Chapter 9
Zinc

9.1 Introduction

Zinc (Zn) has been known from ancient times as an alloy with copper. It was used in India and China in the 5th century. The first real knowledge of smelting comes from India and China, the latter producing zinc on a moderate scale in the early 1700s, a sample of Chinese zinc dated 1745 having been found to contain 98.9% zinc. Production of zinc started in Great Britain in 1740 by the process of distillation. In Belgium the horizontal-retort process was developed in 1806. By-products include cadmium, sulphuric acid and fertilizers. The original Belgian thermal process still remains the basis for modern zinc distillation. In this method the roasted or sintered concentrate (or both) is reduced by strongly heating with coal in vertical retorts. Metallic zinc distills and is collected as liquid metal in condensers. Produced zinc contains 1–2% lead and was formerly known as spelter. By fractionating spelter, 99.99% zinc can be obtained.

9.2 Sources

The important ores of zinc are sphalerite (ZnS) and marmatite [(ZnFe)S]. Less common ores are zincite (ZnO), smithsonite ($ZnO.CO_2$), and franklinite. The oxidized zinc ore calamine ($Zn_2O.SiO_3$) was at one time the main source of zinc. Zinc ore is widely distributed, the most important sources being USA, Canada, Australia, Mexico, Germany, Poland and India. However, with the successful separation of sulphide minerals by flotation, its importance has considerably decreased. Sphalerite (ZnS) and marmatite [(ZnFe)S] are the main economic ores, which are always found with the lead mineral galena; they are separated by flotation.

Zinc ores/minerals:

(1) Zinc blende or sphalerite (ZnS).
(2) Smithstone ($ZnCO_3$).
(3) Calamine ($Zn_2SiO_4.H_2O$).

Zinc ores are often a low grade ores which contain 2–7.5% Zn. By mineral beneficiation process (i.e. flotation), separation of sulphides of Pb, Cu take places and concentration of zinc (ZnS) is produced. Zinc concentration contains 47 to 60% Zn, 1.5 to 2.5% Pb, 3.5% Cu, 3 to 10% Fe, 0.2% Cd and 29 to 33% S; apart from those minor quantities of Tl, In, Ga, Ge, Se and Te are also present.

9.3   Extraction of Zinc

There are two routes of extraction of zinc: pyrometallurgical process, and hydrometallurgical process followed by electrometallurgical process.

9.3.1   Pyrometallurgical Process

The techniques of smelting and converting are applied for Cu_2S in copper metallurgy. But for ZnS, they are not possible due to high melting point of ZnS even at 1500 °C. Hence, a different method is applied in zinc extraction.

Flow sheet for pyrometallurgical process is shown in Fig. 9.1. After grinding of ore, separation of sulphides of lead and copper is done; and concentration of zinc (50–60% Zn) is produced.

9.3.1.1   Roasting

Oxidation of zinc concentrate (ZnS) is necessary for the subsequent reduction and recovery of zinc metal. Oxidation is carried out by roasting, either a partial roast followed by sintering or in one operation as a dead roast. Complete elimination of sulphur is desirable as any remaining after roasting ties up twice its weight of zinc, which is lost in subsequent operation. The zinc sulphide concentrate always contains some lead sulphide which is eliminated during initial stages of roasting, i.e. by volatilization; hence, the multiple hearth roaster is used. The roaster has eight hearths and a top drier hearth. The remaining lead sulphide is removed during sintering at high temperature. Heating is unnecessary when a partial roast is done, for the blende contains sufficient sulphur to support combustion down to 7–8% sulphur; but for dead roasting, external heating is necessary to drive off the last few per cent of sulphur; this is provided by a firebox on the bottom hearth, either oil or gas is used as fuel.
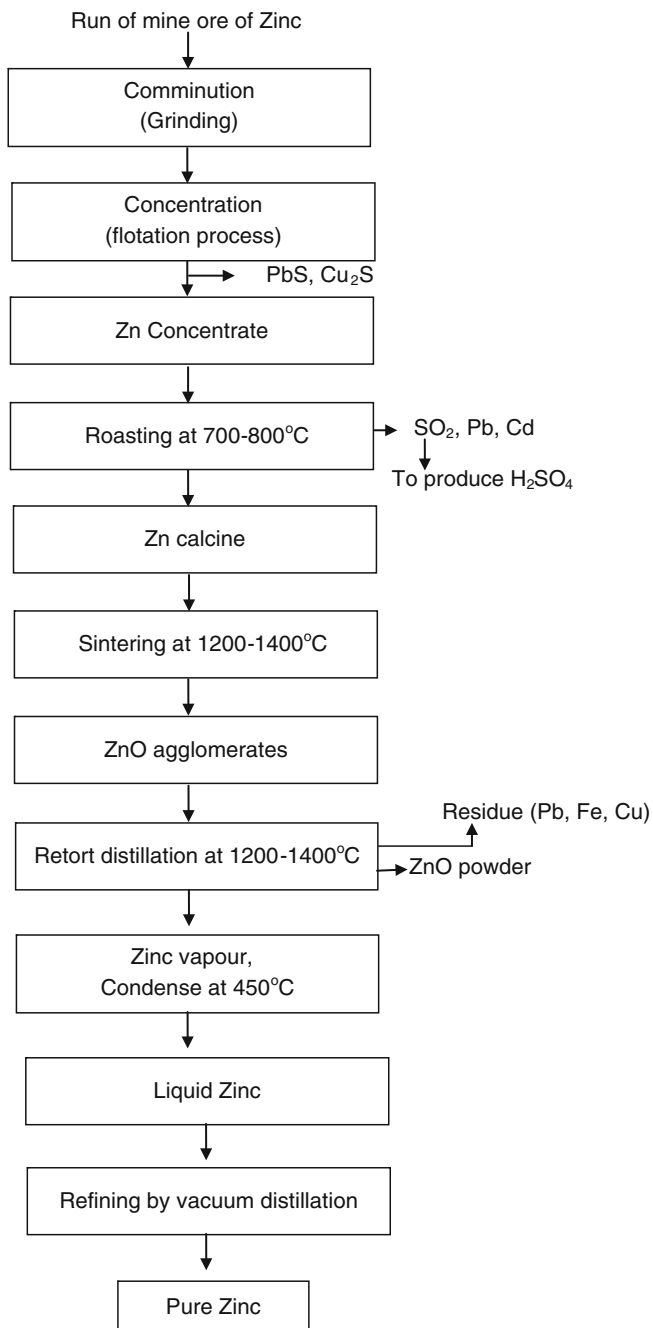
Run of mine ore of Zinc

Comminution
(Grinding)

Concentration
(flotation process)

→ PbS, Cu$_2$S

Zn Concentrate

Roasting at 700-800°C → SO$_2$, Pb, Cd

To produce H$_2$SO$_4$

Zn calcine

Sintering at 1200-1400°C

ZnO agglomerates

Residue (Pb, Fe, Cu)

Retort distillation at 1200-1400°C → ZnO powder

Zinc vapour,
Condense at 450°C

Liquid Zinc

Refining by vacuum distillation

Pure Zinc

Fig. 9.1 Flow diagram for extraction of zinc by pyrometallurgical process

Partial roasting of zinc concentration (ZnS) is done at 700–800 °C to zinc calcine (ZnO, which contain 1–4% S). For a dead roasting a higher temperature (1000 °C) is required.

$$2ZnS + 3O_2 = 2ZnO + 2SO_2 \tag{9.1}$$

Presently, roasting is carried out in a suspension roaster or fluidized bed roaster instead of earlier in a conventional hearth roaster, because the former has certain advantages: (a) it is autogenous; (b) good control over the temperature; and (c) high roasting rate.

Then sintering of zinc calcine (ZnO) is done at 1200–1400 °C in a Dwight-Lloyd sintering machine to provide lump feed for retort distillation and to eliminate residual sulphur, cadmium and lead.

9.3.1.2 Retort Distillation

In horizontal retort process, 2 m long retorts, each having a diameter of 25 cm and a thickness of 5–6 cm, are lined up in a gas fired furnace in batches of several numbers at a time. Retorts cannot make of metals because most of metals produce alloy with zinc when heated at high temperature. The retorts are generally made of fireclay. The retorts are first charged with mixture of fine size ZnO and an excess of coal (30–40% by weight), then heated to a maximum temperature to volatilize zinc which is subsequently condensed. Theoretically, one part of carbon will reduce seven parts of zinc oxide, but in practice it has been found necessary to use four to five times this amount, principally to keep the carbon dioxide concentration as low as possible ($C + CO_2 = 2CO$), and also to protect the retorts by holding up the molten slag. This large excess of carbon, over that the theoretically required, is necessary to insure complete reduction and to maintain a reducing atmosphere in the retort by reducing any carbon dioxide that may be formed.

The furnace is gradually heated up to 1400 °C, distillation start around 1100 °C. The first gas to come off is coal gas, burning with a luminous flame; as the reduction proceeds, and carbon monoxide is given off, the luminosity diminishes and the flame becomes purple. The beginning of zinc distillation is marked by the flame of bluish-white colour and generally at this stage the prolongs are fitted to the condensers. Finally, when all the distillable zinc has been expelled, the flame loses its bluish tinge and becomes purple again, indicating that the cycle has been completed. Temperature of condenser is important: if it becomes too low (below 400 °C) excessive blue powder forms, and if too high, zinc vapour will pass off uncondensed. A temperature of 1400 °C is generally maintained in the furnace, and retorts temperature being 100–200 °C lower.

Reduction of zinc oxide by carbon is a strongly endothermic reaction, which requires temperature in the range of 1200–1400 °C.

$$ZnO(s) + C(s) = Zn(g) + CO(g) \, \Delta H_f^\circ = 238.49 \, kJ \tag{9.2}$$
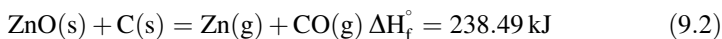
The liberated zinc vapour is extremely sensitive to oxidation and it is necessary to carry out the distillation in a closed system. The carbon monoxide forms in reaction (9.2), then further reduces to zinc oxide:

$$ZnO(s) + CO(g) = Zn(g) + CO_2(g) \, \Delta H_f^\circ = 75.31 \, kJ \tag{9.3}$$
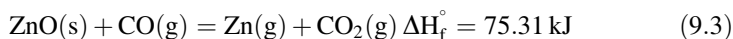
At high temperature the carbon dioxide is unstable, so it reacts with more carbon present in the system to form carbon monoxide:

$$C(s) + CO_2(g) = 2CO \tag{9.4}$$

Zinc boils at 907 °C, and carbon does not reduce zinc oxide until 1120 °C, so zinc is liberated in the vapour form. In this state it is not only susceptible to oxidation by the ordinary oxidizing agents such as air and water vapour, but it is capable of oxidizing by carbon dioxide. Reactions (9.3 and 9.4) are reversible reactions, but the concentration must be very high before the backward reactions take place. With zinc vapour [reaction (9.3)], however, the backward reaction occurs with small concentrations of carbon dioxide. In general, condition of reduction is $(p_{co}/p_{co2})_{gas \, phase} > (p_{co}/p_{co2})_{equilibrium}$, so p_{co} should be maintained at a high level in order to prevent the oxidation of zinc vapour to zinc oxide due to presence of CO_2 gas. If the zinc vapour is much diluted with other gases, it condenses not to liquid zinc but to a mixture of solid zinc encrusted with zinc oxide, which is known as blue powder.

9.3.1.3 Vertical Retorts

Vertical retorts are made of carborundum, as refractory by mixing with 6–12% of clay. Carborundum is nothing but silicon carbide (SiC), which has a melting point above 2700 °C. The conductivity of silicon carbide is about five times higher than that of fireclay. Vertical retort is a shaft of rectangular cross-section. The height of the heating zone is about 7.5 m, and inside dimensions of retort cross-section average 300 × 1500 mm.

Generally, gas is used to heat the retort by burning of gases in chambers. Modern vertical retort is heated by electrical energy. The graphite electrodes are introduced through the silicon carbide walls near the bottom of the retort. The electrical energy provides the heat to the system. The charge is introduced as briquettes from the top and slag is discharged continuously from the bottom. Modern vertical retorts are provided with automatic charging and discharging systems which help the handling of raw materials as well as products.

The roasted zinc concentrate, coking coal and coal tar (as binder), after a through mixing, the charge is passed through a briquetting machine. The briquettes are

Table 9.1 Comparisons between horizontal and vertical retorts

| Horizontal retort	Vertical retort
1. Fine-sized roasted zinc concentrate and coal or coke act as charge materials	1. Sinter/briquette of roasted zinc concentrate and coal or coke act as charge materials
2. It is batch process	2. It is continuous process
3. It is difficult to mechanize and hence involves large manual labour (29–43 man-hours)	3. It can be easily mechanized and hence involves less manual labour (7.7–12.5 man-hours)
4. It has less capacity (800–1000 kg/day) and less recovery of zinc (86–88%)	4. It has more capacity (7–10 tonne/day) and high recovery of zinc (90–94%)
5. Size of retort is smaller (2 m long, 0.25 m diameter and 0.05–0.06 m thickness)	5. Size of retort is larger (10 m long, and 0.3 x 1.5 m cross-section)
6. Retorts are made of fireclay	6. Retorts are made of silicon carbide

heated to 750–900 °C to strengthen briquettes and make them adequately porous. Distillation in vertical retorts is no different in chemistry than the standard horizontal retort technique. Since the conductivity of silicon carbide is higher and therefore zinc is removed more completely, zinc content in slag is generally less than 5%.

A condenser is lined with refractory brick and provided with internal partitions that lengthen the path of gases. The zinc vapour is condensed very fast in order to avoid the formation of blue powder (ZnO + Zn). 3–4% zinc, all iron, gangue, copper, and precious metals are contained in the residues of the retort processes. Zinc recovery is about 95%. The comparisons between horizontal and vertical retorts are shown in Table 9.1.

Zinc vapours are condensed to metal and some are oxidized. Besides zinc, retort slag always carries lead, copper and noble metals; therefore they require additional treatment. A top layer of zinc containing some lead (about 0.8%) and an intermediate layer of zinc and iron (15–20%) is called hard metal, which is recycled to the retorts. Bottom lead layer is further smelted to recover the lead. The zinc layer is refined by fractional distillation due to wide difference in the boiling points of zinc (907 °C), cadmium (780 °C) and lead (1620 °C); therefore, easy separation of one metal from the other.

9.3.1.4 Physical Chemistry of Zinc Smelting

The reaction taking place in a retort may be written as (in general):

$$(x + 2y)ZnO(s) + (x + y)C(s) = (x + 2y)Zn(g) + xCO(g) + yCO_2(g) \quad (9.5)$$
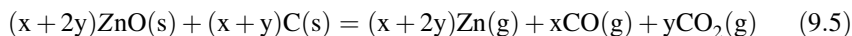
When zinc oxide and carbon are heated together, variable amounts of zinc, carbon monoxide and carbon dioxide are produced. This reaction (9.5) is the sum of the following reactions:

$$xZnO(s) + xC(s) = xZn(g) + xCO(g) \tag{9.6}$$

$$2yZnO(s) + yC(s) = 2yZn(g) + yCO_2(g) \tag{9.7}$$
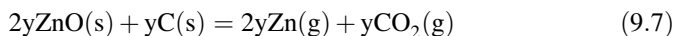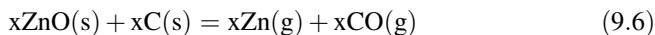
It is significant that the so-called temperature of reduction of zinc oxide had been reported by investigators over the range of 780 to 1310 °C. These divergences had been attributed in the past to differences in the physical form of zinc oxide and carbon, to differences in the gas pressure, and to allotropic modifications. It is certain that no amount of continued heating at a definite pressure will cause gas-free carbon to reduce zinc oxide continuously below a certain temperature. It is also obvious that attempts to measure the temperature at which reduction takes place have measured only the temperature at which the rate of reaction becomes measurable. At higher temperatures, where the reaction takes place at any definite temperature, either zinc oxide or carbon, or both, disappear from the system. In other words, if a system containing zinc oxide and carbon is vented at a definite pressure, a condition of equilibrium can exist at only one temperature. Below this temperature, reduction by carbon does not take place, and above it continuous reaction takes place. This is the system which is unstable as far as chemical equilibrium is concerned.

Reactions within the charge in a retort produce water vapour, hydrocarbons, carbon monoxide and carbon dioxide; but only the last two (CO and CO_2) are the important factors in the production of *blue powder*, which is a mixture of zinc and zinc oxide.

Zinc is a moderately strong basic metal and may be used to reduce carbon monoxide:

$$Zn(g) + CO(g) = ZnO(s) + C(s) \tag{9.8}$$
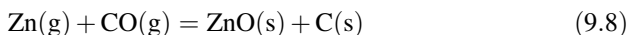
This would necessarily involve the reversal of the producer gas reaction:

$$2CO(g) = CO_2(g) + C(s) \tag{9.9}$$

$$CO_2(g) + Zn(g) = ZnO(s) + CO(g) \tag{9.10}$$
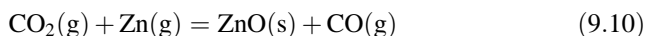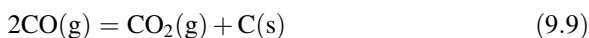
The reaction (9.8) is the combination of the reactions (9.10) and (9.9).

It has been shown that reaction (9.9) is slow below 1100 °C but reaction (9.10) is perceptible above 300 °C and very fast above 550 °C, so that the rate at which zinc is oxidized is determined by the slowest step. Large amounts of carbon dioxide would be present in the equilibrium mixture at temperature below 850 °C, but at this temperature the rate of the reaction is so slow that equilibrium would be obtained only in week or month. Catalysts are known that would increase this rate, but they are not present in the charge. Therefore, the reaction with carbon monoxide probably accounts for the formation of only a part of the blue powder.

9.3.2 Hydrometallurgical Process

(a) Hydrometallurgical processes are used for the extraction of zinc from the low
    grade ores. These processes produce high purity zinc and also lead to a higher
    rate of recovery of valuable by-products. Figure 9.2 shows the flow sheet of
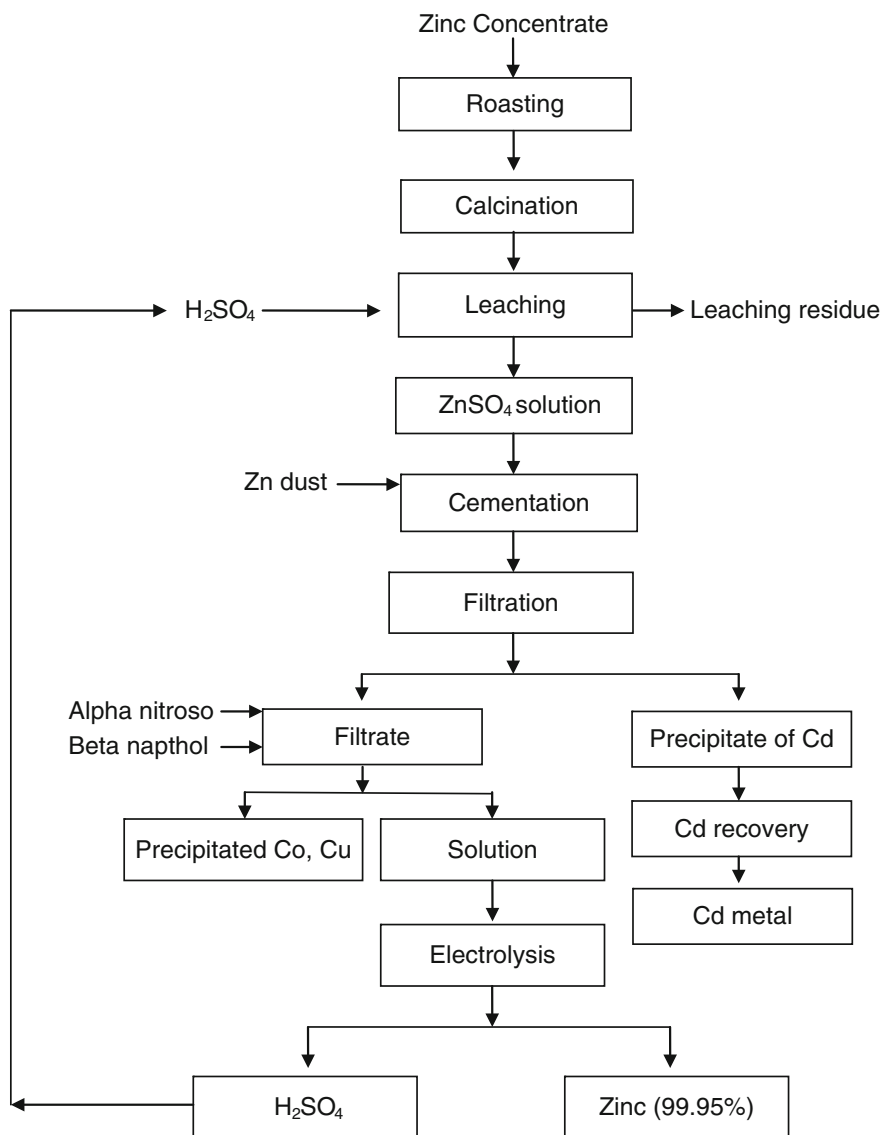   hydrometallurgical process.

Fig. 9.2 Flow diagram for extraction of zinc by hydrometallurgical process

Before leaching, the zinc sulphide concentrate is first roasted. Roasting for leaching must be very carefully controlled to produce the right proportions of zinc oxide and zinc sulphate. The zinc sulphate must be present in sufficient amount to make up for the sulphuric acid lost in dissolving the oxide and processing the residues. The roasted zinc concentrate is dissolved in sulphuric acid and the valuable by-products are precipitated out.

$$ZnO + H_2SO_4 = ZnSO_4 + H_2O \tag{9.11}$$

Zinc dust is added to the leach zinc sulphate solution to precipitate cadmium (i.e. cementation process) for recovery of Cd; Co and Cu are also precipitated out. Precipitation of cobalt from leach solution is done by adding α-nitroso-β-napthol. Then electrolysis of the purified leach solution ($ZnSO_4 + H_2SO_4$) of 5.3 pH is done by using a cell with an anode of cast Pb-Ag (1%) alloy and rolled high-purity aluminium sheet as cathode. Metallic zinc is deposited at cathode and oxygen gas is released at anode. Cu and Fe present in solution reduce the current efficiency of the electrolyte bath.

(b) Acid-pressure leaching of zinc concentrates was developed in Canada. To obtain high zinc recovery in the leaching process, zinc concentrate should be very fine sizes. Continuous-pressure leaching is carried out in two to three compartments, along with autoclaves. After leaching, the slurry is cooled by two-stage flashing at atmospheric pressure. After a solid–liquid separation and residue is washed properly, the liquor is passed for sulphur removal by neutralization. After neutralization, iron is removed from the leach liquor. In the first stage, the liquor is neutralized at 80–90 °C and pH is maintained at 3.5–4.0 with limestone. Air is spurged into the neutralization reactor to oxidize iron for hydrolyses and precipitation. In the second stage, zinc dross is used for further neutralization to pH 4.5. In the second stage, copper losses are significant; and so that is recycled. A purification process is carried out by zinc dust before coming to electro-winning.

(c) In the conventional process, certain impurities (like selenium, mercury, fluoride, and chloride) are removed during the roasting of the zinc concentrates. In the direct leaching process, selenium, mercury, and fluoride, are removed either in the leach residues or during the iron precipitation steps. It is well known that selenium is difficult to remove from leach liquors of copper concentrates. Since selenium is very harmful in the zinc electro-winning step, separate purification procedures are followed to keep its level low, which is acceptable in the electro-winning cells. Any chloride present in the zinc leach liquor has to be removed prior to electro-winning by either ion exchange or silver chloride precipitation.

9.4   Properties

Atomic weight of zinc is 65.38, specific gravity is 7.14; melting point and boiling point are 419 °C and 907 °C respectively. The relatively high corrosion resistance of zinc maks it useful as a protective coating (galvanizing) on steel. Zinc, being electro-negative to iron, is slowly corroding zinc by corrosive media, leaving the iron undamaged and protects iron. If the coating is damaged at any point, its protective properties remain unaffected, since base sections of iron are not attacked. On cast condition, zinc possesses a tensile strength of 3.15 to 7.87 kg/mm^2; after cold work that is increased to 18.9–25.2 kg/mm^2.

Zinc dissolves in strong acids (like HCl, H_2SO_4) with an evolution of hydrogen. Zinc oxide (ZnO) is a fine crystalline white powder obtained by oxidation of zinc vapour in the air. Zinc oxide is a non-fusible substance which volatilizes at a temperature above 1800 °C without melting. Reduction of zinc oxide can be done by carbon at the temperature 950 °C.

9.5   Applications

After cold work, tensile strength is drastically increased; hence, zinc is not used where high stresses are likely to be encountered; but it can be used for ordinary applications such as roofing, metal linings, dry batteries etc. By rolling, the metal is easily worked to make foil, due to ductility of zinc.

High purity zinc (99.99%) is used for manufacturing of die casting parts, wire, foil and anodes. High grade zinc (99.95%) is used for production of wire, zinc oxide, and high grade brasses. Foundry grade zinc (98.5%) is used for making sheet and strip by rolling; foundry work for brass and other alloys castings. Zinc (98%) is used for galvanizing, formation of zinc dust and brass. Zinc acts as an alloying element in brass and bronze. The bulk of the metal is consumed as an alloying element of brass and in the form of galvanized steel sheet.

Small articles are exposed to zinc dust at elevated temperatures (350–400 °C); zinc diffuses at the surface, and this method is known as sherardizing. This process is used for steel windows. Springs, aeroplane components, bolts, nuts and small castings of intricate design can be made from zinc and its alloys. Almost any metal may be applied by spraying, since zinc has a low melting point (420 °C) and corrosion prevention property, hence being used to a greater extent than any other metal. Anti-corrosion paints based on metallic zinc powder form, a convenient alternative to metal spraying.

On account of low melting point and prevention of corrosion, zinc is used to spray on the other metals. Zinc in the form of wire or powder is loaded into a pistol, where it is melted and atomized by compressed air; then is projected at the target object. The main applications of sprayed zinc coating are for steel bridges, ships, storage tanks etc.

   The copper-zinc alloys can be divided into two main groups: (a) first group contains 30–37% Zn, which has adequate ductility and strength for cold deformation into sheets and wire; (b) second group contains 37–45% Zn, which is much less plastic when cold and is therefore worked above 500 °C. The zinc die-cast alloys contain small amounts of Al, Cu and Mg. The most widely used of these zinc die-casting alloys contain up to 4% Al with small amounts (0.02%) of Mg.

   Zinc oxide is used for high grade pigments and pharmaceutical use. Zinc oxide is extensively used in the manufacture of oil and other types of paints owing to its white colour and high covering power.