Chapter 6
Thorium

6.1 Introduction

The discovery of thorium (Th) is attributed to Berzelius in 1828. The name thorium was derived from *Thor*, Scandinavian god of war. Interest in the metal and its oxide lagged until about 1884. The interest in thorium for nuclear energy application is increased owing to its abundance in the Earth's crust 0.0012% thorium as compared to 0.0004% uranium. Thorium is a major potential source for increasing the world's supply of nuclear fuel. It is a fertile material, for producing U^{233}, in a nuclear reaction similar to the conversion of U^{238} to Pu^{239}. Th^{232} captures a neutron and subsequently emits two β particles to become U^{233}, a long-lived fissionable isotope.

$$_{90}Th^{232} + {}_{0}n^{1} \rightarrow {}_{90}Th^{233} + \gamma \tag{6.1}$$

$$_{90}Th^{233} \rightarrow {}_{91}Pa^{233} + {}_{-1}\beta^{0} \tag{6.2}$$

$$_{91}Pa^{233} \rightarrow {}_{92}U^{233} + {}_{-1}\beta^{0} \tag{6.3}$$

Thorium, like uranium, is a radioactive element in nature and emits α particle. The metal has a high density, low strength, and poor corrosion resistance in water. These properties, together with its high cost, have prevented its use as an engineering material. The use of thorium metal instead would offer the advantages of case of fabrication, and good thermal conductivity. Thorium metal has a relatively high melting point (1750 °C) and has good dimensional stability under irradiation.

S.K. Dutta and D.R. Lodhari, *Extraction of Nuclear and Non-ferrous Metals*,
Topics in Mining, Metallurgy and Materials Engineering,
https://doi.org/10.1007/978-981-10-5172-2_6

6.2 Sources

Thorium occurs in a large number of minerals associated with uranium and the rare earths metals. Those which contain a high amount of the element, such as thorianite ($ThO_2 + UO_2$) and thorite ($ThSiO_4$) are scarce.

The major source of the thorium metal is monazite. This mineral occurs associated with silica and other minerals in the so-called monazite sands. The largest deposits of these sands are in India and Brazil. Other countries are Australia, Ceylon, South Africa, Canada and the USA.

The major sources of monazite in India are found in Kerala (at the sea-coast of Travancore) and Tamil Nadu; monazite is also found on Bihar. The *black sands* of the Kerala sea-coast contain ilmenite ($FeTiO_3$), garnet, monazite, quartz, rutile and other minerals. They get their name from the black colour of the ilmenite. The monazite content of these sands is 4–5%. First separation done by nature is carried further by man with the help of magnetic or electrostatic separators, a concentration of 97–99% of monazite is obtained. Monazite contains thoria (ThO_2), uranium oxide (U_3O_8), phosphate and rare earths metals oxides. Monazite of the Kerala sea-coast contains 8–9% ThO_2, 0.3–0.4% U_3O_8, 59% RE_2O_3 (where RE are cerium, Ce; lanthanum, La: holmium, Ho; thulium, Tu etc.).

6.3 Extraction of Thorium

Extraction of thorium metal from monazite sand is shown in flow-diagram (Fig. 6.1). Thorium oxide is present in monazite in rather lower concentration (8–9%) than cerium (Ce), lanthanum (La) and yttrium (Y) rare earths metal oxides (59%). This created technical difficulties for separation of thorium from rare earths metals. There are, in general, two chemical processes commonly used for separation: (a) sulphuric acid method; (b) caustic soda method.

6.3.1 Separation of Thorium Compound from Monazite

6.3.1.1 Sulphuric Acid Method

Separation of thorium compound from monazite by sulphuric acid method has been in commercial use for many decades. The monazite sands are decomposed chemically in an excess of concentrated (93%) H_2SO_4 at a temperature of 210 °C for a period of 1 to 5 h, depending on the sand particle size. The pasty mass which is produced is cooled and cold water is added to dissolve the thorium, uranium, and rare earth metals (RE). Thus, monazite sulphate solution is formed and separated from the insolubles, primarily consisting of silica.

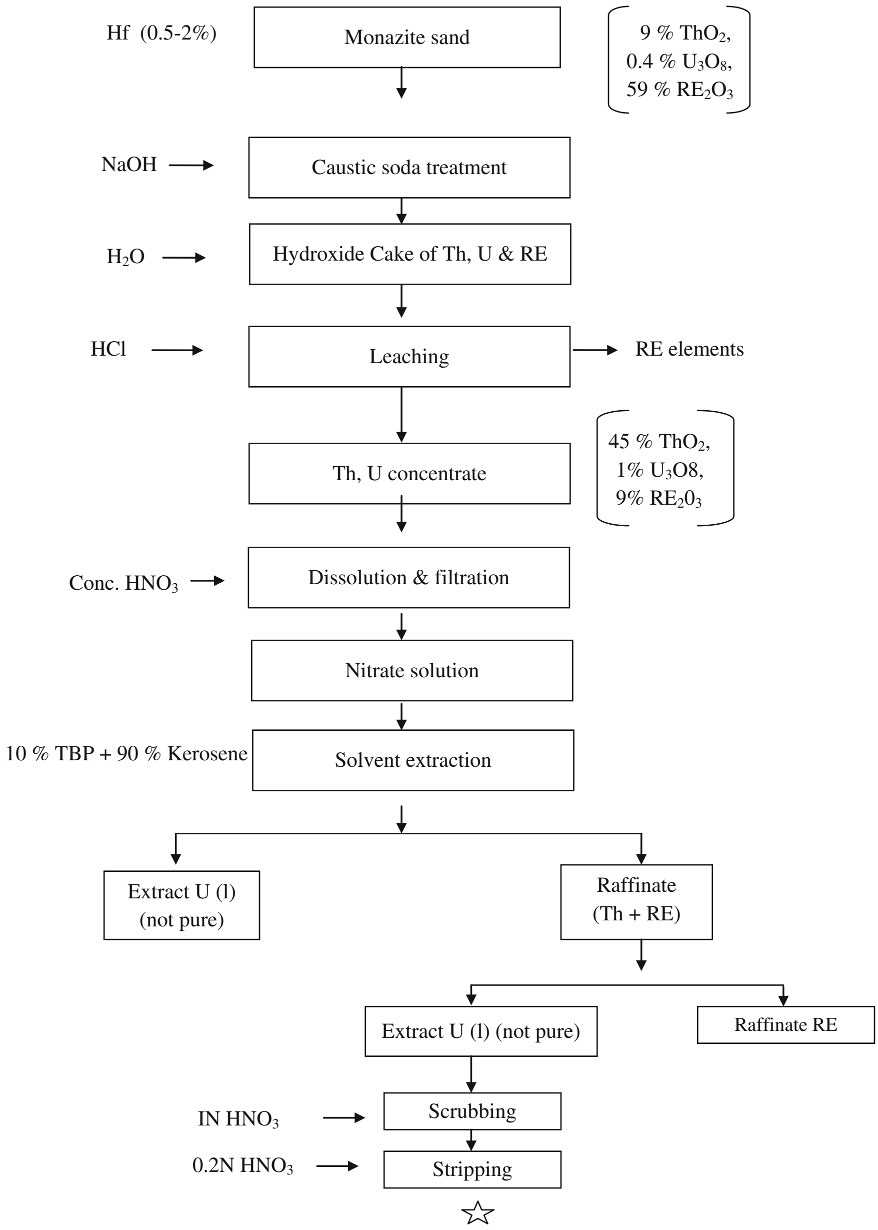

Fig. 6.1 Flow sheet for the extraction of thorium metal

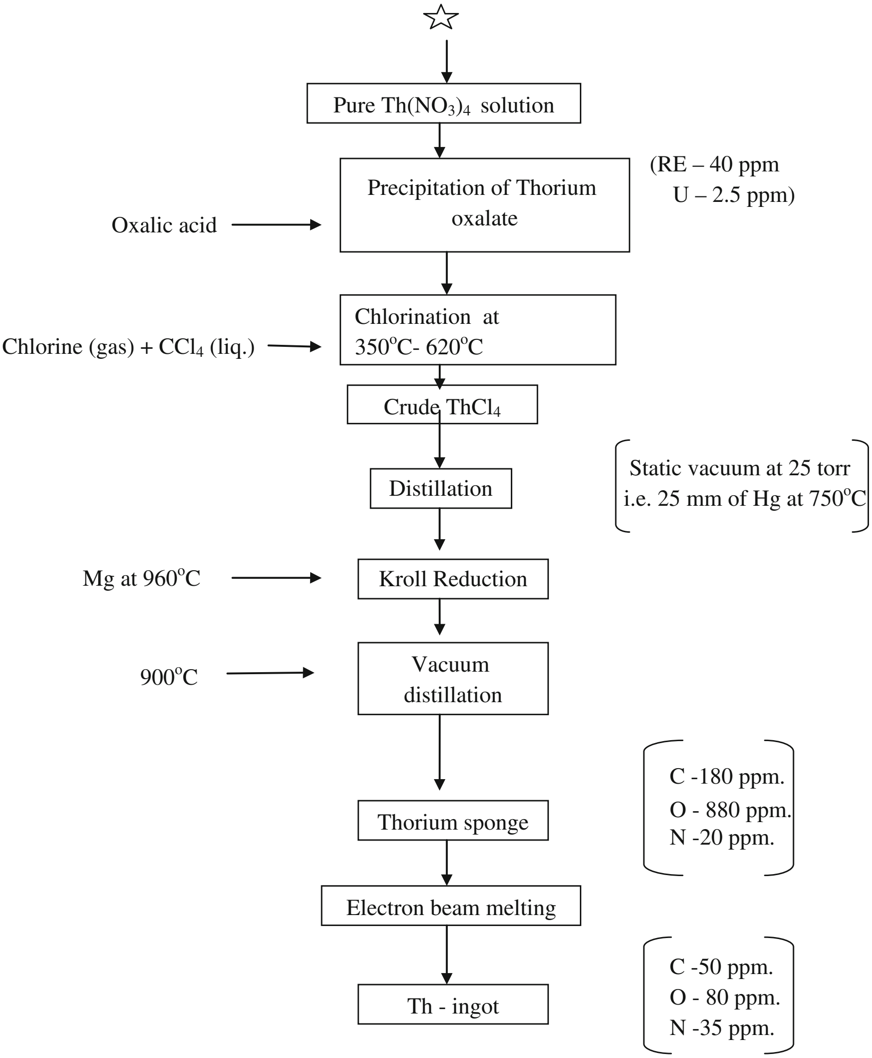

Fig. 6.1 (continued)

$$ThO_2 + 2H_2SO_4 = Th(SO_4)_2 + 2H_2O \tag{6.4}$$

$$U_3O_8 + 7H_2SO_4 = 3UO_2(SO_4)_2 + 6H_2O + H_2S \tag{6.5}$$

$$RE_2O_3 + 3H_2SO_4 = RE_2(SO_4)_3 + 3H_2O \tag{6.6}$$

Then that is treated with ammonium hydroxide to get a p_H of 1.0 for the solution. Some 99% of the thorium and about 5% of the rare earths metals are precipitated from the solution.

$$Th(SO_4)_2 + 4NH_4OH = Th(OH)_4 + 2(NH_4)_2SO_4 \tag{6.7}$$

$$RE_2(SO_4)_3 + 6NH_4OH = 2RE(OH)_3 + 3(NH_4)_2SO_4 \tag{6.8}$$

Because of the much larger quantities of rare earths present originally in the ore, the precipitates are filtered off and treated with nitric acid to redissolve the thorium, which is then extracted selectively by solvent extraction method with TBP (tributyl phosphate).

$$Th(OH)_4 + 4HNO_3 = Th(NO_3)_4 + 4H_2O \tag{6.9}$$

The sulphuric acid method has the disadvantage of allowing sulphate and phosphate ions to remain with the thorium; those ions interfere with the subsequent purification process.

6.3.1.2 Sodium Hydroxide Method

Finely ground (−325 mesh) monazite sands are chemically decomposed with 45% concentrated sodium hydroxide (NaOH) solution at 138 °C for about 3 h to obtain precipitations of Th, RE and U hydroxides.

$$ThO_2 + 4NaOH = Th(OH)_4 + 2Na_2O \tag{6.10}$$

$$U_3O_8 + 12NaOH = 3U(OH)_4 + 6Na_2O \tag{6.11}$$

$$RE_2O_3 + 6NaOH = 2RE(OH)_3 + 3Na_2O \tag{6.12}$$

The residue is concentrated by evaporation to form a cake, which is dissolved in 37% HCl at 80 °C. HCl dissolves the bulk of the rare earths metals and partially neutralized with NaOH to p_H 5.8. Thus all the thorium, uranium and only a small percentage of some rare earths metals are precipitated.

$$Th(OH)_4 + 4HCl = ThCl_4 + 4H_2O \tag{6.13}$$

$$U(OH)_4 + 4HCl = UCl_4 + 4H_2O \tag{6.14}$$

$$RE(OH)_3 + 3HCl = RECl_3 + 3H_2O \tag{6.15}$$

$$ThCl_4 + 4NaOH = Th(OH)_4 + 4NaCl \quad (6.16)$$

$$UCl_4 + 4NaOH = U(OH)_4 + 4NaCl \quad (6.17)$$

The precipitates (Th–U concentrate contain 40–50% ThO_2, 11% U_3O_8, 8–10% RE_2O_3) are filtered, washed, and treated with concentrate HNO_3 to redissolve the uranium and thorium to form nitrate solution.

$$Th(OH)_4 + 4HNO_3 = Th(NO_3)_4 + 4H_2O \quad (6.18)$$

$$U(OH)_4 + 4HNO_3 = U(NO_3)_4 + 4H_2O \quad (6.19)$$

Solvent extraction with TBP (tributyl phosphate) is used to separate uranium and thorium from nitrate solution. Extraction with 10% TBP gets uranium in the organic phase leaving thorium and rare earths metals in the aqueous phase. The raffinate is next contacted with 50% TBP to extract thorium in organic phase.

Scrubbing of impurities from the extract is done with dilute (1 N) HNO_3 and the thorium is stripped from the scrubbed extract by slightly acidified water [(0.2 N) HNO_3]. Thorium nitrate solution obtains in pure condition.

6.3.2 Thorium Oxalate Formation

Oxalic acid is reacted with thorium nitrate to precipitate of thorium oxalate (which contain Al-3, Ca-40, U-2 to 2.5, Ni-1, Cu-1, Fe-20, RE-40, Si-30, B-0.1, Cd-0.4, Zr-100 ppm).

$$Th(NO_3)_4 + 2H_2C_2O_4 = Th(C_2O_4)_2 + 4HNO_3 \quad (6.20)$$

6.3.3 Chlorination of Thorium Oxalate

The precipitate is heated for 2 h at 260 °C in argon atmosphere to remove moisture and to get dried thorium oxalate. The temperature is raised slowly to 350 °C and chlorine gas is than admitted into the reactor for converting thorium oxalate to thorium-oxy-chloride ($ThOCl_2$).

$$2Th(C_2O_4)_2 + 4Cl_2 = 2ThOCl_2 + 7CO_2 + CCl_4 \quad (6.21)$$

Chlorination is finally completed to $ThCl_4$ formation at 620 °C by passing a mixture of CCl_4–Cl_2 or CO–Cl_2 or CCl_4–CO_2.

$$2ThOCl_2 + CCl_4 + Cl_2 = 2ThCl_4 + CO_2 + Cl_2 (99\%\,\text{yield}) \tag{6.22}$$

$$ThOCl_2 + CO + Cl_2 = ThCl_4 + CO_2 \quad (98\%\,\text{yield}) \tag{6.23}$$

$$2ThOCl_2 + CCl_4 + CO_2 = 2ThCl_4 + 2CO_2 \quad (93\%\,\text{yield}) \tag{6.24}$$

6.3.4 Purification of $ThCl_4$

$ThCl_4$ is prepared from oxalate usually containing some residual $ThOCl_2$ and unreacted ThO_2. For producing high purity metal, $ThCl_4$ should not contain oxygen-bearing compounds and carbon. Vacuum sublimation of $ThCl_4$ is done at 750 °C at argon pressure (25 mm of Hg). Distilled $ThCl_4$ is condensed on an air-cooled tube. The vacuum sublimed $ThCl_4$ is white, dense and crystalline.

6.3.5 Reduction of $ThCl_4$

(a) By Magnesium: $ThCl_4$ is reduced with Mg to get thorium sponge. Sufficient quantity of Mg (freshly pickled and acetone dried) is used to reduce $ThCl_4$ to form Th-20 wt% Mg liquid alloy. During the reduction, the temperature is maintained at 960 °C and a positive pressure of argon, kept arround 10 cm of Hg. Two hours heating is required for completion of the reaction. As the Th–Mg alloy is not completely liquid at this temperature, the temperature of the system is raised to 1050 °C to ensure good slag and alloy separation.

$$ThCl_4 + 3Mg = Th - Mg + 2MgCl_2 \tag{6.25}$$

Vacuum distillation is done to separate the thorium metal from Th–Mg alloy and $MgCl_2$. The charge is slowly heated under vacuum and the distillation is carried out at a holding temperature of 900 °C and final vacuum of 0.06 μ (6×10^{-5} mm of Hg) and holding time is 10 h (94% yield). After the vacuum distillation, the system is cooled to about 75 °C and then filled with argon for further cooling to room temperature. Before dismantling the system, the sponge (C-180, O-880, N-20 in ppm) is given a conditioning treatment with a mixture of air and argon to avoid sudden oxidation during handling.

b) By Sodium: The reaction between the $ThCl_4$ and Na is initiated by heating the mixture charge to about 525 °C, and the treatment is continued with subsequent heating at 800 °C for about 10 h.

$$ThCl_4 + 5Na = Th - Na + 4NaCl \tag{6.26}$$

The by-product, NaCl, and the excess Na from the charge are removed from the Th–Na alloy by heating in a vacuum at 900 °C for 16 h.

6.3.6 *Purification of Thorium Metal*

Thorium sponge is purified by electron beam melting at constant power level for different lengths of time to obtain thorium ingot (C-50, O-80, N-35 in ppm). The thorium sponge is then subsequently arc melted to get solid thorium ingot.

6.4 Production of Thorium Powder

(a) Reduction of ThO_2 by Ca: The reduction of ThO_2 by Ca in the presence of $CaCl_2$, according to the reaction:

$$ThO_2 + 2Ca + (2.4\,CaCl_2) = Th + 2CaO + (2.4\,CaCl_2) \tag{6.27}$$

The actual charge includes 3 mol excess of Ca. The mixed charge was heated to 950 °C in a closed steel bomb, under an inert gas atmosphere for 1 h during which the calcium reduces the thoria. The products are cooled and are leached with dilute acetic acid to dissolve the CaO and the unreacted Ca. The thorium metal remains as a powder and is washed successively with water, alcohol and ether. After that the powder is vacuum dried, it is compacted at 3.15–15.75 kg/mm^2 and then vacuum sintered at temperature up to 1450 °C for about 30 min to produce a dense ductile metal with purity better than 99.77%. The principal impurity is oxygen which is present about 0.15–0.17%.

Further improvement on this process is achieved by elimination of $CaCl_2$ in the reaction and use of a thin walled cup in place of the closed bomb, and reaction takes place under a static pressure of argon gas. Thorium powder (99.8%) is recovered by leaching the charge with dilute acetic acid, water, alcohol and ether; followed by vacuum drying.

(b) Fused Salt Electrolysis: Small scale production of pure thorium powder has been achieved by electrolysis of $ThCl_4$ in either NaCl or a mixture of NaCl and KCl. A high yield (90%) of good quality metal was produced by fused NaCl salt method, but preparation of the chloride from the nitrate feed material was found to be faster in the NaCl–KCl fused salt system. A bath with a 2:1 ratio of NaCl to KCl is heated at a temperature of 780–850 °C in a graphite crucible which served as anode. The cathode is made of Mo metal, which is suspended centrally in the bath; and electrolyte is the mixture of $Th(NO_3)_4$ and NaCl–KCl (chloride must be low in oxide and moisture content to obtain a pure product; also free from Fe, Ni, Zr, Cu, and Mn impurities, which are more electro-positive than thorium. These impurities are almost completely deposited on the cathode along with thorium).

$$Th(NO_3)_4 + 4NaCl/4KCl = ThCl_4 + 4NaNO_3/4KNO_3 \tag{6.28}$$

$$ThCl_4 = Th^{4+} + 4Cl^- \tag{6.29}$$

$$\text{At anode}: 4Cl^- - 4e = 2Cl_2 \tag{6.30}$$

$$\text{At cathode}: Th^{4+} + 4e = Th \tag{6.31}$$

Thorium powder is deposited on Mo cathode, the cathode along with deposit are slowly taken out from the electrolyte bath; deposits are washed with dilute H_2SO_4, and dried.

6.5 Production of Massive Thorium Metal

Thorium Fluoride Reduction: Thorium oxide is converted to the ThF_4 with anhydrous hydrofluoric acid (HF).

$$ThO_2 + 4HF = ThF_4 + 2H_2O \tag{6.32}$$

ThF_4 is mixed with a 20% excess of redistilled and sized (to remove the fines) Ca metal and with anhydrous $ZnCl_2$. The mixture is then charged to a refractory lined steel bomb. At about 640 °C the $ZnCl_2$ reacts exothermically with Ca and provides additional heat to the primary reaction.

$$ZnCl_2 + Ca = Zn + CaCl_2 \tag{6.33}$$

$$ThF_4 + 2Ca = Th + 2CaCl_2 \tag{6.34}$$

$$ThF_4 + 3Zn = Th - Zn + 2ZnF_2 \tag{6.35}$$

The reaction that ensues generates sufficient heat to fuse the products, Th–Zn alloy and slag. Zinc in turn reacts with the thorium at about 1200 °C to form alloy of low melting point; and the slag contains CaF_2–$CaCl_2$–ZnF_2. The dense molten alloy collects at the bottom of the bomb and under the thick layer of fused slag. Th–Zn alloy is recovered after the products have solidified in position and cooled to room temperature. This alloy is one large massive piece of metal, referred to as a *biscuit*, which is free of adhering slag. The biscuit is then placed in a graphite crucible and slowly heated for several hours under vacuum to a temperature of 900–1200 °C to distill the Zn. Holding the biscuit for 1 h at this temperature leaves a fraction of a percent of Zn in the sponge. Holding at this temperature for up to 8 h removes essentially all of the Zn.

Remelting of the sponge is done by induction furnace at 1800 °C; the main impurities in the casting are about 0.05% C (from the graphite moulds used in dezincing and in casting), about 0.02% Be (from bio-crucible), 0.02% N, about 1.25% oxide (as ThO_2) and trace amounts of Al, Fe and Si. Consumable electrode arc melting is also used to minimize contamination during the melting process. This gives lower O, Al, Si contents than in induction furnace process.

6.6 Properties

Pure thorium is a soft metal and paramagnetic in nature. The melting temperature is affected by small amounts of impurities, melting temperature range from a low of 1120 °C to a high of 1750 °C, boiling point is 4200 °C. When etched, its surface has a silvery-white lustre but darkens when exposed to air for prolonged periods. Thorium has a FCC structure at room temperature. At high temperature (about 1400 °C) allotropic transformation to the BCC structure takes place.

Crystal structure: (a) FCC → Room temperature to 1400 °C → a_0 = 5.086 Å at 25 °C

(b) BCC → 1400 °C to 1750 °C → a_0 = 4.11 Å at 1450 °C.

The atomic mass of thorium is 232.05. The theoretical density of the thorium at room temperature, based on the average lattice parameter of 5.086 Å, is 11,720 kg/m^3. Density of Ca reduced cast metal is between 11,500 kg/m^3 and 11,600 kg/m^3; and arc melted metal is 11,660 kg/m^3. Thermal conductivity as well as electrical resistivity increase with increasing temperature.

Amount as well as kind of impurities present have varying effects on the mechanical properties of thorium. Because of the chemical reactivity of hot thorium with oxygen and nitrogen of the air, it is necessary to have an irert gas protective atmosphere during hot fabrication. An important consideration in selecting a solid fuel material for a nuclear reactor regarding its corrosion behaviour with respect to the coolant. Ideally, the fuel should be fully corrosion resistant since it may be exposed to the coolant through failure of the protective cladding. Corrosion of thorium in air is increased with increasing temperature, above 400 °C there is a rapid increase in the corrosion rate.

Thorium forms a protective adherent film in boiling water (95–200 °C). Weight change is 1×10^{-4} mg/cm^2/h.

$$Th + 2H_2O = ThO_2 + 2H_2 \tag{6.36}$$

$$2Th + 3H_2 = 2ThH_3 \tag{6.37}$$

$$2ThH_3 + 4H_2O = 2ThO_2 + 7H_2 \tag{6.38}$$

Most thorium alloys have less corrosion resistance than unalloyed thorium in high temperature water. The Th–Zr alloys show an increased resistance in high temperature water. In water at 200 °C, the rate of weight loss is least for Th–10% Zr alloy. Alloys with small amounts of C, Si, Ti and Zr have better corrosion resistance than pure thorium in high temperature water.

Ingots of commercial grade thorium can be readily worked either hot or cold by most mechanical fabrication processes. The FCC metal has low hardness, low strength, and high ductility at room temperature. During cold rolling, drawing of thorium without intermediate annealing, the metal increases in hardness only moderately up to 40% reduction in area. Futher cold rolling up to 99% reduction shows very little increase in hardness. The chemical reactivity of thorium must be considered when heating for hot working. The heating may be carried out in a fused salt bath, or the thorium metal may be jacketed with another metal such as copper. Thorium metal can be machined easily.

6.7 Applications

(a) Nuclear use: Thorium is important as a potential source of atomic energy. Just as natural uranium-238 can, by absorption of a neutron, be converted into a new element plutonium, of critical value in the release of atomic energy, so thorium-232 can become a new isotope of uranium-233. An important difference exists, however, in that natural uranium-238 contains its own nuclear fuel; thorium having no naturally occurring isotopes has no such advantage and therefore in any thorium atomic energy pile, fuel in the shape of plutonium or uranium-235 has to be supplied. For this reason thorium cannot yet compete with uranium in the production of atomic energy. The major applications of thorium are in nuclear power. The form of the thorium for use in nuclear applications includes the metal, alloys and compounds. Thorium is used to form U^{233}.

(b) Non-nuclear use: Thorium is an important alloying element in magnesium because it contributes high strength properties and creep resistance to magnesium at elevated temperature. Although thorium metal has a density similar to lead, the amounts necessary to impart these desirable properties to magnesium are sufficiently low (about 3%) to give light-weight alloys that are definitely advantageous for use in aeroplane and missile construction. Thorium metal is used as a non-energy application, like use as a low density alloy (a few percent Th in Mg) with superior high temperature properties.

Other non-nuclear uses of thorium include application in several lamps of the gaseous discharge type, due to its high electron-emission properties. The metal has been used in photoelectric tubes for the measurement of a wide band of the ultraviolet spectrum, and it is also used in germicidal lamps of the cold cathode type.