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LECTURE NOTES ON NONFERROUS METALLURGY (MTE 528)

BY

ENGR. UDOCHUKWU MARK

DEPARTMENT OF MATERIALS & METALLURGICAL ENGINEERING
SCHOOL OF ENGINEERING & ENGINEERING TECHNOLOGY,
FEDERAL UNIVERSITY OF TECHNOLOGY, OWERRI



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**COURSE CODE: MTE 528 COURSE TITLE: NONFERROUS METALLURGY COURSE
CREDIT LOAD: [L-Lectures = 2; T-Tutorials = 0; P-Practical = 0; U-Credit Unit = 2]**

COURSE CONTENT

- ❖ A general survey of nonferrous metals and alloys of engineering importance. Basis for their uses. Low density materials.
- ❖ Metallurgy of the alloys of aluminium e.g. Al-Mg-Si, Al-Mn, Al-Zn alloys. Basis for alloying, Age hardening of Al-alloys. Deformability and strength, deformation defects.
- ❖ Beryllium and magnesium based alloys, Production characteristics.
- ❖ Metallurgy of titanium alloys, High temperature applications, Aerospace applications, α - and β phase stabilizers. Commercial titanium alloys.
- ❖ Copper and Zinc based alloys. Common grades of brasses and their importance.

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ASSESSMENT

There will be two types of assessment in this course. The first one comprises an **assignment** and a **quiz** and the second is the examination at the end of the course. The assignment and quiz count for 30% of your total course mark. At the end of the course, you are required to write an **examination** of about two to three hours duration. This examination will count for 70% of your total course mark. The table below shows how the actual marks will be distributed.

Assessment	Actual Marks	% of Course Marks
Assignment	20 marks	20%
Quiz	10 marks	10%
Final Examination	70 marks	70%
Total	100 marks	100%

PREAMBLE

Metallurgy is the scientific study of the extraction, refining, alloying, and fabrication of metals and of their structure and properties. This definition embraces all branches of metallurgy, namely Chemical Metallurgy (extraction and corrosion), Physical Metallurgy and Mechanical Metallurgy. In the study of nonferrous metallurgy, we shall briefly touch all the branches of metallurgy but with respect to selected nonferrous metals and their alloys.

Why study nonferrous metallurgy? In finding answers to this poser, we may need to ponder the following questions.

- *In the history of mankind, which came first: copper or steel?*
 - *Why is tungsten used for light bulb filaments?*
 - *What materials are used as “catalysts” in the automobile catalytic converter? What do they “convert?”*
 - *What materials are used to manufacture biomedical implants for hip prostheses?*
 - *What materials power the aerospace age?*
- We shall find answers to these questions and more as we progress in this course.

ANCIENT HISTORY OF METALLURGY

Nonferrous metals were the first metals used by humans for metallurgy. Gold, silver and copper [coinage metals] existed in their native crystalline yet metallic form. These crystals, though rare, were enough to attract the attention of humans. Less susceptible to oxygen [corrosion or oxidation resistance] than most other metals, they can be found even in weathered outcroppings. Copper was the first metal to be forged; it was soft enough to be fashioned into various objects by cold forging, and it could be melted in a crucible. Gold, silver and copper replaced some of the functions of other materials, such as wood and stone, owing to their ability to be shaped into various forms for different uses. Due to their rarity, gold, silver and copper artifacts were treated as luxury items and handled with great care. The use of copper also heralded the transition from the Stone Age to the short-lived Copper Age. The Bronze Age, which succeeded the Copper Age, was again heralded by the invention of bronze, an alloy of copper with the nonferrous metal tin. As early as Gen. 4:22, Tubal-Cain forged all kinds of tools out of copper (possibly as bronze or

brass) and iron; authenticating that these metals were well known in antiquity [Exo. 25:3; Deut. 8:9]

THE CLASSIFICATION OF METALS – ECONOMIC PERSPECTIVE

Out of over 100 known elements, about 80 are metals, but only 8 of these namely Fe, Al, Cu, Pb, Sn, Mg, Zn and Ni are sufficiently abundant and cheap to provide common engineering materials (Table 1). It can be seen that O, Si, Al, Fe, Ca, Na, Mg, K, Ti, H and Cu dominate more than 98% of the Earth’s crust. About 15 other metals (the most important of which are Au, Ag, Cr, Mn, Ti, Co, W, Be) fulfill specific often indispensable applications.

The Periodic Table classifies metals, metalloids, and nonmetals according to their chemical properties; it does not indicate their relative economic importance (Table 2). The fact that iron and its alloys (pure iron, wrought iron, steels and cast irons) are by far the most important metals from the perspective of production and use, has led to the classification of metals as **ferrous** (iron and its alloys) and **nonferrous** (all other metals and metalloids). In effect, metals are divided into two groups: iron and others. This is justified because the production of iron in one year exceeds the production of all other metals combined in ten years. Although the usage of nonferrous metals is much less than that of ferrous metals, their practical importance is very great and thus calls for closer studies. For example, it is nonferrous metallurgy that provides materials for aerospace (where high strength and low weight are desirable) and for electricity distribution in the form of Al and Cu cables of high conductivity. In many applications (e.g. transportation and construction), weight is a critical factor. To relate the strength of the material to its weight, a **specific strength**, or **strength-to-weight ratio**, is defined as

specific strength $\frac{\text{trench}}{\text{ensity}}$. Table 3 compares the specific strength of steel, some high-strength nonferrous alloys, and polymer-matrix composites. Some applications of metals are given in Table 4.

When Columbus discovered the New World [1492 A.D.], not more than half a dozen metals were known to Man. Today, man has isolated all seventy of them and 'constructed' a number of new ones, such as plutonium and neptunium, which previously did not exist in nature. One may wonder if all these metals will be useful to the engineer. Nevertheless, who would have thought, even as late as the 1950s,

say, that by the end of the twentieth century we would have used samarium and neodymium (in magnets), hafnium (in nuclear plant), yttrium and lanthanum (in high temperature alloys) and erbium (in cancer therapy generators)?

NONFERROUS METALS

The nonferrous metals may be divided into numerous groups according to their production, properties, use, and occurrence (Table 5). This

classification is arbitrary since one metal may be placed in more than one group.

Primary Metals: From the inception of the Nineteenth Century, copper, nickel, lead, zinc, and tin and their alloys found use as substitutes for iron in industrial applications that required particular properties in which cast irons and steels were lacking (e.g. corrosion resistance). This explains why these metals are known as primary metals. Typical uses of primary metals are as shown in Table 6.

Table 1: Relative Abundance of Elements in the Lithosphere (Earth's Crust)

Element	%	Element	%	Element	%	Element	%
Actinium	$3 \cdot 10^{-14}$	Europium	$1 \cdot 10^{-4}$	Neodymium	$1.7 \cdot 10^{-3}$	Scandium	$5 \cdot 10^{-4}$
Aluminum	8.13	Fluorine	$8 \cdot 10^{-2}$	Neon	-	Selenium	$9 \cdot 10^{-6}$
Americium	-	Francium	-	Neptunium	-	Silicon	27.72
Antimony	$1 \cdot 10^{-4}$	Gadolinium	$5 \cdot 10^{-4}$	Nickel	$8.0 \cdot 10^{-3}$	Silver	$2 \cdot 10^{-6}$
Argon	-	Gallium	$1.5 \cdot 10^{-3}$	Niobium	$2.4 \cdot 10^{-3}$	Sodium	2.83
Arsenic	$5 \cdot 10^{-4}$	Germanium	$7 \cdot 10^{-4}$	Nitrogen	-	Strontium	$1.5 \cdot 10^{-2}$
Astatine	-	Gold	$1 \cdot 10^{-7}$	Osmium	-	Sulfur	$5.2 \cdot 10^{-2}$
Barium	$4.3 \cdot 10^{-2}$	Hafnium	$4.5 \cdot 10^{-4}$	Oxygen	46.6	Tantalum	$2.1 \cdot 10^{-4}$
Beryllium	$6 \cdot 10^{-4}$	Helium	-	Palladium	$1 \cdot 10^{-6}$	Technetium	-
Bismuth	$2 \cdot 10^{-5}$	Holmium	$1.15 \cdot 10^{-4}$	Phosphorus	0.12	Tellurium	$1.8 \cdot 10^{-7}$
Boron	$1.0 \cdot 10^{-3}$	Hydrogen	0.14	Platinum	$5 \cdot 10^{-7}$	Terbium	$2 \cdot 10^{-4}$
Bromine	$2.5 \cdot 10^{-4}$	Indium	$1.0 \cdot 10^{-5}$	Plutonium	-	Thallium	$3 \cdot 10^{-5}$
Cadmium	$1.5 \cdot 10^{-5}$	Iodine	$3 \cdot 10^{-6}$	Polonium	$3 \cdot 10^{-14}$	Thorium	$1.1 \cdot 10^{-3}$
Calcium	3.63	Iridium	$1.0 \cdot 10^{-7}$	Potassium	2.59	Thulium	$2.0 \cdot 10^{-5}$
Carbon	$3.2 \cdot 10^{-2}$	Iron	5.00	Praseodymium	$5 \cdot 10^{-4}$	Tin	$4.0 \cdot 10^{-3}$
Cerium	$2.5 \cdot 10^{-3}$	Krypton	-	Promethium	-	Titanium	0.44
Cesium	$3.2 \cdot 10^{-4}$	Lanthanum	$1.7 \cdot 10^{-3}$	Protactinium	$8 \cdot 10^{-11}$	Tungsten	$1.0 \cdot 10^{-4}$
Chlorine	$4.8 \cdot 10^{-2}$	Lead	$1.5 \cdot 10^{-3}$	Radium	$1.3 \cdot 10^{-10}$	Uranium	$4 \cdot 10^{-4}$
Chromium	$2.0 \cdot 10^{-2}$	Lithium	$6.5 \cdot 10^{-3}$	Radon	-	Vanadium	$1.5 \cdot 10^{-2}$
Cobalt	$2.3 \cdot 10^{-3}$	Lutetium	$7.5 \cdot 10^{-5}$	Rhenium	$1.0 \cdot 10^{-7}$	Xenon	-
Copper	$7.0 \cdot 10^{-3}$	Magnesium	2.09	Rhodium	$1 \cdot 10^{-7}$	Ytterbium	$1.5 \cdot 10^{-4}$
Curium	-	Manganese	0.10	Rubidium	$3.1 \cdot 10^{-2}$	Yttrium	$1.0 \cdot 10^{-3}$
Dysprosium	$2 \cdot 10^{-4}$	Mercury	$5 \cdot 10^{-6}$	Ruthenium	-	Zinc	$8.0 \cdot 10^{-3}$
Erbium	$1.5 \cdot 10^{-4}$	Molybdenum	$2.3 \cdot 10^{-4}$	Samarium	$3 \cdot 10^{-4}$	Zirconium	$2.2 \cdot 10^{-2}$

Abundance range	Element
Over 10%	O (46.6); Si (27.7)
1-10%	Al (8.1); Fe (5.0); Ca (3.6); K (2.6); Na (2.8); Mg (2.1)
0.1-1%	C; H; Mn; P; Ti
0.01-0.1%	Ba; Cl; Cr; F; Rb; S; Sr; V; Zr
0.001-0.01%	Cu; Ce; Co; Ga; La; Li; Nb; Ni; Pb; Sn; Th; Zn; Yt
1-10 ppm	As; B; Br; Cs; Ge; Hf; Mo; Sb; Ta; U; W; and most of the rare Earths
0.1-1 ppm	Bi; Cd; I; Ir; Tl
0.01-0.1 ppm	Ag; Pd; Se
0.001-0.01 ppm	Au; Ir; Os; Pt; Re; Rh; Ru

Table 2: The Periodic Table of the elements; numbers in parentheses are the atomic weights of the most stable or common isotopes (from Puddephatt and Monaghan, 1986; by permission of Oxford University Press. Note that 1, 2, 3 ... or IA, IIA, IIIB... and IA, IIA, IIIA ... are the New and Previous IUPAC notations respectively. Note also that most of the elements are *metals*, those within the thick boundary are *nonmetals*; close to these are mutilated boxes containing the *metalloids* or *intermediates*)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
IA	IIA	IIIB	IVB	VB	VIB	VII B	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	O
IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIII			IB	IIB	IIIB	IVB	VB	VIB	VII B	O
¹ H 1.008																	² He 4.003
³ Li 6.941	⁴ Be 9.012											⁵ B 10.81	⁶ C 12.01	⁷ N 14.01	⁸ O 16.00	⁹ F 19.00	¹⁰ Ne 20.18
¹¹ Na 22.99	¹² Mg 24.31											¹³ Al 26.98	¹⁴ Si 28.09	¹⁵ P 30.97	¹⁶ S 32.45	¹⁷ Cl 35.45	¹⁸ Ar 39.95
¹⁹ K 39.10	²⁰ Ca 40.08	²¹ Sc 44.96	²² Ti 47.90	²³ V 50.94	²⁴ Cr 52.00	²⁵ Mn 54.94	²⁶ Fe 55.85	²⁷ Co 58.93	²⁸ Ni 58.71	²⁹ Cu 63.55	³⁰ Zn 65.37	³¹ Ga 69.72	³² Ge 72.92	³³ As 74.92	³⁴ Se 78.96	³⁵ Br 79.90	³⁶ Kr 83.80
³⁷ Rb 85.47	³⁸ Sr 87.62	³⁹ Y 88.91	⁴⁰ Zr 91.22	⁴¹ Nb 92.91	⁴² Mo 95.94	⁴³ Tc 98.91	⁴⁴ Ru 101.1	⁴⁵ Rh 102.9	⁴⁶ Pd 106.4	⁴⁷ Ag 107.9	⁴⁸ Cd 112.4	⁴⁹ In 114.8	⁵⁰ Sn 118.7	⁵¹ Sb 121.8	⁵² Te 127.6	⁵³ I 126.9	⁵⁴ Xe 131.3
⁵⁵ Cs 132.9	⁵⁶ Ba 137.3	⁵⁷ La 138.9	⁷² Hf 178.5	⁷³ Ta 180.9	⁷⁴ W 183.9	⁷⁵ Re 186.2	⁷⁶ Os 190.2	⁷⁷ Ir 192.2	⁷⁸ Pt 195.1	⁷⁹ Au 197.0	⁸⁰ Hg 200.6	⁸¹ Tl 204.4	⁸² Pb 207.2	⁸³ Bi 209.0	⁸⁴ Po (210)	⁸⁵ At (210)	⁸⁶ Rn (222)
⁸⁷ Fr (223)	⁸⁸ Ra (226.0)	⁸⁹ Ac (227)	¹⁰⁴ Unq	¹⁰⁵ Unp	¹⁰⁶ Unh	¹⁰⁷ Uns											
←s-block→		←d-block→										←p-block→					
Lanthanides			⁵⁷ La 138.9	⁵⁸ Ce 140.1	⁵⁹ Pr 140.9	⁶⁰ Nd 144.2	⁶¹ Pm (147)	⁶² Sm 150.4	⁶³ Eu 152.0	⁶⁴ Gd 157.3	⁶⁵ Tb 158.9	⁶⁶ Dy 162.5	⁶⁷ Ho 164.9	⁶⁸ Er 167.3	⁶⁹ Tm 168.9	⁷⁰ Yb 173.0	⁷¹ Lu 175.0
Actinides			⁸⁹ Ac (227)	⁹⁰ Th 232.0	⁹¹ Pa 231.0	⁹² U 238.0	⁹³ Np 237.0	⁹⁴ Pu (242)	⁹⁵ Am (243)	⁹⁶ Cm (248)	⁹⁷ Bk (247)	⁹⁸ Cf (251)	⁹⁹ Es (254)	¹⁰⁰ Fm (253)	¹⁰¹ Md (256)	¹⁰² No (254)	¹⁰³ Lr (257)
←f-block→																	

Table 3: Specific Strength and cost of nonferrous metals, steels, and polymer composites

Material	Density		Tensile Strength	Specific Strength	Cost per lb
	g/cm ³	(lb/in ³)	(psi)	(in.)	(S) ^b
Aluminum	2.70	(0.097)	83,000	8.6 × 10 ⁵	0.60
Beryllium	1.85	(0.067)	55,000	8.2 × 10 ⁵	350.00
Copper	8.93	(0.322)	150,000	4.7 × 10 ⁵	0.71
Lead	11.36	(0.410)	10,000	0.2 × 10 ⁵	0.45
Magnesium	1.74	(0.063)	55,000	8.7 × 10 ⁵	1.50
Nickel	8.90	(0.321)	180,000	5.6 × 10 ⁵	4.10
Titanium	4.51	(0.163)	160,000	9.8 × 10 ⁵	4.00
Tungsten	19.25	(0.695)	150,000	2.2 × 10 ⁵	4.00
Zinc	7.13	(0.257)	75,000	2.9 × 10 ⁵	0.40
Steels	~7.87	(0.284)	200,000	7.0 × 10 ⁵	0.10
Aramid/epoxy (Kevlar, vol. fraction of fibers 0.6, longitudinal tension)	1.4	(0.05)	200,000	4.0 × 10 ⁵	—
Aramid/epoxy (Kevlar, vol. fraction of fibers 0.6, transverse tension) ^a	1.4	(0.05)	4,300	0.86 × 10 ⁴	—
Glass/epoxy (Vol. fraction of E-glass fibers 0.6, longitudinal tension)	2.1	(0.075)	150,000	2.0 × 10 ⁶	—
Glass/epoxy (Vol. fraction of E-glass fibers 0.6, transverse tension)	2.1	(0.075)	7,000	9.3 × 10 ⁴	—

^a Data for composites from Harper, C.A., Handbook of Materials Product Design, 3rd ed. 2001; McGraw-Hill. Commodity composites are relatively inexpensive; high-performance composites are expensive.

^b Costs based on average prices for the years 1998 to 2002.

Table 4: Applications and Natural Occurrence of Selected Metals

S/N	Metal Selected	Selected Applications ^a	Primary Locations ^b
1	Li	Batteries, glasses, aerospace components	US, Chile, China, Argent
2	Na	Dyes, pigments, lamps, photoelectric cells	Chile, Peru, US
3	K	Nuclear reactors, respiratory equipment	Ger., Can., France, Spain
4	Be	X-ray tubes, ship/aircraft navigation systems	US, Africa, Brazil, Rs.
5	Mg	Auto parts, coatings, photoengraving	US, Can., S. Amer., Asia
6	Ca	Lighter flints, lights, plastics stabilizer	US, Can., S. Amer., Asia
7	Sr	Glasses, ceramics, paints, TV tubes	Mexico
8	Sc	High-intensity lamps, nuclear reactors	China, US, Aus., Ind.
9	Y	Coatings, capacitors, superconductors, lasers	China, US, Aus., Ind.
10	Ti	Golf clubs, surgical implants, jet engines	US, Aus., S.A., Norway
11	Zr	Prosthetic devices, nuclear reactors	Ind.,US, Aus., S.A.
12	V	Tools, ceramics, batteries, magnets	US, Mex., Peru, Rs., S.A
13	Nb	Heat shields, electromagnets, spaceships	Japan, Rs., Can., Brazil
14	Ta	Aircraft turbines, rocket nozzles, HT vessels	Aus., Brazil, Thailand, Can.
15	Cr	Corrosion-resistant coatings, tools	S.A., Turk., Rs., Cuba, Phil.
16	Mo	Lubricants, lamp filaments, integrated circuits	US, Aus., Swe.
17	W	Filaments, coatings, missiles, tools, paints	US, Asia, S. Amer., Rs.
18	Mn	Steels, paints, batteries	US, Can., France, Ger., Ind.
19	Fe	Autos, tools, structural materials	US, Can., China, Brazil, Rs.
20	Ru	Coatings, superconductors, electrodes	S.A., Rs., US
21	Os	Fountain pen tips, pacemakers, forensics	S.A., Rs., US
22	Co	Magnets, batteries, recording media	Can., N. Africa, Swe.
23	Rh	Catalytic converters, coatings, crucibles	S.A., Rs., US
24	Ir	HT crucibles, spark plugs	S.A., Rs., US

25	Ni	Batteries, coatings, currency	Can., Rs., Aus.
26	Pd	Jewelry, dental crowns, surgical instruments	S.A., Rs., US
27	Pt	Jewelry, coatings, surgical implants, lighters	S.A., Rs., US
28	Cu	Conductive wire, pipes, currency	Chile, US, Can.
29	Ag	Jewelry, dental fillings, photography	Mex., Peru, US, Can.
30	Au	Jewelry, integrated circuits, heat shields, coatings	S.A., US, Aus., Can.
31	Zn	Coatings, pipes, highway guard rails	US, Can., Aus., China
32	Cd	Alloys, batteries, nuclear reactors	Canada, Aus., Mex.
33	Al	Auto parts, ceramics, coatings, paints	Brazil, Jamaica, Asia
34	Sn	Alloys, plating, flat glass	Bolivia, Brazil, Malaysia
35	Pb	HT vessels, pipes, sound absorbent materials	Aus., US, China, Peru
36	Ce	Lighter flints, ceramic capacitors, magnets	China, US, Aus., Ind.
37	Eu	Television screens, nuclear reactors	China, US, Aus., Ind.
38	Er	Lasers, catalysts, phosphors	China, US, Aus., Ind.

^aThese selected applications may be for the pure metal or other alloys or compounds. ^bCan. = Canada, Rs. = Russia, Aus. = Australia, Ind. = India, S.A. = South Africa.

Group	Metals	Remarks
Primary	Cu, Pb, Zn, Sn, Ni	Extensively used; second in importance to iron.
Secondary	As, Sb, Bi, Cd, Hg, Co	Mainly by-products of primary metals but also form their own deposits. Used in almost equal amounts (10–20 thousand tons annually).
Light	Be, Mg, Al, Ti	Low specific gravity (below 4.5), used mainly as material of construction.
Precious	Au, Ag, Pt, Os, Ir, Ru, Rh, Pd	Do not rust; highly priced.
Refractory	W, Mo, Nb, Ta, Ti, Zr, Hf, V, Re, Cr	Melting points above 1650 °C. Mainly used as alloying elements in steel but also used in the elemental form. Some resist high temperature without oxidation.
Scattered	Sc, Ge, Ga, In, Tl, Hf, Re, Se, Te	Do not form minerals of their own. Distributed in extremely minute amounts in the earth's crust.
Radioactive	Po, Ra, Ac, Th, Pa, U, Pu	Undergo radioactive decay. Some of them (U, Pu, and Th) undergo fission. Plutonium prepared artificially in nuclear reactors.
Rare earths	Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	Always occur together, similar chemical properties. Not rare as the name implies.
Ferroalloy metals	Cr, Mn, Si, B	Were once mainly used as alloying elements to steel, but now also used in elemental form.
Alkali	Li, Na, K, Rb, Cs	Soft and highly reactive.
Alkaline earths	Be, Mg, Ca, Sr, Ba	Higher melting point and less reactive than the alkali metals

Table 5: Commercial classification of nonferrous metals and metalloids

Secondary Metals: This group includes the metals cadmium, cobalt, and mercury and the metalloids arsenic, antimony, and bismuth. They are mainly by-products of the primary metals but also form their own deposits. They are used worldwide in almost equal amounts of about 20 000 tons annually. Table 7 shows the typical uses of secondary metals.

Light Metals: These are beryllium, aluminium, magnesium, and titanium. They are used in pure state and in alloys, characterized by lightweight and high strength hence they are valuable materials of construction (Table 8). They are reactive metals and difficult to prepare and became known in the metallic state relatively recent.

Precious Metals: This group of metals (also known as **noble metals**) is composed of gold, silver, and the

six platinum group metals: platinum, osmium (the densest element), iridium, ruthenium, rhodium, and palladium. They are all common in that they do not rust, and are highly priced – used as jewelries (Table 9).

Refractory Metals: This group of metals is composed of the transition metals tungsten, molybdenum, niobium, tantalum, titanium, zirconium, hafnium, vanadium, rhenium, and chromium and they all have high melting points. For example, tungsten melts at 3380°C, rhenium at 3180 °C, molybdenum at 2610 °C. They are mainly used as alloying elements in steel but also are used in the elemental form. Some resist high temperature without oxidation, and some are very hard, having excellent wear and abrasion resistance (Table 10).

Scattered Metals: This group of metals and metalloids is composed of scandium, germanium, gallium, indium, thallium, hafnium, rhenium, selenium, and tellurium. They do not form minerals of their own but occur in very small amounts in the ores of other common metals. Thus gallium occurs with aluminium in bauxite, selenium and tellurium in copper and nickel sulfide ores, etc. (Table 11). As a result of processing a large tonnage of ores each year, these metals are enriched in certain fractions and are usually recovered.

Radioactive Metals: These metals have the highest atomic weights in the Periodic Table starting from polonium, and include radium, actinium, thorium, protactinium, uranium, and the transmutation metals that do not occur in nature. **Rare Earth Metals:** Rare earths are a group of 13 metals that occur together and have similar chemical properties. These are cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutecium. Another member of this group is promethium, whose position in the Periodic Table is between neodymium and samarium does not occur in nature but is found in the fission products of uranium. To this group is always added lanthanum and yttrium because they also have similar properties and are associated with these metals in nature. These metals are not rare – they are widely distributed in nature and it is preferable to call them the lanthanides in reference to the first member of the group. They form their own ore deposits and also occur in phosphate rock, in iron ores, and others.

Table 6: Typical uses of primary metals

Metal	Use	%
Copper	Electrical	50
	Buildings	20
	Engineering and transport	25
	Other	5
		<u>100</u>
Lead	Batteries	35
	Pipes, sheets	15
	Gasoline additive	12
	Cable sheathing	10
	Pigments, chemicals	10
	Alloys, solder	10
	Other	7
		<u>100</u>
Zinc	Galvanizing	40
	Die casting	27
	Alloys	18
	Sheet, wire, etc.	8
	Zinc compounds	5
	Other	2
		<u>100</u>
Tin	Tinplate	50
	Solder	20
	Alloys	15
	Chemicals	3
	Other	12
		<u>100</u>
Nickel	Stainless steel	28
	Cast irons and alloy steels	20
	Nonferrous alloys	20
	High-temperature alloys	12
	Electroplating	16
	Catalysts	1
	Other	3
		<u>100</u>

Table 8: Typical uses of light metals

Metal	Use	%
Beryllium	Electric industry	37
	Electronic industry	16
	Nuclear reactors	20
	Aerospace	18
	Others	9
		<u>100</u>
Aluminum	Buildings	30
	Transportation (automotive, aircrafts)	20
	Electrical	15
	Packaging	15
	Others (reducing agent, paint)	20
		<u>100</u>
Titanium	Jet engine	84
	Chemical industry	16
		<u>100</u>
Magnesium	As metal and alloy (reducing agent)	65
	As oxide for refractories	7
	Fertilizer, paper, etc.	28
		<u>100</u>

Table 7: Typical uses of secondary metals

Metal	Use	%
Antimony	Batteries	47
	Pigments, chemicals	18
	Fire retardants	11
	Rubber, plastics	8
	Glass, ceramics	6
	Bearing alloys	4
	Other	6
	<u>100</u>	
Cadmium	Cadmium plating	50
	Plastics stabilizer	20
	Pigments	15
	Ni-Cd batteries	7
	Other	8
	<u>100</u>	
Cobalt	Alloys	45
	Magnets	30
	Paint driers	10
	Ceramics	5
	Catalysts	5
	Other	5
	<u>100</u>	
Mercury	Caustic-chlorine cells	35
	Batteries, electrical	28
	Biocidal paints	14
	Instruments	10
	Dental	5
	Agriculture	3
	Other	6
	<u>100</u>	

The annual consumption of lanthanides is about 30 000 tons. They are finding use as deoxidizers, in alloys, in the production of cast iron and steel, as catalysts, in lighter flints and flares, in the glass and ceramic industry, in optical glass as well as glass polishers, in the manufacture of ferrites for use as magnetic materials for electric motors, materials for electric motors, electronic circuits, and computers. Europium and yttrium are used in the manufacture of phosphors, producing the bright reds and greens of colour television. Because of neutron-absorption properties they are used in the manufacture of control rods in nuclear reactors. They have many other applications, e.g., in the production of more efficient fluorescent lighting, portable X-ray sources, better X-ray screens, fibre optics, quick-drying paints, synthetic gems, and others.

Table 9: Typical uses of precious metals

Metal	Use	%
Gold	Jewelry and arts	70
	Dental	9
	Space and defence	8
	Other	13
	<u>100</u>	
Silver	Silverware	29
	Photography	28
	Electrical	22
	Brazes, solder	10
	Silver batteries	3
	Other	8
	<u>100</u>	
Platinum	Catalysts	60
	Electrical	17
	Glass forming	9
	Dental, medical	5
	Jewelry, etc.	4
	Other	5
	<u>100</u>	

Table 10: Typical uses of refractory metals

Table 11: Parent ores of scattered metals

Metal	Parent ore	Concentration in ore, %	Major use
Gallium	Bauxite	0.01	Semiconductor
Germanium	Zinc sulfide	Trace	Semiconductor
Hafnium	Zircon sand	1	Nuclear reactors, control rods
Indium	Zinc sulfide	Trace	Semiconductor
Rhenium	Molybdenite concentrates from porphyry copper ores	0.07	Refractory metal
Scandium	Uranium and thorium	Trace	
Selenium	Copper sulfides	Trace	Photoelectric cells
Tellurium	Copper sulfides	Trace	
Thallium	Zinc sulfide	Trace	

Metal	Use	%
Vanadium	Ferrous alloys	80
	Nonferrous alloys	10
	Catalyst (V_2O_5)	10
		100
Chromium	Metallurgical (stainless steel)	58
	Refractories (oxide)	30
	Chemical industry (tanning of leather, electroplating)	12
		100
Molybdenum	Steel industry	80
	Chemicals	20
		100
Tungsten	Tungsten carbides	53
	Alloy steels	23
	Electrical lamps	13
	Chemicals	4
	Other	7
		100

Ferroalloy Metals: This group of metals is composed of chromium, manganese, silicon, and boron. They were once mainly used as alloying elements to steel in form of ferroalloys but now are also used in the elemental form. Thus chromium is used as a protective coating by electroplating on iron, silicon is used in the preparation of semiconductors and to convert energy from the sun directly into electricity. Manganese is used as an alloying element with aluminium and copper. Manganese dioxide is a powerful oxidizing agent. Boron carbide and boron nitride are hard materials second only to diamond.

Alkali Metals: This group is the first in the Periodic Table. Their name is derived from the fact that when reacted with water they form alkalis. Soft and highly reactive, usually not used as metals except lithium as an alloying element for aluminium, sodium as a reducing agent either alone or as an amalgam, and an alloy of 50% Na and 50% K known as NaK is used as a coolant in nuclear reactors.

The economic deposits of the alkali metals are mainly found in nature as salt deposits or in surface and subsurface waters except lithium which may also be found as a silicate; the last member of the group, francium, does not occur in nature. At one time sodium carbonate was recovered from the ashes left after burning wood by leaching with water, while potassium carbonate was recovered similarly but from ashes left after burning seaweeds.

Alkaline Earth Metals: This is the second group of the Periodic Table whose name originates from the fact that these metals form stable oxides (earths) that have alkaline reaction. For example, calcium forms the oxide CaO that dissolves in water to form calcium hydroxide. The first two members, beryllium and magnesium are of useful mechanical properties and being light, are used as light metals. The last member, radium is radioactive and of no importance as a metal.

Strontium and barium are of limited use.

SPECIFIC NONFERROUS METALS & ALLOYS

We shall be treating individual nonferrous metals and their important alloys. In accordance with the course content [syllabus & curriculum], we shall consider the following: 1.) Aluminium and its alloys; 2.) Beryllium, Magnesium and their alloys; 3.) Copper, Zinc, and their alloys; 4.) Titanium and its alloys. 5.) Nickel, Tin, Niobium and Tantalum may also be considered if time permits.

ALUMINIUM

Aluminum, Al is a silvery-white lustrous metallic element belonging to group 13 or IIIA (formerly IIIB) of the Periodic Table. It has the following property data: atomic number = 13, relative atomic mass = 27, face-centred cubic (FCC) crystal structure, lattice constant, $a = 4.0467\text{\AA}$, density = 2.7 g/cm^3 , melting point = 660°C and boiling point = 2467°C . Aluminium comprises 8% of the earth's crust by weight and is, therefore, the most abundant structural metal. As the most abundant metal in the earth's crust, aluminum is found in all aluminosilicate minerals, particularly clays, shale, schist and granite; but commercially it is extracted from **bauxite** by the electrolytic reduction of alumina, Al_2O_3 . The production of aluminium since 1965 has surpassed that of copper and now comes next to iron. It is competing with copper in the electric industry and as a material of construction. Although the electrical conductivity of aluminum is slightly lower than that of copper, it is still economical to use in preference to copper in power cables because of its lighter weight. As a material of construction, aluminum can be anodized to get a protective oxide film, which can be dyed to give a colorful appearance.

Aluminium is the most heavily consumed nonferrous metal in the world, with annual consumption at 24 million tons, according to 2003 figures. About 75% of the annual consumption is **primary aluminium** (that is, aluminium extracted from ore, as opposed to **secondary aluminium**, which is derived from scrap metal processing).

The ancient Greeks and Romans used alum $\{\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}\}$ in medicine as an astringent, and in dyeing processes. In 1761 de Morveau proposed the name —aluminl for the base metal in alum. In 1807, Davy proposed the name aluminium for the metal, undiscovered at that time, and later agreed to change it to aluminum. Shortly thereafter,

the name aluminium was adopted by IUPAC to conform to the —iuml ending of most elements. Aluminium has remained the IUPAC spelling and therefore the international standard, though Americans still refer to aluminium as —aluminuml.

The process of primary aluminium production can be divided into three independent stages, which are, as a rule, carried out at different plants.

These are:

- The actual mining of the necessary raw materials (bauxite and a variety of other ores);
- The processing of the ores and preparation of alumina (aluminium oxide);
- Production of primary aluminium from alumina.

Production (Extraction) of Aluminium

Since Humphry Davy announced in 1808 his belief that the plentiful compound alumina was the earth (oxide) of an undiscovered metal, scientists had been making efforts to obtain this new metal. Davy never made any aluminum himself; but in 1825, the Danish scientist Hans Christian Oersted (1777-1851) published his successful experiment in producing a tiny sample of the metal in the laboratory by reducing aluminum chloride with potassium amalgam. Potassium was isolated a few years earlier by Davy.

Two years later, Friedrich Wöhler (1800-1882) in Germany produced tiny globules of aluminum by the same method, and was able to demonstrate the metal's lightweight and malleability. Henri Sainte-Claire Deville in France in 1854 showed that cheaper sodium could also be used, and the first commercial plant producing small quantities of aluminum was begun in 1855. Since potassium and sodium were produced electrolytically, the process was expensive. In 1886, following the development of large-scale equipment for generating electrical power, Paul Héroult in France, and Charles Hall in the United States, independently developed a process for the direct electrolytic decomposition of Al_2O_3 . They discovered that when an electric current is passed through molten cryolite (Na_3AlF_6) containing dissolved Al_2O_3 at $980\text{--}1000^\circ\text{C}$, molten aluminum is deposited at the cathode and carbon dioxide is liberated at the carbon anode. This discovery, coupled with the process developed by Karl Josef Bayer in 1888 for the production of alumina resulted in the modern process for the production of aluminum.

In the manufacture of aluminum, there are two main stages. The first embraces the production of pure Al_2O_3 from bauxite, and the second is the reduction of this Al_2O_3 to the metal in a bath of fused cryolite.

Bauxite and the Bayer's Process

Bauxite, the principal ore of alumina varies greatly in appearance and composition, but comprises mixtures of hydrated aluminium salts with impurities in the form of oxides of iron, silicon, titanium, etc. The name bauxite is derived from the village of *Les Beaux** near Marseille in Southern France where the mineral was originally mined [*Note that *bauxite* was formerly spelt *beauxite*]. Most large deposits occur in tropical and semi-tropical regions – mainly Jamaica, Vienna, Surinam, West Africa (Ghana, Sierra Leone,), India, Russia, Hungary, Malaysia and North Australia (see Table 12). Bauxite deposits are of three main forms – **blanket**, **interlayered** and **pocket deposits**. Most of the tropical deposits are of the blanket type about 20 feet thick and are mined by both open cast and

underground methods. Pocket deposits are mined by open cast methods.

Table 12: World Bauxite Resources (January 1985 Figures)

Strictly speaking, bauxite is not a particular mineral (i.e. with fixed chemical formula), but designates various kinds of aluminum ores consisting mainly of aluminum hydroxide (see

Table 13). Three aluminum hydroxide minerals occur in bauxite: **gibbsite**, **böhmite**, and **diaspore**. They differ considerably in their physical properties, as shown in Table 14. A bauxite

deposit consists mainly of either one of these types, although cases are known when mixed hydroxides are present in one ore. Bauxites vary in color from cream to dark brown when the iron content is high. Table 15 shows the composition of a typical bauxite.

Table 13: Minerals Found in Bauxites

Minerals	Chemical composition
Gibbsite (hydrargillite)	$\alpha\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$
Böhmite	$\alpha\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$
Diaspore	$\beta\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$
Hematite	$\alpha\text{-Fe}_2\text{O}_3$
Goethite	$\alpha\text{-FeOOH}$
Magnetite	Fe_3O_4
Siderite	FeCO_3
Ilmenite	FeTiO_3
Anatase	TiO_2
Rutile	TiO_2
Brookite	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$
Kaolinite	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
Quartz	SiO_2

Table 14: Aluminium Minerals in Bauxite

	Gibbsite (hydrargillite)	Böhmite	Diaspore
Formula	$\gamma\text{-Al(OH)}_3$	$\gamma\text{-AlOOH}$	$\alpha\text{-AlOOH}$
$\text{Al}_2\text{O}_3\text{:H}_2\text{O}$ ratio	1:3	1:1	1:1
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Hardness (Moh)	2.5–3.5	3.5–4	6.5–7
Specific gravity	2.42	3.01	3.44
Refractive index	1.568	1.649	1.702
Temperature of rapid dehydration	150°C	350°C	450°C
Product of dehydration	$\chi\text{-Al}_2\text{O}_3$	$\gamma\text{-Al}_2\text{O}_3$	$\alpha\text{-Al}_2\text{O}_3$
Solubility in 100 g/l Na_2O	128	54	Insoluble
Solution at 125°C; g/l Al_2O_3			

**Table 15:
Composition of
Bauxites**

	Percentage
Al_2O_3	40–60
SiO_2	1–6
Fe_2O_3	2–25
TiO_2	1–5
$\text{CaO}+\text{MgO}$	0.2–0.6
Loss on ignition	10–30
Ga_2O_3	0.01
K_2O	0.01
P_2O_5	0.02–0.4
V_2O_5	0.01–0.1
$\text{Ln}_2\text{O}_3^{\text{a}}$	0.01
F	0.01–0.05

Typical

^aLn – lanthanide.

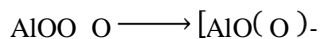
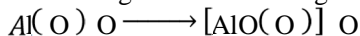
Mined bauxite is commonly subjected to crushing, washing and drying processes (**beneficiation or mineral processing**) to improve its quality. The first step in the extraction of aluminium is to reduce the bauxite to pure alumina (Al_2O_3). There are several methods but the **Bayer Process** is the most popular and usually the most efficient. The use of sodium hydroxide to leach bauxite was invented in 1892 by Karl Josef Bayer as a process for obtaining pure aluminum hydroxide, which can be calcined, to pure Al_2O_3 suitable for processing to the metal. The process involves three steps: selective dissolution of aluminum hydroxide from bauxite, precipitation of pure aluminum hydroxide from the solution, and calcination of the hydroxide to Al_2O_3 . Historically, the precipitation step was invented before the leaching step.

Crushed bauxite is usually washed to remove fine particles of clay, dried in a rotary kiln, then ground to 60 -100 mesh; the drying process is essential to facilitate grinding. Drying temperature should be less than the temperature of dehydration of aluminum hydroxides; otherwise, the solubility will be impaired.

The bauxite is treated under pressure with hot caustic soda (NaOH) which dissolves the alumina to form sodium aluminate. The residue known as red mud containing iron oxide (Fe_2O_3), titania (TiO_2) and silica (SiO_2), is filtered off and discarded. Aluminium oxide trihydrate ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) is precipitated from the liquor, washed and calcined in rotary kilns at about 980°C to give alumina in the form of white powders. The yield of alumina in the Bayer Process is approximately 1kg of alumina for each 2 kg of high grade bauxite.

About 90 million tonnes of bauxite are treated annually by this process. About 2 tonnes of bauxite yield 1 tonne of Al_2O_3 from which 0.5 tonne aluminum is produced. In addition, 2 tonnes of bauxite produce 1 tonne of waste minerals called red mud.

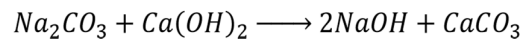
Figure 1 shows a flow sheet of the process. The reactions in leaching are the following:



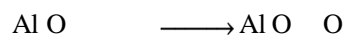
Leaching is usually carried out in mild-steel autoclaves, with direct steam injection for heating and agitation. Operating conditions depend on the type of minerals in the bauxite. Bauxites containing gibbsite are leached at a lower temperature, with

lower NaOH concentration, and for a shorter time than those containing böhmite and diaspore. The more concentrated the NaOH, the faster the rate; however, highly concentrated solutions will require excessive dilution in the later stage of precipitation, which presents difficulties in handling and filtration. Therefore, there must be an optimum concentration which compromises between digestion time and subsequent operations. Leaching time could be shortened to 374 min if the process is conducted in tube autoclaves at 330°C and 25,000 kPa; also, the settling properties of the mud are improved. In tube autoclaves, the slurry is pumped into an externally heated thick-walled tube about 30 cm in diameter and 30 – 50 m long. The major part of the heat is supplied by the slurry leaving the tube. Only at the extreme side of the tube, steam from an outside source is used for heating.

Sometimes, NaOH is formed in situ in the autoclaves by adding sodium carbonate and calcium hydroxide:



To a leach solution containing 200_250 g/l Na_2CO_3 , enough lime is added such that the solution contains about 140 g/l NaOH. Leaching is carried out at 140°C for about 1 hr. This method applies only to gibbsite, because in the case of böhmite or diaspore, a sodium hydroxide concentration above that which can be obtained directly from Na_2CO_3 and lime is required. Therefore, it is necessary to prepare NaOH separately and concentrate it by evaporation for use in leaching. The final operation in the production of alumina is the calcination of the hydroxide:



Electrolytic Reduction Of Al_2O_3

Since metallic aluminium has a strong affinity for oxygen (see Ellingham diagram), traditional smelting methods such as pyrometallurgy or carbothermy cannot reduce the alumina. The invention of the Hall-Heroult reduction process was a major breakthrough for commercial extraction of aluminium. In this process, about 20 kWh and 2 kg of alumina are consumed for each kg of aluminium produced. Due to this need for large quantities of electrical energy, aluminium smelting is always done in areas with cheap sources of electrical power, preferably hydroelectric power or generating sets associated with natural gas deposits.

Because high grade ore and cheap power are vital to the existence of the aluminium industry, much effort is being expended on the exploration

and development of new sources of raw materials [e.g. Nigeria needs to develop techniques to produce alumina from her abundant kaolinite clay deposits] and new sources of energy such as magnetohydrodynamic energy or nuclear power.

Recent work on direct reduction of aluminium ores has not been commercially successful and the industry is looking to cheap atomic power as a future source of energy supply.

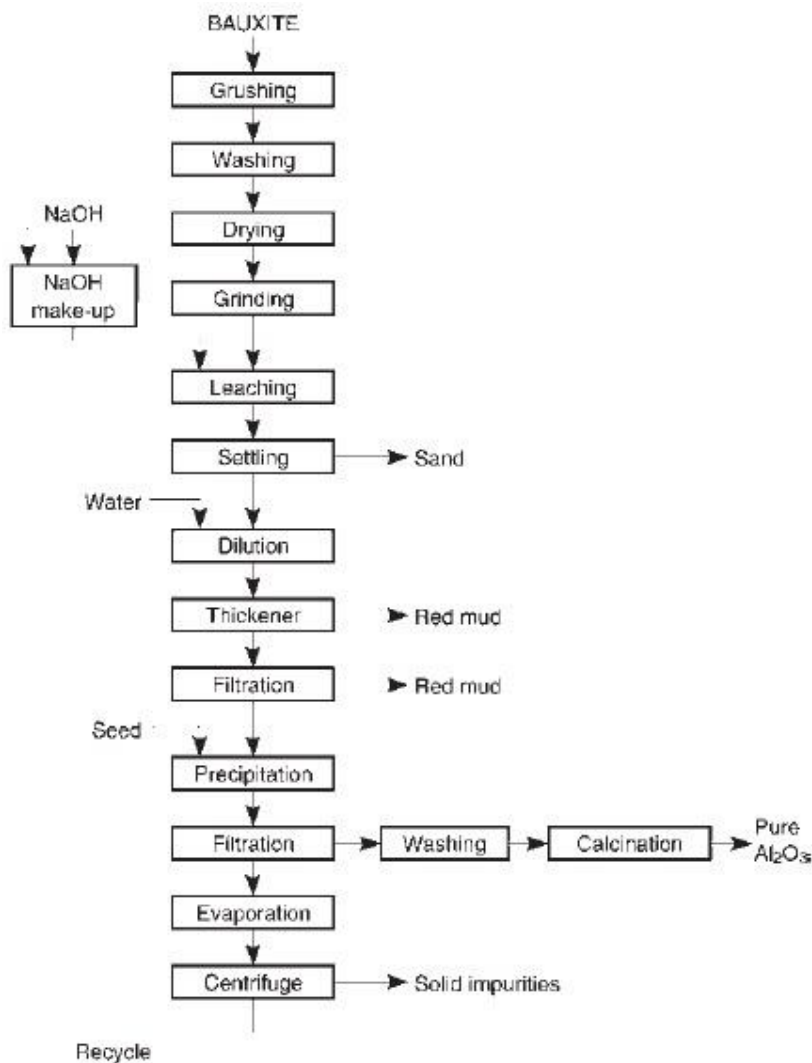


Figure 1: Flow sheet of the Bayer process

A reduction plant for aluminium is made up of one or two *pot lines* comprising a number of large steel boxes or **pots** or **electrolytic cells** lined with carbon (graphite) about 6 inches thick forming the cathode. One or more carbon anodes are dipped into each pot and are either prebaked from petroleum coke and pitch or are of the self-baking type in which the coke and pitch are continuously added as the electrode burns away. Each cell takes a direct current of between 10, 000 to 100, 000 amperes depending on its size, and operates at about 6 volts. It is usual to connect up to 150 pots in series

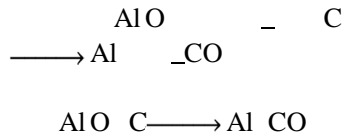
[forming a **pot line**]; the dc power being fed from tanks of rectifiers. The electrolyte employed is cryolite, a double fluoride of sodium and aluminium ($3\text{NaF} \cdot \text{AlF}_3$ or Na_3AlF_6).

Formally, natural cryolite from Ivigtût on the west coast of Greenland was used. But now synthetic cryolite produced in an extension of the Bayer Process for alumina is the usual material. The cryolite is loaded into cells as powders and melted by electric current. Alumina is then dissolved in the molten cryolite and decomposed by electrolysis into oxygen and metallic aluminium. The metallic

aluminium falls to the bottom of the cell. When the electrical resistance of the cell falls

to about 10 times its normal value, more alumina is added. The metallic aluminium is siphoned from the pots and either cast into blocks for remelting and alloying or continuously cast into large slabs for subsequent rolling or extrusion.

The cathodic product is molten aluminium and the product discharged on the anode is largely CO_2 and minor amounts of CO . The overall cell reaction may be represented by:



Cryolite was found to be the best molten salt for electrolyzing Al_2O_3 for the following reasons:

- It is a good solvent of alumina.
- It has a greater decomposition potential than alumina.
- It is a good conductor.
- It can be free of metallic impurities that could be deposited.
- It has a low melting point.
- It has sufficient fluidity.
- It has a density less than that of aluminium at the working temperature. ➤ It has a low vapor pressure.
- It does not react with the electrodes or with the products of electrolysis.

The solubility of Al_2O_3 depends on electrolyte composition and temperature. Alumina and Na_3AlF_6 form a

eutectic at 960°C with 11% Al_2O_3 . The solubility limit of Al_2O_3 at 1000°C is 13% Al_2O_3 . For the dissolution of alumina in cryolite, the most important factor is the nature of the alumina used: the rate is faster with lower α alumina content and larger specific area. The percentage of Al_2O_3 in the bath must be carefully controlled within narrow limits for the following reasons:

- Shortage in Al_2O_3 will cause operating difficulties – the **anode effect** (i.e. gas accumulation at the anode causing decreased current efficiency).
- Increased amount of Al_2O_3 will cause its deposition as a sludge under the metal layer.

The electrolyte is agitated by:

- The bubbles of gas given off at the anodes.
- The magnetic field effect produced by the large currents passing through the anode bus bars, the cell walls, and the **lining** (see later).

Agitation is essential to help solubilize the alumina. Were there no agitation, the alumina would sink to the bottom of the cell and accumulate under the metal layer, thus, acting as an insulator to the cathodic carbon. However, too violent an agitation will increase the possibility of short-circuiting in the cell (anode – cathode distance decreases greatly). A schematic diagram of aluminium extraction cell is shown in Figure 2 while Figure 3 is a flow sheet illustrating the extraction of aluminium from alumina.

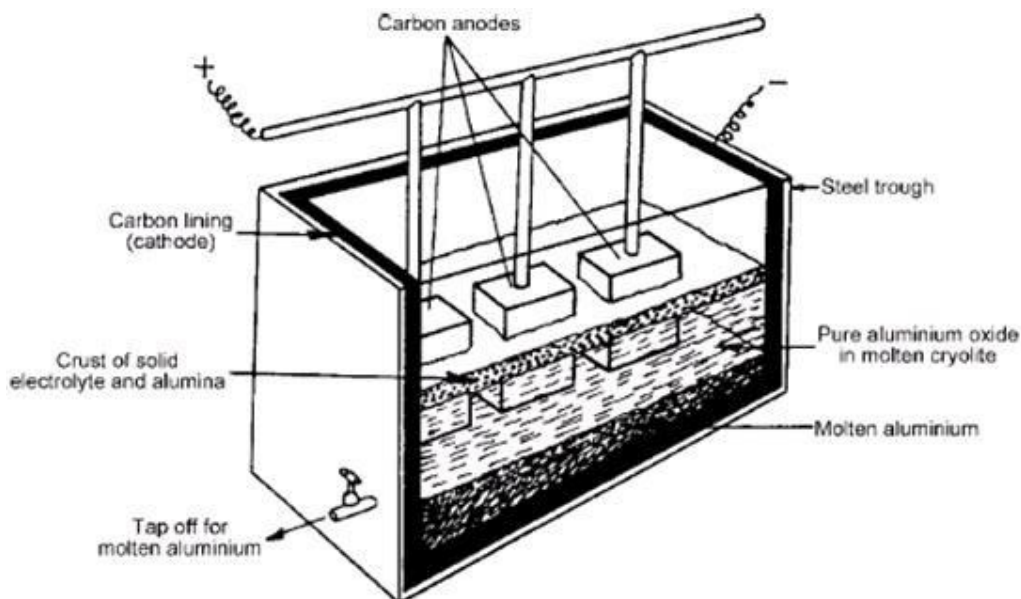


Figure 2: Schematic of Aluminium Extraction Cell

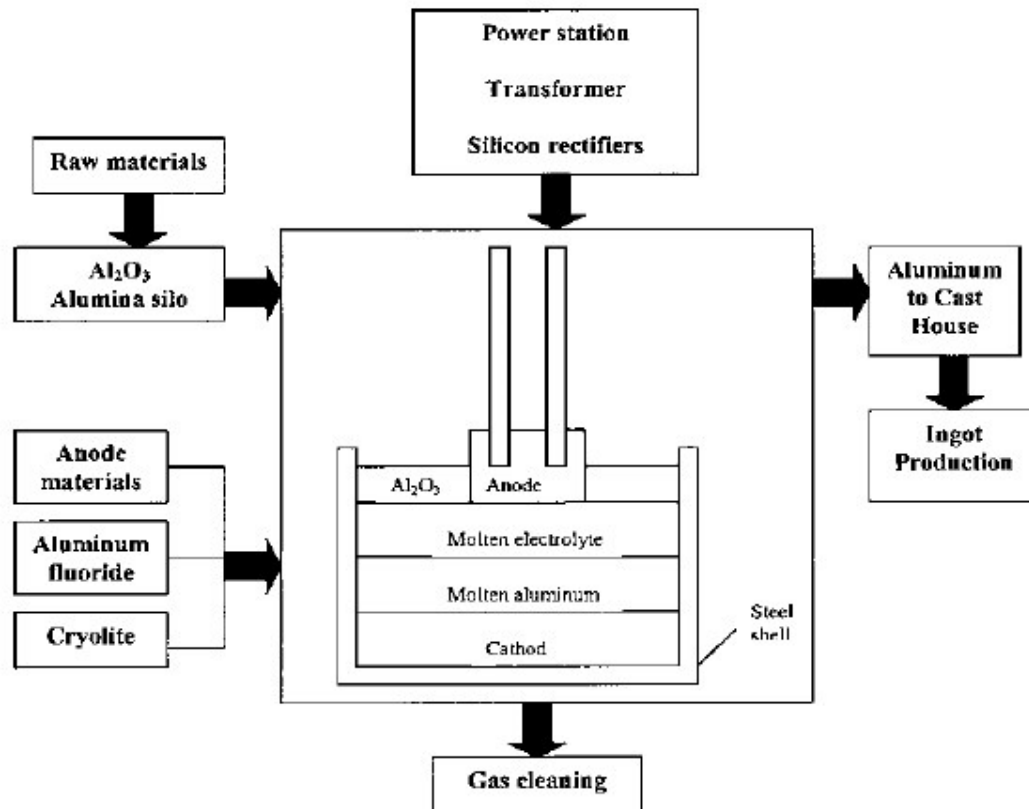


Figure 3: Flow sheet for aluminium production from alumina

Properties and Uses of Aluminium

Pure aluminium is a silvery coloured metal whose main characteristic is lightness. Although chemically very reactive, Al is protected against deterioration by a thin tough oxide layer (skin, film or coat) that forms spontaneously on the surface and accounts for the high durability of Al exposed to the atmosphere. An electrolytic process known as **anodizing** or **anodic oxidation** can thicken this oxide layer artificially. The resulting film can be , Si or Cu in a process known as alloying to produce aluminium alloys.

The term aluminium is used in industry to mean whole range of aluminium alloys, which are used commercially. Different alloying elements give different properties and a wide range of materials can be produced with properties suitable for different industrial applications. For instance, one type of Al alloy has very high strength for use in aircraft; another has high resistance to seawater and is used in ships; and another takes a high polish and is used in architecture.

coloured and is the basis for the production of coloured aluminium, e.g. profiles used for architectural and decorative applications as well as in chemical plants where protection is needed.

Although pure Al is not very strong [strength is about 6 TSi (tonnes per square inch) compared to about 28 TSi for mild steel] its strength can be increased up to 60% by cold working in a rolling mill. However, much greater increases in strength can be obtained by the addition of small quantities of other elements such as Mg

Although the strength of Al can be increased by **cold working**, a number of them can be made even stronger by **heat treatment** in which the metal is heated below its melting point (660°C) and then suddenly quenched. It is usual to have a second heat treatment or **aging process**. Aging then gives a stable structure of high strength which can only be destroyed by reheating to a high temperature.

The melting point of Al is about 660°C but it has a high specific heat capacity. Thus although the melting point is about thrice smaller than that of steel, the heat required to melt a tonne of each is about the same. At the same time Al has a very high

heat conductivity, hence its use as a heat exchanger in industry and in domestic cooking utensils (in which its chemical inertness is an advantage). Aluminium is a good electrical conductor surpassed only by silver and copper among the common metals.

On weight basis, Al is a better conductor, kg for kg for any other metal, and this accounts for its widespread use in overhead conductors; and in recent years for underground cables and transformer windings. The rising price of Cu encourages this trend. Aluminium will take a high polish, becoming a good reflector of light, hence its use in decoration and thermal insulation.

Available Forms of Aluminium

- ❖ **Remelt Ingot:** Al from the smelter is supplied in the form of ingots of different shapes. The first step in the production of commercial forms is the remelting of the ingot followed by degasification and other purification treatments, and the addition of alloying elements as may be required. The metal is then cast into ingots (usually by a semi-continuous chill process) for rolling or extrusion.
- ❖ **Sheets:** Al sheets are of thicknesses between 0.01 and 0.05 inches and supplied in coiled form. It may be of pure Al or any of the alloys and can be supplied with different surface finishes; such as lacquered or stone enamels, or coated with high purity Al to increase durability or decorative properties.
- ❖ **Foils:** Sheet materials below about 0.008 inch are known as foil and have wide-scale application in packaging industries. It is used for paper-insulated and electrolytic capacitor electrodes in the electrical industry, and is being used increasingly in place of round wire for coil winding in transformers and electromagnets.
- ❖ **Plates:** This is flat material over ¼ inch thick up to a maximum of 6 inches. Using modern machinery, plates can be produced in large pieces up to 10 feet wide and 50 feet long weighing up to 2.5 tonnes.
- ❖ **Extruded Sections:** Al being amenable to extrusion can be produced by extrusion into long lengths of cross-section over 38 feet in length. Al profiles or rails are made by extrusion.
- ❖ **Wires:** Al wire is of importance to electrical industry. It is produced by conventional wire drawing processes. A circular rod $\frac{3}{8}$ inch in diameter is first produced by continuous casting; the rod is then reduced to wire by pulling it through a hardened steel die of successively small diameter.

Uses of Aluminium

Al is virtually used in every area of modern life. The principal uses of aluminium include:

- ❖ **Building/Construction:** Roofing and siding sheets are by far the largest individual use which Al is put. More and more building components (e.g. frames for windows and doors) are made from aluminium.
- ❖ **Transportation:** Aircraft still accounts for a large part of the transport usage of aluminium. Large passenger ships are being made of aluminium superstructure to save weight and space. Railway rolling stock, particularly for urban services is often all aluminium. In road transport, commercial vehicles have Al to save weight while the amount of Al in private vehicles increases every year. This is mainly in the form of strips, window frames, etc. and in cast engine components. Several cars have Al cylinder blocks in steel liners and a large increase in these is expected if an Al cylinder is developed that does not need a steel liner.
- ❖ **Consumer Products:** These include domestic equipment of all kinds including hollow ware and other decorative and utilitarian goods found in hardware stores.
- ❖ **Electrical:** The principal electrical use is for overhead cables in which standard Al cables are used, often with a steel core to impart higher strength. It is called **aluminium conductor steel-reinforced cable (ACSR cable)** and is a specific type of high-capacity, high-strength stranded cable typically used in overhead power lines. The outer strands are aluminium, chosen for its excellent conductivity, low weight and low cost. The center strand is of steel for the strength required to support the weight without stretching the aluminum due to its ductility. This gives the cable an overall high tensile strength. In Europe particularly the UK, underground cables with stranded or solid Al conductors are becoming important and form a market comparable to that of overhead conductors. Such cables may have tubular Al outer sheets corrugated for flexibility. Transformer windings in Al are becoming more popular and this may be wires or flat wide strips. Al seems likely to be used increasingly for small wiring cables for houses, shops and offices.

- ❖ **Packaging:** The food and drug industries use aluminum extensively because it is nontoxic, non-adsorptive, and splinter-proof. It also minimizes bacterial growth, forms colorless salts, and can be steam cleaned. Al packaging may be divided into rigid containers such as food cans, and flexible containers such as collapsible tubes [e.g. toothpastes and creams] and foil wrappings. Both of these uses employ large quantities of Al, but the flexible market is the larger. In most countries, the rigid containers in Al is restricted to non-sterilized foods such as jams, coffee etc. and other materials such as pharmaceuticals. The market for foil and foil pack in Al is rarely extensive and the use of Al in —easy open cans was initially for beer but now is spreading to other drinks and juices.
- ❖ **Engineering Uses:** Al is a normal engineering material both for load bearing parts and castings for machinery. It is chosen for all uses where lightweight and strength are required, including machine tools and portable equipment. Chemical engineering uses vast quantities of Al for tanks and equipment where high resistance to corrosion attack is needed. It is widely used for low temperature applications (*cryogenic applications*) because its properties do not fall as the temperature drops, and it is not subject to brittle fracture, being an fcc metal. Many aluminium products used in engineering are *forgings*, *powder metallurgy* (P/M) parts or even *metal matrix composites* (MMCs).
- ❖ **Domestic Uses:** The familiar Al cooking utensils are domestic wares. A recent development is the use of thin plastic coating on Al to get a non-stick surface. Composite Al-Cu and Al-Stainless steel utensils have been made but they do not have any apparent advantage over the pure metal.

Alloys of Aluminium

Commercially pure Al from the smelter is relatively soft and of value in situations where high strength is not required, e.g. in decoration, packaging, electrical conductors and domestic cooking utensils. Several million tonnes per year are consumed in this form.

The addition of small quantities of other elements produces dramatic changes in properties and a number of such alloys are of great commercial importance. Some of the principal alloy systems are

briefly discussed below but many others have been developed for special purposes. These alloys are for making sheets, plates and extruded Sections:

- a) **Al – Mg Alloy System:** Alloys containing up to 5% Mg have good strength and notable resistance to corrosion. They are therefore used for shipbuilding and in chemical engineering. Cold working can increase the strength of these alloys, not heat treatment. The Al-Mg binary phase diagram is shown in Figure 4.
- b) **Al – Mg – Si Alloy System:** This system sometimes known as *‘aluminium silicide group’* gives a range of medium strength heat-treatable alloys used largely in engineering structures and architecture. Figure 5 is the AlSi binary phase diagram.
- c) **Al – Cu Alloy System:** The addition of up to 4% Cu with other elements in smaller quantities gives alloys of very high strength used principally in the aircraft industry. The resistance to atmospheric corrosion, however, is not good. Thus, the material is often supplied with a surface coating of pure aluminium. Figure 6 shows the Al-Cu binary phase diagram.
- d) **Al – Zn – Mg Alloy System:** There are two classes of heat treatable alloys in this range; one gives medium strength readily weldable alloys much favoured in Europe while the other gives ultra-high strength material whose strength can exceed that of steel – almost used exclusively in the aircraft industry. The Al-Zn binary phase diagram is shown in Figure 7.
- e) **Al – Li Alloy System:** These have been developed primarily to reduce the weight of aircraft and aerospace structures; more recently, they have been investigated for use in cryogenic applications (for example, liquid oxygen and hydrogen fuel tanks for aerospace vehicles). Commercial aluminum-lithium alloys are targeted as advanced materials for aerospace technology primarily because of their low density, high specific modulus, and excellent fatigue and cryogenic toughness properties. Figure 8 shows the Al-Li binary phase diagram while Figure 9 illustrates the uses of Al-Li alloys in a commercial aircraft. Although military applications are treated as classified information; for the most part, however, they can be generically viewed in much the same way as commercial applications.

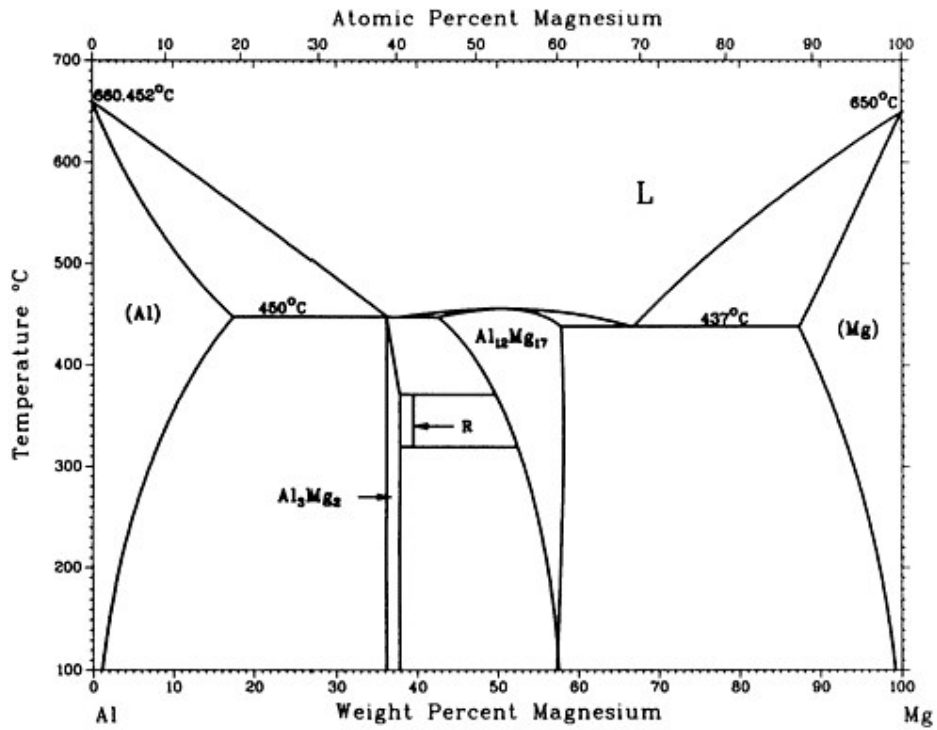


Figure 4: Aluminium – Magnesium Binary Alloy Phase Diagram

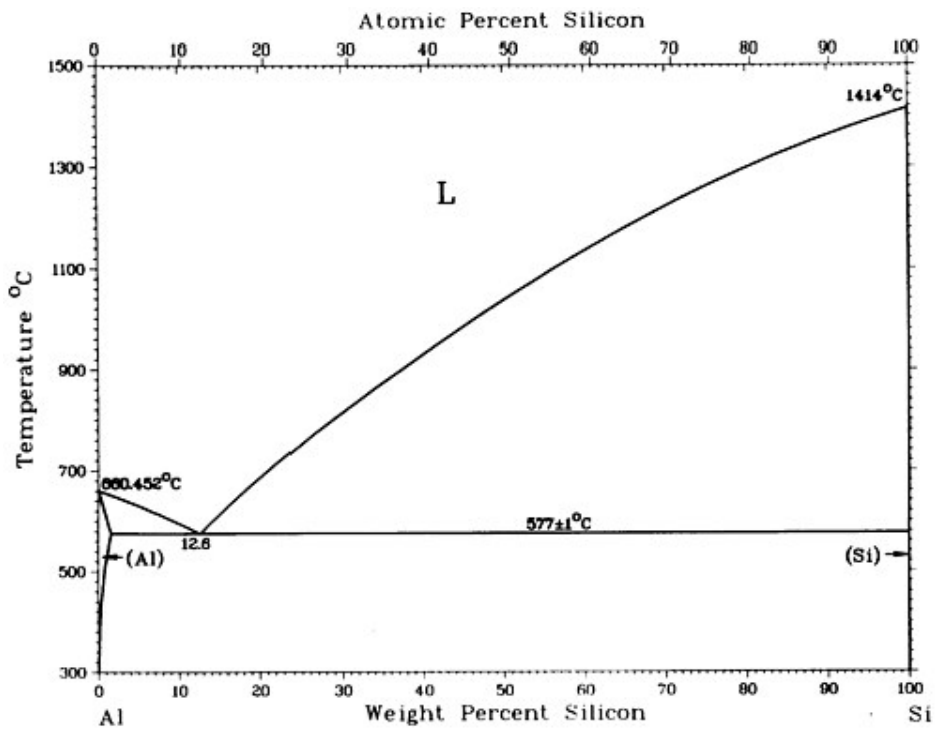


Figure 5: Aluminium – Silicon Binary Alloy Phase Diagram

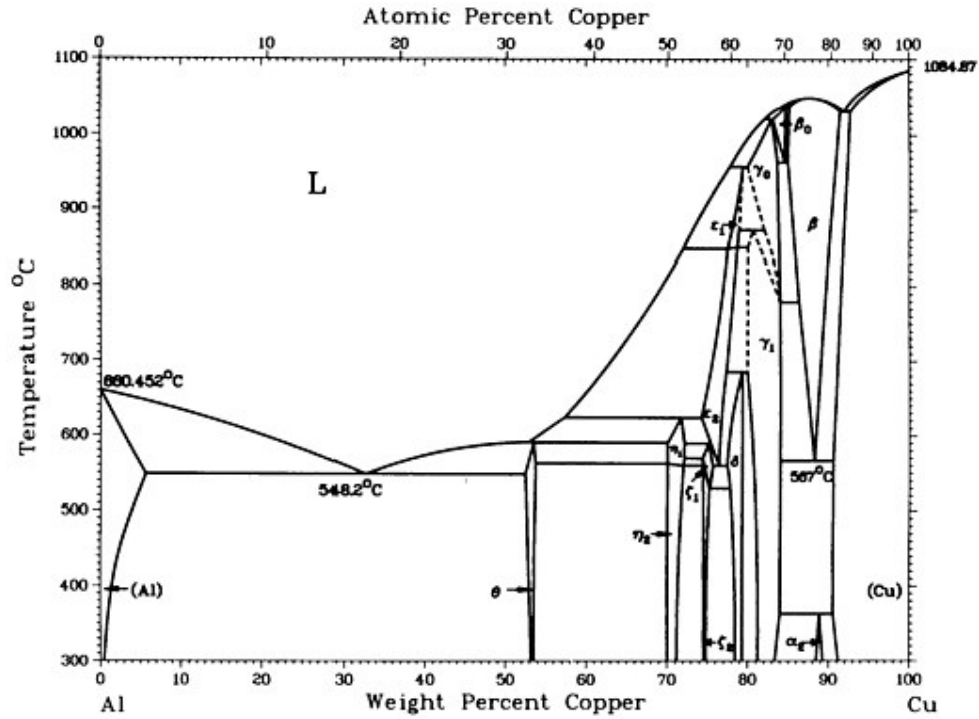


Figure 6: Aluminium – Copper Binary Alloy Phase Diagram

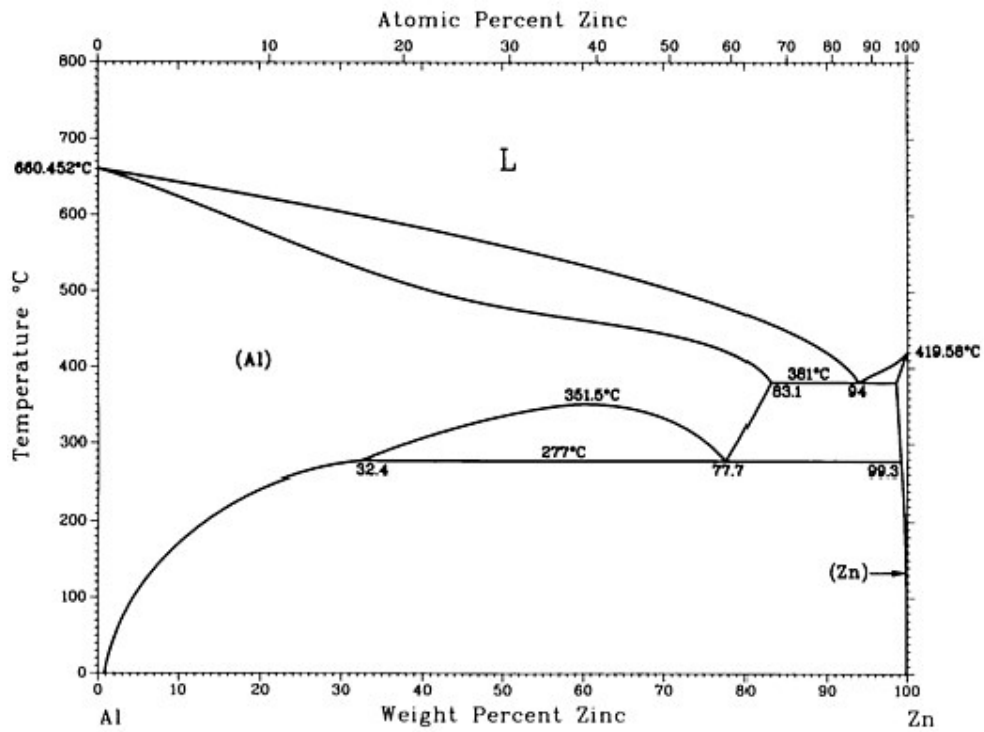


Figure 7: Aluminium – Zinc Binary Alloy Phase Diagram

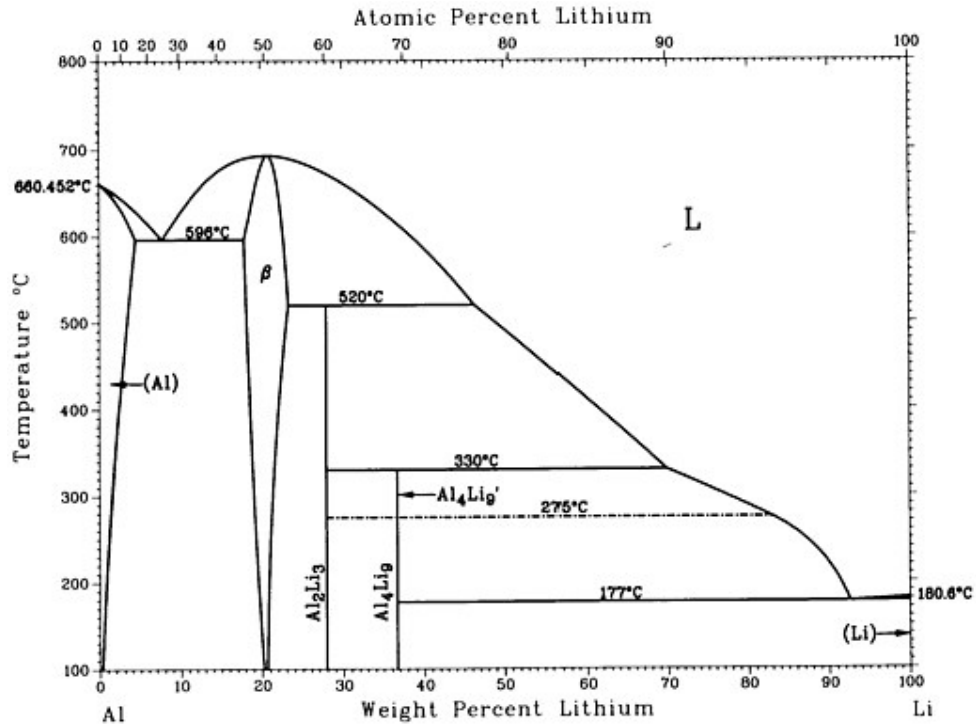


Figure 8: Aluminium – Lithium Binary Alloy Phase Diagram

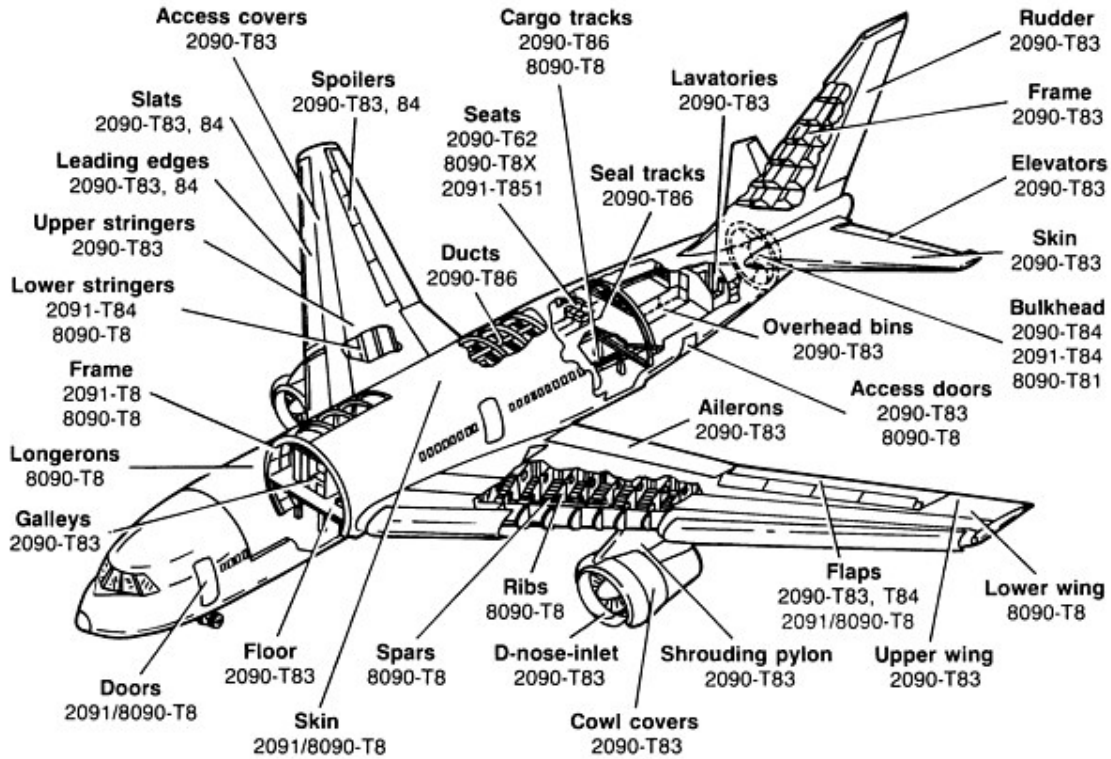


Figure 9: Use of aluminum-lithium alloys in a commercial aircraft

Designation of Aluminium Alloys

The word aluminium can be misleading since it is used for both the pure metal and for the alloys. Practically all commercial products are composed of aluminium alloys. For aluminium to be considered as unalloyed it must have a minimum content of 99.00% of aluminium. Most unalloyed specifications range from 99.00 to 99.75% minimum aluminium. To assist in the smelting process elements such as bismuth and titanium are added, while chromium, manganese, and zirconium are added for grain control during solidification of large ingots. Elements such as copper, magnesium, nickel, and zinc are added to impart properties such as strength, formability, stability at elevated temperature, etc. Some unintentional impurities are present coming from trace elements contained in the ore, from pickup from ceramic furnace linings, or from the use of scrap metal in recycling.

There are three types of composition listings in use. First there is the *nominal*, or *target*, composition of the alloy. This is used in discussing the generic types of alloys, their uses, etc. Second are the alloy limits registered with the Aluminum Association which are the specification limits against which alloys are produced. In these limits intentional alloying elements are defined with allowable ranges. The usual impurity elements are listed as the maximum amount allowed. Rare trace elements are grouped into an each other category. Each trace element cannot exceed a specified each amount and the total of all trace elements cannot exceed the slightly higher total amount. The third listing consists of the elements actually present as found in an analyzed sample.

When the melt is analyzed the intended elements must be within the prescribed ranges, but not necessarily near the midpoint if the range is wide. Specified impurity elements must be at or below the maximum limit. Individual nonspecified impurities should be less than the 0.05% each level with the total less than 0.15%. Every sample will not contain all of the impurity elements, but some amount of iron and silicon are usually present except in ultra-refined pure aluminum. Certain alloys are produced in several levels of purity, with the less pure levels being less expensive and the higher purity levels improving some property. For example, when the iron and silicon levels are both less than 0.10%, toughness is improved. It is important to know that other metallic elements are

present and necessary for desired properties. Many elements combine with one another and with aluminum to produce intermetallic compounds that are either soluble or insoluble in the aluminum matrix. The presence of second-phase particles is normal and they can be seen and identified by metallographic examination. Al alloys can be subdivided into two major groups, **wrought alloys** and **cast alloys**, based on the method of their fabrication. Wrought alloys which are shaped by plastic deformation have compositions and microstructures slightly different from casting alloys. Within each group we can subdivide the alloys into **heat treatable alloys** and **non-heat treatable alloys**. Heat treatable alloys are *age hardening* whereas non-heat treatable alloys are strengthened by *solid-solution strengthening*, *strain-hardening (work hardening)* or *dispersion strengthening*.

Cast and wrought alloy nomenclatures have been developed. The Aluminum Association system is the most widely recognized. Their alloy identification system employs different nomenclatures for wrought and cast alloys, but divides alloys into families for simplification. For wrought alloys a *four-digit system* is used to produce a list of wrought composition families. The first number specifies the first or principal alloying element, and the remaining numbers refer to the specific composition of the alloy. For example, the 1xxx or 1 series [1S] denote commercially pure aluminium, with greater than 99% Al. The 1 series cannot be aged. In the 2xxx through 7xxx alloy groups the second digit indicates an alloy modification. If the second digit is zero, the alloy is the original alloy, while numbers 1 through 9 are assigned consecutively as the original alloy becomes modified. The last two digits serve only to identify the different alloys in the group and have no numerical significance.

- ✓ 1xxx – Controlled unalloyed (pure) compositions. Used primarily in electrical and chemical industries.
- ✓ 2xxx – Alloys in which Cu is the principal alloying element, though other elements, notably Mg, may be specified. They are ageable. Used in aerospace applications.
- ✓ 3xxx – Alloys in which Mn is the principal alloying element. Age-hardenable only when Mg is added. Used in architectural applications

- ✓ 4xxx – Alloys in which Si is the principal alloying element. Used in welding rods and brazing sheets
 - ✓ 5xxx – Alloys in which Mg is the principal alloying element. Used in maritime applications.
 - ✓ 6xxx – Alloys in which Mg and Si are the principal alloying elements. They are very common compositions characterizing miscellaneous castable and age-hardenable. Used for pistons. compositions.
 - ✓ 7xxx – Alloys in which Zn is the principal alloying element, but other elements such as Cu and Mg are specified. Comprises nearly 90% of all shaped castings produced.
 - ✓ 8xxx – Alloys including Sn and some Li principal alloying elements. They are very common compositions characterizing miscellaneous castable and age-hardenable. Used for pistons. compositions.
 - ✓ 9xxx – Reserved for future use.
- Tables 15 and 16 give more details. The nominal Cu, Mg, Cr and Zr may be specified. They are chemical composition of representative aluminum age-hardenable and are the strongest Al alloys. wrought alloys are given in Table 17.

Table 15: Wrought Aluminium and Aluminium Alloy Designation

Series designation	Alloying materials
1XXX	99.9% min. Al
2XXX	Al-Cu, Al-Cu-Mg, Al-Cu-Mg-Li, Al-Cu-Mg-Si
3XXX	Al-Mn, Al-Mn-Mg
4XXX	Al-Si
5XXX	Al-Mg, Al-Mg-Mn
6XXX	Al-Mg-Si, Al-Mg-Si-Mn, Al-Mg-Si, Cu
7XXX	Al-Zn, Al-Zn-Mg, Al-Zn-Mg-Mn, Al-Zn-Mg-Cu

Table 16: Major Alloying Elements for Wrought Alloys

Series designation	Major alloying ingredient
1XXX	Aluminum ≥99.0%
2XXX	Copper
3XXX	Manganese
4XXX	Silicon
5XXX	Magnesium
6XXX	Magnesium and silicon
7XXX	Zinc
8XXX	Other elements
9XXX	Unused series

Casting compositions are described by a threedigit system followed by a decimal value. The decimal .0 in all cases pertains to casting alloy limits. Decimals .1, and .2 concern ingot compositions, which after melting and processing should result in chemistries conforming to casting specification requirements. Alloy families for casting compositions are:

- ✓ 1xx.x – Controlled unalloyed (pure) compositions, especially for rotor manufacture.
- ✓ 2xx.x – Alloys in which Cu is the principal alloying element, but other alloying elements may be specified.
- ✓ 3xx.x – Alloys in which Si is the principal alloying element, but other alloying elements

- ✓ 6xx.x – Unused
- ✓ 7xx.x – Alloys in which Zn is the principal alloying element, but other alloying elements such as Cu and Mg may be specified
- ✓ 8xx.x – Alloys in which Sn is the principal alloying element
- ✓ 9xx.x – Unused

NB: Al casting alloys must contain some silicon.

Temper Designations of Aluminium Alloys

Temper shows the degree of hardness imparted to the metal because of processing or manufacturing techniques. The Aluminum Association has adopted a temper designation system that is used for all product forms, excluding ingots. Aluminum alloys are hardened and strengthened by either deformation at room temperature, referred to as strain hardening, and designated by the letter H, or

by an aging heat treatment designated by the letter T. When a wrought alloy is annealed to attain its softest condition the letter O is used in the temper designation. If the product has been shaped without the solution-treated (as-quenched) condition. The hardened and heat-treated conditions are subdivided according to the degree of temper designations.

any attempt to control the amount of hardening the letter F (as-fabricated) is used for the temper designation. The letter W is used for

strain hardening and the type of heat-treating strain-hardened and heat-treated conditions are (called aging). Table 18 gives a summary of further

Table 17: Nominal Chemical Composition of Representative Aluminium Wrought Alloys

Alloy	Percent of alloying elements								
	Si	Cu	Mn	Mg	Cr	Zn	Ti	V	Zr
<i>Non-heat-treatable alloys</i>									
1060	99.60% min. Al								
1100	99.00% min. Al								
1350	99.50% min. Al								
3003		0.12	1.2						
3004			1.2	1.0					
5052				2.5	0.25				
5454			0.8	2.7	0.12				
5456			0.8	5.1	0.12				
5083			0.7	4.4	0.15				
5086			0.45	4.0	0.15				
7072*						1.0			
<i>Heat-treatable alloys</i>									
2014	0.8	4.4	0.8	0.50					
2219		6.3	0.30				0.06	0.10	0.18
2024		4.4	0.6	1.5					
6061	0.6	0.28		1.0	0.20				
6063	0.4			0.7					
7005			0.45	1.4	0.13	4.5	0.04		0.14
7050		2.3		2.2		6.2			
7075		1.6		2.5	0.23	5.6			

*Cladding for Alclad products

Table 18: Temper Designations of Aluminium Alloys

Temper Designation	Meaning
F	As-fabricated (e.g. hot worked, forged, cast)
O	Annealed (i.e. in the softest possible condition)
H	Cold worked i.e. work hardened or strain hardened
W	Solution Treated (i.e. as-quenched after solutionizing)
T	Age hardened or precipitation hardened
Strain Hardened Subdivisions	
H1X	<i>Strain Hardened Only</i> [The second digit indicates the degree of strain hardening. Full strain hardening is represented by H18. This is produced at about 75% reduction in area at room temperature. A product strained to about half maximum strain hardening is designated by H14, which is attained by approximately 35% reduction in area at room temperatures.]
H2X	<i>Strain Hardened and Partially Annealed</i> [The second digit indicates tempers ranging from quarter hard to full hard obtained by partial annealing of a room worked material. Typical tempers are H22, H24, H26, and H28. The highest number represents the highest hardness and strength, as in the H1X series.]

H3X	<i>Strain Hardened and Stabilized</i> [Alloys whose mechanical properties have been stabilized by a low temperature heat treatment or because of heat introduced during fabrication are included in the H3X series. This designation applies only to those alloys that, unless stabilized, gradually age soften at room temperature. As before, a second digit is used to indicate the degree of strain hardness remaining after stabilization. Typical designations are H32, H34, H36, and H38, again the highest number relating to the highest hardness and strength.]
Heat Treated Subdivisions	
T1	Cooled from an elevated process temperature and aged (natural aging) at ambient temperature to a substantially stable condition.
T2	Cooled from an elevated-temperature forming process, cold worked and naturally aged to a substantially stable condition.
T3	Solution heat treated, cold worked, and naturally aged to a substantially stable condition. Solution heat treatment involves heating the product to an elevated temperature, usually in the 932–1022°F (500–550°C) range. At this temperature the alloy becomes a single-phase solid solution which is cooled rapidly (quenched) so that a second phase does not form. This is designated as the W condition, which is an unstable condition. Consequently properties for this condition will not be found in the handbooks.
T4	Solution heat treated and naturally aged to a substantially stable condition.
T5	Cooled from an elevated-temperature forming process and artificially aged (holding for a specific time a temperature above the ambient temperature)
T6	Solution heat treated and artificially aged. The aging process is usually maintained until maximum or near maximum strength is achieved.
T7	Solution heat treated and over-aged. Products that have been aged beyond the point of maximum strength to provide some special characteristics such as improved corrosion resistance or ease of forming are included in this designation.
T8	Solution heat treated, artificially aged, and cold worked.
T9	Solution treated, artificially aged, and cold worked.
T10	Cooled from an elevated-temperature forming process, cold worked, and artificially aged.

Mechanical and Physical Properties of Aluminium Alloys

Pure aluminum can only be strengthened by solid solution strengthening up to the solid solubility limit of the strengthening element. Heat-treatable alloys are strengthened by solution heat treatment and by precipitation heat treatment. All alloys can

be cold worked to increase strength. This decreases properties such as elongation, forming, and toughness. The effect of strengthening mechanism on aluminium alloys is shown in Table 19 while Table 20 gives the typical physical properties of selected Al alloys.

Material	Yield Strength	Tensile Strength	Ductility (% Elongation)	ie d trength of oy ie d trength of ure
Pure Al (99.999%), Annealed	6,500	2,500	60	-
Commercially Pure Al (99%)	13,000	5,000	45	2.0
Solid Solution Strengthened 1.2% Mn Alloy	16,000	6,000	35	2.4
75% Cold Worked Pure Al	24,000	22,000	15	8.8
Dispersion strengthened 5% Mg Alloy	42,000	22,000	35	8.8
Age Hardened Alloy, 5% Zn, 2.5% Mg	33,000	73,000	11	29.2

Table 20: Typical Physical Properties of Selected Wrought Al Alloys

Alloy	Density (g/cm ³)	Electrical conductivity (% IACS)	Thermal conductivity at 25°C (W/mK)	Coefficient of thermal expansion (10 ⁻⁶ /°C)
1100-0	2.70	61	222	24
2014-T6	2.80	34	154	22
2024-T4	2.70	30	121	23
3003-H14	2.73	41	159	23
3004-H38	2.72	42	163	24
4032-T6	2.68	35	138	19
5005-0	2.69	52	200	24
5050-H34	2.69	50	193	24
5052-H34	2.68	30	138	24
5054-H32	2.67	33	130	23
6061-T6	2.69	43	165	24
6063-T6	2.70	53	200	20
7075-T6	2.81	33	130	24

Age Hardening (or Precipitation Hardening)

Age hardening effect was discovered in 1901 by Alfred Wilm (1869 – 1937), a German metallurgist who invented the alloy Al-3.5-5.5%Cu-Mg-Mn [Mg and Mn being <1%], now known as duraluminium, which is used extensively in aircraft. This discovery was made after hardness measurements on Al-Cu alloy specimens were serendipitously found to increase in hardness at room temperature. This increase in hardness was identified after his measurements were interrupted by a weekend, and when resumed on the Monday the hardness had increased. The term age hardening implies that time or age caused the alloys to harden. Scientific enquiries into the phenomenon have proved that a new phase(s) precipitated in the material and caused the hardening effect, i.e. precipitation hardening.

Age hardening, or **precipitation hardening**, is produced by a sequence of phase transformations that leads to a *uniform dispersion* of nanoscale, coherent precipitates in a softer, more ductile matrix. The inadvertent occurrence of this process may have helped the Wright brothers, who, on December 17, 1903, made the first controllable flight that changed the world forever. Gayle and co-workers showed that the aluminium alloy used by the Wright brothers for making the engine of the first airplane ever flown picked up copper from the casting mold. The age hardening occurred inadvertently as the mold remained hot during the casting process. The application of age hardening started with the Wright brothers' historic flight and, even today, aluminium alloys used for aircrafts are strengthened using this technique. Age or precipitation hardening is probably one of the earliest examples of *nanostructured materials* that have found widespread applications.

A weakness associated with this mechanism is that age-hardened alloys can be used over a limited range of temperatures. At higher temperatures, the precipitates formed initially begin to grow and eventually dissolve if the temperatures are high enough. This is where alloys in which *dispersion strengthening* is achieved by using a second phase that is insoluble are more effective than age-hardened alloys.

Once again, the sole aim of age hardening or precipitation hardening process is to produce a uniform dispersion of a fine coherent precipitate in a softer more ductile matrix. However, we have pertinent questions to deal with. How do precipitates form in precipitation hardening? How do they grow or age? Can the precipitates grow too much, or **overage**, so that they cannot provide maximum dispersion strengthening? Answers to these questions can be found by following the microstructural evolution in the sequence of phase transformations that are necessary for age hardening. We shall use the Al-Cu system as a classic example to illustrate these ideas. The Al-4%Cu alloy is a practical example of an age hardenable alloy. Figure 10 shows the age hardening and work hardening alloys of aluminium.

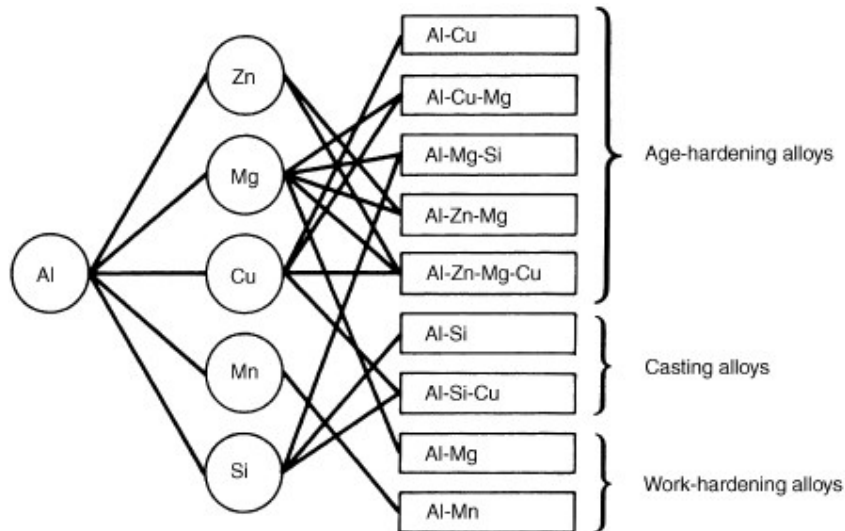


Figure 10: Principal alloys of aluminium and their strengthening mechanism

The aluminium-rich end of the Al-Cu system is shown in Figure 11 in which the three steps involved in agehardening heat treatment and the microstructures produced in each step are illustrated. As shown, the Al-Cu system has the following characteristics that are relevant to age hardening:

- 1) **Solvus:** - The *solubility line* that separates a single-phase solid region from a two-phase solid region in the phase diagram. The phases involved in this case are α and $(\alpha + \theta)$. For Al-4%Cu alloy, the solvus temperature is approximately 510°C.
- 2) **Liquidus:** - The solubility line in the phase diagram above which no solid can exist on heating.
- 3) **Solidus:** - The solubility line in the phase diagram below which no liquid can exist on cooling.
- 4) **Eutectic:** - The composition with the lowest melting point (or lowest freezing point). The eutectic composition for Al-Cu system is 5.65wt% Cu and 94.35wt% Al. The eutectic temperature is 548°C.

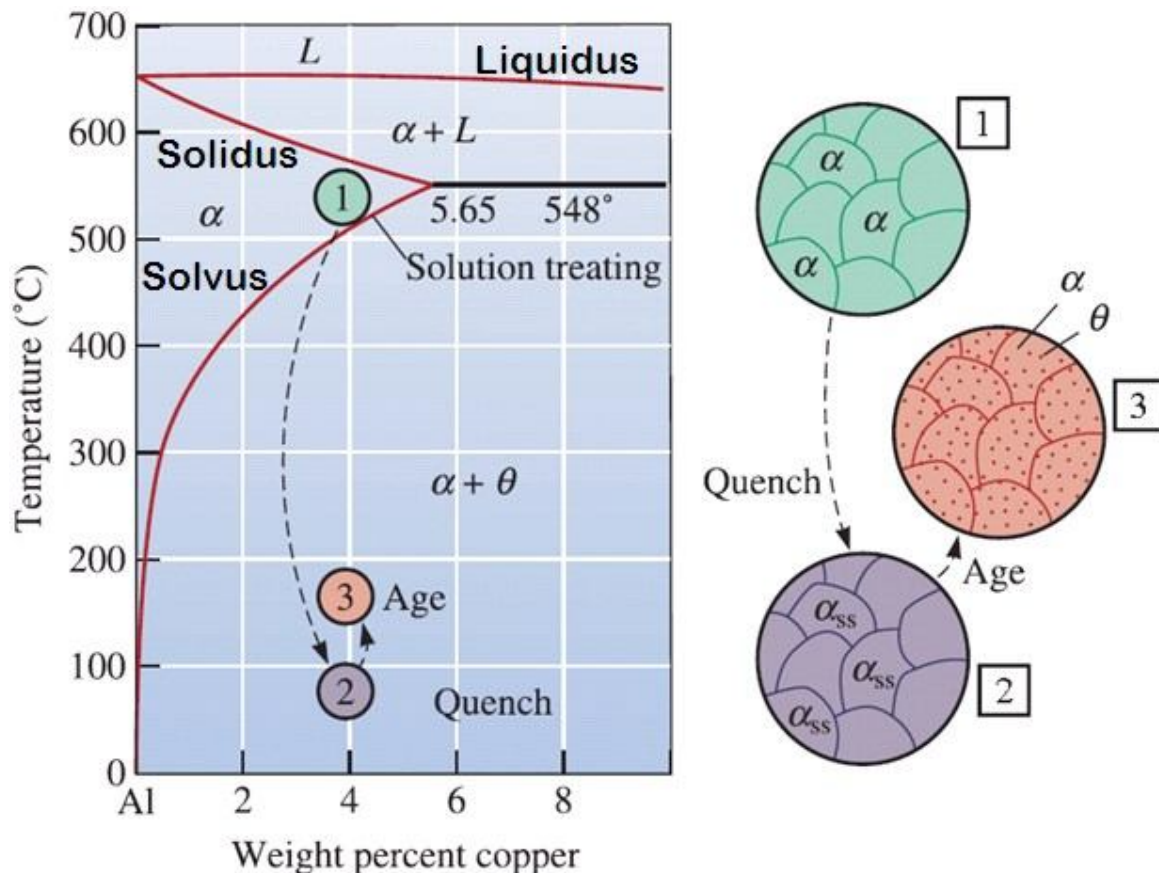


Figure 11: Aluminium-rich End of the Al-Cu System Showing the Three Steps Involved in AgeHardening Process and the Corresponding Microstructures

The three steps involved in age hardening heat treatment (Figure 12) are discussed as follows.

Step 1 – Solution Treatment [or Solutionizing]: In the **solution treatment**, the alloy is first heated to a temperature above the solvus temperature and held until a homogeneous solid solution α is produced. This step dissolves the θ phase precipitate and reduces any micro-chemical segregation present in the original alloy. The alloy could be heated to just below the solidus temperature to increase the rate of homogenization; however, the presence of a non-equilibrium eutectic micro-constituent may cause melting (resulting to **hot shortness**). Hence, the Al-4% Cu alloy is solution treated between the solvus and the eutectic temperatures, that is, between 500°C and 548°C in order to ensure that hot shortness does not occur.

Step 2 – Quenching: After solution treatment, the alloy contains only α in its structure and it is rapidly cooled, or quenched; the atoms not having time to diffuse to potential nucleation sites, so the θ phase does not form. After the quench, the structure still contains only α but this α is a **supersaturated solid solution** containing excess copper, and it is not an equilibrium structure. It is a metastable structure, a supersaturated α and is designated by α_{ss} .

Step 3 – Ageing/Aging (or Precipitation Treatment): Finally, the supersaturated α (that is, α_{ss}) is heated to a temperature below the solvus temperature. At this **ageing temperature**, atoms are able to diffuse only short distances. Because α_{ss} is metastable, the extra copper atoms diffuse to numerous nucleation sites and precipitates form and grow. Eventually, if the alloy is held for a sufficient time at the ageing temperature, the equilibrium $\alpha+\theta$ structure is produced. The θ is actually the intermetallic compound CuAl_2 . If the alloy is allowed to age at room temperature after quenching, **natural ageing** is implied; but if done at a slightly higher temperature (but below the solvus temperature), **artificial ageing** is implied. Artificial ageing is faster than natural ageing, i.e. the time required to develop maximum strengthening in the alloy is significantly reduced with artificial ageing.

Note that even though the structure that is formed has two equilibrium phases (i.e., $\alpha+\theta$), the morphology of the phases is different from the structure that would have been obtained by the slow cooling of this alloy.

When we go through the three steps described previously, we produce the θ phase in the form of ultra-fine uniformly dispersed second-phase precipitate particles. This is what we need for effective precipitation strengthening.

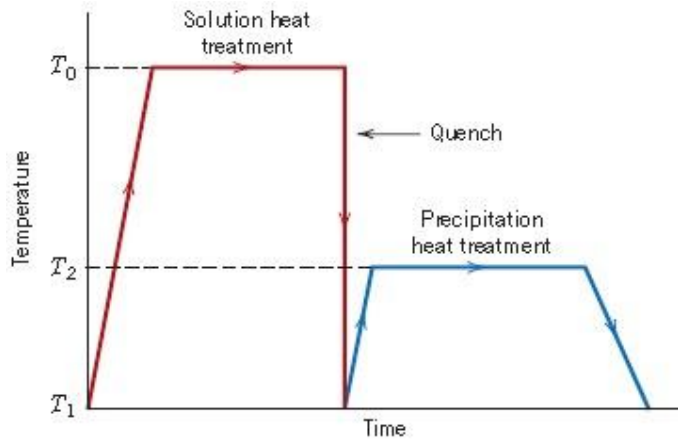


Figure 12: Schematic diagram showing both solution and precipitation heat treatments for precipitation hardening

Requirements for Age Hardening

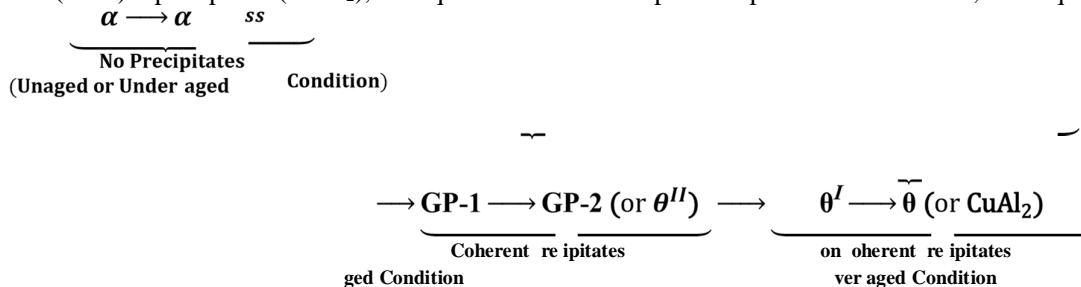
Not all alloys are age hardenable. Four conditions must be satisfied for an alloy to have an age-hardening response during heat treatment:

- The alloy system must display decreasing solid solubility with decreasing temperature. In other words, the alloy must form a single phase on heating above the **solvus line**, and then enter a two-phase region on cooling.
- The alloy must be quenchable so that the rapid cooling to room temperature suppresses the forming of a precipitate. Some alloys cannot be cooled rapidly enough to suppress the formation of the precipitate. Quenching may, however, introduce residual stresses that cause distortion of the part. To minimize residual stresses, aluminum alloys are quenched in hot water at about 80°C.
- The matrix should be relatively soft and ductile, and the precipitate should be hard and brittle. In most age hardenable alloys, the precipitate is a hard, brittle intermetallic compound.
- A coherent precipitate must form.

A number of important alloys, including certain stainless steels and alloys based on aluminum, magnesium, titanium, nickel, chromium, iron, and copper, meet these conditions and are age hardenable.

Under Ageing and Over Ageing

During the ageing of Al-Cu alloys, a continuous series of precipitates form before the equilibrium phase θ is produced. At the start of the ageing, the Cu atoms concentrate on the $\{00\}$ planes in α matrix and produce very thin precipitates called **GP-1 zones** [i.e. **Guinier–Preston Zones**]. As ageing continues more Cu atoms diffuse to the precipitates and the GP-1 zones thicken into thin discs known as **GP-2 zones**. With continued diffusion the precipitates (GP-2 zones) develop a greater degree of order and are called θ^I , and finally a tetragonal (BCT) θ precipitate (CuAl_2), the equilibrium or stable phase is produced. Therefore, the sequence is:



The non-equilibrium precipitates, GP-1 and GP-2 (θ'') are **coherent precipitates**. They are said to be coherent with the Al matrix since the copper atoms just replace the Al atoms in the lattice thereby straining the Al lattice. The strength of the alloy increases with **ageing time** as coherent phases (non-equilibrium precipitates) grow in size during the initial stages of the ageing treatment. When coherent precipitates are present, the alloy is in the aged condition, i.e. age-hardened condition. Maximum strength coincides with the formation of the θ'' (**GP-2 zones**) phase, which may be preserved upon cooling the alloy to room temperature.

Over-aging results from continued particle growth and the development of θ' and θ phases. The θ and θ' precipitates are said to be **incoherent**, i.e. they have a distinct crystal structure different from the matrix. When the stable or equilibrium non-coherent θ phase precipitates, the alloy goes into the **over-aged condition**, i.e. softened condition. The θ still provides some dispersion strengthening, but with time the θ grains grow larger and become less numerous, and even the simple dispersion strengthening effect diminishes.

Ageing below the GP-2 zones (θ'') may be regarded as **under ageing** as the dispersion strengthening effect is either minimal or non-existent. Figure 13 illustrates the effect of ageing time on strength or hardness.

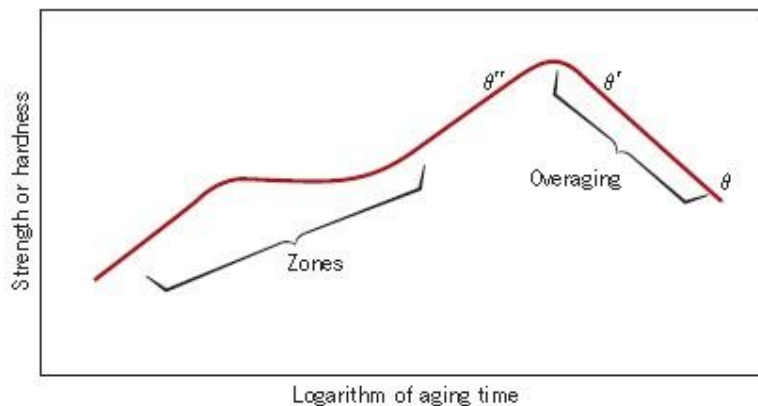


Figure 13: Schematic diagram showing strength and hardness as a function of aging time at constant temperature during the precipitation heat treatment

Age-Hardenable Alloys at High Temperatures

Selecting an age-hardened Al-4% Cu alloy for use at high temperatures will not be a sound decision. At service temperatures ranging from 100°C to 500°C, the alloy overages and loses its strength. Above 500°C, the second phase re-dissolves in the matrix, and we do not even obtain dispersion strengthening. In general, the aluminum age-hardenable alloys are best suited for service near room temperature; however, some magnesium alloys may maintain their strength to about 250°C and certain nickel superalloys resist overaging at 1000°C.

We may also have problems when welding age-hardenable alloys. During welding, the metal adjacent to the weld is heated. The *heat-affected zone* (HAZ) contains two principal zones. The lower temperature zone near the unaffected base metal is exposed to temperatures just below the solvus and may overage. The higher temperature zone is solution treated, eliminating the effects of age hardening. If the solution-treated zone cools slowly, stable θ may form at the grain boundaries, embrittling the weld area. For very fast welding processes such as electron-beam welding, complete reheat treatment of the area after welding, or welding the alloy in the solution-treated condition improve the quality of the weld. Welding of nickel-based superalloys strengthened by precipitation hardening does not pose such problems since the precipitation process is sluggish and the welding process simply acts as a solution and quenching treatment. The process of friction stir welding has also been recently used for welding of Al and Al-Li alloys for aerospace and aircraft applications.

BERYLLIUM

Beryllium is the first element in group 2 or IIA of the Periodic Table. It was formerly called *glucinium*, chiefly in France, because of the pronounced sweetish taste of its salts. Both the finely divided metal and its compounds have serious toxic effects on the lungs. The metal beryllium constitutes about 6 ppm (0.0006%) of the lithosphere. It occurs in concentrated form in various minerals. The total exploitable world reserves of

beryllium are estimated at 200 000 tonnes. Beryllium has a hexagonal closed packed (hcp) crystal structure; the atomic weight is 9.01 g/mol; the melting and boiling points are respectively, 1287°C and 2472°C.

Raw Materials

Beryllium got its name from the semi-precious mineral beryl, a beryllium aluminium cyclosilicate with the chemical formula $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$ or $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$. Pure beryl is colourless (i.e. white), but it is frequently tinted by impurities; possible colours being green, blue, yellow, and red. It is used as a gemstone and has five varieties: emerald, aquamarine, heliodor,morganite, and red beryl. The gemstone **emerald** (green in colour), is beryl in which a small fraction of Al^{3+} is replaced by Cr^{3+} . For **aquamarine** (blue-green in colour), the impurity ion is Fe^{2+} . **Heliodor** (yellow in colour) contains Fe^{3+} ions as dopants. **Morganite** and **Red Beryl** have Mn^{2+} and Mn^{3+} impurities, the colours being pink and red, respectively. Beryl contains about 11% BeO or about 4% Be and is often obtained as a by-product of feldspar quarrying. In addition to the Al_2O_3 and SiO_2 , principal impurities in the ores include alkali metals, alkaline-earth metals, iron, manganese, and phosphorus. The largest deposits are found in Brazil, Argentina, India, Mozambique, Madagascar, Uganda, Zimbabwe, South Africa, and the former USSR.

Until the late 1960s, beryl was the only beryllium mineral having industrial importance. In 1969 Brush Wellmann Inc. began the processing of **bertrandite** ores in Utah. This is presently the most important commercial beryllium mineral. Its formula is $4\text{BeO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$, but ores contain only 0.2 – 0.35% Be. Chrysoberyl, $\text{BeO} \cdot \text{Al}_2\text{O}_3$; phenakite, $2\text{BeO} \cdot \text{SiO}_2$; euclase, $\text{BeAlSiO}_4(\text{OH})$; and the precious varieties of beryl, emerald and aquamarine, are highly prized as gemstones. About 40 other beryllium-bearing minerals are known.

Production History

Vauquelin discovered BeO while analyzing varieties of beryl including emerald and aquamarine in 1797. Working independently, Wöhler and Bussy in 1828, prepared elemental Be by reduction of BeCl_2 with potassium. In 1899 Lebeau obtained Be crystals by electrolysis of molten sodium beryllium fluoride. Industrial production of Be began in 1916 in several countries. The publication of the phase diagrams of Be with Fe, Ni, and Cu by Østerheld in 1916, led to the first important use of Be in 1931, namely, as an additive, about 2%, in age-hardenable copper alloys.

The demand for Be increased around 1950 with the development of nuclear reactors because the nuclear properties and low density of Be seemed to indicate that the metal would be especially suitable as a moderator (neutron absorber) for nonstationary nuclear reactors of the types used in airplane, space craft, ships, and submarines. However, Be was a disappointment because it swells and becomes brittle when exposed to the simultaneous action of radioactivity and heat. However, the increased research activity in Be technology associated with this period produced significant advances in the chemistry, physics, and processing technology of beryllium.

Since the end of the 1950s, there has been increased interest in Be as a structural material, especially in aeronautical and astronautical uses because its mechanical and thermal properties relative to weight are superior to those of all other materials. Most of the Be produced today is used for military purposes. Greater use in the civilian sector is hindered mainly by the high price, the toxicity, and the room-temperature susceptibility to brittle fracture of the metal. On the other hand, BeO (beryllia) is finding increasing use in electrical engineering as an electrical insulator.

Processing of Beryllium Ores

Since the density of beryl is close to that of quartz, concentration by density is not possible. Hand sorting has been the chief means of separation. Flotation is successful only for a few ores. An automatic machine, the Beryl Picker, has been used recently: the ore is first γ -irradiated to render the Be atoms radioactive. A sorter guided by a neutron counter then selects the beryl crystals out.

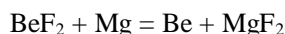
The recovery of Be from both beryl and bertrandite includes several stages. The ores are first converted to an acid-soluble form by fusion. Complex chemical processes are then used to obtain comparatively pure $\text{Be}(\text{OH})_2$ or BeO and then BeCl_2 or BeF_2 . These halogenides (halides) are reduced to metallic Be with other metals or by melt (fusion) electrolysis. The beryllium metal obtained is subjected to one or more refining processes and then to further treatment by powder metallurgy or in some cases fusion metallurgy.

Beryllium Extraction

The chief difficulties encountered in the extraction of beryllium are the reactivity and high melting point of the metal and the extreme stability of oxide. Of the many possible methods of producing beryllium, two are used on industrial scale currently: fusion electrolysis and reduction of halides by metals. Only calcium is able to reduce the extremely stable BeO directly under standard conditions. However, Ca forms the very stable intermetallic compound CaBe. Reduction of BeO with Ti, Zr, or C at high temperatures is theoretically possible; but the volatile Be would have to be distilled off from the reaction zone immediately.

a) Reduction of Be Halides [BeF₂ or BeCl₂] with Metals

Beryllium is extracted by heating beryl with sodium hexafluorosilicate, Na₂SiF₆, to produce BeF₂, which is then reduced to the element by magnesium. This reduction of the fluoride by magnesium is known as *magnesiothermic reduction*. Calcium cannot be used for this purpose because it would interact with beryllium to form a stable intermetallic phase (CaBe). The reduction of beryllium fluoride by magnesium follows the reaction:



Magnesiothermic reduction of BeF₂ is the most viable commercial method for the production of beryllium metal. The reaction is exothermic, but the enthalpy change is not large enough to permit a thermit-type reduction, as in the case of uranium. In the Ellingham diagram for fluorides the beryllium fluoride and magnesium fluoride lines are located relatively close to each other and unlike uranium, which forms a tetrafluoride, beryllium forms only a difluoride. The reduction is therefore, carried out by heating the reactants together in a graphite crucible in an induction furnace.

When stoichiometric quantities of beryllium fluoride and magnesium are used, the reduced beryllium metal does not fuse and the separation of the slag from the metal becomes very difficult. This problem has been solved by the use of excess beryllium fluoride (about 40%) in the reaction mixture. The unreacted beryllium fluoride, which forms a thin coating over the magnesium fluoride crystals, dissolves rapidly during the water leaching stage, disintegrating the slag and releasing the beryllium pebbles. The unreacted BeF₂ is separated from the MgF₂ and returned to the process.

The reaction cannot be performed without external heating because the heat of reaction is not great and because BeF₂ must be processed in the form of relatively large particles due to its toxicity and hygroscopicity. The reaction of beryllium fluoride with magnesium goes to completion at around 1000°C. However, in practice, the temperature is raised rapidly to 1400 °C at the end of the reaction. This is well above the melting points of beryllium and magnesium fluoride. The molten slag-metal mixture is poured into a water-cooled graphite mould for solidification. Beryllium pebbles float to the surface of the slag due to the low density of beryllium. The solidified mass is then wet ball-milled to separate the beryllium pebbles from the slag.

Beryllium is a toxic element, and the reduction operation is therefore carried out in a well-ventilated special double enclosure. The furnace controls are located outside the enclosure. The ball milling of the reduced mass is carried out in walk in-type fume hoods. The magnesium-reduced beryllium pebbles generally assay 96% beryllium and are always associated with residual magnesium and slag. These pebbles are purified to about 99.5% by vacuum induction melting in beryllia crucibles at temperatures of about 1400°C.

The ingots are machined and machined scarf is milled to produce beryllium powder. The ground metal powder is pressed and sintered under vacuum. The product is called vacuum hot-pressed beryllium, and this is machined for component manufacture.

The reduction may be performed in the presence of an alloying component such as copper or aluminum to obtain a *master alloy*. Such alloys may also be produced by carbothermic smelting of the oxide in the presence of the alloying constituent. The carbothermic route constitutes a cheaper mode of production, when making the alloys is the sole objective.

The reduction of BeCl₂ with Mg or Na or the reduction of BeF₂ with Na is more cumbersome than magnesiothermic reduction of BeF₂, and does not currently have any economic importance.

b) Fusion Electrolysis of BeF₂ or BeCl₂

All practical electrolytic methods of production are based on the decomposition of BeF₂ or BeCl₂ mixed with halides of the alkali metals or alkaline-earth metals. The halides of alkali or alkaline-earth metals are necessary to form a stable melt electrolyte with good conducting properties since the molten Be halides are covalently bonded resulting to their poor electrical conductivity.

Only BeF₂ has a sufficiently large interval between melting point (554°C) and boiling point (1169°C) at atmospheric pressure. The electrolysis of BeF₂ is carried out above the melting point of Be (1287°C) at 1290 - 1400°C. However, the method of extraction by electrolyzing BeF₂ is now obsolete.

Based on fusion electrolysis, Be is mainly extracted by electrolysis of a fused mixture of beryllium chloride (BeCl₂) and sodium chloride (NaCl). As noted previously, the NaCl is added to increase conductivity of the melt, since BeCl₂, because of its considerable covalent character, is a poor conductor. The electrolysis of BeCl₂ can be carried out at temperatures so low that the metal neither melts nor oxidizes. The Be is obtained as solid flakes, which are separated by washing out the electrolyte.

Mixtures of approximately equal parts of BeCl₂ and NaCl are electrolyzed at approximately 350 - 400°C. The composition of the electrolyte is held as constant as possible. The apparatus consists of two identical nickel vessels hanging in electric furnaces. The crucible covers contain the anode and can be placed alternately on each crucible, the crucible themselves serve as cathodes. During electrolysis (using 4 – 6V, 0.08A per cm² of cathode surface area) the metal is deposited as flakes on the cathode wall. When the BeCl₂ concentration in the melt has fallen to about 45%, the melt is siphoned into the second crucible, in which BeCl₂ and NaCl have previously been melted down in quantities corresponding to the quantities consumed by the electrolysis in the first crucible. In this way the bath is again given its original composition. The crucible covers are then exchanged, and electrolysis is started in the second crucible. The chlorine generated at the anode during electrolysis is collected and used in the production of BeCl₂.

c) Refining and Further Processing of Pebbles and Flakes

The as-reduced beryllium *pebbles* (magnesiothermally reduced) or *flakes* (electrolytically reduced) still contain many impurities, which have to be removed or reduced before the metal can be used to fabricate structural pieces. The main impurities in electrolytic beryllium are Na and Cl. The main impurities in magnesiothermic beryllium is Mg and MgF₂. Other impurities include BeO, carbon (from the graphite crucible), and metals, particularly Al, Fe and Si. Some of the impurities have adverse effects on the mechanical properties and corrosion resistance of beryllium or are reactor poisons. Commercial grades of Be are refined exclusively by vacuum melting in BeO or MgO crucibles and casting in graphite ingot moulds. The ingots weigh approximately 200 kg. Their surfaces are machined (skinned) to remove the high carbon content material adjacent to the mould wall.

The melting of magnesium-reduced beryllium in a high vacuum produces a degree of purity comparable to that of electrolytic beryllium. Melting the electrolytic flakes in a vacuum further reduces the content of halides and low-boiling metals. A very pure grade of Be, particularly with respect to the content of oxide, Al, Fe, Si, C and halides, can be produced by electrolytic purification.

Uses of Beryllium

Beryllium is a hard, light, strong metal of high melting point and resistance to corrosion, an unusual combination of properties and an unusual one to engineers. The low density of Be combined with its high strength, high melting point, and resistance to oxidation is the basis for its use in structural parts that must be light and are exposed to inertial or centrifugal forces. In addition, it has a high modulus of elasticity, which gives light-weight components a high degree of rigidity. Another area of use is in so-called dimensionally stable parts, in which high microyield strength and good thermal conductivity and reflexivity are exploited. It is an excellent heat sink, and therefore used especially for brake systems of airplanes. Though affected by radiation damage when used as nuclear moderator and reflector, its favourable nuclear properties have been exploited in weapons systems and in various physical instruments. Beryllium single crystals are the most efficient material for neutron monochromators. Beryllium foil is widely used as windows in energy-dispersive X-ray analyzers. Beryllium compound (the silicate with zinc) is used as fluorescent pigments or luminescent phosphors in fluorescent light tubes and TV tubes.

Beryllium is unreactive in air because of a passivating layer of an inert oxide film on its surface, which makes it very resistant to corrosion. This inertness, combined with the fact that it is one of the lightest metals, results in its use in alloys to make precision instruments, aircraft, and missiles. It is highly transparent to X-rays due to its low atomic number (and thus electron count) and is used for X-ray tube windows. [NB: X-rays readily penetrate metals of low atomic number]. Beryllium is also used as a moderator for nuclear reactions (where it slows down fast-moving neutrons through inelastic collisions) because the beryllium nucleus is a very weak absorber of neutrons and the metal has a high melting point.

Beryllium is lighter than aluminum, with a density of 1.848 g/cm^3 , yet it is stiffer than steel, with a modulus of elasticity of $42 \times 10^6 \text{ psi}$ (290 GPa). Beryllium alloys, which have yield strengths of 30,000 to 50,000 psi (200–350 MPa), have high specific strengths and maintain both strength and stiffness to high temperatures. Instrument grade beryllium is used in inertial guidance systems where the elastic deformation must be minimal; structural grades are used in aerospace applications; and nuclear applications take advantage of the transparency of beryllium to electromagnetic radiation.

Its chief alloy is *beryllium-bronze* (98 % Cu, 2 % Be) which, after suitable heat treatment, has remarkable properties [see the Cu-Be system in Figure 14]. For example, it is as hard and tough as the best steels; its power to withstand continual flexing without showing fatigue is greatly superior to that of steel; its resistance to corrosion is as good as that of stainless steel; it does not cause sparks when struck. Consequently, it has replaced steel in making valve springs and other engine components subject to continual vibration and for tools to be used near explosive gases or solids.

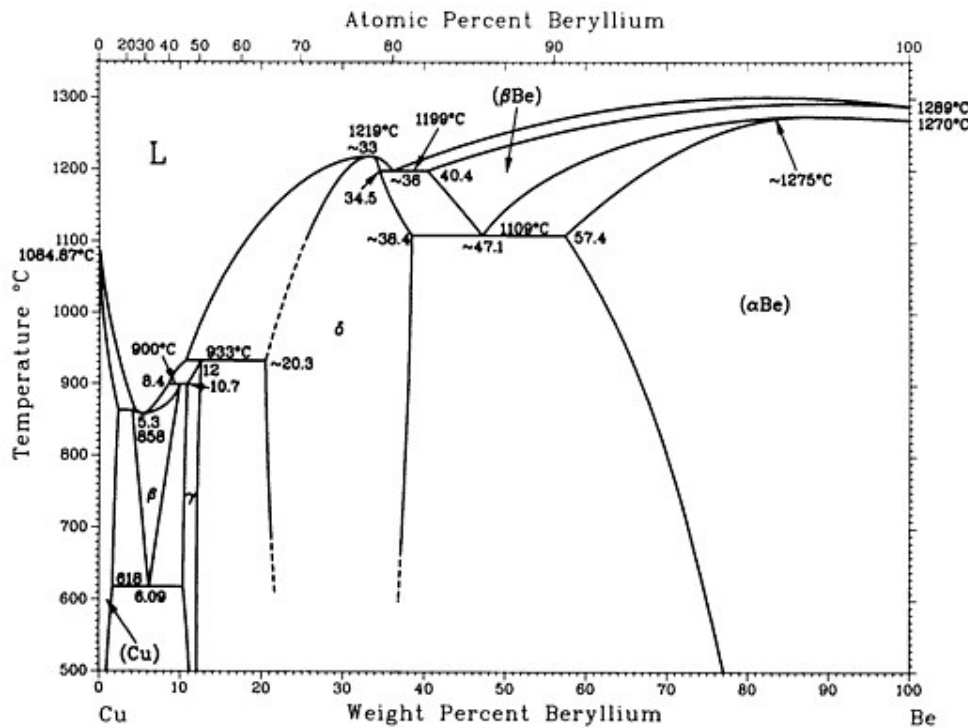


Figure 14: Copper – Beryllium Binary Alloy Phase Diagram

Beryllium is used in aluminum alloys containing magnesium to reduce oxidation at elevated temperatures. Up to 0.1% Be is used in aluminizing baths for steel to improve adhesion of the aluminum film and restrict the formation of the deleterious iron-aluminum complex. The mechanism of protection is attributed to beryllium diffusion to the surface and the formation of a protective layer. Oxidation and discoloration of wrought aluminum-magnesium products are greatly reduced by small amounts of beryllium because of the diffusion of beryllium to the surface and the formation of an oxide of high-volume ratio. Beryllium does not affect the corrosion resistance of aluminum.

Recently a series of beryllium-aluminium alloys [known as *lockalloys*] has been introduced, containing in the region of 60 per cent beryllium. Their main attribute is a low density of 2.16 kg/m^3 combined with a tensile strength of 310 MPa (giving a strength/weight ratio of $150 \text{ kg m}^2\text{s}^{-2}$) with a percentage elongation of 3.5. The Al-Be binary system is as shown in Figure 15. These alloys are used as investment castings for such components as secondary structural members in US Army helicopters and guidance components for advanced missiles and satellite. Naturally, due to the high cost of beryllium and its processing, these are expensive alloys. Since Al does not form any beryllides (intermetallic compound with Be), lockalloy contains Be grains embedded or dispersed in the ductile Al phase (matrix) with a more or less uniform distribution. This combination has a comparatively high modulus of elasticity, low density, and comparatively useful deformation behaviour at room temperature; having a notch sensitivity lower than that of commercial beryllium.

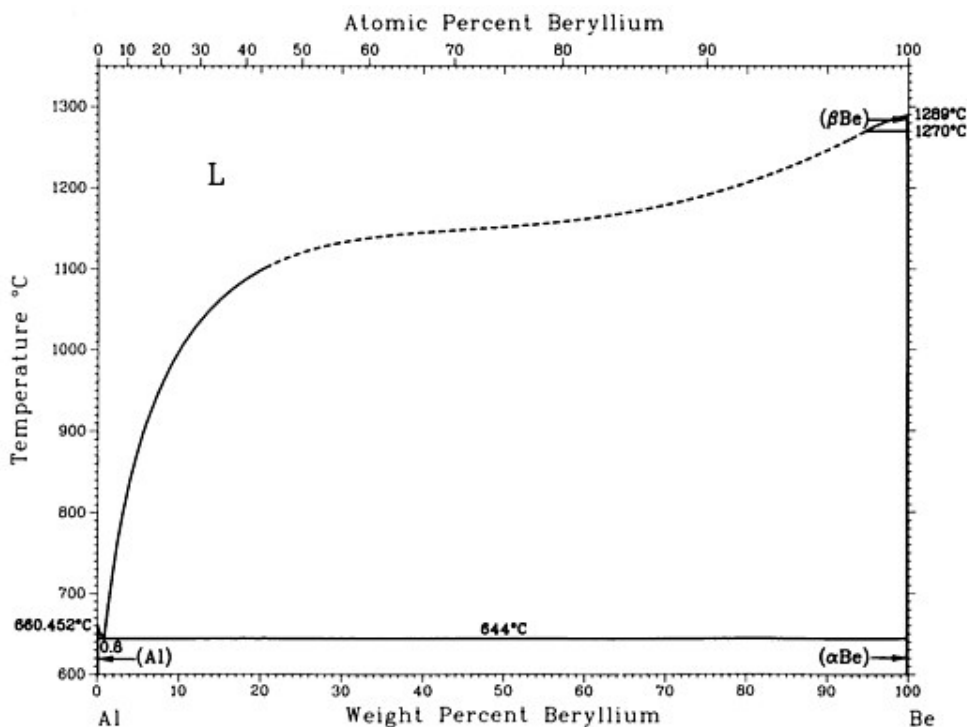


Figure 15: Aluminium – Beryllium Binary Alloy Phase Diagram

Beryllium is generally held to < 8 ppm in welding filler metal, and its content should be limited in wrought alloys that may be welded. Beryllium fluoride (BeF_2), a white, freely soluble, low melting salt is sometimes used as an additive to welding and soldering fluxes because it dissolves metal oxides readily.

Beryllium, as well as magnesium and calcium are also used in metallurgy as deoxidants; in which case small quantities are added to the molten metal to reduce oxides and sulphides to the metal, their compounds formed separating as slag in the process. They are also added to molten metals during casting, to remove dissolved oxygen and nitrogen, which cause blowholes when the casting solidifies. Another use is to produce high vacua in radio valves by removal of residual oxygen and nitrogen as the oxide and nitride.

Unfortunately, beryllium is expensive, brittle, reactive, and toxic. Its production is quite complicated, and hence, the applications of Be alloys are very limited. Beryllium oxide (BeO), which is also toxic in a powder form, is used to make high-thermal conductivity ceramics.

Beryllium poisoning is an allergic disease, a problem of individual hypersensitivity that is related to intensity and duration of exposure. Inhalation of dust containing beryllium compounds may lead to acute poisoning. Beryllium is not used in aluminum alloys that may contact food or beverages. *Berylliosis*, a form of metal poisoning with beryllium, is a persistent form of pneumonia that can result in severe lung damage. Beryllium metal, alloys, and ceramic beryllium (i.e. compounds) can be handled safely without special precautions as long

as the fabrication process does not require high temperatures [to avoid the fume or vapour] or produce particles smaller than 0 μm [to avoid the dust].

MAGNESIUM

Magnesium is the eighth most abundant element in the Earth's crust constituting about 2.1% of the lithosphere. It occurs naturally in a number of minerals such as *dolomite* (CaCO₃·MgCO₃) and *magnesite* (MgCO₃) and is the third most abundant element dissolved in seawater (after Cl and Na), from which it is commercially extracted [see Table 21]. A litre of seawater contains more than 1 g of magnesium ions. Magnesium is a silvery white metal that belongs to group 2 or IIA of the Periodic Table, just below beryllium. Magnesium has a dense hexagonal closed packed (hcp) crystal structure; the atomic weight is 24.31 g/mol with density 1.74g/cm³; the melting and boiling points are respectively, 650°C and 1107°C.

Production History

The history of elementary magnesium started in 1755, when Joseph Black, a Scottish chemist, discovered that magnesia (MgO) contained a new element, magnesium. Black was unable to isolate this element. Magnesia had previously been known as "white stone" or "white earth" (magnesia lithos or magnesia carnea). It is generally accepted that the name originates from an area in Thessaly, Northern Greece, where in ancient times the material had been excavated and exported to countries around the Mediterranean.

Actually, the British chemist and scientist Sir Humphrey Davy is honored as the discoverer, because it was he who isolated the metal in 1808, when he decomposed wet magnesium sulphate by electrolysis using a voltaic cell and a mercury cathode. Exactly 20 years later the Frenchman Antoine Alexandre Brutun Bussy isolated the metal by fusing dehydrated magnesium chloride with potassium at elevated temperatures. Then Michael Faraday, the famous British scientist and a former assistant to Sir Humphrey, reduced dehydrated magnesium chloride by electrolysis and obtained pure metallic magnesium in 1833.

A German, Robert-Wilhelm Bunsen, after having developed the carbon-zinc electric cell in 1841, produced metallic magnesium in 1852, also starting from fused and dehydrated magnesium chloride. Besides smaller attempts in some European countries, magnesium found steady interest only in Germany, which, in 1868, was the only producer in the world, using the metal mostly as powder or ribbon for flashlights and other pyrotechnical purposes, and as a reducing agent in the production of aluminum. The first industrial production of Mg by electrolysis of molten *carnallite* (MgCl₂·KCl) began in 1886 in Hemelingen (Germany). In 1940, L.M. Pidgeon pioneered the first industrial pyrometallurgical extraction of magnesium in Canada; using metallothermic reduction of dolomite.

Raw Materials

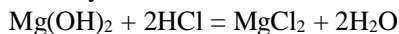
Magnesium does not occur in nature in elemental form but in the form of compounds in seawater, minerals, brines, and rocks. The major raw material sources for Mg extraction are the minerals *magnesite* (MgCO₃), *dolomite* (CaCO₃·MgCO₃), and *brucite* [Mg(OH)₂]; magnesium-rich salts such as *carnallite* (MgCl₂·KCl·6H₂O), *kieserite* (MgSO₄·H₂O), *bischofite* (MgCl₂·H₂O), *kainite* (KCl·MgSO₄·3H₂O), *langbeinite* (K₂SO₄·MgSO₄), and serpentine (3MgO·2SiO₂·2H₂O); and magnesium-rich brines and seawater (Mg²⁺_(aq.)). Magnesium-rich brines are obtained as by-products from potash production or from surface or underground brine deposits. For example, Israel's metallurgical and chemical industries are developed on the resources from the Dead Sea, the most concentrated salt lake on the Earth. Table 21 compares the compositions of general seawater and Dead Sea water.

Table 21: Composition of General Seawater and Dead Sea Water

<u>Material</u>	<u>Sea water composition [%]</u>	<u>Dead Sea water composition [%]</u>
Magnesium	0.1290	4.20
Chlorine	1.9500	20.80
Potash	0.0380	0.75

Bromine	0.0670	0.60
Sodium	1.0770	3.50
Calcium	0.0412	1.60

The extraction from seawater relies on the fact that magnesium hydroxide is less soluble than calcium hydroxide because the solubility of the salts of mononegative anions increases down the group. Either CaO (quicklime) or Ca(OH)₂ (slaked lime) is added to seawater and Mg(OH)₂ precipitates. The hydroxide is converted to the chloride by treatment with hydrochloric acid:



The surface of the Dead Sea, 418 m (1,371 ft.) below sea level as of 2006, is the lowest water surface on earth. The lake is 80 km (50 mi) long and has a maximum width of 18 km (11 mi); its area is 1,020 sq. km (394 sq. mi). The Dead Sea is fed mainly by the Jordan River, which enters the lake from the north. Several smaller streams also enter the sea, chiefly from the east. The lake has no outlet, and the heavy inflow of fresh water is carried off solely by evaporation, which is rapid in the hot desert climate. Due to large-scale projects by Israel and Jordan to divert water from the Jordan River for irrigation and other water needs, the surface of the Dead Sea has been dropping for at least the past 50 years. Nearly nine times as salty as the ocean, the Dead Sea contains at a depth of 305 m (1,000 ft) some 27 percent solid substances: sodium chloride (common salt), magnesium chloride, calcium chloride, potassium chloride, magnesium bromide, and many other substances. Because of the density of solids in the water, the human body easily floats on the surface. The lake contains no life of any sort except for a few kinds of microbes; sea fish put into its waters soon die. The Dead Sea is economically important as a source of potash, bromine, gypsum, salt, and other chemical products, which are extracted inexpensively. The lake is closely associated with biblical history; the sites of the cities of Sodom and Gomorrah [where Lot's wife turned to a pillar of salt] are believed to lie beneath the lake.

Production Problems and Parameters

Magnesium is produced commercially by electrolysis of MgCl₂ melts and by metallothermic reduction of MgO with silicon. A wide variety of processes are used. The extraction of Mg by electrolysis consists of two steps: (i) preparation of the MgCl₂ cell feed and (ii) electrolysis. Electrolysis of MgCl₂ in aqueous solution liberates hydrogen, not magnesium, at the cathode. Attempts to electrolyze magnesium salts in organic solvents have not been successful. Carbothermic reduction of MgO is not used industrially; the main challenges being high reaction temperatures (1,800 – 2000°C) and rapid cooling of reaction gases to suppress MgO formation.

One of the features of the magnesium industry is the wide variety of production processes. Relative to an industry, which has been manufacturing a product commercially for close to one hundred years; it is somewhat strange that there are over 10 different processes for producing magnesium. Unlike many other industries, there is no one particular dominant technology used for most of the world's production. The large number of production technologies stems from the differences in basic parameters of the production processes. Below are the basic parameters, which differentiate the various production methods.

a. Raw materials: There are six principal sources of raw materials for the production of magnesium: magnesite, dolomite, bischofite, carnallite, serpentine and seawater. These sources differ in the magnesium content, in production methods, and in their origin. Some are mined from mines, some in open mining, others originate in various processes carried out on sea water and salt lakes, and another material originates from the waste of the asbestos production process.

b. Materials and method of reduction: Magnesium always appears in nature in ionic form with the following electron arrangement: 1S²2S²2P⁶3S². This arrangement is characterized by the low ionization energies relative to the two most external electrons, which are at the 3S level. This is the reason why univalent or trivalent magnesium is not found in nature, only bivalent. The low standard reduction potential of magnesium is the reason why no metallic magnesium is found in nature:



All production technologies, therefore, require a reduction agent that can transfer two electrons to the magnesium. The reduction agents are: electric current operated at the appropriate potential, coal in various forms, silicone-based materials (FeSi), CaC₂ and aluminum. The accepted division in literature, for thermal and

electrochemical technologies stems in fact from this central feature. All the electrochemical technologies use direct current electricity form, which passes through the electrolysis cells and discharges chlorine and magnesium ions into gaseous chlorine and metallic magnesium. The thermal methods are based on heating of magnesia (MgO) in the presence of various reduction materials, to a variety of temperatures. At a particular temperature the reduction reaction takes place and the magnesium becomes metal, usually in its gaseous form.

c. Production temperatures: Maximum temperatures in the various production processes are in the range of 655-1,900°C, which is a very large temperature range for a production process of one particular material. In general, electrochemical production processes take place within the lower production temperature range, usually between 655-720°C, while the thermal reduction production processes take place within the higher temperature ranges, usually between 900-1,900°C.

d. By-products: The by-products from the various methods are, in fact dependent on the composition of the raw materials. If the basic raw material is bischofite or carnallite, we shall obtain, in addition to magnesium, chlorine and by-products related to the components of the original material. In the case of carnallite, in addition to chlorine there will be KCl-rich salt (70%), which serves in the production of fertilizers. With processes in which the basic raw material does not contain chlorine, no surplus chlorine will be produced, since the chlorine produced will be recycled into the production process. Most processes will actually require the addition of chlorine from external sources such as magnesium chloride or HCl.

Pyrometallurgical Reduction: Pidgeon/Magnetherm Process

Metallothermic processes for magnesium production are based on the reduction of MgO with ferrosilicon (FeSi). The only ores used in the production of magnesium with thermal reduction technology are dolomite and magnesite. These ores are extracted through customary mining methods, mainly through open mining. The ore extracted from the mine undergoes calcination at temperatures of 700 – 1000°C to produce the MgO. At this temperature the material releases CO₂ gas, according to the following equations:



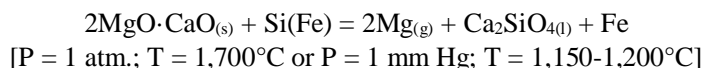
Following calcination the material is ground into a fine powder. Another main raw material that is used in thermal reduction is an alloy of silicon and iron called Ferrosilicon. The silicon content in this alloy is 6585%, and at times the mix also contains small quantities of aluminum.

An additional material, which was used in the past as a thermal reduction agent, is Calcium carbide.

The Pidgeon Process

The most important example of the use of silicon as a reducing agent in producing metals (**silicothermy**) is the **Pidgeon process** for the production of magnesium. [NB: Silicon is generally considered to be a congener of carbon (used in carbothermy) and this is also reflected in the application of silicon as a reducing agent for metal oxides. Silicon forms a fairly stable solid oxide silica or silicon (IV) oxide (SiO₂) and also a stable gaseous oxide silicon (II) oxide (SiO), both of which can be useful in oxide reduction reactions]. The process stands as one of the illustrious examples of application of physico-chemical principles of metal extraction.

This process was developed in the 1940s in Ontario Canada, by Prof. Pidgeon and the Timminco company. Lately, this process has received new attention and constitutes a central process in the magnesium production especially in China. A schematic illustration of the retort used in this process is shown in Figure 16 and the reaction is as follows:



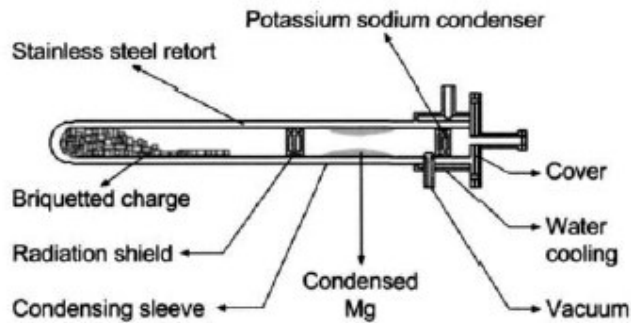
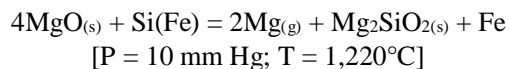


Figure 16: A retort used in the pidgeon process

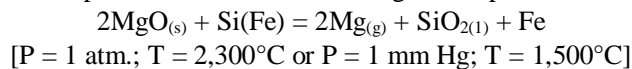
The dimensions of the retort are 2.7–3.3 m with a diameter of 28–35 cm. The capacity of the retort is about 120 kg. The source of energy in the process carried out in China is normally coal, while the calcination process and the heating furnaces require 14–20 tonnes of coal for the production of one tonne of magnesium.

On completion of the process, a **magnesium crown** is obtained, weighing 12–20 kg, which is then extracted from the upper part of the retort. Due to the usually high temperature, the magnesium in this case will contain high concentrations of aluminum, manganese, iron and other impurities.

The above process can also be carried out with magnesite as an alternative to dolomite; the working conditions are almost identical and the reaction in this case is:



Another version of the above process is carried out at a higher temperature, according to the reaction:

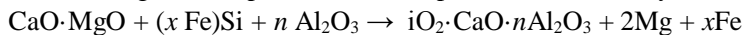


The advantage of this reaction is the higher output from each retort (up to about 80%), while the disadvantages in this case are many. The main one being the higher temperature required for the process, 1,500°C, about 300°C more than with the regular process. Work at a higher temperature usually causes the evaporation of impurities and a lower quality of material. In addition, there is accelerated amortization of tools and this in addition to the higher cost of energy and the need for accessibility to magnesite.

The Magnetherm Process

The Pidgeon process is largely being replaced by the **Magnetherm process**, which has been developed in France in the 950s and 960s by ociete Francaise d'Electrometallurgie, Marignac and the large aluminum production company Pechiney. Later, it was also used by Northwest Alloys in the United States. The Magnetherm process, is essentially a modern variant of the Pidgeon process, and is carried out in a large reactor (height 5.7 m, diameter 4.3 m) shown schematically in Figure 17. The reactor consists of a specific feeding system for raw materials, electric energy, and a vacuum system. The process flowsheet is as shown in Figure 18. The furnace consists of a vacuum tight steel shell lined with refractory concrete and thermal insulation. The hearth is lined with carbon blocks and its bottom is connected to a power source. Electric power is fed through the electrode-molten slag-hearth to provide the requisite thermal energy. The charge consists of calcined dolomite, ferrosilicon and calcined bauxite. Heat is generated internally in the furnace by the passage of electric current, through the molten slag, between the carbon electrodes. Alumina lowers the melting point of the calcium silicate slag, and the slag is molten at the reaction temperature of about 1550 °C. The pressure in the reactor is kept at about 8 torr (8 mm Hg). The magnesium produced in the reaction boils out into the condenser which is maintained at 650°C. Magnesium vapor condenses and collects as a liquid in the water-cooled steel crucible attached to the condenser, and then solidifies. Up to 7 tonnes of magnesium can be collected in the crucible. The process is continued after tapping the slag and the residual ferrosilicon at regular intervals from the furnace.

Sufficient slag is left in the reactor so that the central electrode remains immersed in it and heating can be continued. The reaction of the Magnetherm process can be represented chemically as:



The main characteristic of this technology is the heating and production furnace in which the heating takes place with electrodes using alternating current (Figure 17). Such heating requires liquid slag, which will conduct electricity, and therefore, in addition to calcined dolomite and the reduction silicon, alumina is also added. The furnace in the Magnetherm process operates within a temperature range of 1,300-1,700°C. This high temperature range stems from a number of reasons and variations in the process. The first reason is the difficulty in maintaining low pressures in the furnace with a large volume, and, therefore, it is necessary to work at higher temperatures. At times, a certain quantity of magnesite, which has undergone calcination, is also added, to increase the reaction temperature. Another variation of the process that can also influence the temperature is the addition of metallic aluminum as an alternative to silicon (making the process aluminothermic).

The Magnetherm process is batch production process and a complete cycle lasts normally 16-24 h. The magnesium fumes rise and accumulate in the cooled condenser in the liquid or solid state. The furnace usually produces between 3 and 8 tonnes of magnesium a day, according to its size. As a rule, 7 tonnes of raw material are required in order to produce 1 tonne of magnesium.

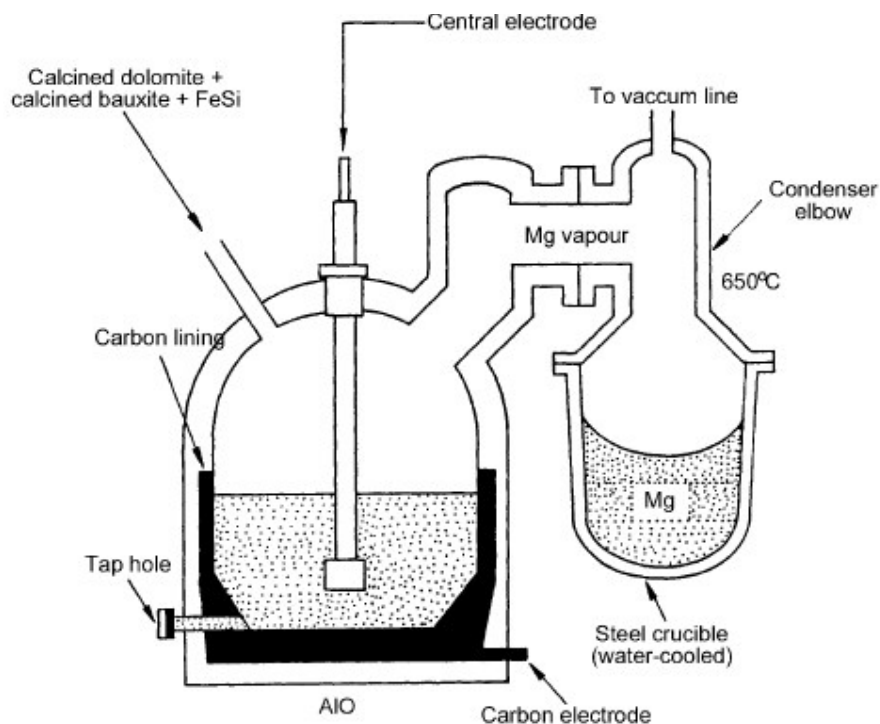


Figure 17: Reactor Assembly for the Magnetherm Process

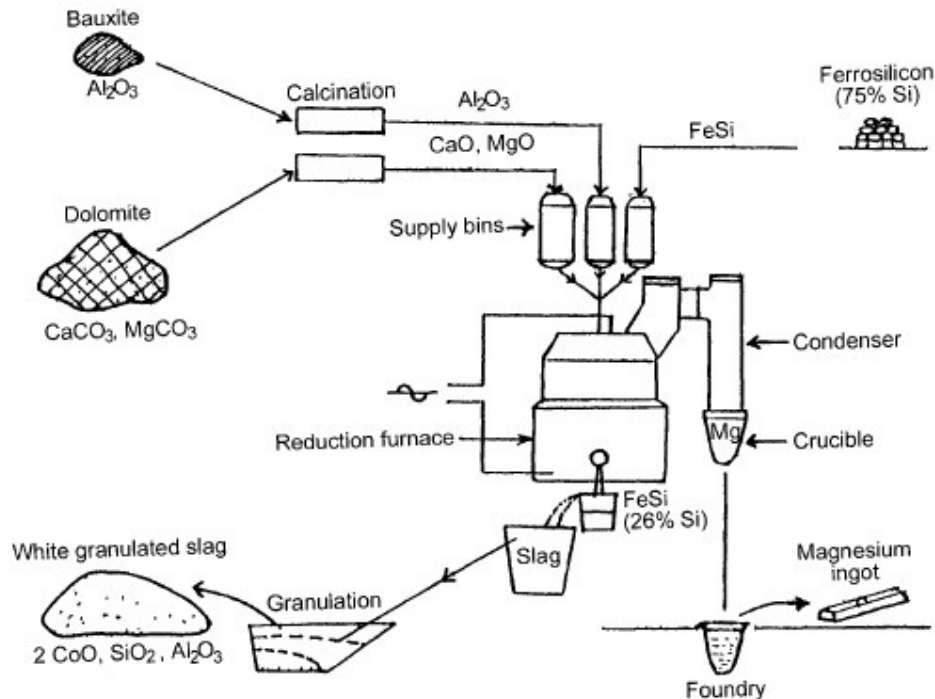


Figure 18: Magnetherm Process Flowsheet

Thermal magnesium, i.e., magnesium produced by the Pidgeon process and by the Magnetherm process at constitutes only 30% of the total magnesium production. The rest is produced electrolytically in which the leading examples are (i) the Dow electrolytic reduction process, and (ii) Norsk hydro process.

Electrometallurgical Reduction: Dow and Norsk Hydro Processes

Magnesium chloride cell feeds in industrial use consists of anhydrous (dehydrated) $\text{MgCl}_{2(s)}$ or $\text{MgCl}_{2(l)}$; dehydrated carnalite ($\text{MgCl}_2 \cdot \text{KCl}_{(s)}$); or $\text{MgCl}_2 \cdot 1.5 \text{H}_2\text{O}$. Cell feeds contain 3-8% alkali chlorides and minor impurities of C, SiO_2 , MgO, O^- , B, and heavy-metal compounds. Alkali chlorides accumulate in the electrolytic cell as major constituents of the electrolyte. Metallic and nonmetallic impurities are undesirable because they adversely affect cell performance and the corrosion resistance of magnesium. The use of pure dehydrated MgCl_2 allows coproduction of highly concentrated chlorine gas and electrolysis at high current efficiencies. Dehydrated carnalite (which contains only 50% MgCl_2) leads to accumulation of significant tonnages of KCl-rich electrolyte in the electrolysis leading to high power consumption in electrolysis. The water content of $\text{MgCl}_2 \cdot 1.5\text{H}_2\text{O}$ results in high consumption of anode carbon and formation of sludge in the cell; power consumption is high.

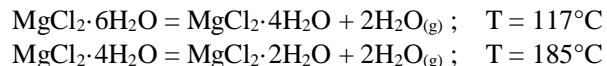
The two main routes to the production of dehydrated MgCl_2 cell feed are: (i) chlorination of magnesia (MgO) or magnesite (MgCO_3) in the presence of carbon or CO and (ii) dehydration of aqueous MgCl_2 solutions (brines, seawater) or hydrous carnalite ($\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$).

The electrolysis stage is performed in the electrolysis cells. The optimal electrolyte for the production of magnesium must have low resistance, high density, and a low price. Magnesium chloride does not have high conductivity and, therefore, the accepted values for its use are relatively low (8-25%), this despite the fact that it is in fact the material undergoing electrolysis. The other materials are determined according to other technological constraints

The Dow Process

The process developed at Dow Chemical Company, in the USA (see Figure 19) is unique, due to the fact that the material fed into the electrolysis cells still contains a significant amount of water - about 27%. That is, the cell feed is hydrous magnesium chloride, $\text{MgCl}_2 \cdot 1.5\text{H}_2\text{O}$. A solution of magnesium chloride is introduced directly into the spray dryer and comes into direct contact with burning gases, predominantly natural gas.

During this process the following reactions take place:



The products of this stage are granules of $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$. The additional dehydration is, in fact, carried out in the electrolysis cell, by the chlorine, which is created in the cell and the graphite anodes, which are used up at a fast rate.

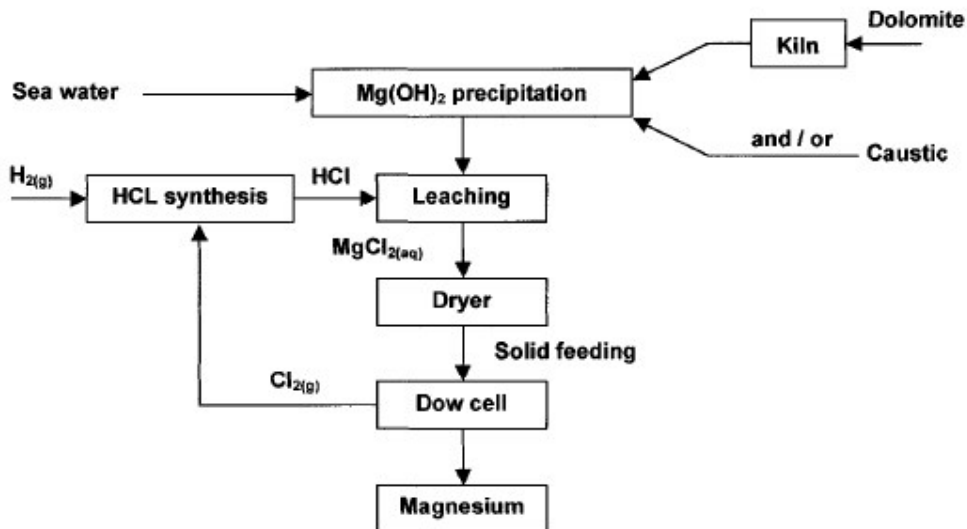
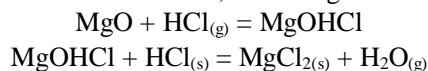


Figure 19: Dow Processes (USA)

Norsk Hydro Process (The Hydro Magnesium Process)

In the Hydro Magnesium process (developed in Norway and presently used in Canada), during the preliminary drying process, the magnesium chloride solution is heated in the evaporator by the residual heat from the process until almost pure bischofite with a water content of 45-50% is obtained ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$). The bischofite, which is melted during this process is turned into prills (granules or pellets) in the prilling tower. One of the main reasons for the transfer to prills is the wish to reduce the quantities of dust during the next drying stages.

The next drying stage is performed in a fluidized bed dryer. At this stage, the bischofite with six molecules of water is dried by hot air to $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$. The last stage of drying, to extract anhydrous magnesium chloride is carried out by gaseous HCl drying at temperatures of about 330°C . The reason for performing this stage with heated gaseous HCl is the difficulty in preventing hydrolysis, and the wish to obtain solid and dry magnesium chloride with magnesium oxide qualities of about 0.1%, according to the reactions:



From the above reactions, it appears that the use of gaseous HCl will fundamentally reduce the hydrolysis reactions, thus reducing the concentration of magnesium oxide in the product. A further point is that opposite reactions to hydrolysis take place with HCl, which also reduce the concentration of magnesium oxide. The HCl from the drying process is transferred to the raw materials extraction and preparation process, according to Figure 20.

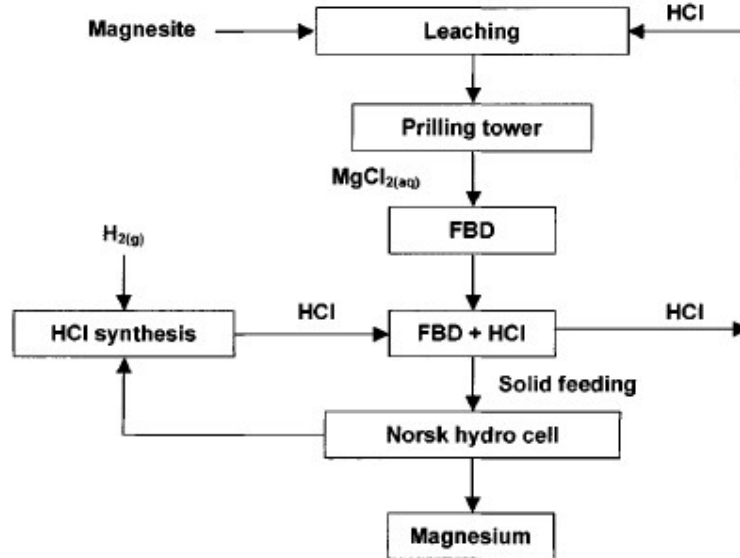
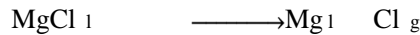


Figure 20: Norsk Hydro Process (Canada)

Magnesium chloride is electrolyzed in a molten mixture with alkali chlorides at 700 – 800°C, the main reaction being:



The electrolyte is contained in brick-lined vessels or a steel shell. The magnesium rises to the surface because it is lighter than the electrolyte.

Industrial electrolytic cells differ in electrode configuration, flow pattern of the electrolyte, and collection system for reaction products. The Dow cell and Norsk Hydro cell are shown in Figures 21 and 22 respectively. Steel cathodes and graphite anodes are arranged vertically or at an angle. Electrodes may be monopolar, bipolar, or a combination of both, with interpolar gaps ranging from 3 to 12 cm and current densities from 2000 to 8000 A/m².

The composition and primary characteristics of electrolytes used vary, containing 8 – 20% MgCl₂. Other chlorides (BaCl₂, LiCl, NaCl and KCl) may be added to influence the density; LiCl also increases the conductivity of the melt.

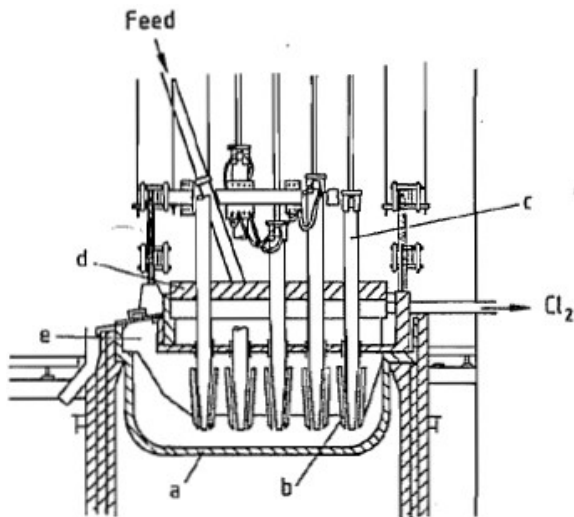


Figure 21: Dow Cell: a) Steel mantle; b) Steel

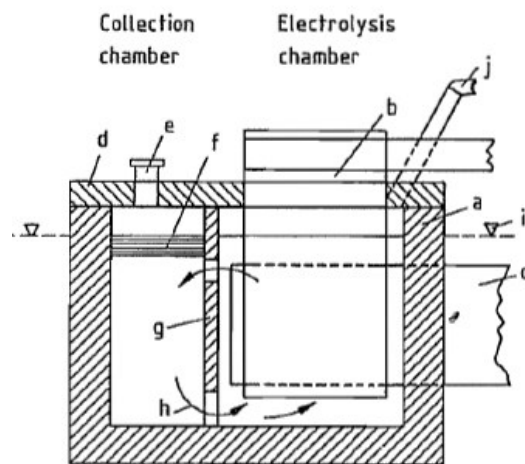


Figure 22: Norsk Hydro Cell: a) Refractory material; b) Graphite anode; c) Steel cathode;

cathode; c) Graphite anode; d) Refractory d) Refractory cover; e) Metal outlet; f) Metal cover; e) Magnesium collection compartment (Magnesium); g) Partition wall; h) Electrolyte flow; i) Electrolyte level; j) Chlorine outlet

MgCl₂ and Mg react with atmospheric oxygen or with oxygen-containing compounds to form MgO, which has a low solubility in the melt. The oxide can form a layer on the cathode surface, resulting in higher electrical resistance. MgO with entrapped electrolyte and Mg globules form a sludge at the bottom of the cell which must be removed at intervals. The amount of sludge is significantly lower in sealed as opposed to open cell designs.

Theoretically, 2.918 tonnes of Cl₂ is produced per tonne of Mg; commercial cells operating with dehydrated MgCl₂ may yield 2.7 – 2.8 tonnes of Cl₂ with a concentration of ≥ 95%. The chlorine gas from cells operated on dehydrated cell feed contains small amounts of air, dust from the electrolyte components, and minor amounts of chlorinated hydrocarbons requiring efficient systems for collection and destruction. Electrolytic magnesium contains typically 99.8% ≥ Mg.

Advantages and Disadvantages of Electrolytic Production Versus Thermal Reduction Methods

It would be reasonable that magnesium plants be established according to the availability of raw materials and energy. The use of Pidgeon technology in China involves the burning of coal as the source of energy for the process. The amount of coal required to produce 1tonne of magnesium is 20-25 tonnes for the preparation of FeSi, calcination of dolomite, heating the retorts, and re-melting and casting the magnesium ingots. This energy consumption in China for the production of magnesium is almost double that required for the electrochemical processes common to the countries in the West. The burning of such large quantities of coal is not compatible with environmental concerns, since it is accompanied by the discharge of very large quantities of SO_x into the atmosphere.

A summary of the comparison between electrolytic and thermal reduction processes for magnesium production is shown in Table 23. This clearly indicates that although the capital investment for electrolytic production is higher compared to thermal reduction process, the operating costs for magnesium production by thermal reduction are significantly higher and certainly not justified if compared by the same economic criteria.

Table 23: Comparison Between Electrolytic and Thermal Reduction Processes

Parameter for Comparison	Electrolytic Technology	Thermal Reduction Technology
Raw material	Magnesite, Dolomite, Bischofite, Carnalite, Serpentine, Seawater	Dolomite, Magnesite Coal, gas
Energy sources	Hydropower, Gas, Fossil fuel	
Energy consumption per tonne of Mg [MWh]	18 – 28	45 – 80 Batch process
Operational conditions	Continuous process	
Capital investment per tonne of Mg [US\$]	10,000 – 18,000	Up to 2,000
Operational manpower	X	Up to 5X

Refining and Casting

All magnesium extraction processes are followed by refining to remove impurities and casting to convert the metal to ingots, billets, slabs, or granules.

Properties and Uses of Magnesium and Its Alloys

Perhaps the most outstanding characteristic of magnesium is its density, 1.7 g/cm^3 , which is the lowest of all the structural metals. Apart from lithium, magnesium has the lowest relative density of the metals used in general engineering. Therefore, its alloys are used where lightweight is an important consideration (e.g., in aircraft components). Castings and forgings in the aircraft industry account for much of the magnesium alloys produced, e.g. landing-wheels, petrol-tanks, oil-tanks, crankcases, and air-screws, as well as other engine parts in both piston and jet engines. The automobile industry of course makes use of magnesium-base alloys.

At room temperature, magnesium and its alloys are difficult to deform; in fact, only small degrees of cold work may be imposed without annealing. Consequently, most fabrication is by casting or hot working at temperatures between 200 and 350°C. Magnesium, like aluminum, has a moderately low melting temperature but it melts at a slightly lower temperature (651°C) than aluminum.

As in aluminum alloys, the solubility of alloying elements in magnesium at room temperature is limited, causing only a small degree of solid-solution strengthening. The solubility of many alloying elements increases with temperature. Therefore, alloys may be strengthened by either dispersion strengthening or age hardening. Some age-hardened magnesium alloys, such as those containing Zr, Th, Ag, or Ce, have good resistance to over-aging at temperatures as high as 300°C. Alloys containing up to 9% Li have exceptionally lightweight.

Advanced magnesium alloys include those with very low levels of impurities and those containing large amounts (>5%) of cerium and other rare earth elements. These alloys form a protective MgO film that improves corrosion resistance. Rapid solidification processing (RST) permits larger amounts of alloying elements to be dissolved in the magnesium, further improving corrosion resistance. Improvements in strength, particularly at high temperatures, can be obtained by introducing ceramic particles or fibers such as silicon carbide into the metal.

These alloys are also classified as either cast or wrought, and some of them are heat-treatable. Aluminum, zinc, manganese, and some of the rare earths are the major alloying elements. Manganese helps to improve corrosion resistance, whilst zirconium acts as a grain-refiner. The 'rare earths' and thorium give a further increase in strength, particularly at high temperatures. A composition–temper designation scheme similar to that for aluminum alloys is also used. Table 24 lists several common magnesium alloys, their compositions, properties, and applications. These alloys are used in aircraft and missile applications, as well as in luggage. Furthermore, in the last several years the demand for magnesium alloys has increased dramatically in a host of different industries. For many applications, magnesium alloys have replaced engineering plastics that have comparable densities inasmuch as the magnesium materials are stiffer, more recyclable, and less costly to produce. For example, magnesium is now employed in a variety of handheld devices (e.g., chain saws, power tools, hedge clippers), in automobiles (e.g., steering wheels and columns, seat frames, transmission cases), and in audio-video-computer-communications equipment (e.g., laptop computers, camcorders, TV sets, cellular telephones).

Table 24: Compositions, Mechanical Properties, and Typical Applications for Six Common Magnesium alloys

ASTM Number	UNS Number	Composition (wt%)*	Condition	Mechanical Properties			Typical Applications
				Tensile Strength [MPa (ksi)]	Yield Strength [MPa (ksi)]	Ductility [%EL in 50 mm (2 in.)]	
AZ31B	M11311	90 Al, 1.0 Zn, 0.2 Mn	As extruded	<i>Wrought Alloys</i>			Structures and tubing, cathodic protection
				262 (38)	200 (29)	15	
HK31A	M13310	90 Th, 0.6 Zr	Strain hardened, partially annealed	255 (37)	200 (29)	9	
ZK60A	M16600	5.5 Zn, 0.45 Zr	Artificially aged	350 (51)	285 (41)	11	Forgings of maximum strength for aircraft
AZ91D	M11916	90 Al, 0.15 Mn, 0.7 Zn	As cast	<i>Cast Alloys</i>			
				290 (33)	150 (22)	3	Die-cast parts for automobiles, luggage, and electronic devices
AM60A	M10600	60 Al, 0.13 Mn	As cast	220 (32)	130 (19)	6	
AS41A	M10410	43 Al, 1.0 Si, 0.35 Mn	As cast	210 (31)	140 (20)	6	Die castings requiring good creep resistance

*The balance of the composition is magnesium.

Chemically, magnesium alloys are relatively unstable and especially susceptible to corrosion in marine environments. On the other hand, corrosion or oxidation resistance is reasonably good in the normal atmosphere; it is believed that this behavior is due to impurities rather than being an inherent characteristic of Mg alloys. Fine magnesium powder ignites easily when heated in air; consequently, care should be exercised when handling it in this state. Because of its great affinity for oxygen, magnesium burns with an intense hot flame and was used as the main constituent of incendiary bombs during the Second World War. This great affinity for oxygen makes it also more difficult to deal with in the foundry than other light alloys. To prevent it taking fire, it is melted under a layer of molten flux and, during the casting process; 'flowers of sulphur' are shaken on to the stream of molten metal as it leaves the crucible. The sulphur burns in preference to magnesium.

Magnesium is a desulphurizing and nodularizing agent in iron and steel making. It triggers the transformation of laminar carbon to globules in nodular iron. Magnesium is also used in the Kroll process for the production of titanium and zirconium, the reduction of UF₄ to uranium metal, and the production of beryllium and hafnium.

The electronegative character of Mg makes the metal suitable for corrosion abatement in the popular cathodic protection by sacrificial anode method. Pure Mg (preferably atomized powder) combines readily with hydrogen to form magnesium hydride which can be released in a reversible process. Magnesium hydride has a higher concentration of hydrogen per unit volume than liquid hydrogen. The reversibility [absorption and desorption] of the process is dependent on the surface activity of the powder. As a carrier for hydrogen, Mg can be used for fuel-cell applications.

TITANIUM

Titanium is probably the most important and most widely used of those metals whose technology was developed in the latter half of the twentieth century. As well as being strong and corrosion-resistant, it is also a very light metal and since it has a relative density of 4.5, only just half that of steel, this gives it an excellent strength-to-weight ratio (termed '*specific strength*'). It is as corrosion-resistant as 18/8 stainless steel but will also withstand the extreme corrosiveness of salt water. It has a high melting point of 1668°C. It is this combination of high strength, low density and excellent corrosion resistance that has led to the expansion of the

use of titanium in the aerospace, chemical and engineering industries since the late 1940s. It is now no longer a 'new' metal but quite a commonly used metal.

Although discovered in Cornwall by an English priest, Rev. W. Gregory, as long ago as 1791, the industrial production of titanium did not begin until the late 1940s and that was to fulfill the needs of aerospace engineers. This was not due to any scarcity of its ores - it is in fact the tenth element in order of abundance in the Earth's crust and fifty times more abundant than copper - but principally because molten titanium reacts chemically with most other substances, making it difficult, and hence extremely expensive, to extract, melt, cast, and shape commercially. Nevertheless, although chemically very reactive, once it has been successfully shaped, titanium has an excellent corrosion resistance because, like aluminium, its surface becomes coated with a dense impervious film of oxide, which effectively seals it from further atmospheric attack.

History of Titanium

Rev. William Gregory, a clergyman and amateur mineralogist found its oxide in a dark, magnetic iron sand [ilmenite, (FeO·TiO₂)] in Cornwall (UK), and first suspected the element titanium as a new, unknown element in 1791. In 1795, Klaproth, a German chemist, analyzed rutile (TiO₂) from Hungary and identified an oxide of an unknown element, the same as the one reported by Gregory. Klaproth named the element *titanium* after the *Titans*, the powerful sons (gods) of the earth mother in Greek mythology [see *Titanic*]. During the 19th century, several attempts were made to extract the metal from its oxide. In 1825, Berzelius produced very impure metal. In the following year (1826), Dumas was able to convert its oxide to its tetrachloride (TiCl₄), and in 1887 Wilson and Peterson reduced the tetrachloride with sodium to make small quantities of brittle titanium of 95% purity. At this time, Ti in the form of an impure alloy with iron was used as a deoxidizing agent for steels. The production of ductile, high purity titanium still proved to be difficult, because of the strong tendency of this metal to react with oxygen, nitrogen and carbon. Early demonstrations of the reduction of TiCl₄ using either Na or Mg produced small quantities of brittle titanium metal.

In 1910, Hunter of the General Electric Company made Ti of 99.5% purity by sodium-reduction [sodiodermy] of the tetrachloride in an enclosed bomb. In 1922, van Arkel produced a pure, ductile metal by reducing potassium hexafluorotitanate (K₂TiF₆) with sodium in an inert atmosphere. It was not until well into the 20th century (1937-1940) that a commercially attractive process for making pure ductile Ti was developed by Dr. W. Kroll in Luxembourg. This process involved the reduction of TiCl₄ with magnesium [*magnesiothermy*] in an inert gas atmosphere following Hunter's bomb process. The resulting titanium is called —*titanium sponge* because of its porous and spongy appearance. Wartman of the Bureau of Mines then developed a method of treating the titanium sponge so obtained by melting it in an electric arc furnace under vacuum using a tungsten electrode. This famous Kroll process has remained essentially unchanged and is the dominant process for titanium production today.

It is noteworthy that the industrial capacity of TiCl₄ production existed before the interest in metallic titanium developed. This is because TiCl₄ is the feedstock for synthetic, high purity TiO₂ used in paint. Even today, only 5% of the TiCl₄ production is used to produce titanium metal.

Occurrence and Processing

Titanium is present in the earth's crust at a level of about 0.53% and is therefore the fourth most abundant structural metal after aluminum, iron, and magnesium. The most important mineral sources are **ilmenite** (FeTiO₃) and **rutile** (TiO₂). Rutile is found in beach sand in Australia, Mexico and in Trivacore, South India; rock deposits of the mixed oxides, ilmenite (FeTiO₃ or FeO·TiO₂) and **titanomagnetite** [(FeTi)O₄] are extensive in Norway, The Transvaal (South Africa), USA, Canada and former USSR.

The resources can be divided into two broad categories: **natural resources**, and **secondary resources**. The natural resources are **ilmenite**, **rutile** (tetragonal TiO₂), **anatase** (tetragonal TiO₂), **brookite** (orthorhombic TiO₂) **pseudo-brookite**, **leuxozene**, **arizonite**, **perovskite**, **laporite**, and **sphine**. The secondary resources are red mud, synthetic rutile, titania slag, and ferrotitanium. Among the natural resources, the most important titanium-bearing minerals are ilmenite, (FeO·TiO₂) and rutile, (TiO₂). The former represents about 90% of the world's titanium reserves while the latter accounts for the balance of 10%. About 95% of the titanium minerals processed annually are utilized for the preparation of pure titanium dioxide which is used as a pigment.

Natural rutile, because of its high titanium oxide content and its low impurity levels, is the preferred feed on some accounts. Since ilmenite is more abundant than rutile, it is of considerable technical importance. Processes have been established for the beneficiation of ilmenite to produce a rutile substitute. Beneficiated ilmenite yields a product known as —synthetic rutile— a material that can be treated in the same way as rutile to produce the titanium dioxide pigment.

Beneficiation or Processing

The mined ores are separated from siliceous gangue by the conventional technique of froth flotation, specific gravity methods and, for ores containing titanomagnetite, magnetic separation. Typical ore concentrates contain 95% titanium dioxide or titania (TiO₂) from rutile, 40 – 80% TiO₂ from ilmenite and about 10% TiO₂ from titanomagnetite. Smelting of ilmenite ores to produce pig iron leaves a high Ti slag containing about 70% TiO₂.

Although a large number of technologies are known to have been developed for the beneficiation of ilmenite, only a limited number of processes are found to be in use. These may broadly be grouped under three heads: (i) partial reduction of iron oxide followed by acid leaching; (ii) full (metallization of iron oxides) reduction followed by aeration (oxidation), desliming acid leaching; and (iii) full ((metallization of iron oxides) reduction followed by smelting (tappings: pig iron and titania slag) followed by acid washing/leaching of the slag. Partial reduction and leaching process bear the advantages such as least (direct) energy consumption, utilization of waste acids, and good-quality product. This route is, however, associated with pollution-related problems. The metallization and desliming approach has registered success (particularly in Australia), as the process has the advantages of lower operating costs and fewer pollution-related problems. The reduction smelting (electric arc) process is perhaps the most attractive avenue because pig iron is produced as a co-product and the slag (acid-washed) has received acceptability and marketability.

The technology for the production of titania slag by direct reduction smelting in electric arc furnaces (particularly for smelting of iron titanates and ilmenites having lower amounts of titania) is very old and the process has been in vogue in Canada, Norway, South Africa, CIS (countries of former USSR), and Japan. The slag which contains about 80% TiO₂ has been (and is still being) used for the production TiO₂ pigment by the sulphate route. The USA and CIS have used the process involving chlorination of slags with the without ilmenite and in the presence or absence of chloride melts. In current lines, the development of a process involving reduction smelting in plasma arc furnaces for the production of pig iron and titania slag from ilmenites has been reported and according to published literature, this process is becoming more exploited on a commercial basis.

Extraction of Titanium

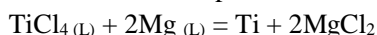
Titania or titanium (IV) oxide (TiO₂) is chemically very stable and cannot be reduced to the pure metal by the common reducing agents such as carbon or hydrogen. Furthermore, O₂, N₂, C and H₂ are soluble in the metal, making it brittle [embrittlement] and must be excluded if ductile Ti is to be produced. The metal is produced by converting TiO₂ to TiCl₄, which is reduced with Mg or Na to form a titanium sponge or finely divided granules.

Titanium tetrachloride (TiCl₄) is manufactured by passing chlorine gas over [i.e. chlorination] an intimate mixture of titanium dioxide (TiO₂) and coke [bonded with coal-tar to form briquettes] in a vessel at 800°C. Reaction temperature is maintained by resistance heating with carbon electrodes and by heat generated autogenously by the reaction:



The chlorination temperature can be lowered by prefiring the TiO₂ with carbon and ammonia at high temperature to form titanium carbide (TiC) or titanium cyanonitride (TiCN). The impure product of the chlorination process is refined by filtration, fractional distillation, and by refluxing with carbon disulphide (CS₂) and hydrogen sulphide (H₂S) to remove vanadium oxychloride (VOCl₂), an impurity with a boiling point similar to that of TiCl₄. Titanium tetrachloride is a yellow liquid boiling at 136° C, which hydrolyzes readily in contact with moist air.

The next stage in metal production is reduction of TiCl₄. The process, now known as the **Kroll process**, was originally developed in 1940 by Wilhelm F. Kroll for the production of titanium. It is based on the reaction:



The process was adopted for zirconium subsequently. In the Kroll process, TiCl_4 is fed into a clean reaction vessel containing molten Mg at 800 – 900°C and an inert atmosphere of argon. The liquid Mg reduces the TiCl_4 to form spongy masses of titanium metal. Reaction temperature is maintained by controlling the rate of addition of the tetrachloride. Sufficient TiCl_4 is added to react with 85 to 90% of the Mg present; then as much MgCl_2 as possible is tapped off and the product is allowed to cool in the inert atmosphere. The spongy mass of Ti containing residual Mg and MgCl_2 is evolved from the reaction vessel into a dry atmosphere and the titanium sponge is separated by leaching with cold hydrochloric acid and by vacuum distillation at 900°C. MgCl_2 is leached out while Mg is distilled off.

Further refining of the raw titanium metal is not usually necessary but can be achieved by the **Van Arkel–de Boer process** [i.e. **iodide refining process**] or by electrorefining in fused salt baths. Iodide refining is one of the important methods for the purification of titanium, zirconium, and hafnium. The method is based on the reversibility of a reaction between a metal and iodine. Formation of the metal iodide occurs at a relatively low temperature, and decomposition of the iodide occurs at a much higher temperature. Even though the free energy change associated with the reaction remains negative in the temperature range considered, the iodide decomposes at higher temperatures because of the low pressure maintained in the reaction vessel and dissociation of the iodine molecule to monatomic iodine. The reactor used for this process is so designed that the iodine liberated during the decomposition reaction travels back and reacts with the crude metal, forming fresh tetraiodide. Iodine thus functions as a vehicle for carrying the pure metal. The process can be represented as:



The reduction of TiCl_4 with sodium to produce titanium metal granules is essentially similar to the Kroll magnesium process, although final vacuum distillation is not needed. The major disadvantages of Mg or Na reduction is that it can only be separated as a batch process.

Electrolytic reduction of molten salts containing titanium chloride and fluorotitanates can produce very pure metal and is being developed as a commercial process.

Melting and Conversion of Titanium Ingot

Due to its high reactivity and melting point (1668°C), titanium cannot be melted in air using conventional refractory materials. Production of Ti and Ti alloy ingot is therefore achieved by arc-melting (in vacuum or an inert atmosphere) an electrode of Ti sponge or granules compacted with a uniform distribution of the required alloy additions. The melting crucible is made of copper and is vigorously cooled with water or with liquid sodium-potassium alloy. Ingot size is from 1 to 10 tonnes. Conversion of Ti ingots into useful shapes follow conventional metal working practices, equipment used for steel being generally more suitable than that used in other nonferrous metal production. Ti and its alloys are supplied for manufacture of components as billets and bars for forging or machining and as plates, sheets, wire, extruded sections and tubes.

Properties of Titanium

Titanium is a silvery-grey transition metal with atomic number of 22 and atomic weight 47.9 g/mol belonging to group 4 or IVA of the Periodic Table. The density of pure Ti is 4.51 g/cm³ and the melting and boiling points are 1668°C and 3260°C respectively. The melting point is raised by impurities such as oxygen, nitrogen and carbon. The specific heat capacity of Ti is about 0.126 Cal/g·°C at room temperature. Thermal conductivity of pure Ti is 0.04 Cal/cm·°C. Alloying lowers the thermal conductivity to between 0.015 and 0.030 Cal/cm·°C depending upon the alloy additions. The strength and ductility of Ti depend on purity. Iodine refined metal (99.9% Ti) has a tensile strength of about 15 Tsi. Commercially pure Ti melted from sponge or granules has a strength of 20 to 30 Tsi which can be increased to 50 Tsi at the expense of ductility. By the addition of oxygen, the modulus of elasticity is about 16×10⁶ Psi. The fatigue limit of Ti is 45 to 60% of the UTS.

Although strengths of up to 50 Tsi can be obtained with commercially pure Ti containing high impurity levels of oxygen, carbon and nitrogen, these impurities lead to reduced ductility. It is necessary to alloy Ti with other metals to achieve higher strength with good ductility and in particular, good creep resistance at temperatures of 150 to 500°C.

Addition of beta-stabilizing elements improves the forgeability of Ti alloys and leads to duplex structure of α - and β -phases which, by suitable heat treatment, can be modified in composition and distribution to provide Ti alloys varying widely in strength, ductility, creep resistance and toughness.

With larger additions of beta-stabilizing elements it is possible to retain the high temperature beta allotrope on cooling to room temperature. Limited use has been made of heat-treatable metastable β -alloys, but they have higher density than α - and α - β alloys. Complex alloys containing two or more alpha-stabilizers with one or more beta-stabilizers or compound-forming additions generally have superior mechanical properties to the simpler alloys. Ti alloys are classified by phases present at room temperature.

The excellent corrosion resistance of Ti to many chemicals is due to the formation of a thin passive surface oxide film. The protective TiO_2 film provides excellent resistance to corrosion and contamination below 535°C . Above 535°C , the oxide film breaks down, and small atoms such as carbon, oxygen, nitrogen, and hydrogen embrittle the titanium. Ti is resistant to oxidizing acids, most organic acids, chloride solutions and moist chlorine gas, sulphuric and dilute mineral acids and alkaline solutions. Hydrofluoric acid at temperatures above 700°C makes Ti to oxidize rapidly in air and oxygen dissolves into the metal causing hardening and embrittlement.

High strength, low density, and excellent corrosion resistance are the main properties that make titanium attractive for a variety of applications. Examples include aircraft (high strength in combination with low density), aero-engines (high strength, low density, and good creep resistance up to about 550°C), biomedical devices (corrosion resistance and high strength), and components in chemical processing equipment (corrosion resistance). The relatively high cost of titanium has hindered wider use, for example in automotive applications.

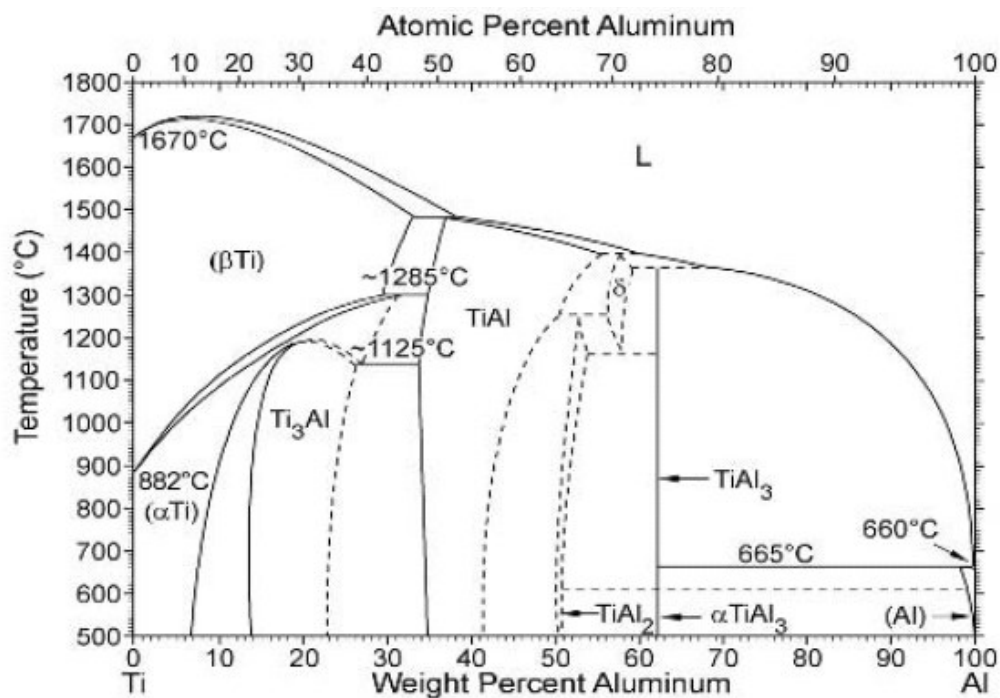


Figure 23: Ti-Al Binary System

Titanium Alloys

Titanium exists in two crystallographic forms. At room temperature, unalloyed (commercially pure) titanium has a hexagonal close-packed hcp crystal structure referred to as alpha α phase. At 883°C (1621°F), this transforms to a body-centered cubic bcc structure known as beta β phase. The manipulation of these crystallographic variations through alloying additions and thermomechanical processing is the basis for the development of a wide range of alloys and properties. These phases also provide a convenient way to categorize titanium mill products. Based on the phases present, titanium alloys can be classified as either α alloys, β alloys, or α β alloys. The relative amounts of alpha and beta phases in any particular alloy has a significant effect on its tensile strength, ductility, creep properties, weldability and ease of formability.

Aluminium is the most important alloy addition because it strengthens alpha titanium (α -Ti) and also reduces density, thus improving an already favourable high strength-to-weight ratio. Al additions are limited to 6.4 wt% because higher levels can cause embrittlement. The Ti-Al binary system is shown in Figure 23. It is common practice to refer to a titanium alloy by its structure:

Alpha titanium alloys contain elements such as aluminum and tin. These α -stabilizing elements work by either inhibiting change in the phase transformation temperature or by causing it to increase. Alpha alloys generally have creep resistance superior to β alloys, and are preferred for high-temperature applications, e.g. steam turbine blades. The most common of the all- α alloys contains 5% Al and 2.5% Sn, which provide solid solution strengthening to the CP α . The α -alloys are annealed at high temperatures in the β region. Rapid cooling gives an acicular, or Widmanstätten, α -grain structure that provides good resistance to fatigue. The absence of a ductile-to-brittle transition, a feature of β alloys, makes α alloys suitable for cryogenic applications. Alpha alloys are characterized by satisfactory strength, toughness, and weldability, but poorer forgeability than β alloys. This latter characteristic results in a greater tendency for forging defects. Smaller reductions and frequent reheating can minimize these problems. Unlike β alloys, alpha alloys cannot be strengthened by heat treatment. They most often are used in the annealed or recrystallized condition to eliminate residual stresses caused by working.

Near alpha-titanium alloys are almost entirely alpha phase with a small amount of the beta phase dispersed through the alpha. Such alloys are obtained by adding small amounts of molybdenum and vanadium to what otherwise would have been an alpha alloy. An example is Ti-8%Al-1%Mo-1%V which is normally used in the annealed condition, and used for airframe and jet engine parts which require high strengths, good creep resistance and toughness up to temperatures of about 850°C. For maximum creep resistance above 450°C, near alpha alloys are used and they have good weldability.

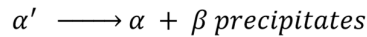
Beta titanium alloys contain transition elements such as vanadium, niobium, and molybdenum, which tend to decrease the temperature of the α to β phase transition and thus promote development of the bcc β phase. Although large additions of vanadium or molybdenum produce an entirely β structure at room temperature, none of the β alloys actually are alloyed to that extent. Instead, they are rich in β -stabilizers, so that rapid cooling produces a metastable structure composed of all β . Strengthening is obtained both from the large amount of solid-solution strengthening alloying elements and by aging the metastable β structure to permit α to precipitate. They have excellent forgeability over a wider range of forging temperatures than α alloys, and β alloy sheet is cold formable in the solution-treated condition. Beta alloys have excellent hardenability, and respond readily to heat treatment. A common thermal treatment involves solution treatment followed by aging at temperatures of 450 to 650°C. This treatment results in formation of finely dispersed α particles in the retained β . In the high strength condition, the alloys have low ductility as well as poor fatigue performance. A typical β -titanium alloy is Ti-13%V-11%Cr-3%Al. Applications include high-strength fasteners, beams, and other fittings for aerospace applications.

Alpha + beta titanium alloys have compositions that support a mixture of α and β phases and may contain between 10 and 50% β phase at room temperature. Although this particular alloy is relatively difficult to form even in the annealed condition, α + β alloys generally have good formability. The properties of these alloys can be controlled through heat treatment, which is used to adjust the amounts and types of β phase present. Solution treatment followed by aging at 480 to 650°C precipitates α , resulting in a fine mixture of α and β in a matrix of retained or transformed β phase. They tend to be high strength materials with tensile strengths of 900-1250 MPa and have good creep resistance up to about 350-400°C.

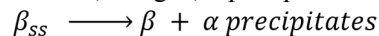
With proper balancing of the α and β stabilizers, a mixture of α and β is produced at room temperature. Ti – 6% Al – 4% V, an example of this approach, is by far the most common of all the titanium alloys. The Al stabilizes the α -phase while the V stabilizes the β -phase. Because the alloys contain two phases, heat treatments can be used to control the microstructure and properties.

Annealing provides a combination of high ductility, uniform properties, and good strength. The alloy is heated just below the β -transus temperature, permitting a small amount of α to remain and prevent grain growth. Slow cooling causes equiaxed α grains to form; the equiaxed structure provides good ductility and formability while making it difficult for fatigue cracks to nucleate. Faster cooling, particularly from above the α - β transus

temperature, produces an acicular—or —basketweave— α phase. Although fatigue cracks may nucleate more easily in this structure, cracks must follow a tortuous path along the boundaries between α and β . This condition results in a low-fatigue crack growth rate, good fracture toughness, and good resistance to creep. Two possible microstructures can be produced when the β phase is quenched from a high temperature. The β transforms to titanium martensite (α') in an alloy that crosses the M_s line on cooling. The titanium martensite is a relatively soft supersaturated phase. When α' is reheated, tempering occurs by the precipitation of β from the supersaturated α' :



Fine β precipitates initially increase the strength compared with the α' , opposite to what is found when a steel martensite is tempered; however, softening occurs when tempering is done at too high a temperature. More highly alloyed α - β compositions are age hardened. When the β in these alloys is quenched, β_{ss} , which is supersaturated in titanium, remains. When β_{ss} is aged, α precipitates in a Widmanstätten structure:



The formation of this structure leads to improved strength and fracture toughness. Components for airframes, rockets, jet engines, and landing gear are typical applications for the heat-treated α - β alloys. Some alloys, including the Ti – 6% Al – 4% V alloy, are superplastic and can be deformed as much as 1000%. This alloy is also used for making implants for human bodies. Titanium alloys are considered **biocompatible** (i.e., they are not rejected by the body). By developing porous coatings of bone-like ceramic compositions known as **hydroxyapatite**, it is possible to make titanium implants **bioactive** or **bioadhesive** (i.e., the natural bone can grow into the hydroxyapatite coating). The following three examples illustrate applications of titanium alloys.

Applications of Titanium and Its Alloys

The rapid growth of the titanium industry is testimony to the metal's high specific strength and corrosion resistance. With density about 55% that of steel, titanium alloys are widely used for highly loaded aerospace components that operate at low to moderately elevated temperatures, including both airframe and jet engine components. Titanium's corrosion resistance is based on the formation of a stable, protective oxide layer. This passivating behavior makes the metal useful in applications ranging from chemical processing equipment to **surgical implants and biomedical implants** such as hip prostheses.

Ti is used in applications where its particular properties of high strength-to-weight ratio, good creep strength at temperatures up to 500°C and excellent corrosion resistance offer design efficiency and economy over conventional and cheaper metals. Major outlets for Ti are in the aerospace and chemical engineering industries. Ti alloys are used for compressor wheels, blades and casings of gas turbine engines and in airframe and space vehicle structures for high strength and heat resistance. Low temperature pressure vessels for rocket motors frequently are Ti particularly α - β alloys for its good cryogenic properties.

Unalloyed titanium (commercially pure) is used for its superior corrosion resistance. Impurities, such as oxygen, increase the strength of the titanium but reduce corrosion resistance. Applications include heat exchangers, piping, reactors, pumps, and valves for the chemical and petrochemical industries.

When it is combined with niobium, a superconductive intermetallic compound is formed; when it is combined with nickel, the resulting alloy displays the **shape-memory effect**; when it is combined with aluminum, a new class of intermetallic alloys is produced. Titanium alloys are used for sports equipment such as the heads of golf clubs.

Titanium and its alloys are used in the form of wrought products, castings, P/M parts, metal-matrix composites, and ordered intermetallics. Table 25 presents several titanium alloys along with their typical properties and applications. They are commonly utilized in airplane structures, space vehicles, and surgical implants, and in the petroleum and chemical industries.

In Japan, titanium has become established as a roofing material, particularly for 'prestige' buildings. Since weight-for-weight titanium is some times more expensive than competitors like copper and stainless steel, this may seem surprising. However, since titanium is strong, light-gauge material can be used, thus reducing the cost per unit area covered. More important still, this light-gauge material coupled with the low relative density of the metal means that much less massive support members are necessary in roof construction. Titanium has a high resistance to corrosion and is able to cope with the very corrosive marine atmospheres prevalent in most of

Japan. This reduces maintenance costs relative to other metals, so that when all of these points are considered, it is claimed that titanium can compete, particularly when the architecturally pleasing result is taken into account.

Table 25: Compositions, Mechanical Properties, and Typical applications for Several Common Titanium Alloys

Alloy Type	Common Name (UNS Number)	Composition (wt%)	Condition	Average Mechanical Properties			Typical Applications
				Tensile Strength [MPa (ksi)]	Yield Strength [MPa (ksi)]	Ductility [%EL in 50 mm (2 in.)]	
Commercially pure	Unalloyed (R50250)	99.5 Ti	Annealed	240 (35)	170 (25)	24	Jet engine shrouds, cases and airframe skins, corrosion-resistant equipment for marine and chemical processing industries
α	Ti-5Al-2.5Sn (R54500)	5 Al, 2.5 Sn, balance Ti	Annealed	826 (120)	784 (114)	16	Gas turbine engine casings and rings; chemical processing equipment requiring strength to temperatures of 480°C (900°F)
Near α	Ti-8Al-1Mo-1V (R54810)	8 Al, 1 Mo, 1 V, balance Ti	Annealed (duplex)	930 (138)	890 (129)	15	Forgings for jet engine components (compressor disks, plates, and hubs)
α - β	Ti-6Al-4V (R56400)	6 Al, 4 V, balance Ti	Annealed	947 (137)	877 (127)	14	High-strength prosthetic implants, chemical-processing equipment, airframe structural components
α - β	Ti-6Al-6V-2Sn (R56600)	6 Al, 2 Sn, 6 V, 0.75 Cu, balance Ti	Annealed	1030 (153)	985 (143)	14	Rocket engine case airframe applications and high-strength airframe structures
β	Ti-10V-2Fe-3Al	10 V, 2 Fe, 3 Al, balance Ti	Solution + aging	1223 (178)	1130 (167)	10	Best combination of high strength and toughness of any commercial titanium alloy; used for applications requiring uniformity of tensile properties at surface and center locations; high-strength airframe components

In selecting Ti alloys for engineering applications, one needs to consider the susceptibility of near alpha alloys to stress corrosion cracking (SSC) in salt-water environments and poor fatigue performance of beta alloys.

Assignment 1

Shape-Memory Alloys were referred to as “Metallurgical Solution Looking for a Problem” in *Metallurgia*, Vol. 51, No. 1, January 1984, pp. 26–29: (a) Describe the shape memory effect, and then explain the mechanism (in terms of phase transformations, etc.) that is responsible for this phenomenon. (b) Identify any three alloy systems exhibiting this effect. (c) Suggest three practical applications in which an alloy displaying this shape memory effect may be utilized. (d) Why did the author of the paper cited above call SMAs „metallurgical solutions looking for a problem“?

Assignment 2

Discuss the rationale for biomedical applications of titanium and its alloys. Use hip prosthesis materials for a case study.

[NB: These subjects will be discussed in the next class. You are therefore expected to turn in your assignments before the next class, i.e. 12.35 pm on Thursday, 16 August 2012. Remember to provide a full list of all references used]

Titanium and Shape Memory Effect (SME)

Shape memory alloys (alloys displaying shape-memory effect) have the unique characteristic of being able to recover their initial geometric shape after they have been plastically deformed. This recovery after deformation at a lower temperature occurs on reheating to a few hundred degrees Celsius. This reversibility of geometric shape is referred to as the **shape-memory effect (SME)**. Shape-memory effect is a unique property possessed by some alloys that undergo the martensitic reaction. These alloys can be processed using a sophisticated thermo-mechanical treatment to produce a martensitic structure. At the end of the treatment process, the material is deformed to a predetermined shape. The metal can then be deformed into a second shape, but when the temperature is increased, the metal changes back to its original shape!

Alloys based on the nominal composition of the compound TiNi (known as *titanol*) have been recognized to exhibit the shape memory effect for many years. One of the original shape memory alloys dates back to 1950 and was based on AuCd. The temperature range over which this strain reversal is possible is very sensitive to the alloy composition but SME occurring from -150°C to $+150^{\circ}\text{C}$ is readily achievable. Under the right conditions of composition and temperature, this class of materials also exhibits the capability to deform elastically over large strain ranges. This latter characteristic is known as superelastic behavior. At present, the TiNi class of SME alloys is among the most widely used. For this reason, a short discussion of shape memory alloys and applications of titanium based shape memory alloys is necessary here.

Mechanism of the Shape Memory Effect

The compound TiNi has a bcc (CsCl prototype) structure which transforms martensitically to a monoclinic (AuCd prototype) structure when cooled below the martensite start (M_s) temperature, as shown schematically in Figure 24. The martensite is internally twinned. The twins represent the mode of lattice invariant deformation using the standard terminology from the crystallographic theory of martensite. Part B of Figure 25 shows these twins. Upon deformation, the martensite untwins, as shown in part C of Figure 25, leaving a shape change equivalent to the volume fraction of twins multiplied by the twinning shear. In TiNi this reversible shape change can be equivalent to as much as an 8% shear strain. If the material containing the deformed (untwined) martensite is reheated to above the austenite start temperature (A_s) shown in Figure 24, the martensite becomes unstable and reverts to the parent phase. When this occurs, the original shape of the starting piece is recovered, as shown in part A of Figure 25. This reversible martensitic phase transformation is the basis for the shape memory effect, not only in compounds based on TiNi but also in a variety of other alloys based on Cu, Au, Ag, and Fe.

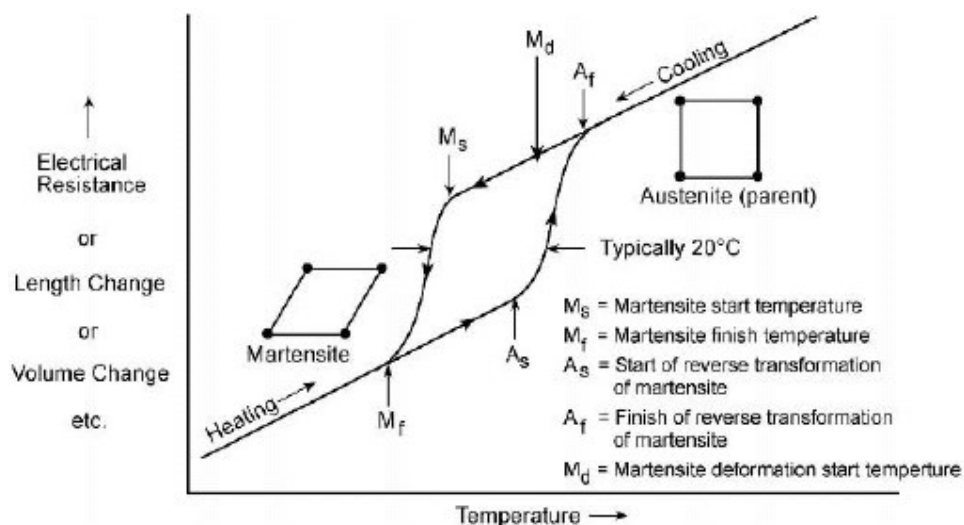


Figure 24: Schematic diagram showing the transformation sequence of a TiNi alloy during cooling and reheating, the martensite deformation start temperature is also shown

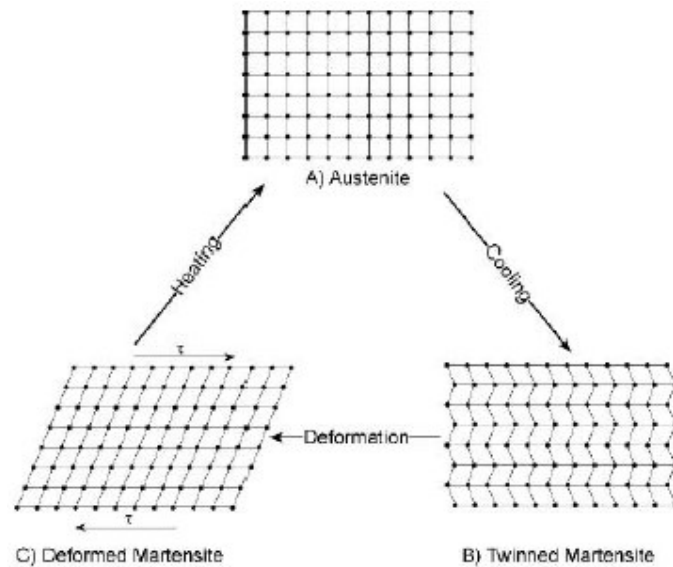


Figure 25: Diagram showing the transformation from austenite to martensite and the shape change that occurs when the martensite untwins during deformation

In general, a shape-memory alloy is polymorphic—that is, it may have two crystal structures (or phases), and the shape-memory effect involves phase transformations between them. One phase (termed an *austenite phase*) has a body-centered cubic structure that exists at elevated temperatures; its structure is represented schematically by the inset shown at stage 1 of Figure 26. Upon cooling, the austenite transforms spontaneously to a martensite phase, which is similar to the martensitic transformation for the iron–carbon system—that is, it is diffusionless, involves an orderly shift of large groups of atoms, and occurs very rapidly, and the degree of transformation is dependent on temperature. The temperatures at which the transformation begins and ends are indicated by M_s and M_f labels on the left vertical axis of Figure 26. In addition, this martensite is heavily twinned, as represented schematically by the stage 2 inset, Figure 26. Under the influence of an applied stress, deformation of martensite (i.e., the passage from stage 2 to stage 3, Figure 26) occurs by the migration of twin boundaries—some twinned regions grow while others shrink; this deformed martensitic structure is represented by the stage 3 inset.

Furthermore, when the stress is removed, the deformed shape is retained at this temperature. Upon subsequent heating to the initial temperature, the material reverts back to i.e., —remembers its original size and shape (stage 4). This stage 3–stage 4 process is accompanied by a phase transformation from the deformed martensite to the original high-temperature austenite phase. For these shape-memory alloys, the martensite-to-austenite transformation occurs over a temperature range, between temperatures denoted by A_s austenite start and A_f austenite finish labels on the right vertical axis of Figure 26. Of course, this deformation–transformation cycle may be repeated for the shape-memory material.

The original shape (to be remembered) is created by heating to well above the A_f temperature (such that the transformation to austenite is complete) and then restraining the material to the desired memory shape for a sufficient time period. For example, for Nitinol alloys, a one-hour treatment at 500°C is necessary. Although the deformation experienced by shape-memory alloys is semi-permanent, it is not truly —plastic deformation, neither is it strictly —elastic. Rather, it is termed *thermoelastic*, because deformation is nonpermanent when the deformed material is subsequently heat-treated. The Maximum recoverable deformation strains for thermoelastic materials are on the order of 8%.

For Nitinol family of alloys, transformation temperatures can be made to vary over a wide temperature range (between about –200°C and 110°C), by altering the Ni–Ti ratio, and also by the addition of other elements.

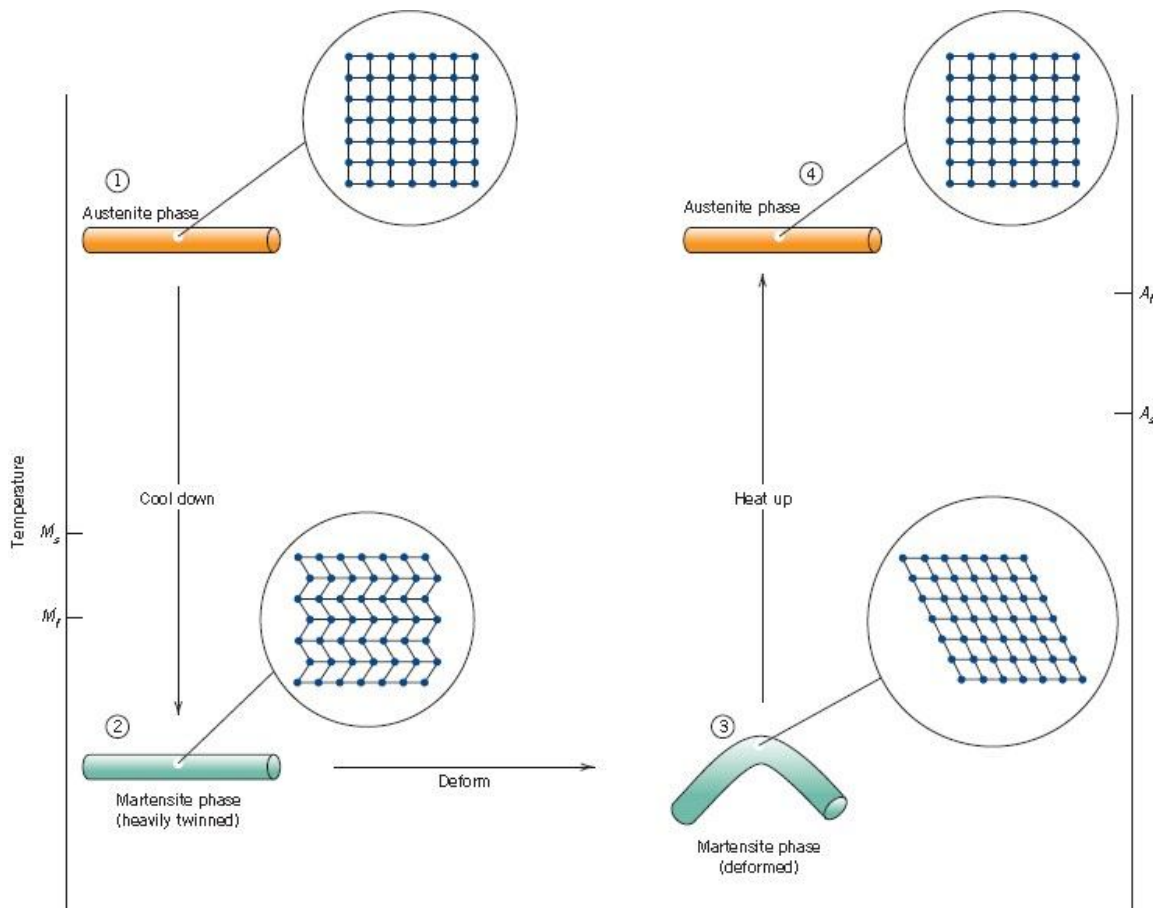


Figure 26: Diagram illustrating the shape-memory effect. The insets are schematic representations of the crystal structure at the four stages. ‘ M_s ’ and ‘ M_f ’ denote temperatures at which the martensitic transformation begins and ends. Likewise for the austenite transformation, ‘ A_s ’ and ‘ A_f ’ represent beginning and end transformation temperatures.

Titanium and Shape-Memory Alloys (SMAs)

The *shape-memory alloys* (or *SMAs*) are a relatively new group of metals that exhibit an interesting (and practical) phenomenon known as shape-memory effect (SME). As shown in the preceding section, one of these materials, after being deformed, has the ability to return to its pre-deformed size and shape upon being subjected to an appropriate heat treatment—that is, the material “remembers” its previous size and shape. Deformation normally is carried out at a relatively low temperature, whereas shape memory occurs upon heating. Alloys that demonstrate this phenomenon only upon heating are said to have a *one-way shape memory*. Some of these materials experience size/shape changes on both heating and cooling; these are termed *two-way shape memory alloys*.

As noted already, nickel–titanium alloys (their trade name is *Nitinol*, which is really an acronym for *nickel–titanium naval ordnance laboratory*; Naval Ordnance Laboratory being where this alloy was first discovered) are classic examples of SMAs. In addition to the family of Ni–Ti alloys there are other alloys that exhibit the shape memory effect. These are Ag–Cd, Au–Cd, Cu–Al–Ni, Cu–Sn, Cu–Zn, combinations of Cu–Zn with Al, or Si or Sn, In–Ti, Ni–Al, Fe–Pt, Mn–Cu, and Fe–Mn–Si. Note that not all compositions of either the two or three elements yield an alloy with shape memory effect, but only certain compositions.

More recently, a special class of materials known as *ferromagnetic shape memory alloys* also has been developed. Examples of ferromagnetic shape-memory alloys include Ni₂MnGa, Fe–Pd, and Fe₃Pt. Unlike Ni–Ti, these materials show a shape-memory effect in response to a magnetic field. Most commercial shapememory alloys including Ni–Ti are not ferromagnetic.

In a sense, viscoelastic polymers can be said to show shape-memory effect, since the viscous component is recovered over time. Thus, many polymers do have a memory of their shape! Recently, researchers have developed new shape-memory plastics.

SMA's are a class of *smart* or *intelligent materials*, i.e. materials that can sense an external stimulus (such as stress, temperature change, magnetic field, pH change, etc.) in their environment and respond in a timely and predetermined manner. Shape-memory alloys exhibit a memory that can be triggered by stress or temperature change or even presence or absence of a magnetic field as in the case of ferromagnetic SMA's. *Actively smart materials* can even initiate a response (i.e., they function as a sensor and an actuator). Shapememory alloys are a family of *passively smart materials* in that they merely sense a change in stress or temperature

Applications of Shape-Memory Alloys [SMAs]

There is a host of applications for alloys displaying SME—for example, eyeglass frames, actuators for smart systems, tooth-straightening braces (orthodontic braces), collapsible antennas for cellular phones, greenhouse window openers, antiscald control valves on showers, women's foundation garments, fire sprinkler valves, and in biomedical applications (such as blood-clot filters, self-extending coronary stents, and bone anchors).

Flaps that change direction of airflow depending upon temperature have been developed and used for air conditioners using SMA's. Shape-memory alloys also show a **superelastic** behavior. Recoverable strains up to 10% are possible. This is why shape-memory alloys have been used so successfully in such applications as orthodontic wires or braces, eyeglass frames, and antennas for cellular phones. In these applications, we make use of the superelastic (and not the shape memory) effect.

Nitinol has been used in military, medical, safety, and robotics applications. Specific applications include hydraulic lines used on F-14 fighter planes, medical tweezers and sutures, anchors for attaching tendons to bones, stents for cardiac arteries, eyeglass frames, and antiscalding valves used in water faucets and showers.

One important SMA application is in weldless, shrink-to-fit pipe couplers used for hydraulic lines on aircraft, for joints on undersea pipelines, and for plumbing on ships and submarines (Figure 27). Each coupler (in the form of a cylindrical sleeve) is fabricated so as to have an inside diameter slightly smaller than the outside diameter of the pipes to be joined. It is then stretched (circumferentially) at some temperature well below the ambient. Next the coupler is fitted over the pipe junction and then heated to room temperature; heating causes the coupler to shrink back to its original diameter, thus creating a tight seal between the two pipe sections.

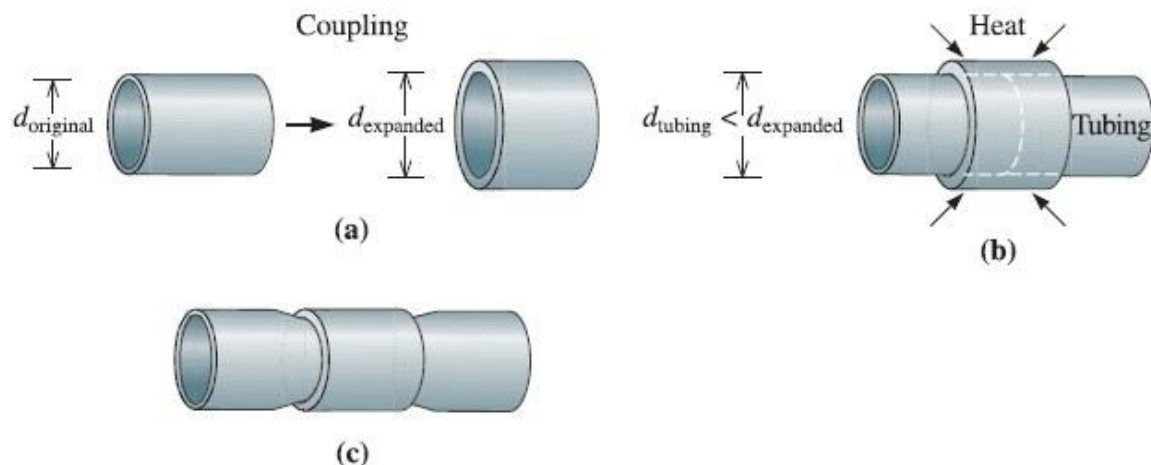


Figure 27: Use of shape-memory alloys for coupling tubing; (a) A memory alloy coupling is expanded so that (b) it fits over the tubing, when the coupling is reheated, (c) it shrinks back to its original diameter, squeezing the tubing for a tight fit.

Biomedical Applications of Ti Alloys

The use of titanium in the biomedical field has become a well-established area because titanium fulfills the property requirements better than any competing material (stainless steels, Co-Cr alloys, CP niobium, and CP tantalum; CP stands for ‘commercially pure’). The properties which are of interest for biomedical applications are corrosion resistance, biocompatibility, bioadhesion (bone ingrowth), modulus of elasticity (should be as close as possible to the modulus of bone which is in the range of 10–30 GPa), fatigue strength, and good processibility including joining and casting.

Especially the excellent corrosion resistance and biocompatibility make titanium the material of choice. Even the price of titanium, which is normally the drawback for its application, is only slightly higher as compared to the Co-Cr alloys and to the types of stainless steel used. Compared to CP niobium and CP tantalum the price of titanium is much lower. There are numerous different medical devices using titanium materials, e.g. bone plates, screws, hip joint implants, stents, heart valves, and various other kinds of fixtures also used in the dental area.

Three groups of titanium (CP titanium, α + β -titanium alloys, and β -titanium alloys) are used in the biomedical area. In addition, there are devices that use shape memory alloys based on the compound TiNi. Traditionally, CP titanium and the Ti-6Al-4V alloy were the first titanium materials used for biomedical applications and even today these two materials are used in most applications. Because of the suspicion of long-term toxicity problems with vanadium, the α + β -alloys Ti-5Al-2.5Fe and Ti-6Al-7Nb were developed in the 1980's. These two alloys have similar microstructures and properties as the Ti-6Al-4V alloy. Then in the 1990's, a variety of β -titanium alloys were developed, mainly because of the higher fatigue strength and the lower modulus of elasticity as compared to α + β -titanium alloys. These two properties are important for applications such as hip joint implants as will be discussed next.

Materials for Hip Prosthesis: A Case Study

What type of a material would you choose for an implant to be used for a total hip replacement implant? A hip prosthesis is intended to replace part of the worn out or damaged femur bone. (Figure 28, right.) The implant has a metal head and fits down the cavity of the femur. We need to consider the following factors: biocompatibility, corrosion resistance, high fracture toughness, excellent fatigue life (so that implants last for many years since it is difficult to do the surgery as patients get older), and wear resistance.

We also need to consider the stiffness. If the alloy chosen is too stiff compared to the bone, most of the load will be carried by the implant. This leads to weakening of the remaining bone and, in turn, can make the implant loose. Thus, we need a material that has a high tensile strength, corrosion resistance, biocompatibility, and fracture toughness. These requirements suggest 316 stainless steel or Ti-6Al-4V. Neither of these materials are ferromagnetic, and both are opaque to x-rays. This is good for magnetic resonance and x-ray imaging. Titanium alloys are not very hard and can wear out. Stainless steels are harder, but they are much stiffer than bone. Titanium is biocompatible and would be a better choice. Perhaps a composite material in which the stem is made from a Ti-6Al-4V alloy and the head is made from a wear resistant, corrosion resistant, and relatively tough ceramic, such as alumina, may be an answer. The inside of the socket could be made from an ultra-high density (ultrahigh molecular weight) polyethylene that has a very low friction coefficient. The surface of the implant could be made porous so as to encourage the bone to grow. Another option is to coat the implant with a material like porous **hydroxyapatite** to encourage bone growth.

The most demanding application for biomedical implants requiring a high fatigue strength is the stem of a hip joint implant. A schematic of a complete artificial hip joint is shown in Figure 29. The titanium alloy stem has a ceramic head (usually Al_2O_3 or ZrO_2) which can rotate in a cup made out of ultrahigh molecular weight polyethylene (UHMWPE). This combination of materials has a very low friction coefficient. The UHMWPE cup is usually held by a snap-in mechanism in a metal backed shell (not shown in Figure 29) which in turn is fixed to the bone by screws. Both the metal backed shell and the screws also are made out of titanium (Ti-6Al4V or CP titanium). The most common titanium alloy used for the hip joint stem is Ti-6Al-4V. The stem blanks are usually α β forged and stress relieved, therefore the microstructure is either mill-annealed or fully equiaxed depending on the details of the processing route. As an alternative manufacturing method to forging, investment casting of the hip stem can be used. In this case, the desired surface roughness of the stem can be directly obtained by designing it into the casting.

To facilitate better bioadhesion (bone ingrowth) the surface of the finished stem is very important. In general, the bone ingrowth behavior improves with increasing roughness of the stem surface. Various surface finishing methods are used (machining, etching, blasting with Al_2O_3 , porous coatings, plasma spraying, etc.). One popular surface treatment is plasma spraying of **hydroxyapatite** (main component of bone tissue) as bioactive coating on the titanium implant.

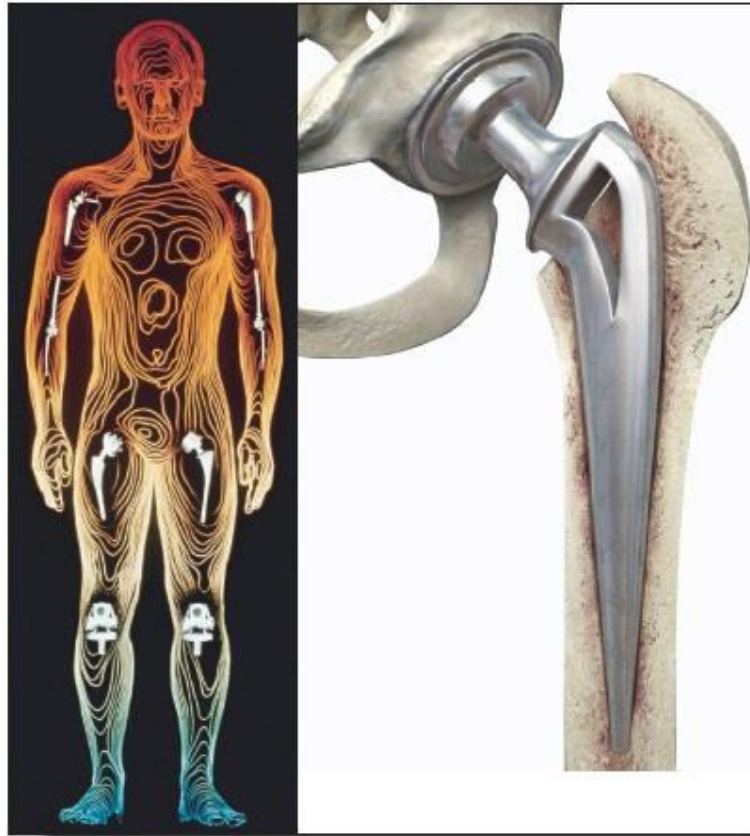


Figure 28: Increasingly, artificial implants are being incorporated into the human body. Some examples of commonly replaced joints are shown in the diagram on the left. Every year, approximately 500,000 people receive a hip implant such as that shown in the photo on the right. The implant must be made from a biocompatible material that has strong fracture toughness and an excellent fatigue life, and it must be corrosion resistant and possess a stiffness similar to that of bone. Nonferrous alloys based on titanium are often used for this application, as are cobalt-chrome alloys [Adapted from Askeland, D. R., Fulay, P. P. and Wright, W.J. (2011): *The Science and Engineering of Materials, Sixth Edition*; Connecticut: Cengage Learning, p.538].

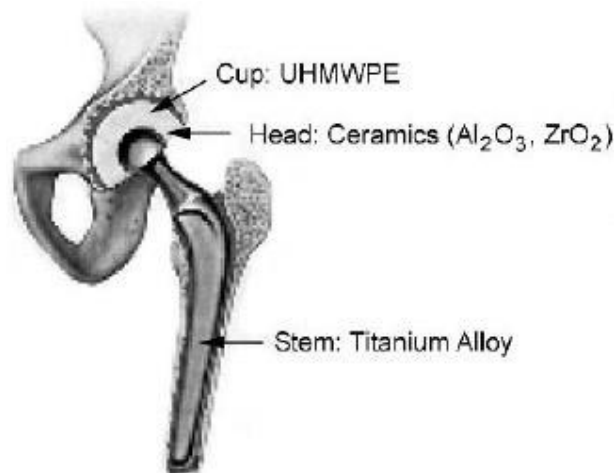


Figure 29: Schematic of an artificial hip joint

COPPER

Copper, the red metal, apart from gold, has been known since the early days of the human race. [In fact, iron pyrite (FeS₂) which associates with copper or gold was known as the **foo 's go d** because of its yellow colour and metallic lustre]. Copper has always been one of the significant materials, and today is rated as the most frequently used heavy nonferrous metal.

History

According to mythology, the goddess Venus (Aphrodite) was born on the Mediterranean island of Cyprus, where copper was exploited millennia before Christ. Therefore, in early times the Romans named it cyprium, later called cuprum. This name remains the Latin origin of the symbol Cu for copper.

It is usually believed that the **Stone Age** was followed by the **Bronze Age**, but it seems very likely that metallic copper was used in Egypt some 1500 years before bronze - a copper-tin alloy. That is, a short-lived **Copper Age** existed before or alongside the **Bronze Age**. Since copper is more easily corroded than bronze, only limited evidence of this early use of copper remains. Nevertheless, we can regard copper as the most ancient metal of any engineering significance. Brass (a copper-zinc alloy) was in classical times, made by smelting together ores of copper and zinc. The extraction of metallic zinc was not possible at that time, in fact not until the sixteenth century. The Romans made their brass by smelting copper along with the zinc ore calamine (zinc carbonate). The Romans used brass for coinage and ornaments, and bronze for fittings on important buildings, e.g. bronze pillars, tiles, and doors. In ancient times, the World's output of copper - mainly for bronze manufacture - was ultimately outstripped by that of iron and, during the twentieth century, also by aluminium.

In former days, the bulk of the world's requirements of copper was smelted in Swansea, from ore mined in Cornwall, Wales, or Spain. Later, deposits of ore were discovered in the Americas and Australia, and shipped to Swansea to be smelted, but it was subsequently realized that it would be far more economical to smelt the ore at the mine. Thus, Britain ceased to be the centre of the copper industry. Today, the USA and Russia, along with Chile, Canada, Zambia, Zaire (Congo DR) and Peru, are the leading producers of copper.

Occurrence, Processing and Extraction

Copper occurs in nature as elemental copper (**native copper**) and was also extracted successfully from minerals long before iron, since the relatively lower temperatures required for the extraction could be achieved more easily. More than 200 minerals contain copper in definable amounts, but only about 20 are important as copper ores (Table 26) or as semi-precious stones (turquoise and malachite). Copper is a typical chalcophilic element; therefore, its principal minerals are sulphides, mostly chalcopyrite, bornite, and chalcocite, often accompanied by pyrite (also called iron pyrite), galena, or sphalerite. One or more of these may occur in an individual deposit.

Table 26: The Most Important Copper Minerals

Mineral	Formula	Copper	Crystal system	Density, g/cm ³
Native copper	Cu	≤ 99.92	cubic	8.9
Chalcocite	Cu ₂ S	79.9	orthorhombic	5.5–5.8
Digenite	Cu ₉ S ₅	78.0	cubic	5.6
Covellite	CuS	66.5	hexagonal	4.7
Chalcopyrite	CuFeS ₂	34.6	tetragonal	4.1–4.3
Bornite	Cu ₅ FeS ₄ /Cu ₃ FeS ₃	55.5–69.7	tetragonal	4.9–5.3
Tennantite	Cu ₁₂ As ₄ S ₁₃	42–52	cubic	4.4–4.8
Tetraedrite	Cu ₁₂ Sb ₄ S ₁₃	30–45	cubic	4.6–5.1
Enargite	Cu ₃ AsS ₄	48.4	orthorhombic	4.4–4.5
Bourmonite	CuPbSbS ₃	13.0	orthorhombic	5.7–5.9
Cuprite	Cu ₂ O	88.8	cubic	6.15
Tenorite	CuO	79.9	monoclinic	6.4
Malachite	CuCO ₃ ·Cu(OH) ₂	57.5	monoclinic	4.0
Azurite	2CuCO ₃ ·Cu(OH) ₂	55.3	monoclinic	3.8
Chrysocolla	CuSiO ₃ ·nH ₂ O	30–36	(amorphous)	1.9–2.3
Dioptase	Cu ₆ [Si ₆ O ₁₈]·6H ₂ O	40.3	rhombohedral	3.3
Brochantite	CuSO ₄ ·3Cu(OH) ₂	56.2	monoclinic	4.0
Antlerite	CuSO ₄ ·2Cu(OH) ₂	53.8	orthorhombic	3.9
Chalcanthite	CuSO ₄ ·5H ₂ O	25.5	triclinic	2.2–2.3
Atacamite	CuCl ₂ ·3Cu(OH) ₂	59.5	orthorhombic	3.75

Copper is typically produced by a pyrometallurgical process. The copper ore containing high-sulphur contents is concentrated, then converted into a molten immiscible liquid containing copper sulphide-iron sulphide and is known as a **copper matte**. This is done in a **flash smelter**. In a separate reactor, known as a **copper converter**, oxygen introduced to the matte converts the iron sulphide to iron oxide and the copper sulphide to an impure copper called **blister copper**, which is then purified electrolytically. Other methods for copper extraction include leaching copper from low-sulphur ores with a weak acid, then electrolytically extracting the copper from the solution.

Copper is extracted almost entirely from ores based on **copper pyrites** (a mineral in which copper is chemically combined with iron and sulphur). The metallurgy of the process is rather complex, but is essentially as follows:

1. The ore is 'concentrated'; that is, it is treated by 'wet' processes (**flotation**) to remove as much as possible of the earthy waste, or 'gangue'.
2. The concentrate is then heated in a current of air, to burn away much of the sulphur (a process called **roasting**). At the same time, other impurities, such as iron and silicon, oxidize to form a **slag**, which floats on top of the purified molten copper sulphide (called '**matte**').
3. The molten matte is separated from the slag, and treated in a Pierce-Smith converter, the operation of which resembles to some extent that of the furnace used in steel-making by the 'oxygen process'. Some of the copper sulphide is oxidized, and the copper oxide thus formed reacts chemically with the remainder of the sulphide, producing crude copper.

The crude copper is then refined by either:

- Re-melting it in a furnace, so that the impurities are oxidized, and are lost as a slag, or:
- Electrolysis, in which an ingot of impure copper is used as the anode, whilst a thin sheet of pure copper serves as the cathode. During electrolysis, the anode gradually dissolves, and high-purity copper is deposited on the cathode. '**Cathode copper**' so formed is 99.97 per cent pure.

Properties of copper

The most important physical property of copper is its *very high electrical conductivity*. In this respect, it is second only to silver; if we take the electrical conductivity of silver to be 100 units, then that of pure copper reaches 97, followed by gold at 71 and aluminium at 58. Consequently, the greater part of the world's production of metallic copper is used in the electrical/electronic industries. Much of the copper used for electrical purposes is of very high purity, as the presence of impurities reduces the electrical conductivity, often very seriously. Thus, the introduction of only 0.04 per cent phosphorus will reduce the electrical conductivity by almost 25 per cent. Other elements have less effect, e.g. 1.0 per cent cadmium, added to copper used for telephone-wires in order to strengthen them, has little effect on the conductivity.

The thermal conductivity and corrosion-resistance of copper are also high, making it a useful material for the manufacture of radiators, boilers, and other heating equipment. Since copper is also very malleable and ductile, it can be rolled, drawn, deep-drawn, and forged with ease. In recent years, the cost of copper production has risen steeply; so for many purposes - electrical and otherwise - it has been replaced by aluminium, even though the electrical and thermal conductivities of the latter are inferior to those of copper.

Copper alloys also are unusual in that they may be selected to produce an appropriate decorative color. Pure copper is red; zinc additions produce a yellow color; and nickel produces a silver color. Copper can corrode easily, forming a basic copper sulfate [CuSO₄·3Cu(OH)₂]. This is a green compound (patina) that is insoluble in water (but soluble in acids). This **green patina** provides an attractive finish for many applications. The Statue of Liberty [in the USA] is green because of the green patina of the oxidized copper skin that covers the steel structure.

Commercially Pure Copper

Commercial grades of 'pure' copper are available in a number of forms:

1. **Oxygen-free high-conductivity (OFHC) copper:** This is derived from the electrolytically refined variety. The cathodes are melted, cast, rolled, and then drawn to wire or strip for electrical purposes. This grade is usually 99.97 per cent pure and is of the highest electrical conductivity. It is widely used for electronic components. OFHC copper has extremely low oxygen and other impurity contents, produced for many electrical applications is also required to be of 100% IACS (International Annealed Copper Standard).
2. **Tough-pitch copper:** This is a fire-refined variety, which contains small amounts of copper oxide as the main impurity. Since this oxide is present in the microstructure as tiny globules, which have little effect on the mechanical properties but reduce the electrical conductivity by about 10 per cent, it is suitable for purposes where maximum electrical conductivity is not required. It is unsuitable where gas-welding processes are involved because reactions between the oxide globules and hydrogen in the welding gas cause extreme brittleness:



Steam is insoluble in solid copper and forms fissures at the crystal boundaries.

3. **Deoxidized copper:** This is made from tough-pitch grade copper by treating it with a small amount of phosphorus just before casting, in order to remove the oxide globules. Whilst phosphorus-deoxidized copper may be valuable for processes where welding is involved, it is definitely not suitable for electrical purposes because of the big reduction in electrical conductivity (up to 30% reduction) introduced by the presence of dissolved phosphorus.

An example of the use of copper is in the production of printed circuit-boards. A board, made of a polymer or polymer-composite material is used as the substrate. The surface is chemically treated so that it has enough conductivity to allow electroplating in which copper is plated over the entire surface to a depth of about 100 µm. A layer of photoresist film is then rolled, in a vacuum to avoid air bubbles, onto the copper. A mask with the required pattern of conductors is then placed over the resist and ultraviolet light shone onto it. Where the mask transmits the UV, the photoresist polymer becomes insoluble in the 'developer', whilst the unexposed areas can be dissolved. The dissolved areas thus reveal the copper. Spraying with nitric acid then dissolves the exposed copper and so leaves bare board, i.e. a pattern of insulators, with the pattern of conductors being the unexposed, unattacked copper.

Alloys of Copper

The tensile strength of hard-rolled copper reaches about 375 MPa, so for most engineering purposes where greater strength is required, copper must be suitably alloyed. Alloys of copper are less widely used than they were previously. The growing price of copper relative to its increasing scarcity, coupled with the fact that the quality of cheaper alternatives has improved in recent years, has led to the replacement of copper alloys for many purposes. Moreover, improved shaping techniques have allowed less ductile materials to be employed; thus, deep-drawing quality mild steel is now often used where ductile brass was once considered to be essential.

Nevertheless, copper alloys are still of considerable importance and the following are discussed: i. Brasses: copper-zinc alloys

- SME brasses
- i. Bronzes: copper-tin alloys
 - Phosphor bronzes: copper-tin-phosphorus alloys
 - Gunmetals: copper-tin-zinc alloys
- ii. Aluminium bronzes: copper-aluminium alloys
- iii. Cupro-nickels: copper-nickel alloys
 - Nickel silvers: copper-zinc-nickel alloys
- iv. Beryllium bronzes: copper-beryllium alloys

The brasses: These are copper-base alloys containing up to 45 per cent zinc and, sometimes, small amounts of other metals, the chief of which are tin, lead, aluminium, manganese, and iron. The equilibrium diagram (Figure 30) shows that plain copper-zinc alloys with up to approximately 37 per cent zinc have a structure consisting of a single phase - that labelled α . Phases occupying such a position on an equilibrium diagram are solid solutions. Such solutions are invariably tough and ductile and this particular one is no exception, being the basis of one of the most malleable and ductile metallurgical materials in common use. Brasses containing between 10 and 35 per cent zinc are widely used for deep drawing and general presswork - the maximum ductility being attained in the case of 70-30 brass, commonly known as '*cartridge metal*', since it is used in the deep-drawing of cartridge- and shell-cases of all calibres. Many of these however are now produced in modern low-nitrogen, deep drawing quality mild steel.

Brasses with more than 37 per cent zinc contain the phase β' . This is a hard, somewhat brittle substance, so a 60-40 brass lacks ductility. If such a brass is heated to 454°C (Figure 30), the phase β' changes to β , which is soft and malleable. As the temperature is increased further, the α phase present dissolves in β , until at X the structure is entirely malleable β . Therefore, 60-40 brasses are best hot-worked at about 700°C. This treatment also breaks up the coarse cast structure and replaces it with a fine granular structure. Thus, brasses with less than 37 per cent zinc are usually cold-working alloys, whilst those with more than 37 per cent zinc are hot-working alloys. A copper-zinc alloy containing more than 50 per cent zinc would be useless for engineering purposes, since it would contain the very brittle phase γ Figure .

Up to 1 per cent tin is sometimes added to brasses, to improve their resistance to corrosion, particularly under marine conditions. Lead is insoluble in both molten and solid brass, and exists in the structure as tiny globules. About 2 per cent lead will improve machinability of brass. Small amounts of arsenic are said to improve corrosion-resistance and inhibit dezincification.

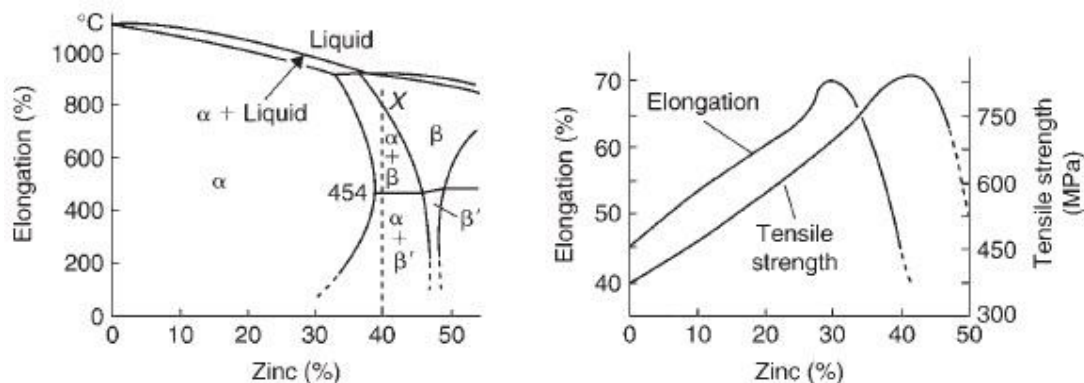


Figure 30: The section of the copper-zinc equilibrium diagram, which covers brasses of engineering importance.

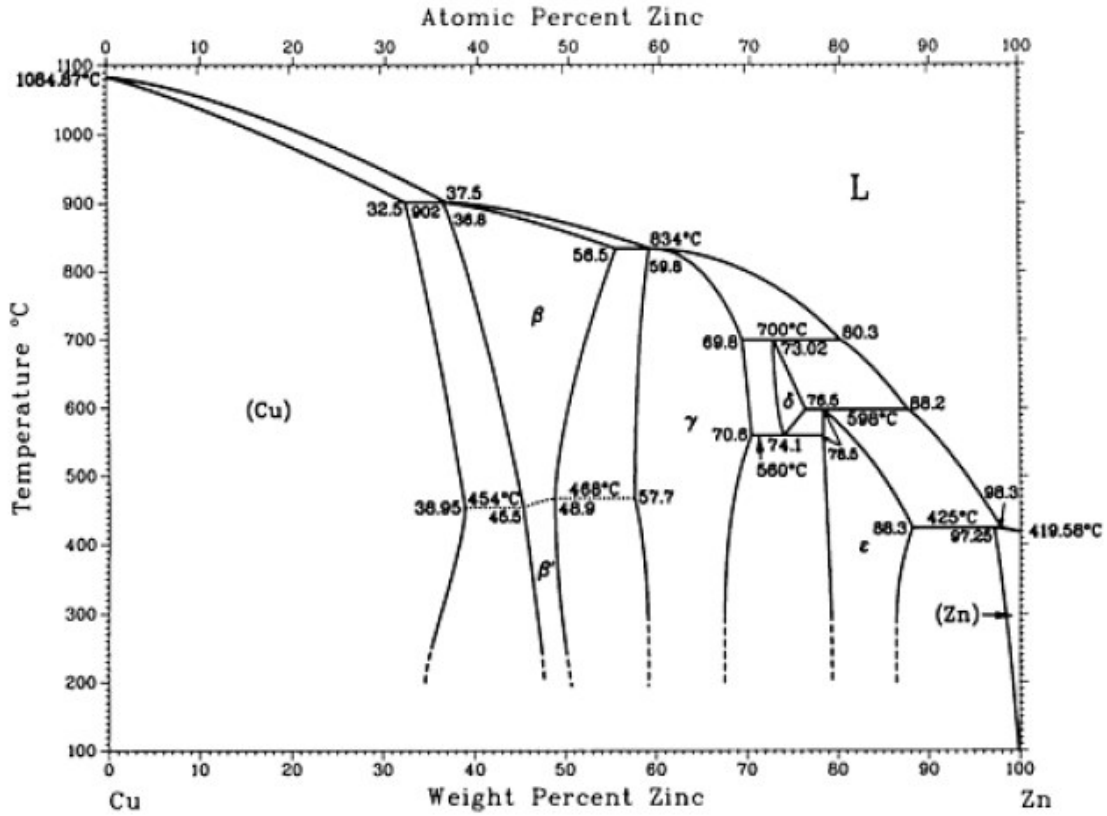


Figure 31: Complete Cu-Zn Phase Diagram

Manganese, iron and aluminium all increase the tensile strength of a brass, and are therefore used in high-tensile brasses. These alloys are sometimes, rather misleadingly, known as 'manganese bronzes'. Additions of up to 2 per cent aluminium are also used to improve the corrosion resistance of some brasses. Table 27 shows the composition, typical properties and uses of the more important brasses.

Table 27: Composition, Typical Properties and Uses of Important Brasses

BS 2870 designation	Composition %			Condition	Typical mechanical properties		Uses							
	Cu	Zn	Other elements		Tensile strength MPa	Elong. %								
CZ 101	90	10		Soft	280	55	<i>Gilding metal</i> – used for imitation jewellery, because of its gold-like colour, good ductility, and its ability to be brazed and enamelled.							
				Hard	510	4								
CZ 106	70	30		Soft	320	70	<i>Cartridge brass</i> – deep-drawing brass of maximum ductility. Used particularly for the manufacture of cartridge- and shell-cases.							
				Hard	700	5								
CZ 107	65	35		Soft	320	65	<i>Standard brass</i> – a good general-purpose cold-working alloy when the high ductility of 70–30 brass is not required. Widely used for press-work and limited deep-drawing.							
				Hard	700	4								
CZ 108	63	37		Soft	340	55	<i>Common brass</i> – a general-purpose alloy, suitable for limited cold-working operations.							
				Hard	725	4								
CZ 123	60	40		Hot-rolled	370	40	<i>Yellow or Muntz metal</i> – hot-rolled plate. Can be cold-worked only to a limited extent. Also extruded as rods and tubes.							
CZ 120 2Pb	59	39	Pb 2	Extruded-rod	450	30	<i>Free-cutting brass</i> – very suitable for high-speed machining, but can be deformed only slightly by cold-work.							
CZ 112	62	37	Sn 1	Extruded	420	35	<i>'Naval brass'</i> – structural uses, also forgings. Tin raises corrosion-resistance, especially in sea water.							
								58	Rem.	Mn 1.5, Al 1.5, Fe 1, Pb 1, Sn 0.6	Extruded	500	15	<i>High-tensile brass</i> ('manganese bronze') – pump-rods, stampings and pressings. Also marine castings such as propellers, water-turbine runners, rudders, etc.

Copper 'shape memory alloys' [SME Brasses]: 'Shape memory' is a phenomenon associated with a limited number of alloys. The important characteristic of these alloys is the ability to exist in two distinct shapes or crystal structures, one above and one below a critical transformation temperature. As the temperature falls below this critical temperature, a martensitic type of structure forms. As the temperature is raised again, the martensite reverts to the original structure. This *reversible change* in structure is linked to a change in dimensions and the alloy thus exhibits a 'memory' of the high and low temperature shapes. SME brasses ('Shape memory effect' brasses) contain 55-80 per cent copper, 2-8 per cent aluminium and the balance zinc. By choosing a suitable composition, transition temperatures between -70°C and 130°C can be achieved. The force associated with the change in shape can be used to operate temperature-sensitive devices, the snap on/off positions often being obtained by using a compensating bias spring. Such devices are used in automatic greenhouse ventilators, thermostatic radiator valves, de-icing switches, electric kettle switches and valves in solar heating systems.

Tin bronzes: Tin bronze was almost certainly the first metallurgical *alloy* to be used by Man and it is a sobering thought that for roughly half of the 4000 years of history during which he has been using metallurgical alloys, bronze was his sole material. Though tin bronzes have relatively limited uses these days - due in part to the high

prices of both copper and tin - they still find application for special purposes. Tin bronzes, contain up to 18 per cent tin, sometimes with smaller amounts of phosphorus, zinc, or lead.

The complete copper-tin equilibrium diagram (Figure 32) is a rather complex one and its interpretation is rendered more difficult by the fact that tin bronzes need to be cooled extremely slowly indeed - *far more slowly than is ever likely to prevail in a normal industrial casting process* – if microstructural equilibrium is to be attained.

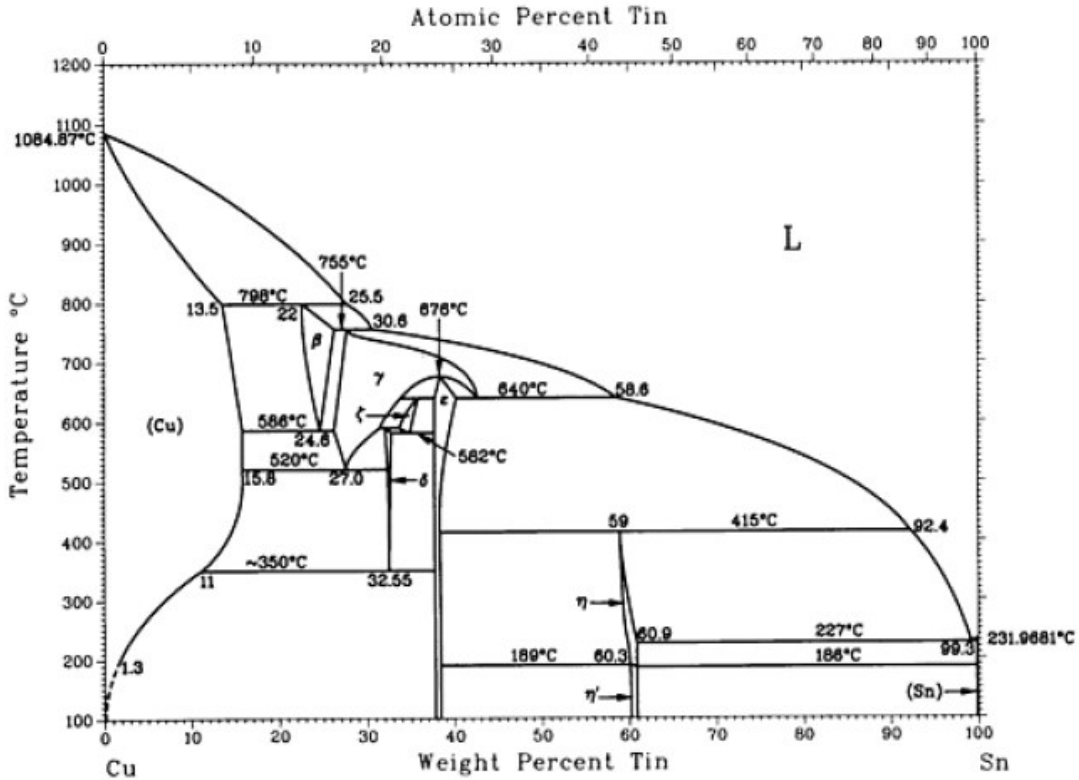


Figure 32: Complete Cu-Sn Phase Diagram

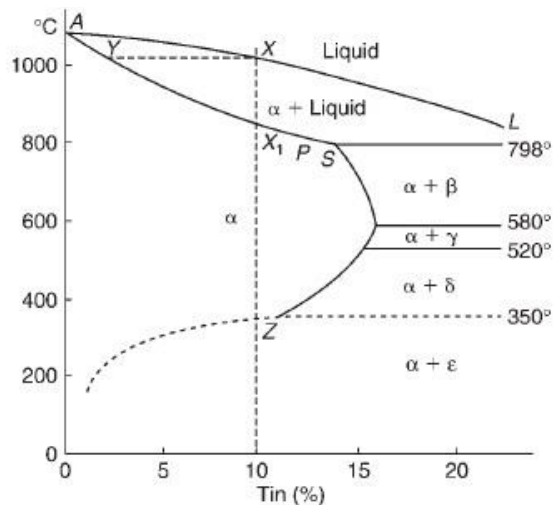


Figure 33: Part of the Cu-Sn equilibrium diagram. The phase δ is an intermetallic compound $\text{Cu}_{31}\text{Sn}_8$ whilst ϵ is the intermetallic compound Cu_3Sn , but this latter will never be present in a bronze casting, which solidifies and cools under normal industrial conditions.

Let us simplify this by assuming, from a simple interpretation of the diagram (Figure 33), that a cast 10 per cent tin bronze which begins to solidify at X (about 1000°C) will be completely solid at X_1 (about 850°C) as a

polycrystalline mass of a solid solution, which then cools without further change until at Z particles of the intermetallic compound ϵ begin to form within the α crystals. Sadly, the transformations which take place are not nearly so simple.

First, the wide range between the liquidus line AL and the solidus AS is an indication that extensive coring takes place in tin bronzes as they solidify. Thus, the molten bronze containing 10 per cent tin begins to solidify at X by forming dendrites of composition Y (about 2 per cent tin). Since these dendrites contain only about 2 per cent tin this means that the remaining liquid has been left much richer in tin, i.e. its composition moves to the right along AL. Cooling is too rapid for the microstructure to attain equilibrium and solidification is not complete until the temperature has fallen to 798°C when the remaining liquid will probably contain about 20 per cent tin. This will then solidify as a mixture of α and β , as indicated by the diagram.

As the now solid alloy cools to 586°C, the $\alpha + \beta$ mixture transforms to $\alpha + \gamma$ which at 520°C transforms further to $\alpha + \delta$. As the temperature falls lower, transformations become increasingly sluggish and so the change to a structure of $\alpha + \epsilon$ at 350°C does not occur at the speed at which the temperature is falling. So under industrial conditions of cooling, we are left with a final microstructure of heavily cored α solid solution with a network and particles of the brittle intermetallic compound δ ($\text{Cu}_{31}\text{Sn}_8$) at the α dendrite boundaries.

The networks of the δ phase at the crystal boundaries of the solid solution α makes the 10 per cent tin bronze rather brittle under shock. Commercial tin bronzes can be divided into two groups:

- a. Wrought tin bronzes containing up to approximately 7 per cent tin. These alloys are generally supplied as rolled sheet and strip, or as drawn rod, wire, and turbine-blading.
- b. Cast tin bronzes containing 10 to 18 per cent tin, used mainly for high-duty bearings. Table 28 shows data on tin bronzes.

Table 28: Properties and Uses of Tin Bronzes and Phosphor Bronzes

BS spec. number	Composition %			Condition	Typical mechanical properties		Uses
	Cu	Sn	Other elements		Tensile strength MPa	Elong. %	
	95.5	3	Zn 1.5	Soft Hard	320 725	65 5	Coinage bronze – British ‘copper’ coinage now contains rather less tin (0.5%) and more zinc (2.5%).
2870/ PB 101	96	3.75	P 0.1	Soft Hard	340 740	65 15	Low-tin bronze – springs and instrument parts. Good elastic properties and corrosion-resistance.
2870/ PB 102	94	5.5	P 0.2	Soft Hard	350 700	65 15	Drawn phosphor bronze – generally used in the work-hardened condition; steam-turbine blading. Other components subjected to friction or corrosive conditions.
1400/ PB1-B	89	10	P 0.5	Sand cast	280	15	Cast phosphor bronze – supplied as cast sticks for turning small bearings, etc.
	81	18	P 0.5	Sand cast	170	2	High-tin bronze – bearings subjected to heavy loads – bridge and turntable bearings.
1400/ G1-C	88	10	Zn 2, Ni 2 (max)	Sand cast	290	16	Admiralty gunmetal – pumps, valves and miscellaneous castings (mainly for marine work, because of its high corrosion-resistance); also for statuary, because of good casting properties.
1400/ LG2-A	85	5	Zn 5, Pb 5, Ni 2 (max)	Sand cast	220	13	Leaded gunmetal (or ‘red brass’) – a substitute for Admiralty gunmetal; also where pressure tightness is required.
1400/ LB5-B	75	5	Pb 20, Ni 2 (max)	Sand cast	160	6	Leaded bronze – a bearing alloy; can be bonded to steel shafts for added strength.

Phosphor bronze: Most of the tin bronzes mentioned above contain up to 0.05 per cent phosphorus, left over from the deoxidation process which is carried out before casting. Sometimes, however, phosphorus is added -

in amounts up to 1.0 per cent - as a deliberate alloying element, and only then should the material be termed 'phosphor bronze'. The effect of phosphorus is to increase the tensile strength and corrosion-resistance, whilst, in the case of cast bearing alloys, reducing the coefficient of friction. See Table 28 for data on phosphor bronzes.

Gunmetal: This contains 10 per cent tin and 2 per cent zinc, the latter acting as a deoxidizer, and also improving fluidity during casting. Since zinc is considerably cheaper than tin, the total cost of the alloy is reduced. Gunmetal is no longer used for naval armaments, but it is used as a bearing alloy, and also where a strong, corrosion-resistant casting is required. See Table 28 for data on gunmetals.

Coinage bronze: This is a wrought alloy containing 3 per cent tin and, in the interests of economy, 1.5 per cent zinc. In Britain, even more of the tin has been replaced by zinc (see Table 28).

Leaded bronzes: Up to 2.0 per cent lead is sometimes added to bronzes, in order to improve machinability. Some special bearing bronzes contain up to 24 per cent lead, and will carry greater loads than will 'white metal' bearings. Since the thermal conductivity of these bronzes is also high, they can work at higher speeds, as heat is dissipated more quickly. See Table 28 for data on a leaded bronze.

Aluminium bronzes: Like brasses, the aluminium bronzes can be divided into two groups: the cold-working alloys, and the hot-working alloys [see Al-Cu system of Figures 6 and 11]. Cold-working alloys contain approximately 5 per cent aluminium and are ductile and malleable, since they are a completely solid solution in structure. They have a good capacity for cold-work. As they also have a good resistance to corrosion, and a colour similar to that of 22 carat gold, they were widely used for cheap jewellery and imitation wedding rings in those less permissive days when such things were deemed necessary; but for decorative purposes they have been replaced by coloured anodized aluminium and other cheaper materials.

The hot-working alloys contain in the region of 10 per cent aluminium and, if allowed to cool slowly, the structure is brittle, due to the precipitation of a hard compound within it. When this structure is heated to approximately 800°C, it changes to one which is a completely solid solution, and hence malleable; so alloys of this composition can be hot-worked successfully. Similar alloys are also used for casting to shape by both sand- and die-casting methods. To prevent precipitation of the brittle compound mentioned above, castings are usually ejected from the mould as quickly as possible, so that they cool rapidly.

An interesting feature of the 10 per cent alloy is that it can be heat-treated in a manner similar to that for steel. A hard martensitic type of structure is produced on quenching from 900°C, and its properties can be modified by tempering. Despite these apparently attractive possibilities, heat-treatment of aluminium bronze is not widely employed, and such of these alloys as are used find application mainly because of their good corrosion-resistance, retention of strength at high temperatures, and good wearing properties.

Aluminium bronze is a difficult alloy to cast successfully, because, at its casting temperature (above 1000°C) aluminium oxidizes readily. This leads to aluminium oxide dross becoming entrapped in the casting, unless special casting techniques are employed, and an increase in the cost of the process inevitably results. Compositions and uses of some aluminium bronzes are given in Table 29.

Table 29: Properties and Uses of Aluminium Bronzes

BS spec. number	Composition %			Condition	Typical mechanical properties		Uses
	Cu	Al	Other elements		Tensile strength MPa	Elong. %	
	Rem.	7.5	Fe, Mn, and Ni up to 2.5 total	Hot-worked	430	45	Chemical engineering, particularly at fairly high temperatures.
2472/CA 104	80	10	Fe 5, Ni 5	Forged	725	20	Forged propeller-shafts, spindles, etc. for marine work. Can be heat-treated by quenching and tempering.
1400/AB1-B	Rem.	9.5	Fe 2.5, Ni and Mn up to 1.0 each (optional)	Cast	520	30	The most widely used aluminium bronze for both die- and sand-casting. Used in chemical plant and marine conditions – pump-castings, valve-parts, gears, propellers, etc.

Copper-nickel alloys: The metals copper and nickel 'mix' in all proportions in the solid state; that is, a copper-nickel alloy of any composition consists of only one phase - a uniform solid solution. For this reason, all copper-nickel alloys are relatively ductile and malleable, since there can never be any brittle phase present in the structure. In the cast state, a copper-nickel alloy may be cored, but this coring can never lead to the precipitation of a brittle phase. In other words, the metallurgy of these alloys is very simple - and not particularly interesting as a result. Cupro-nickels may be either hot-worked or cold-worked, and are shaped by rolling, forging, pressing, drawing, and spinning. Their corrosion-resistance is high, and only the high cost of both metals limits the wider use of these alloys. Table 30 gives the composition and uses of some cupronickels.

Nickel-silvers: Nickel-silvers contain from 10 to 30 per cent nickel and 55 to 65 per cent copper, the balance being zinc. Like the cupro-nickels, they are uniform solid solutions. Consequently, they are ductile, like the high-copper brasses, but have a 'near-white' colour, making them very suitable for the manufacture of forks, spoons, and other tableware, though in recent years these alloys have been generally replaced by the less attractive stainless steels. When used for such purposes, these nickel-silvers are usually silver-plated - the stamp 'EPNS' means 'electroplated nickel-silver'.

Table 30: Compositions and Uses of Cupro-nickels and Nickel-silvers

BS spec. number	Composition %			Condition	Typical mechanical properties		Uses
	Cu	Ni	Other elements		Tensile strength MPa	Elong. %	
2870/ CN 104	80	20	Mn 0.25	Soft Hard	340 540	45 5	Used for bullet-envelopes, because of high ductility and corrosion-resistance.
2870/ CN 105	75	25	Mn 0.25	Soft Hard	350 600	45 5	Mainly for coinage – the current British 'silver' coinage.
3072/ 3076/ NA 13	29	68	Fe 1.25, Mn 1.25	Soft Hard	560 720	45 20	<i>Monel metal</i> – good mechanical properties, excellent corrosion-resistance. Chemical engineering plant, etc.
3072/ 3076/ NA 18	29	66	Al 2.75, Fe 1.0, Mn 0.4, Ti 0.6	Soft Hard Heat-treated	680 760 1060	40 25 22	'K' <i>Monel</i> – a heat-treatable alloy. Used for motor-boat propeller-shafts.
2870/ NS 106	60	18	Zn Bal., Mn 0.4				<i>Nickel-silver</i> – spoons, forks, etc.
2870/ NX 111	60	10	Zn Bal., Pb 1.5, Mn 0.25				<i>Leaded nickel-silver</i> – Yale-type keys, etc.

The machinability of these - as of all other copper alloys - can be improved by the addition of 2 per cent lead. Such alloys are easy to engrave, and are also useful for the manufacture of Yale-type keys, where the presence of lead makes it much easier to cut the blank to shape. Table 30 gives the composition and uses of some nickel-silvers.

Other copper alloys: The following are some other copper-base alloys, these containing just small amounts of alloying elements which have generally been added to increase tensile strengths.

- ❖ **Beryllium bronze** - Beryllium bronze (or copper-beryllium) contains approximately 1.75 per cent beryllium and 0.2 per cent cobalt. It is a heat treatable alloy, which can be precipitation-hardened in a manner similar to that of some of the aluminium alloys. A glance at the equilibrium diagram (Figure 34) will show why this is so. At room temperature, the slowly cooled structure will consist of the solid solution *a* (in this case, almost pure copper), along with particles of the compound CuBe. If this is heated - that is, solution-treated - at about 800°C, the structure becomes completely *a*, as the CuBe is slowly dissolved by the solid solution. The alloy is then quenched and in this condition is ductile, so that it can be cold-worked. If the alloy is now precipitation-hardened at 275°C for an hour, a tensile strength of up to 1400 MPa is obtained. The addition of 0.2 per cent

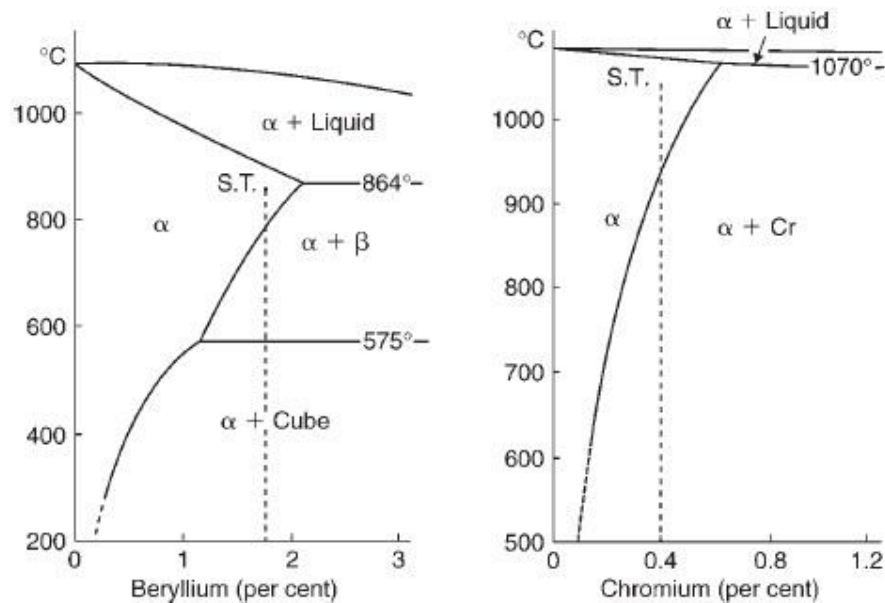


Figure 34: Copper-base alloys which can be precipitation-hardened. In either case, the alloy is solution-treated by heating it to the point S.T., at which the structure becomes uniformly a It is then quenched, to retain this structure, and then precipitation-hardened.

Since beryllium bronze is very hard in the cold-worked/heat-treated state, it is useful for the manufacture of non-sparking tools - chisels and hack-saw blades - for use in gas-works, 'dangerous' mines, explosives factories, or where inflammable vapours are encountered, as in paint and varnish works. Unfortunately, beryllium is a very scarce and expensive metal, and this limits its use in engineering materials.

- ❖ **Copper-chromium** - Copper-chromium contains 0.5 per cent chromium and is also a heat-treatable alloy, as is indicated by the equilibrium diagram in Figure 34. It is used in some electrical industries and in spot welding electrodes, since it combines a high conductivity of about 80 per cent that of pure copper with a reasonable strength of 550 MPa.
- ❖ **Copper-cadmium** - Copper-cadmium contains about 1 per cent cadmium and this raises the tensile strength of the hard drawn alloy to 700 MPa. Since the fall in electrical conductivity due to the cadmium is very small (to about 90 per cent that of pure copper), this material is useful for telephone-wires and other overhead electrical wires.
- ❖ **Copper-tellurium** - Copper-tellurium contains 0.5 per cent tellurium which, being insoluble in pure copper, exists as small globules in the structure. Since tellurium is insoluble, it has little effect on electrical conductivity (only drops to 99.5 per cent that of pure copper) but gives a big improvement in machinability (resembling lead in this respect). It is used for machined high-conductivity items such as terminals and clamps.
- ❖ **Arsenical copper** - Arsenical copper contains 0.4 per cent arsenic. This increases from 200 to 550°C the temperature at which cold-worked copper begins to soften when it is heated. This type of copper was widely used in steam locomotive fireboxes and boiler-tubes, and still finds use in high-temperature steam plant. It is useless for electrical purposes, however, because of the great reduction in electrical conductivity caused by the presence of the arsenic in the solid solution.

ZINC

Zinc is a bluish white metallic element found in group 12 or IIB of the Periodic Table, with molar mass of 65.37g and density of 7.14g/cm³. It crystallizes as HCP and has melting and boiling points of 419.5°C and 906°C respectively. The production of metallic zinc is complicated by the fact that the temperatures necessary to reduce zinc from its ores are higher than the boiling point of zinc, so the metal is produced as a vapour, which readily oxidizes during cooling unless a reducing environment is maintained.

History

Metallic zinc was known in China by about 1600 A.D., but was clearly known in India at least a few hundred years earlier. The Romans knew brass, but this was made from zinc ores not metallic zinc. Coins containing 99% zinc were cast during the Ming Dynasty (1368 - 1644). In a book written in 1637, the Chinese described zinc production by controlled smelting in stacked, hermetically sealed pots. In India, remains of zinc smelting operations found in Sawai Madhopur (Rajasthan) confirm that zinc was produced prior to the 1300s. From the 6th century, zinc was imported into Europe (by the Greeks and Romans) from the East under the names of **Indian Tin**. It is also known as **spelter** in the UK. In 1751, Berzelius isolated metallic zinc and Champion patented a method of production by distillation in 1738.

Occurrence

Zinc is contained in ore deposits widely distributed throughout the world. The most important mines are found in Australia, North and South America, Japan, North and Central Africa, Scandinavia, Germany, Poland, Spain, Italy and the former USSR. Zinc associates with Pb in Ishiagu's **galena/sphalerite** deposit of Ebonyi State, Nigeria. Zinc is often smelted or refined near the mines but large quantities of concentrates are also sent abroad for treatment, notably to Belgium, UK, Germany, Japan and the USA. Over 250, 000 tonnes of mined slab zinc are used each year in the UK; the total annual world consumption is over 3.5×10^6 tonnes, excluding the Communist countries.

Zinc Ores and Their Preparation

Zinc has been extracted from **calamine**, the carbonate which the Romans mixed with copper ores to make brass before zinc itself was recognized as a metal. The word calamine is still used in the UK to describe zinc carbonate (ZnCO₃), and in the USA (where zinc carbonate is known as **smithsonite**) it covers any oxidized zinc ore and very often refers to a silicate. Zinc is now nearly all obtained from sulphide materials which usually also contain lead (and often silver). The most plentiful of these is **zinc blende** or **sphalerite** (ZnS), though **marmatite** [(ZnFe)S] and **franklinite** (a spinel type black magnetic mineral that contains iron, manganese and zinc) are also important.

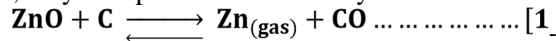
In a few mines, it is possible to pick out sufficiently pure zinc material by hand, however, zinc ores nearly always need to be concentrated before the metal can be extracted. Two methods are in use:

- a) **Wet Gravity Method:** - This takes advantage of the differences in density between mineral particles in the ore and the useless sandy gangue material.
- b) **Flotation Method:** - This is more widely used and is more efficient. This process relies mainly on the reluctance of water to wet the mineral sulphide particles. In the flotation process, the finely crushed ore is agitated with water containing certain chemicals and a suspension of air bubbles are carried to the surface to form a froth, which is skimmed off. The gangue material is readily wetted and, though lighter, sinks to the bottom. By adding suitable reagents [frothers, collectors and modifiers or regulators], it is possible to make some constituents float and others sink, thus permitting the treatment of complex Pb and Zn sulphide ores and the economic separation of each mineral in the concentrated form.

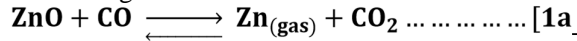
The first stage in the smelting or refining of ZnS concentrates is a roasting process called sintering, which is carried out on a hearth or in a flash roaster. Most of the sulphur is thereby converted to sulphur (IV) oxide (SO₂), which is used for the production of sulphuric acid in the **contact process**. The crude zinc oxide (ZnO) produced is then heated either by thermal smelting or by electrolytic refining.

Thermal Smelting

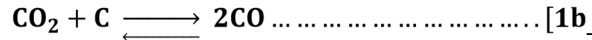
The original **Champion process** for zinc production was a thermal one, and in a modified form, still accounts for about one-third of the metal made. The roasted concentrates are heated to a temperature of about 1100°C with anthracite or a similar carbonaceous material in banks of small horizontal fireclay retorts. The thermal reduction [**carbothermic reduction**] of zinc, which is formed as a vapour and caught as liquid metal in condensers outside the furnace, may be represented chemically as:



The reaction above actually has two stages:



and



The reduction only proceeds at temperatures above the boiling point of zinc and since reaction (1a) tends to reverse as the temperature drops, the proportion of CO₂ must be kept as low as possible (i.e. a strongly reducing atmosphere must be maintained). As a consequence, excess carbon has to be added to the charge so that reaction (1b) is not reversed. A typical retort will produce a daily output of 25 – 40 kg of metal containing 1 % Pb. In the UK this product is known as *good ordinary brand (GOB) zinc* and in North America, as *prime western zinc*. Zinc dust in the finely divided form known as *blue powder* is a by-product of this method of smelting.

New Jersey Process In the late 1900's an important modification was made to the thermal method by the New Jersey Zinc Company. In this process, a briquetted mixture of roasted concentrates and anthracite is heated in a large vertical retort made of silicon carbide bricks, which allows the reduction to take place during the steady descent of the charge. Although the initial cost is high for this continuous plant, labour costs are reduced and production of a daily output of about 7 tonnes (7,000 kg) of metal is possible. Fractional distillation of vertical retort zinc gives a metal of more than 99.99% purity, which is suitable for modern die-casting alloys and a number of other applications.

The ISF Process

In 1957, the Imperial Smelting Corporation announced the successful development of a blast furnace for making zinc, known as **imperial smelting furnace (ISF)** or zinc blast furnace (ZBF). The furnace is fed with a preheated mixture of roasted zinc concentrate and coke, and is supplied with hot air blasts above and below the central take-off point. Zinc vapour is removed in a stream of gas containing CO₂ and CO and condensed rapidly by a spray of molten lead. The lead circulates continuously through heat exchangers for cooling and separating chamber where molten zinc of GOB quality is separated out. Since the charge is heated internally, the ISF process can produce much more zinc daily than the vertical retorts. Pb and Zn can be smelted simultaneously if roasted mixed lead – zinc concentrates are fed in. Low grade concentrates can also be treated by this process and a single unit can make up to 100, 000 tonnes of Zn per annum.

The reduction in the zinc blast furnace follows the same course as in the zinc retort, with the difference that oxygen from the air blast provides the heat by burning the excess carbon and some of the CO. Zn vapour is thus formed in a much greater volume of gas than in a retort. Again, a special condenser is necessary because CO₂ is present. Waste gas from the condenser is utilized to preheat the charge and air blast.

Electrothermal Process

An electrothermal refining process of Swedish origin is also used on a limited scale in America. A mixture of crude oxide and zinc is heated internally by passing a heavy electric current through the charge in this vertical retort process. A similar plant has also been developed for the production of ZnO. One of the drawbacks of this method is the very close control of charge composition necessary to maintain the electrical conductivity at the required value.

Electrolytic Process More than ½ of the world's zinc is refined by electrolytic process, first used commercially during the first World War. Roasted concentrates are first dissolved in sulphuric acid then after an intensive purification of the solution which is treated with zinc dust to precipitate noble metals. Zinc is deposited

electrolytically on aluminium cathode sheets from which it is striped off, melted down and cast into slabs. Metal produced in this way has purity up to 99.95% and exceeding 99.99% when required. This process gives the high grade zinc needed throughout the world for die-casting and other alloys, and for anodes for zinc plating and cathodic protection. It was the successful development of the electrolytic process that led to the large-scale production of zinc outside Europe and USA. This process is used in places with cheap sources of electricity.

Uses of Zinc

Zinc, as a pure metal, finds relatively few applications basically because of its poor mechanical properties. It is relatively weak. Unalloyed zinc used for roofing up to about the 1960s was soft and had a tendency to creep. If the bays of fully supported roofing were too wide, they would eventually sag in the middle. The single largest use of zinc is in the application of zinc coatings (galvanizing) to permit the most efficient use of steel and to conserve energy.

Zinc and zinc alloys are used in the form of coatings, castings, rolled sheets, drawn wire, forgings, and extrusions. Other uses of zinc are as a major constituent in brasses and as a sacrificial anode for marine environments. In its purer form, zinc is available as slabs, ingots, shot, powder, and dust; combined with oxygen, it is available as zinc oxide powder. Impurity limits are very important when zinc is used for alloying purposes. Exceeding impurity limits can result in poor mechanical and corrosion properties. Pure zinc shot is used primarily for additions to electro-galvanizing baths, and zinc powder and dust are used in batteries and in enhanced corrosion-resistant paints. Zinc oxide is used as a pigment in primers and finish paint, as a reducing agent in chemical processes, and as a common additive in the production of rubber products.

About 5% of the world's consumption of zinc is in protective coatings for iron and steel works. Die casting accounts for 25%, brass making 20%, and sheet zinc 10%. With aluminium sheets becoming the dominant roofing material, the use of zinc-coated (or galvanized) iron sheets for roofing applications is on the decline.

1) Zinc Coatings

Due to its excellent resistance to corrosion in most atmospheres, in fresh and salt water, and in contact with any natural and synthetic substances; zinc coatings are widely used for the production of finished products ranging from structural steel works for buildings and bridges to nuts, bolts, chips, strips, sheets, wires and pressings. Five principal methods of application are:

- a) **Zinc Plating (Electro galvanizing):** - Zinc is electrodeposited on the prepared sheet from a solution of zinc salts. The process is used to protect small articles such as bolts, nuts, pressings, etc. which require finer finish than galvanizing can normally provide, this can be specially adapted to provide thin coatings on continuous strip and wire.
- b) **Zinc Spraying [or Metallizing]:** - Atomized particles of molten zinc are deposited on to a grit-blasted steel surface from a special pistol fed with wire or powder. The process is often applied to structural components too large to be dipped [baptized] in a galvanizing bath, or to a large structure, which cannot withstand heating or which, require a thicker coating than can be economically applied by other methods.
- c) **Hot Dip-Galvanizing:** - In this method, articles to be treated are dipped [baptized] after pickling and fluxing in a salt bath of molten zinc at a temperature of about 430 to 460°C. The zinc reacts with the iron or steel to form a series of alloy layers on the surface, each successive layer containing a higher proportion of zinc until in the outer layer, the coating consists of ductile unalloyed zinc. The zinc is thus effectively bonded to the base metal to form a protective coating possessing excellent resistance to corrosion and rough handling.
- d) **Sherardizing:** - Prepared iron and steel articles are heated with zinc dust and sand in a slowly rotating drum until the zinc has formed an alloy coating over their surfaces. The process gives a metallic grey coat, and is limited to small articles because of the difficulty of heating large containers evenly.
- e) **Zinc-Rich Paints:** - These consist of fine zinc dust suspended in a vehicle allowing very high pigmentation and the formation of an electrically conductive dry film. These paints can be applied to any rust-free and scale-free steel structure by brushing, spraying or dipping, and are mainly used to protect factory steel works, ship hulls and parts of car bodies, and to repair damage to other types of

zinc coatings. Automatic grit-blasting and zinc dust paint spraying machines are now widely used in shipyards to protect plates during storage.

2) Rolled Zinc

Rolled zinc sheets and strips are mainly used in dry batteries and in the painting and building industries. The ordinary dry cell operating on the Le Clanché principle uses zinc as a current producing element. Individual cells are made in various shapes and sizes depending on the purpose of the battery.

Another well-established usage of zinc sheet is in printing, as plates for photo-engraving and lithographic work. The zinc sheet is rolled to close thickness tolerances and produced with a controlled uniform fine structure. Zinc sheet and strip are widely used for roofing, gutters, flashings etc. in the UK and Europe; and with the use of proper techniques, gives long maintenance free service.

3) Die-Casting Alloys

The growth of the die-casting industry was helped to a great extent by the development of modern zinc-base alloys. These are rigid and reasonably strong materials, which have the advantage of a low melting point, making it possible to cast them into relatively inexpensive dies. Alloys of high meltingpoint will generally require dies in rather expensive heat-resisting alloy steels.

A very wide range of components, both for the engineering industries and for domestic appliances, is produced in a number of different zinc-base alloys sold under the trade name of **‘Mazak’**. Automobile fittings such as door handles and windscreen-wiper bodies account for possibly the largest consumption, but large quantities of these alloys are also used in electrical equipment, washing machines, radios, alarmclocks, and other domestic equipment.

During the development of these alloys, difficulty was experienced owing to the swelling of the casting during subsequent use, accompanied by a gradual increase in brittleness. These faults were found to be due to intercrystalline corrosion, caused by the presence of small quantities of impurities, such as cadmium, tin and lead. Consequently, very high-grade zinc of „four-nines“ quality, i.e. 99.99 per cent pure, is used for the production of these alloys.

Good-quality zinc-base alloy castings undergo a slight shrinkage, which is normally complete in about 5 weeks (Table 31). Where close tolerances are necessary, a ‘stabilizing’ anneal at 150°C for about three hours should be given before machining. This speeds up any volume change that is likely to occur.

Table 31: Zinc-base Die-casting Alloys

BS 1004 spec.	Composition %, balance Zn		Shrinkage after 5 weeks normal ‘ageing’ mm/mm	Shrinkage after 5 weeks following stabilising mm/mm
	Al	Cu		
Alloy A	4		0.000 32	0.000 20
Alloy B	4	1	0.000 69	0.000 22

In recent decades, these relatively low-strength zinc-base alloys of Table 31 have been replaced for many purposes by plastics mouldings. This, accompanied by a move away from expensive chromium-plated finishes led to a decline in the use of these 4 per cent aluminium alloys. However, a new series of zinc-base alloys [*high-strength zinc-base alloys*] has been developed, containing rather higher quantities of aluminium. They are die-casting alloys but have increased strength and hardness.

As might be expected, these alloys are sensitive to the presence of impurities so that these are kept to the same low limits as those of Table 31. The new alloys (Table 32) have found use in the automobile industry, e.g. ZA27 replacing cast iron for engine mountings. The use of die-casting allows the component to be produced to closer tolerances than does sand-casting. Consequently, the amount of subsequent machining is reduced.

Table 32: High-strength Zinc-base Die-casting Alloys

Alloy designation	Composition %, balance Zn			Condition	Typical mechanical properties		
	Al	Cu	Mg		Tensile strength MPa	Elongation %	Hardness Brinell
ZA8	8.4	1.0	0.02	Sand-cast	262	1.5	85
				Pressure die-cast	375	8	103
ZA12	11.0	0.85	0.02	Sand-cast	396	1.5	100
				Pressure die-cast	403	5.5	100
ZA27	26.5	2.3	0.015	Sand-cast	420	4.5	115
				Pressure die-cast	424	1	119

NICKEL?

TIN?

NIOBIUM [or COLUMBIUM]?

TANTALUM ?



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