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## PRODUCTION OF METALS

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This invention relates to the production of metals and more particularly to the production of thorium. This application is in part a continuation of our copending applications Serial No. 373,512, filed August 11, 1953, and Serial No. 434,648, filed June 4, 1954.

A principal object of the present invention is to provide an improved process for producing high yields of thorium by the reduction of a thorium compound dissolved in a fused salt.

Another object of the invention is to provide a process of the above type which is simple and cheap to operate and which gives a product which can be water leached to separate the thorium from the by-product salt.

Still another object of the invention is to provide an improved process of the above type which is equally applicable to the production of alloys of thorium.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the process involving the several steps and the relation and the order of one or more of such steps with respect to each of the others which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description.

In the present invention, advantage is taken of the well-known ability of certain metals such as the alkali metals and alkaline earth metals to reduce compounds of thorium. For simplicity of illustration, the invention will be particularly described in connection with the formation of thorium by the reduction of a thorium halide dissolved in a fused salt. Equally, the reducing agent will be described as a preferred alkali metal and more particularly as sodium. The reduction reaction between sodium and thorium tetrachloride proceeds rapidly and at relatively low temperatures (i. e., temperatures on the order of the melting point of the by-product halide). However, in the present invention, the reaction conditions are so adjusted that the product thorium consists of crystals of thorium which have a size sufficiently large so as to permit simple leaching with water (containing a small percentage of acid) to dissolve the by-product halide. The size of the individual crystals is such that the surface-to-volume ratio is relatively low, thereby preventing contamination of the product due to the presence of surface oxide. The nature of the product is also such that its surface activity appears to be very low.

In accordance with the present invention, a thorium compound, preferably a halide thereof, is dissolved in a fused salt. The dissolved halide of thorium is then reduced slowly and progressively to thorium metal by addition of a reducing agent such as sodium, potassium, magnesium and the like. The thorium halide content of the fused salt is thus gradually reduced from an average thorium valence of four (when the starting material is thorium tetrachloride) to an average thorium valence

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of zero. This gradual reduction preferably takes place over a relatively long period of time, on the order of at least one hour and preferably longer. The reducing agent is also preferably fed uniformly to the surface of the fused salt during a major portion of the long reduction period.

We have discovered that in such a system crystal growth is strongly promoted if the reducing agent be supplied to the thorium halide fused salt solution via an interposed shielding layer of fused salt which is substantially free of the thorium halide and which is preferably localized by a diaphragm in direct contact with the solution. In one preferred embodiment of the invention, the shielding layer of fused salt is maintained as a distinct layer by means of a diaphragm which permits only very limited circulation between the upper (thorium-free) layer and the lower (thorium-containing) layer. This diaphragm may be, for example, a nickel disc of a diameter almost as large as the reactor diameter. In another embodiment of the invention, the diaphragm is formed in situ and comprises a porous thorium crust. In this case, a solution of thorium tetrachloride in fused sodium chloride is provided in a reactor, and liquid sodium is fed to the surface of the molten salt solution as a thin film distributed substantially uniformly over the surface while the fused salt solution remains quiescent. Under these conditions, a crust of sintered, fine thorium particles forms rapidly at the surface of the salt bath, extending over said surface and adhering to the walls of the reactor and to any other apparatus elements in and adjacent the surface of the bath. This crust is porous and incorporates a layer of fused salt which is substantially free of thorium chloride, at least adjacent and above the top of the crust.

As the process continues, the level of the salt bath will rise due to the manufacture of more by-product salt, but the crust remains where it was formed, adhered to the walls of the reactor, and the thorium crust becomes covered by a layer of molten salt which (due to stratification and diffusion limitations placed on the contents of the bath due to the presence of the crust) is substantially free of thorium chloride. Consequently, further feed of sodium is to the surface of this thorium-chloride-free layer of salt above the thorium crust.

When the crust and shielding layer of thorium-halide-free salt have been established, thorium crystals begin to form, growing out of the under surface of the crust and outwardly from the walls of the reactor. The production of thorium fines, such as initially form the crust, decreases substantially.

The feed of sodium is preferably continued until sufficient sodium has been fed to reduce substantially all of the dissolved thorium chloride to thorium metal. It is also preferred that the thorium chloride solution be relatively concentrated at the start of the reduction so as to assist in forming a self-supporting, porous initial crust. After the crust and thorium-chloride-free salt layer have been formed, the feed rate of sodium to the reactor can be considerably increased, if desired. However, from the standpoint of mechanical simplicity and safety, a constant, relatively slow rate of feed of sodium is preferred.

After the sodium feed is stopped, the reactor is allowed to cool and the solidified contents are leached by means of acidified water, thus removing the salt. The remaining product consists essentially of a mass of loosely adherent, interlaced crystals of thorium extending downwardly from the crust layer of sintered thorium particles and outwardly from the reactor walls.

It will be evident from the foregoing that the diaphragm (which, in the second example just described, is formed of sintered thorium fines) performs two major functions.

First, it helps to segregate the fused layer low in thorium chloride. Second, it forms a supporting stratum from which the thorium crystals may grow.

In order to describe more fully preferred methods of practicing the invention, there are set forth below several non-limiting examples which are merely illustrative of numerous other methods of practicing the invention:

#### Example I

44.0 grams of a solution of thorium tetrachloride in sodium chloride (having the composition  $\text{Na}_2\text{ThCl}_6$ ) is placed in the bottom of a 12 inch by  $1\frac{3}{8}$  inch I. D. stainless steel tube which is closed at one end. A 1.14 inch diameter nickel disc is supported on top of the sodium chloride-thorium tetrachloride mixture. 2 inches of molten sodium chloride is poured into the stainless steel cylinder above the disc. This sodium chloride amounted to 83.9 grams. A sodium feeding crucible is mounted about  $1\frac{1}{2}$  inches above the fused salt barrier layer. This crucible has a hole at the bottom which is filled with a fused salt plug (13 grams of sodium chloride) above the fused salt plug is supported 9.2 grams of sodium. The top of the stainless steel tube is then welded shut. The above charging operations are carried out in a dry box containing an argon atmosphere. The thus sealed tube is then removed from the dry box and gradually moved downwardly into a furnace. As the tube moves into the furnace, the heat thereof progressively melts the charge of salt containing the thorium tetrachloride and then melts the barrier layer of pure salt above the nickel disc. When these two layers of salt are molten, the steel tube is lowered sufficiently into the furnace so as to melt the salt plug in the bottom of the sodium feed cup. This allows the charge of sodium to run out of the cup and to spread across the barrier layer of pure salt above the nickel disc. The tube is maintained in the oven at a temperature of  $800^\circ\text{C}$ . for about 4 hours.

At the conclusion of 4 hours of one such run, the stainless steel tube was removed from the furnace and the charge was allowed to cool to room temperature. The wall of the tube was then machined away and the thorium-containing salt was split into 3 sections. Section 1 contained the material below the nickel disc, section 2 the material one inch above the disc, and section 3 the top one inch of the salt barrier. The three sections were placed in separate beakers and leached with agitation for about two hours. The water leach was followed by an 0.1% HCl leach. This leach liquor was decanted off and the residues washed three times with more water and followed by three methyl alcohol washes. The residues were then dried overnight in a vacuum desiccator. There was no visible indication of excess sodium present, and the samples did not react violently when water was placed in the beakers.

After being vacuum dried overnight, the residue from section 1 was examined under the microscope and the thorium metal was found to be crystalline. The crystals were gem-like in appearance, with the largest being about 1 mm. in cross section. The thorium contained about 75% crystals, the balance being sponge and fines. The thorium was coated with a thin oxide film and unleached salt so it was given three additional 15 minute leaches in 3%  $\text{HNO}_3$ . In the last leach, a small amount of NaF (approximately 0.01%) was added for the last 5 minutes. The thorium was then dried as before and, when viewed under the microscope, showed a bright, shiny surface. The thorium had a bluish tint when viewed with the naked eye.

#### Example II

In still another embodiment of the invention, the reduction is carried out in a large nickel pot (12 inches in diameter and 24 inches in depth). This pot is equipped with a sodium feed tube and a distributor for spraying

the sodium substantially uniformly across the surface of the fused salt charge in the reactor. The reactor is purged of air and charged with 25 pounds of sodium chloride and 80 pounds of thorium tetrachloride. This is heated to  $900^\circ\text{C}$ . and sodium is gradually sprayed across the surface of the molten salt at the rate of approximately 2 pounds per hour for  $9\frac{1}{2}$  hours. The feed of sodium is then stopped and the reactor is maintained at a temperature of about  $900^\circ\text{C}$ . for about 3 hours. The charge is then cooled and the product is leached in 2% nitric acid solution to recover a crop of relatively large thorium crystals.

While several specific examples have been given above, numerous alternative methods may be employed without departing from the spirit of the invention. The temperature of the reaction mass may be varied widely from slightly above the melting point of the salt to temperatures on the order of  $1000^\circ\text{C}$ . and above. Numerous reducing agents other than the sodium may be employed. For example, potassium, calcium, magnesium, lithium and various combinations of these elements may be utilized. Other halides of thorium may be utilized, although, from the standpoint of cost, ease of handling, etc., the tetrachloride is most preferred.

The process, as illustrated in any of the examples, may be practiced with continuous or intermittent feed of thorium chloride, either as such or dissolved in fused salt, this feed being to a portion of the bath below the crust. In such case, an intermittent or continuous overflow or drain of fused salt will normally be provided at a point in the reactor where the fused salt is relatively low in thorium chloride. While agitation of the bath should be minimized, particularly while the crust is forming, some circulation of the bath below the crust may be provided, particularly at later stages of the process, to facilitate complete reduction of the thorium chlorides.

The present invention can be equally employed for the manufacture of alloys by the coreduction of the chlorides, for example, of one of the above four metals with a chloride of vanadium, chromium, manganese, iron, nickel, cobalt, columbium, tantalum, molybdenum, tungsten or silicon. The alloy may be a binary alloy or it may be an alloy containing 3 or 4 constituents. In the manufacture of alloys, the same general conditions of the slow reduction of the thorium compound and reducible compounds of the alloying constituents must be employed. Accordingly, when the expression thorium is used in the appended claims, it is intended to include alloys thereof as well as pure metals.

It should be additionally pointed out that the salt mixture in which the reduction is carried out may be formed of numerous halides, which can be mixed halides, single halides and halides of materials other than the specific reducing agent or agents employed in the reaction. From the standpoint of simplicity of operation and ease of control, it is preferred, however, that the salt be the chloride of the reducing agent. Thus it is quite feasible to employ binary and ternary mixtures of halides having quite low melting points.

It should be pointed out, in connection with a consideration of the various salts which can be employed, that these salts should be completely anhydrous and free of any contaminants such as carbon, nitrogen, oxygen or hydrogen.

Since certain changes may be made in the above process without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A process for manufacturing thorium wherein a thorium halide is dissolved in a bath of a fused salt and is reduced to thorium crystals by supplying a metallic reducing agent to the bath, the reducing agent comprising a metal selected from the class consisting of the

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alkali metals and the alkaline earth metals and the fused salt comprising a halide selected from the class consisting of the alkali metal halides and the alkaline earth metal halides, the improvement of which comprises maintaining between the supply of reducing agent and a major portion of the salt bath containing the dissolved thorium halide a zone comprising fused salt which is substantially free of thorium halide.

2. A process for manufacturing thorium wherein a thorium halide is dissolved in a bath of a fused salt and is reduced to thorium crystals by the addition of a metallic reducing agent, the reducing agent comprising a metal selected from the class consisting of the alkali metals and the alkaline earth metals and the fused salt comprising a halide selected from the class consisting of the alkali metal halides and the alkaline earth metal halides, the improvement of which comprises providing and maintaining in the fused salt bath a zone comprising fused salt low in thorium halide and substantially continuously supplying reducing agent to said zone until a substantial body of thorium crystals is formed in the remaining portion of the bath.

3. The process of claim 2 wherein the feed of the reducing agent to the molten salt is sufficiently gradual to require a reduction period of at least two hours for reducing the average valence of the thorium halide from two or more to a value approaching zero.

4. In a process for producing thorium wherein a halide of thorium is dissolved in a fused salt bath and is reduced to thorium crystals by means of a metallic reducing agent selected from the class consisting of the alkali metals and the alkaline earth metals, the molten salt comprising a halide selected from the group consisting of the alkali metal halides and the alkaline earth metal halides, the improvement which comprises adding molten reducing agent to the surface of the fused salt bath to initially

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form a thorium crust on said bath, and thereafter feeding reducing agent to the upper surface of a layer of fused salt above the crust, the layer of fused salt above the crust being essentially free of dissolved thorium halide and the amount of reducing agent fed being sufficient to reduce substantially all of the contained thorium halide to thorium metal, and maintaining said fused salt molten until substantially all of the contained thorium halide is reduced.

5. In a process for producing thorium wherein a halide of thorium is dissolved in a fused salt bath and is reduced to thorium crystals by means of a metallic reducing agent selected from the class consisting of the alkali metals and the alkaline earth metals, the molten salt comprising a halide selected from the group consisting of the alkali metal halides and the alkaline earth metal halides, the improvement which comprises providing on the surface of the fused salt bath a layer of salt which is substantially free of thorium halides, and thereafter feeding to the top of said thorium-halide-free salt layer sufficient reducing agent to reduce substantially all of the contained thorium halide to thorium metal, and maintaining said fused salt molten until substantially all of the contained thorium halide is reduced.

6. The process of claim 5 wherein the thorium halide is a thorium chloride, the reducing agent comprises sodium and the molten salt bath comprises at least one chloride selected from the group consisting of the alkali metal chlorides and the alkaline earth metal chlorides.

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