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METHOD OF PURIFYING ZIRCONIUM TETRAHALIDE

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This invention relates to a new and improved method for purifying zirconium-containing material, and more particularly to the removal of hafnium tetrahalide from zirconium tetrahalide.

This application is continuation-in-part of Serial No. 360,320, filed on June 8, 1953, now U.S. Patent No. 2,791,485.

All known sources of zirconium contain hafnium in quantities which vary from less than 1% to more than 20%. The chief source of zirconium is the mineral zircon which contains about 1.5% hafnium. In any of the usual methods employed for recovering zirconium from its ores, the associated hafnium is not separated from the zirconium owing to the almost identical properties of these elements and their respective compounds. Elaborate processes based, for example, on slight differences in the solubility of the phosphates of the two elements or ion-exchange methods are necessary to separate the hafnium and zirconium. More recently, separation has been proposed where the hafnium and zirconium are in their tetrahalide form. In general, the first step in such a process has been the decomposition of the zirconium mineral by reduction with carbon in an arc furnace to the respective carbides. Direct halogenation is then carried out to prepare the hafnium and zirconium tetrahalides. The prior art processes are not, however, without serious disadvantages, and generally they are not readily adaptable for commercial operations.

One object of this invention is to provide a method whereby an effective removal of the hafnium is accomplished by direct chemical means as distinct from the physico-chemical methods such as fractional distillation, fractional precipitation, fractional crystallization and ion-exchange processes which are now employed. Another object of this invention is to effect such a high order of hafnium separation that the resulting zirconium product can be regarded as virtually hafnium-free. Other objects of the invention will be apparent from the ensuing description.

It has been found that there is a marked difference in the chemical reducibility of the tetrahalides of zirconium and hafnium. This difference in reducibility forms the basis of the invention, according to which the zirconium tetrahalide is preferentially reduced to one or more lower halides or even to metallic zirconium, while the hafnium tetrahalide remains substantially unchanged. Following selective reduction, the hafnium tetrahalide and any unreduced zirconium tetrahalide, if present are separated from the zirconium tetrahalide reduction product.

As described in detail in Serial No. 360,320, the selective reduction of the zirconium tetrahalide is preferably effected in vacuo or under an inert atmosphere using conventional inert gases such as argon, etc. in the presence of zirconium dihalide and at a temperature within the range of about 250° to 550° C. The zirconium dihalide may be produced in the first instance by treatment of a batch of zirconium and hafnium tetrahalides with finely sub-divided metallic zirconium. Finely divided zirconium metal sponge is another preferred reducing agent. Alternatively, the selective reduction can be achieved by using finely sub-divided magnesium, aluminum, zinc, or other substance of sufficient oxidation-reduction potential as the reducing agent.

The reaction time will ordinarily depend upon the temperatures employed and the nature of the reducing agent, but the selective reduction is usually complete within an hour. The temperature employed will, in turn, depend upon the particular halide and reducing agent. It is, however, important to carefully control the temperature of the reaction in order to avoid overheating which would result in poor separation due to premature disproportionation of the zirconium trihalide. In the ordinary method of carrying out the reaction, mixed hafnium and zirconium tetrahalide vapors are contacted or passed over a solid bed of the reducing agent. As is customary with this type of operation, temperature control is difficult and hot spots often develop which would cause premature disproportionation of the zirconium trihalide or even hafnium tetrahalide reduction. Thus, it would be desirable to be able to carry out the reduction in a reaction medium which would permit easy temperature control and which would not be troubled by hot spot formation. In view of the high temperatures required for reduction, conventional reaction media are of no value. It is to this feature of the reduction operation to which the present invention is especially directed.

In accordance with the present invention it has now been found that certain mixtures of metal salts as melts or fused salts are outstanding reaction media for the selective reduction of the zirconium tetrahalide. Examples of such mixed metal salts include, aluminum chloride plus sodium chloride, lithium chloride plus potassium chloride and similar salt mixtures which will be liquid at temperatures above 300° C. or else will become liquid at 300° C. in the presence of zirconium tetrahalide. In general, at least one of the metal salts will be an alkali metal salt.

The relative proportions of each salt used in formulating the reaction medium is not important, though it is preferred that each salt constitute at least a third of the total composition. Ordinarily, sufficient reaction medium will be employed to permit the desired temperature control and at the same time avoid hot spot formation. Another important characteristic of the reaction medium would be its ability to permit readily the separation of the unreacted hafnium tetrahalide from the reduced zirconium tetrahalide product. It will also be apparent that this type of reaction medium will greatly improve the heat transfer from the source of heat to the reacting substances.

In a more specific embodiment, the invention comprises separating hafnium and zirconium tetrahalides from their mixture, either in vapor or liquid state, by subjecting said mixture to contact with a reducing agent in a reducing zone containing a mixed metal salt reaction medium, particularly useful reducing agents and reaction media for this purpose being listed above. The reducing agent may be added to the reducing zone either prior to or along with the mixed tetrahalide feed. A reaction temperature within the range of about 250° to 450° C. is maintained in said reducing zone during the reaction. The reaction is also preferably carried out in vacuo, though an inert atmosphere, such as provided by argon, may also be effectively employed. In practicing the invention, it is not essential that the reduction be carried out until all of the zirconium tetrahalide is reduced, though the loss of as little zirconium tetrahalide as possible is preferred. The reduction is carried out until the zirconium tetrahalide is reduced to the trihalide, dihalide or metallic state, while the hafnium tetrahalide remains unreduced, and

two immiscible layers result. The top layer contains hafnium tetrahalide and any unreduced zirconium tetrahalide, if present, and most of the salt mixture, while the bottom layer will contain the reduced zirconium tetrahalide product and that part of the salt mixture which is soluble in the reduced tetrahalide. The top layer may be removed readily by decanting or by filtering through sintered glass or metal filters. Separation of the top layer may also be accomplished by further cooling the stratified reaction mixture until solidification occurs. The solidified layers are then removed from the reaction zone and tapped lightly to obtain a physical separation of the top and bottom layers.

The process of the invention is preferably carried out so that substantially all of the zirconium tetrahalide is selectively reduced to zirconium trihalide. Following the separation of the top layer, the bottom layer, containing the zirconium trihalide, is next heated to a temperature within the range of about 300° to 600° C., preferably about 400° to 460° C., to effect disproportionation according to the left-to-right direction of the following reversible reaction:

$$2ZrHal_3 \rightleftharpoons ZrHal_2 + ZrHal_4$$

The gaseous zirconium tetrahalide may then be recovered as a hafnium-free product. The relatively involatile zirconium dihalide may, on the other hand, be employed as the reducing agent to selectively reduce fresh batches of the mixed hafnium and zirconium tetrahalide feed. Alternatively the dihalide may be further disproportionated according to the left-to-right direction of the following reaction:

$$2ZrHal_2 \rightarrow Zr + ZrHal_4$$

Other methods of treating the trihalide to recover hafnium-free zirconium include electrolysis or reduction to metal by the use of reducing agents, such as calcium, magnesium or sodium, according to the techniques known to those familiar with the art.

Prior to any of the above processes the trihalide can be further purified by heating it in a fresh melt of the reaction mediums in order to remove any entrained metal halide impurities such as hafnium and aluminum halides.

The mixed hafnium and zirconium tetrahalide feed useful for the purposes of this invention may be prepared by converting crude zircon or other zirconium-containing mineral to the carbides by reaction with carbon in a graphite resistor furnace. The carbides are then halogenated, e.g. with chlorine gas, in a Monel metal vessel. The selective reduction reaction may then be carried out in a stainless steel vessel. If desired, zirconium metal may be obtained from the hafnium-free zirconium tetrahalide by reduction with magnesium in a stainless steel vessel, followed by vacuum distillation of $MgCl_2$ and excess magnesium from the zirconium sponge in a heat resistant vessel. The zirconium sponge is next melted in a suitable resistor or induction type furnace to form ingots of zirconium.

The invention will be more fully understood by reference to the following examples.

Example I

520 grams of aluminum chloride and 340 grams of sodium chloride were heated in a closed vessel at a temperature of about 250° C. until a homogeneous melt resulted. 70 grams of aluminum powder were added to the melt, and the temperature raised to about 330° C. 210 grams of a mixture of zirconium and hafnium tetrachlorides, containing about 1.7% hafnium based on the total weight of the zirconium and hafnium, were then added to the melt, and the resulting reaction mixture heated to a temperature of about 330° C. for three hours. The reaction product mixture was cooled, and the two distinct layers which had formed were separated. The upper layer, weighing 710 grams, contained about 25 grams of unreduced tetrachlorides having a hafnium content of 5.7% based on the total weight of the hafnium and zirconium. The bottom layer, weighing 430 grams, contained 160 grams of zirconium trichloride having a hafnium content of 1.0% based on the total weight of the hafnium and zirconium.

Example II

52 grams of lithium chloride and 60 grams of potassium chloride were melted in an open vessel under an argon atmosphere at 360° C. 20 grams of a mixture of zirconium and hafnium tetrachlorides, containing 1.7% hafnium based on the total weight of the zirconium and hafnium, and 20 grams of finely divided zirconium metal sponge were slowly fed into the melt over a period of about 15 minutes. The resulting reaction mixture is then heated at a temperature of about 360° C. for 1 hour. The reaction product mixture is then filtered through a heated sintered glass disc. The filtrate weighs 114 grams and contains 6 grams of unreduced tetrachlorides containing 5% hafnium based on the total weight of the hafnium and zirconium. The residue on the filter plate weighs 38 grams and contains 18 grams of zirconium trichloride having a hafnium content of 0.2% based on the total weight of the hafnium and zirconium.

Though separation in accordance with the present invention has been specifically illustrated with respect to the tetrachlorides of hafnium and zirconium, it will be understood other tetrahalides such as tetraiodides and tetrabromides may also be employed. It will be further understood that the operating conditions set forth in the above examples may be varied within the limits indicated in the more general description of the invention and in the appended claims.

What is claimed is:

1. The process for purifying zirconium tetrahalide which comprises reacting a mixture of zirconium and hafnium tetrahalides selected from the group consisting of tetrachlorides, tetrabromides and tetraiodides with a metal reducing agent at a temperature within the range of about 250° to 550° C. in the presence of a reaction medium comprising a mixture of metal salts selected from the group consisting of (A) aluminum halide and sodium halide, and (B) lithium halide and potassium halide, selectively reducing said zirconium tetrahalide to at least a lower valence form and obtaining thereby a reaction product mixture having a top layer containing substantially all of the unreduced tetrahalides and a bottom layer containing the reduced zirconium tetrahalide, and then separating the top layer from the bottom layer.

2. The process of claim 1 wherein said metal reducing agent is aluminum.

3. The process of claim 1 wherein said reducing agent is a zirconium metal.

4. The process of claim 1 wherein said reaction medium comprises a mixture of aluminum chloride and sodium chloride.

5. The process of claim 1 wherein said reaction medium comprises a mixture of lithium chloride and potassium chloride.

6. The process of claim 1 wherein said zirconium tetrahalide is reduced to zirconium trihalide.

7. The process of claim 1 wherein said tetrahalides are tetrachlorides.

8. The process of claim 1 wherein said tetrahalides are tetrabromides.

9. The process of claim 1 wherein said tetrahalides are tetraiodides.

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