44, 573 (1953).
- M. W. Chase, Jr. and co-workers, eds., JANAF Thermochemical Tables, 3rd ed., J. Phys. Chem. Ref. Data. 14 (1985).
- 4. R. A. Andrews, R. T. Webber, and P. A. Spohr, Phys. Rev. 84, 994 (1951).
- 5. C. C. Bidwell and C. L. Hogan, J. Appl. Phys. 18, 776 (1947).
- 6. T. E. Pochapsky, Acta Metall. 1, 747 (1953).
- 7. A. Roll and H. Motz, Z.Metallkd. 48, 272 (1957).
- 8. G. Hass and J. E. Waylonis, J. Opt. Soc. Am. 51, 719 (1961).
- 9. R. P. Madden, L. R. Canfield, and G. Hass, J. Opt. Soc. Am. 53, 620 (1963).
- 10. H. E. Bennett, M. Silver, and E. J. Ashley, J. Opt. Soc. Am. 53, 1089 (1963).
- 11. C. E. Ransley and H. Neufield, J. Inst. Met. 74, 599 (1947-1948).
- 12. W. Eichenauer, K. Hattenbach, and Z. Pebles, Z. Metallkd. 52, 682 (1961).
- T. G. Pearson, *The Chemical Background of the Aluminum Industry*, Monogr. 3, The Royal Institute of Chemistry, 1955.
- 14. P. A. Foster, Jr. J. Am. Ceram. Soc. 43(8), 437 (1960).
- 15. Ibid., 58(7-8), 288 (1975).
- A. Rostum, A. Solheim, and A. Sterten, *Light Metals 1990*, Minerals, Metals, and Materials Society, Warrendale, Pa., 1990, 311–323.
- 17. E. W. Dewing, Can Metall. Q. 13(4), 607 (1974).
- 18. S. K. Ratkje and T. Forland, Light Met. 1, 223 (1976).
- Joint Army-Navy-Air Force Thermochemical Tables, 2nd ed., National Bureau of Standards, Washington, D.C., 1971.
- 20. U.S. Pat. Appl. 2002/0056650 (May 16, 2002), S. P. Ray (to Alcoa, Inc.).
- C. N. Cochran and co-workers, Use of Aluminum in Automobiles—Effect on the Energy Dilemma, SAE Paper 750421, Society of Automotive Engineers, Warrendale, Pa., Feb. 1975.
- 22. A. Wrigley, Am. Metal Market, 108(7), 6 (Jan. 12, 2000).
- 23. P. T. Stroup, Trans. Metall. Soc. AIME 230, 356 (Apr. 1964).
- 24. A. F. Saavedra, C. J. McMinn, and N. E. Richards, in H. Y. Sohn and E. S. Geskin, eds., *Metallurgical Processes for the Year 2000 and Beyond*, Minerals, Metals, and Materials Society, Warrendale, Pa., 1988, 517–534.
- 25. A. Mote and co-workers, Denki Kagaku 55(9), 676 (1987).
- 26. Can. Chem. Process. 51(2), 45; (3), 75 (1967).
- J. F. Elliot, Phys. Chem. of Carbothermic Reduction of Aluminum, DOE/ID/12467-3 (DE89015201), June 16, 1989.
- 28. L. M. Foster, G. Long, and M. S. Hunter, J. Am. Chem. Soc. 21, 1 (1956).
- 29. A. F. Saavedra and R. M. Kibby, J. Met. 40, 32-36 (Nov. 1988).
- 30. H. Ginsberg, Aluminum Düsseldorf 23, 131 (1941).
- 31. L. Evans and W. B. C. Perrycoste, B. I. O. S. Final Report No 1757, Item. No. 21 Manufacture of Super-Purity Aluminum at the Vereinigte Aluminum Werke, Erftwerk, Grevenbroich, UK, March and July 1946.
- 32. W. G. Pfann, J.Met. 4, 747 (July 1952).
- 33. U.S. Pat. 3,303,019 (Feb. 7, 1967), S. C. Jacobs (to Aluminum Company of America).

- 34. P. A. Plunkert, "Aluminum," *Mineral Commodity Summaries*, U.S. Geological Survey, Reston, Va., Jan. 2002.
- 35. P. A. Plunkert, M. George, and L. Roberts, "Aluminum" *Minerals Yearbook*, U.S. Geological Survey, Reston, Va., 2000.
- Nonferrous Metal Data 1960–1999 American Bureau of Metal Statistics, New York, 1960–1999.
- 37. ASTM Annual Book of Standards, Vol. 03.06, Sect. 3, American Society for Testing and Materials, Philadelphia, Pa., 1989.
- "Methods of Chemical and Spectrochemical Analysis of Aluminum" in *Light Metals* and *Their Alloys*, Technical Committee ISO/TC 79, International Organization for Standardization, Geneva, Switzerland, 1979.
- K. Grjotheim, H. Kvande, K. Motzfeldt, and B. J. Welch, Can. Metall. Q. 11(4), 585 (1972).
- 40. C. N. Cochran, W. C. Sleppy, and W. B. Frank, J. Met. 22(9), 54 (1970).
- 41. Aluminum Association of America, Washington, D. C., press release, April 19, 2001.
- B. Dinman, "Aluminum," in E. Bingham, B. Cohrssen, and C. H. Powell, eds., *Patty's* Toxicology, 5th ed., John Wiley & Sons, Inc., New York, 2001 Chapt. 31.
- J. T. Staley, in A. K. Vasudévan and R. D. Doherty, eds., Aluminum Alloys: Contemporary Research and Applications, Academic Press, San Diego, Calif., 1989, pp. 3–31.
- 44. T. Massalski, ed., *Binary Alloy Phase Diagrams*, Vol. 1, American Society for Metals, Metals Park, Ohio, 1986.
- 45. H. M. Flower and P. J. Gregson, Mater. Sci. Tech. 33, 81 (1987).
- 46. H. K. Hardy and J. M. Silcock, J. Inst. Met. 84, 423 (1955).
- 47. L. F. Mondolfo, Aluminum Alloys: Structure and Properties, Butterworths, London, 1976.
- 48. I. J. Polmear, in E. A. Starke, Jr. and T. H. Sanders, Jr., eds., Aluminum Alloys: Their Physical and Mechanical Properties, 1986, pp. 661–674.
- 49. J. R. Pickens, F. H. Heubaum, T. J. Langan, and L. S. Kramer in T. H. Sanders, Jr. and E. A. Starke, Jr., eds., Proc. 5th Int. Conf. on Al-Li Alloys, Vol. 3, Williamsburg, Va., 1989, 1397–1414.
- 50. A. Garg, Y. C. Chang, and J. Howe, Scrip. Met. 24, 677 (1990).
- 51. R. F. Ashton, I. Broveman, P. R. Sperry, and J. T. Staley in Ref. 1, p. 180.
- 52. P. N. Anyalebechi, E. J. Talbot, and D. A. Granger in E. W. Lee, E. H. Chia, and N. J. Kim, eds., *Light Weight Alloys for Aerospace Applications*, The Minerals, Metals, and Materials Society, Warrendale, Pa., 1989.
- D. A. Granger in A. K. Vasudévan and R. D. Doherty, eds., Aluminum Alloys: Contemporary Research and Applications, Academic Press, San Diego, Calif., 1989, pp. 109–135.
- 54. J. T. Staley, R. J. Rioja, R. K. Wyss, and J. Liu, Processing to Improve High Strength Aluminum Alloy Products, 9th Int. Conf. on Production Research, Cincinnati, Ohio, 1987.
- 55. R. J. Bucci, L. N. Mueller, L. B. Vogelsang, and J. W. Gunnick in Ref. 51, pp. 295–322.
- 56. A. Wrigley, Am. Metal Market, 108(38), 6 (Feb. 28, 2000).
- 57. Am. Metal Market, 108(133), 4 (July 12, 2000).

ROBERT E. SANDERS, JR. Alcoa Technical Center