

Fabrication of Thorium and Thorium Dioxide

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Abstract

Thorium based nuclear fuel is of immense interest to India by virtue of the abundance of Thorium and relative shortage of Uranium. Thorium metal tubes were being cold drawn using copper as cladding to prevent die seizure. After cold drawing, the copper was removed by dissolution in nitric acid. Thorium does not dissolve being passivated by nitric acid. Initially the copper cladding was carried out by inserting copper tubes inside and outside the thorium metal tube. In an innovative development, the mechanical cladding with copper was replaced by electroplated copper with a remarkable improvement in thorium tube acceptance rates. Oxalate derived thoria powder was found to require lower compaction pressures compared to ammonium diuranate derived urania powders to attain the same green compact density. However, the green pellets of thoria were fragile and chipped during handling. The strength improved after introducing a ball milling step before compaction and maintaining the green density above the specified value. Alternatively, binders were used later for greater handling strength. Magnesia was conventionally being used as dopant to enhance the sinterability of thoria. The normal sintering temperature for magnesia doped thoria was 1600°C - 1700°C, which was achieved in electrically heated molybdenum element sintering furnaces with reducing atmosphere. 0.25 mole percent addition of niobia to the thoria was found to bring down the sintering temperature to 1150°C. Sintering could be done in ordinary furnaces in air atmosphere using silicon carbide or Kanthal heating elements. Electrical conductivity was measured for both magnesia and niobia doped sintered thoria and used in interpreting differences in sintering behavior.

Keywords

Thorium, Electroplating, Thorium Dioxide, Pelletizing, Sintering, Coring, Electrical Conductivity

1. Introduction

The work reported in this paper was carried out by this author intermittently during the period 1973 to 2007. Most of it was documented as internal reports and some of it was published [1]-[10]. Several other valuable publications are also available from literature [11]-[52]. The importance of thorium for the Indian Nuclear Program became clear when it was found that the country was endowed with large mineral resources of thorium. Early development and production work on thorium metal and thorium oxide was carried out at Bhabha Atomic Research Center, Mumbai. Later, thoria pellets for the research reactors CIRUS and DHRUVA, the Fast Breeder Test Reactor (FBTR) as well as the Pressurized Heavy Water Reactor (PHWR) were made at Nuclear Fuel Complex, Hyderabad. The first core of a 220 MWe PHWR requires 385 depleted uranium bundles for flux flattening. It is possible to use thoria bundles instead of depleted uranium oxide bundles. In such a case only 35 thoria bundles are needed [53]. A few export orders were also executed at Hyderabad such as thoria crucibles for emf measurements in Germany and thoria pellets for fusion fission hybrid research facility LOTUS in Switzerland. Some information is presented in the following sections.

2. Thorium Metal Production

Thorium oxide powder received from Indian Rare Earths Ltd. was re-calcined at 900°C. The calcined powder was mixed with calcium granules and reduced at 900°C under argon atmosphere. The reacted mass was soaked in water, followed by acid leaching, washing and drying. The powder thus produced was highly pyrophoric and contains impurities carbon, oxygen and nitrogen affecting adversely ductility of the bulk metal. Alternatively, thorium oxalate was chlorinated in the presence of carbon. The crude chloride was purified by vacuum sublimation. The purified chloride was reduced with magnesium to get Th-Mg alloy. The alloy was given a pyro vacuum treatment to separate out the magnesium. The thorium sponge thus obtained was less pyrophoric than the powder. Thorium metal powder was compacted at 300 MPa and sintered in vacuum at 1300°C for one hour. 98% TD could be obtained. The sintered material could be cold rolled to more than 90% reduction without intermediate annealing [13].

3. Electroplating Copper on Thorium

Sintered thorium metal was copper jacketed and hot extruded into tubes. The tubes were then cold drawn to meet surface and dimensional requirements in the specifications. Thorium can not be easily drawn as it galls or seizes the drawing die and hence thorium metal tubes need to be clad before drawing. Copper was chosen as the clad material by virtue of its excellent deformability and compatibility with the die during the cold drawing process. The copper clad thorium tubes were drawn and the copper cladding eliminated by dissolution in nitric acid. Thorium metal itself does not dissolve in nitric acid due to quick passivation. Tubes of ID as small as 9.5 mm and wall thickness 0.7 mm were produced. The process of mechanical cladding yielded tubes with wrinkles on the OD which was a cause for rejection. This author had experience in electroless plating and electroplating in the making of Microwave Integrated Circuits which required deposition of copper on alumina substrates [54]. Hence it was decided to try copper deposition on to the thorium tube as an alternative to mechanical cladding. Electroless deposition yields very small thicknesses and used when the cathode is nonconductive. It also requires a number of chemicals for the pre-treatment and plating processes. Electroplating was chosen at the time as a suitable rectifier was readily available.

Copper was deposited in acidic bath using copper sulphate at room temperature. Two anodes were required, a pipe for covering the OD of the thorium tube and a copper rod for ID. The two anodes and the cathode were positioned concentrically maintaining appropriate distances by using a Perspex fixture to hold them in place. Too low a current density yielded coarse copper deposit while a too high a current density yielded a dark deposit. Once these limits are avoided, a large window of current densities is available from plating literature. Separate power supplies were used for the internal anode and external anode to enable independent control of current densities. One would normally expect an increase in plating rate with an increase in current density. But this was not the case with respect to plating on the inner diameter of the thorium tube. The anodic current density for the internal anode was maintained at about half of that of the external anode. This ensured copper deposition of uniform thickness on the inside and outside of the thorium tube. This also prevented passivation of the copper rod and co-deposition of unwanted elements from the bath on to the thorium. The details are shown schemati-

cally in **Figure 1**. A similar method was developed later at Hyderabad by this author to deposit copper on zirconium alloy billets before hot extrusion [55].

Thorium is difficult to plate on. It is due to a thin naturally forming oxide surface film that is often difficult to remove and that reforms quickly when a cleaned surface is exposed to air or water. As a result, adherent electrodeposits are obtained only when either: 1) the oxide film is removed for sufficient time to permit an initial deposit; 2) the film is replaced with another that does not interfere with adhesion; 3) the film is incorporated into the deposit in a compatible manner; or 4) the surface is severely etched to allow mechanical keying between the substrate and deposit [56]. Successful procedures that rely on one or more of the above principles have been documented. However, for our purpose of cold drawing, maximum adhesion has not been aimed at.

4. Thorium Dioxide Pelletizing

Uranium oxide powder was being compacted and sintered on tonnage scale in India since the early seventies. When the requirement of thoria pellets was received, the process parameters of uranium oxide were used for pressing and sintering thorium oxide [15]. However, this led to problems. For example, while a green density of 5.6 to 5.8 g/cc worked fine with uranium oxide, the thorium oxide pellets pressed to the same green density yielded pellets that chipped readily on handling. The thorium oxide powder was supplied by India Rare Earths and it was oxalate derived. It was found that the as received powders were not suitable for compacting directly. Therefore a ball milling step was introduced. Ball milled powder yielded green pellets of density over 6.4 g/cc and these had better green strength than pellets made from unmilled powders and pressed to 5.8 g/cc. The pellets on sintering yielded high sintered densities [3] [4].

However it became difficult to control the air radio-activity levels in the milling process in spite of containment. The separation of the balls from the milled powder too posed a problem. Hence the milling process was

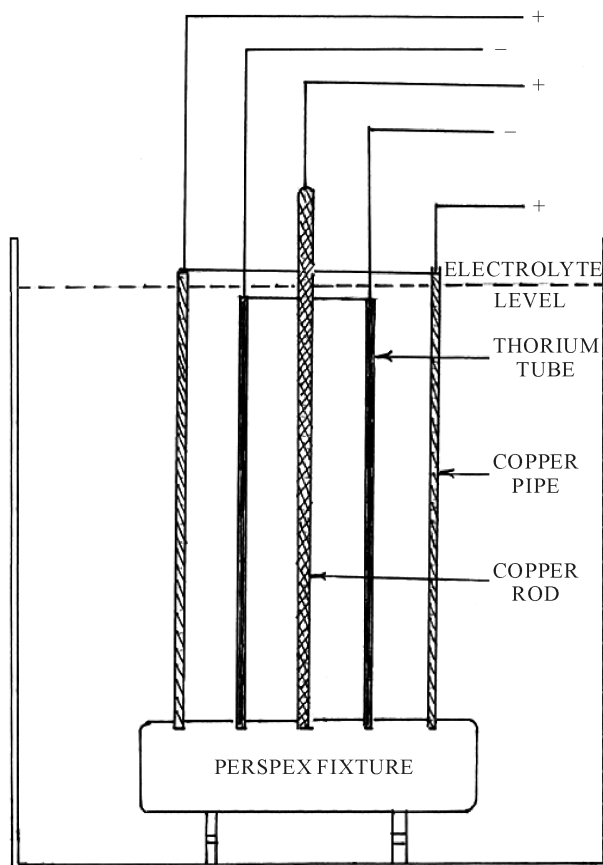


Figure 1. Fixture for holding thorium metal tube, copper rod (internal anode) and copper pipe (external anode).

discontinued. 1% by weight Zinc behenate binder was admixed into the thorium powder to yield strong green pellets and finally dense sintered pellets.

5. Thorium Dioxide Sintering

5.1. Additive Effects on Sinterability

In our early work, it was found that sintering of thorium needed a sintering aid. MgO was being used as sintering aid. MgSO₄ was being added to thorium nitrate solution and co-precipitated as oxalate. The oxalate was calcined to yield thorium oxide with about 250 ppm of Mg.

The thorium pellets were sintered in the same furnaces that were being used for sintering UO₂ pellets, namely, electrically heated molybdenum element furnaces that operated at 1600°C - 1700°C in a reducing atmosphere. Later it was found by this author that thorium oxide could be sintered in air at 1150°C using 0.25 mole percent Nb₂O₅ [3]-[6]. Pellets sintered in a reducing atmosphere ranged in color from bluish gray to white. Those sintered in air ranged from brownish white to white in color. Sintering at 1700°C required round the clock shift operation while sintering at 1150°C in air could be done in two shifts.

5.2. Black Spots in Sintered Thorium

It has been reported that on prolonged heating to 1800°C to 1900°C in vacuum, thorium blackens with loss of oxygen, although the loss is insufficient to be reflected in chemical analysis or lattice parameter measurements. On reheating in air to 1200°C or 1300°C, the white color is restored [57]. Thorium can also become oxygen deficient due to lower valence cation impurities which leave oxygen sites in the crystal lattice vacant. Black spots were noticed by this author in the thorium pellets sintered in hydrogen at 1700°C. On analysis it was found to have been caused by iron contamination from the wear out of steel balls in the milling step. This pointed to the need for use of wear resistant balls such as those made of agate or tungsten carbide.

In one of the experiments, a one mm diameter stainless steel wire piece was introduced in a green thorium pellet. On sintering in hydrogen, a 3 mm diameter black patch resulted. Spectrographic analysis of the black patch revealed the presence of iron, chromium and nickel, the ingredients of stainless steel. The black color is believed to be due to oxygen deficiency in the thorium lattice caused by substitution of Th sites by lower valent Fe, Cr or Ni. Niobia added thorium pellets sintered in hydrogen at 1700°C were totally black in color. The niobium in reducing atmosphere might have acted as a lower valence additive to thorium.

5.3. The Phenomenon of Coring

Thorium pellets could be readily thermal etched to be able to see well defined grain boundaries. A Laser etching technique has been developed for etching thorium for micro structural investigation in reprocessing [24]. Sometimes a cored structure is visible in fractured sintered ceramic pellets. Two types of coring have been mentioned in literature. In one type, reported in thorium and called "picture framing", the grain size in the core was smaller than that in the rim [39]. In another type, reported in alumina, the grain size in the core is much larger than that in the rim [58]. Some of our sintered thorium pellets upon fracturing exhibited a cored structure. The section of the pellet showed a white rim around a glassy inside. In a pellet of 25 mm diameter, the rim thickness varied from pellet to pellet from 1 mm to 3 mm. Zawdzki and Apte [59] studied coring in UO₂ sintered pellets. They found that a cored structure would result when the heating rate was 400°C/hr and when the UO₂ had sulphur impurity of 20 ppm or above. There was no coring when the heating rate was lower, at 250°C/hr for the same material. Coring in Mg doped Alumina was attributed to grain growth inhibition within the cored region. The Mg was thought to have escaped from the rimmed region leading to discontinuous grain growth.

The cored structure appears to be caused by either additives or impurities. Additives are meant for inhibiting grain growth, as MgO in Al₂O₃ and ThO₂. The absence of the additive in the rimmed region of the pellet causes discontinuous grain growth leading to the formation of large grains in the rim [58]. Impurities such as Sulphur are capable of causing discontinuous grain growth and their presence in the core region of the pellet causes discontinuous grain growth and large grains in the core [59]. An analysis of the core region of our sintered thorium pellets pointed to the presence of sulphur content above 500 ppm. The origin of the sulphur may be in the MgSO₄ added to thorium nitrate to provide Mg as sintering aid. The Sulphur appears to have caused discontinuous grain growth leading to larger grain sizes in the cored region. Recalcination of the thorium powder batches

that had shown coring on sintering earlier did not show coring again. This author recommends mechanical addition of MgO to ThO₂ powder instead of MgSO₄ to Th(NO₃)₄ and co-precipitation.

The green density in a compact in uniaxial or biaxial pressing is usually not uniform unlike in isostatic pressing. The rim is of a higher green density than the inside. At fast rates of heating, and for larger diameter pellets, there is a chance that the surface temperature is higher than the core temperature. The skin with a larger number of particle to particle contacts is likely to densify first leading to subsequent constrained sintering of the core. The situation is further aggravated by the absence of grain growth inhibitors or presence of discontinuous grain growth promoters in certain regions of the pellet.

5.4. Evaporation and Condensation of Thorium Dioxide

Two types of sintering furnaces were used for sintering thoria. One type was the pusher type continuous sintering furnace. The other type was a batch sintering furnace. In some sintering runs, the bottom of the water cooled stainless steel lid of the batch sintering furnace was found to have got coated with a white powdery layer, which was identified as thorium oxide. ThO₂ seems to have evaporated in the reducing atmosphere from the pellets being sintered and deposited on the underside of the lid.

6. Electrical Conductivity of Thorium Dioxide with Additives

Electrical conductivity of sintered thoria was determined by this author at the Plasma Physics Division of BARC [8]. Holes were drilled in the thoria disks prepared for conductivity measurements. Initially, the pellets could not be drilled using even diamond drills. Then it was realized that the drill bits were getting damaged due to quick overheating. The thoria disks fully immersed in water could be readily drilled using drill bits of High Speed Steel. For fixing the contact wires to the sintered thoria disc, platinum paste was used. The electrical conductivity of niobia doped thoria was found to be lower than that of magnesia doped thoria in the temperature range 900°C to 1250°C. From defect chemistry considerations, it can be expected that the effect of addition of higher valence Nb₂O₅ to ThO₂ would be to enhance the diffusion of thorium in ThO₂ and to decrease electrical conductivity. The effect of addition of (lower valence) MgO would be to decrease diffusion and enhance the electrical conductivity. The higher diffusivities of otherwise slowly moving cation mean that a lower sintering temperature would suffice for niobium doped ThO₂ than for magnesium doped ThO₂. This has indeed been found to be the case, the sintering temperatures being 1150°C and 1700°C, respectively [5].

7. Dissolution of Thorium Dioxide

It is generally known that it is very difficult to dissolve sintered thoria rejects for recycling in the pelletizing plant as well as in reprocessing after irradiation. At Hyderabad it was found that 1 g of sintered thoria readily dissolved in 10 ml of hot concentrated nitric acid with one drop of hydrofluoric acid. In cases where the HF content was larger, the dissolution either slowed down or stopped. It appears that in higher HF concentrations, a coating of ThF₄ over the ThO₂ might be hindering further dissolution. Niobia doped air sintered thoria required longer time to dissolve compared to hydrogen sintered magnesia doped thoria [9]. Dissolution concerns may have to be addressed while reprocessing after irradiation.

8. Summary

Electroplating of copper instead of mechanical cladding resulted in greater acceptance rates of cold drawn thorium metal tubes. The compaction and sintering parameters for thorium oxide were found to be somewhat different from those of uranium oxide. While the conventional additive MgO required a sintering temperature of 1700°C, achievable in high temperature sintering furnaces with molybdenum elements in a reducing atmosphere, Nb₂O₅ brought down the sintering temperature to 1150°C which could be achieved in ordinary furnaces with air atmosphere. Electrical conductivity measurements on thoria with Mg and Nb additives were made and interpreted with respect to sintering behavior. Coring, that is, the existence of non uniform grain size between the rim of the sintered thoria pellet and the inside is likely when the pellet diameter is large (25 mm) as in the case of CIRUS research reactor pellets, when the heating rates are rapid (400°C/hr) and when there is impurity such as sulphur. Mechanical addition of MgO to ThO₂ powder instead of MgSO₄ to Th(NO₃)₄ for co-precipitation is recommended.

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