Metallurgy ,2nd Part

C9 ,4th Sem

Dr Sukla Chakladar

Associate Professor,RNKWC,Midnapopre

Electrolytic reduction

For more reactive metals like Na,Mg ,Al etc cannot be reduce by carbon reduction process. So they can be reduced by electrolysis and these metals are not obtained by electrolysis from aqueous solution of their salt. So in these cases electrolytes are molten salts.

Some e.gs

Metal	Electrolyte	Reaction at the electrodes
Na	NaOH (Castner's Process)	At Cathode $Na^++e \longrightarrow Na$ At anode $4OH^- \longrightarrow 2H_2O+O_2+4e$
	NaCl(Down's Process)	$Na^++e \longrightarrow Na$(at Cathode) $2Cl^- \longrightarrow Cl_2+2e$(at Anode)
Mg	Molten MgO	$Mg^{2+} +2e \longrightarrow Mg$(Cathode) $O^{2-} \longrightarrow 1/2O_2+e$(Anode)
	$MgCl_2$	$Mg^{2+}+2e \longrightarrow Mg$(Cathode) $2Cl^- \longrightarrow Cl_2+2e$(Anode)
Al	Alumina(Al_2O_3,Na_3AlF_6+CaF_2)	$Al_2O_3 \longrightarrow 2Al^{3+}+3O^{2-}$ $Al^{3+}+3e \longrightarrow Al$(Cathode) $3O^{2-} \longrightarrow 3/2O_2+3e^-$ (Anode)

Hydrometallurgy

Hydrometallurgy involves extraction of metal from ore by preparing an aqueous solution of a salt of the metal and recovering the metal from the solution. The operations usually involved are leaching, or dissolution of the metal or metal compound in water, commonly with additional agents; separation of the waste and purification of the leach solution; and the precipitation of the metal or one of its pure compounds from the leach solution by chemical or electrolytic means.

It involves extraction of less electropositive or less reactive metals like gold and silver. Powdered ore is first dissolved in a suitable reagent by complex formation e.g.

$Ag_2S+4NaCN \longrightarrow 2Na[Ag(CN)_2]+Na_2S$

$4Au+8NaCN+2H_2O+O_2 \longrightarrow 4Na[Au(CN)_2]+4NaOH$

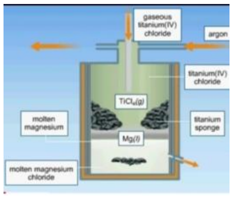
Now a strong electropositive metal added to above salt solution from which metal is obtained.

$2Na[Ag(CN)_2]+Zn \longrightarrow Na_2[Zn(CN)_4] +2Ag$

$2Na[Au(CN)_2]+Zn \longrightarrow Na_2[Zn(CN)_4] +2Au$

Hydrometallurgy is based on the principle that a more electropositive metal displaces a less electropositive metal from its salt.

Electrolytic Kroll Process



Titanium cannot be extracted by reduction with C since it forms TiC with carbon instead of free metal.

$TiO_2(s)+3C(s) \longrightarrow TiC(s)+2CO(g)$

Prior to the Kroll process, titanium was separated from its ores by the chloride process, where a feedstock of refined rutile or ilmenite is reduced with petroleum-derived coke in a fluidized bed reactor at 1000 °C. The product is then treated with chlorine gas, producing $TiCl_4$ and other volatile chlorides, which are then separated by continuous fractional distillation.

The Kroll process is a pyrometallurgical industrial process used to produce metallic titanium. It was invented in 1940 by William J.Kroll.

TiO_2 is reacted with C and Chlorine to produce $TiCl_4$ which is liquid at normal condition and can be purified by distillation.

$TiO_2+2Cl_2(g)+2C(s) \longrightarrow TiCl_4(l)+2CO(g)$

Gaseous $TiCl_4$ is reduced by liquid magnesium at 800–850 °C in a stainless steel retort to ensure complete reduction.

$TiCl_4(g)+2Mg(l) \longrightarrow Ti(s)+2MgCl_2(l)$

Reaction is carried out in Ar atmosphere to prevent the violent reaction of Mg with air..After the reaction is over molten $MgCl_2$ is tapped off. Ti sponge contains upto 30% of impurities (mainly $MgCl_2$). Heating at high temperature removes $MgCl_2$ from Ti sponge. Mg is recovered from $MgCl_2$ by electrolysis.

$MgCl_2 \longrightarrow Mg(l)+Cl_2(g)$

The chlorine is recycled.

Titanium is about six times as expensive as stainless steel.

In the Hunter process, which is not commercial, the $TiCl_4$ from the chloride process is reduced to the metal by sodium.

$TiCl_4(l)+4Na(l) \longrightarrow Ti(s)+4NaCl(l)$

Parting Process

Parting, in metallurgy is the separation of gold and silver by chemical or electrochemical means. Gold and silver are often extracted together from the same ores or recovered as by-products from the extraction of other metal ores and are chemically similar and therefore hard to separate.

A solid mixture of the two, known as bullion, or doré, can be parted by boiling in nitric acid. The silver is dissolved as silver nitrate, leaving a residue of gold that is filtered off and washed; silver is precipitated out of solution by the addition of ferrous sulfate. This is the traditional method used in assaying the content of gold and silver samples.

Most gold and silver are parted electrolytically after being recovered in the slimes left over from copper refining or as a metallic by-product of lead or zinc smelting. The bullion is cast into anodes, which are placed into an electrolytic cell and subjected to an electric current. Silver dissolves in the electrolyte and then deposits onto the cathodes. Gold and trace amounts of silver are recovered in the slimes and are parted either electrolytically or by boiling in sulfuric acid and potassium nitrate to dissolve the silver.

For some years now a new acidless separation process based on the vacuum distillation method, is being used; it is a physical method, which does not use any chemical and therefore it is considered the greenest of the gold parting processes.

Vapour Phase refining

In this refining process of purifying metal:

- The impure metal is heated with a specific reagent that produces a suitable volatile compound as the product.
- Volatile compound is heated strongly, which undergoes decomposition producing pure metal

So the two requirements are:

a) Metal should form a volatile compound with suitable reagent.

b) The volatile compound should be easily decomposable so that the recovery of metal is easy.

Two tmethods of vapour phase refining are:- 1.Mond’s process 2.van Arkel-de Boer process

1.Van Arkel de Boer Process: This method is very useful for removing all the oxygen and nitrogen present in the form of impurity in certain metals like Zr and Ti.

- Used in the refining of Zr and Ti.
- Impure Zr/Ti is heated in an evacuated vessel with iodine
- Volatile $ZrCl_4/TiCl_4$is obtained as product.
- Volatile compound is heated strongly over a tungsten filament to give pure metal(Zr/Ti).The pure metal is thus deposited on the filament.

$$Zr(s)+2I_2(g) \xrightarrow{597^0C} ZrI_4(g) \xrightarrow{1800^0C} Zr(s)+2I_2(g)$$

Impure zirconium | zirconium tetraiodide | Pure zirconium

$$Ti(s)+2I_2(g) \xrightarrow{250^0C} TiI_4(g) \xrightarrow{1427^0C} Ti(s)+2I_2(g)$$

Impure Titanium | Titanium tetraiodide | Pure titanium

2. Mond's Process

- Used for refining of Nickel
- Impure nickel is heated with a stream of CO gas.
- A volatile nickel tetracarbonyl, $Ni(CO)_4$ is produced.
- Impurities are left behind.
- Volatile $Ni(CO)_4$ is heated strongly which decomposes to produce pure nickel.

$$\underset{\text{Impure Nickel}}{\text{Ni (s)}+4\text{CO(g)}} \xrightarrow{57\text{-}77^{0}\text{C}} \underset{\text{Nickel tetracarbonyl}}{\text{Ni(CO)}_4\text{ (g)}} \xrightarrow{177\text{-}197^{0}\text{C}} \underset{\text{Pure Nickel}}{\text{Ni (s)}+4\text{CO(g)}}$$

Zone Refining

Definition: This is a technique for the purification of an impure metal in which a molten region travels through the material to be **refined**, picks up impurities at its advancing edge, and then allows the purified part to recrystallize at its opposite edge.

Zone refining is a very useful method to get metals with very high purity such as silicon and germanium, gallium and tellurium. It is also referred to as zone melting, floating zone process, and traveling melting zone.

Zone refining was discovered by scientist W.G.Pfann and is based in the principle that the impurities have higher solubility in the molten metal as compared to that of solid metal. The difference in the solubility of impurities makes it possible to segregate the impurities in the metals to be refined.

During the process of Zone Refining:

- A circular mobile heater is placed around the impure metal rod which is moved along the rod from one end to the other.
- As the heater shifts from one zone of the metal rod to another, the impurities also shift to the zone with molten metal.
- Finally the impurities get concentrated at one end of the metal rod which is later removed.

Zone refining procedure: The metal rod is placed in a tubular zone refiner. In the Zone Refiner an inert gas atmosphere is maintained. A circular mobile heater is placed around the rod. This heater moves along the rod from one end to the other.

At the time, the heater melts a particular zone or a portion of metal rod along with its impurities. As the heater moves along the rod the molten metal of the previous zone solidifies again. During solidification of the metal impurities of the zone move to newly heated zone or the zone that is in contact with the heater. In another words, as the heater shifts from one zone of the metal rod to another, the impurities also shift to the zone of molten metal. By the time the heater reaches to the other end of the impure metal rod, the impurities get concentrated there. The end of the metal rod with concentrated impurities is then removed and discarded. The same process is repeated again and again till highly purified metal is obtained.