United States Patent [19]

Hurd

[11] **3,801,307**

[45] **Apr. 2, 1974**

[54] **METAL REDUCTION PROCESS**

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[22] Filed: **July 26, 1972**

[21] Appl. No.: **275,257**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 833,378, June 16, 1969, abandoned.

[52] **U.S. Cl.** ..... **75/84.5**, 75/62, 75/84.1 R

[51] **Int. Cl.** **G22b 5/00**, C22b 53/00

[58] **Field of Search** 75/84.5, 62, 84.1

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[57] **ABSTRACT**

An improved metal reduction process permits the efficient production of metals from reducible metal compounds by means of a reducing metal. The reducible metal compound and a stoichiometric amount of a reducing metal are introduced into a sealed reaction zone and heated to a temperature which is above the melting point of the reducing metal but below the temperature at which a reduction reaction between the reducible metal compound and the molten reducing metal will proceed spontaneously. In this temperature range, a reduction reaction is initiated between the reducible metal compound and the molten reducing metal by suddenly disrupting the surface of the molten reducing metal and allowing the reduction reaction to continue to completion.

15 Claims, 7 Drawing Figures

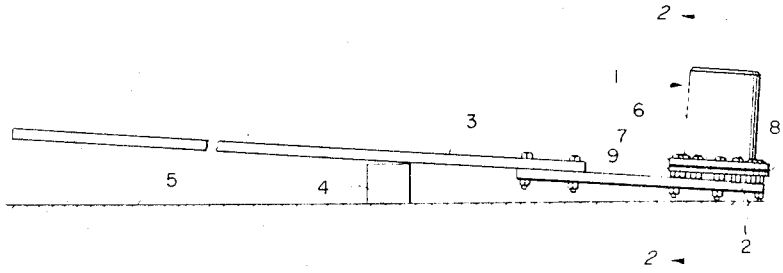


FIG. 1

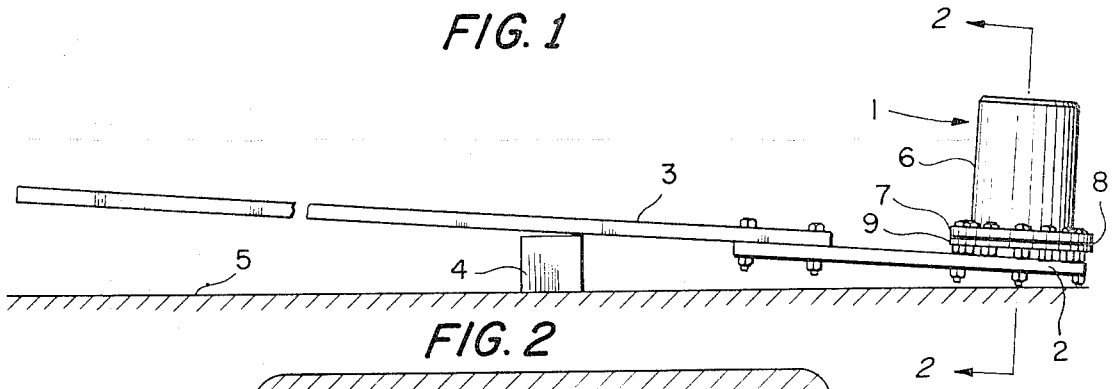
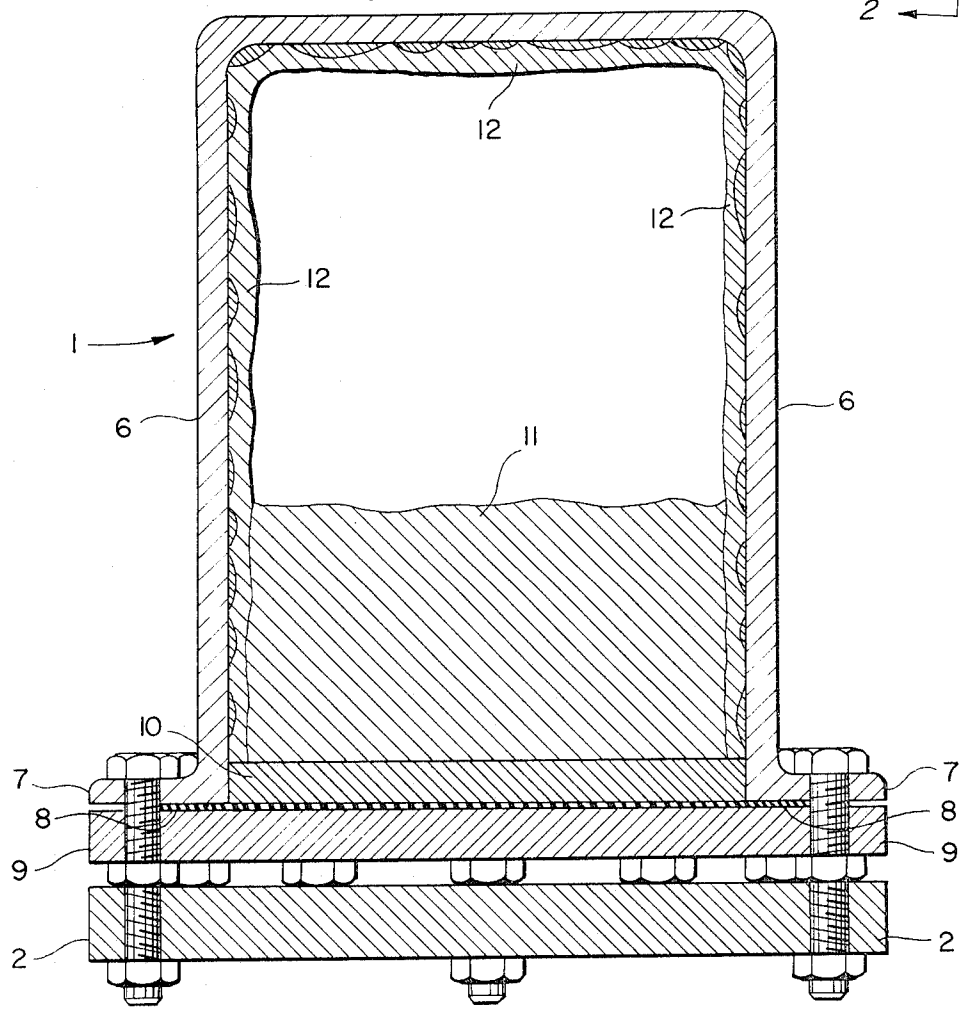


FIG. 2



METAL REDUCTION PROCESS

CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of Ser. No. 833,378, filed June 16, 1969, now abandoned.

BACKGROUND OF THE INVENTION

Numerous processes exist for the production of metals and their alloys from reducible compounds of such metals. For example, titanium and other metals have been produced by processes which involve reacting the corresponding metal halide, such as titanium tetrachloride, with a reducing metal, such as magnesium, under reducing conditions. One existing procedure involves the trickling or other slow addition of titanium tetrachlorideonto or across the top of a large mass of tetrachloride onto magnesium in an effort to reduce the titanium from its polyvalent form to its zero valence state, while producing magnesium chloride as a by-product.

Further, experiments have been conducted by others in which a reducible metal compound and a reducing metal have been placed in a small closed reaction vessel and heated therein, without agitation, to a thermal initiation temperature at which a reduction reaction between the reducible metal compound and the molten reducing metal will proceed spontaneously. However, when such a spontaneous reaction is initiated, the reaction proceeds so rapidly that enormous internal pressures are developed within the closed reaction vessels. Accordingly, it is uncommon for large bulk reactions to be performed by the foregoing procedure on a commercial scale. Instead, industry has relied on procedural modifications involving the slow and incremental addition of one or both of the reactants to a closed reaction zone which is maintained at or near atmospheric pressure. However, this modified procedure also has its disadvantages since the modification involves the time-consuming steps of selecting, monitoring, and changing the rates of addition of the reactants to the closed reaction zone in order to control the temperature of the reaction zone. As an example of the time-consuming nature of the modified procedure, according to one reported procedure used by the U.S. Bureau of Mines, titanium tetrachloride was slowly fed into a reaction vessel above the surface of a large bath of molten magnesium which was enclosed within the reaction vessel. 2 hours after the titanium tetrachloride addition was begun, only 40 percent of the total amount of the reactant had been introduced into the reaction vessel.

SUMMARY OF THE INVENTION

The present invention relates to an improved metal reduction process which permits the efficient production of a metal from its reducible metal compound by reacting substantially all of the reducible metal compound simultaneously with substantially all of a reducing metal in a closed reaction zone without encountering the extremely high pressure conditions or time-consuming steps common to the existing procedures discussed above.

Briefly described, the process of this invention includes the following steps. A reducible metal compound and a reducing metal are introduced into a reaction zone, without any pre-mixing of these reactants, in

amounts usually not more than 10 percent excess of either reactant over the stoichiometric requirements for the complete reduction of the metal compound to the zero valence state of the metal. After the reaction zone is sealed, the reactants are heated therein, without any significant agitation of the reactants, from a temperature below the melting point of the reducing metal to a temperature which is above the melting point of the reducing metal but below the thermal initiation temperature at which the reduction reaction will proceed spontaneously. After the reactants are brought to within the foregoing temperature range, a reduction reaction is initiated between reducible metal compound and the reducing metal by suddenly disrupting the surface of the molten reducing metal and allowing this reaction to continue spontaneously and exothermically to thereby produce the zero valence state of the reduced metal. Subsequently, the reduced metal is withdrawn from the reaction zone.

An important feature of the present invention is that the reactants are maintained at a temperature significantly below the thermal initiation temperature before the reduction reaction is initiated by the sudden disruption of the surface of the molten reducing metal. The thermal initiation temperature in this case is defined as the temperature to which the reactants must be heated at rest in a sealed reaction vessel to cause the reaction to proceed spontaneously without disrupting the surface of the molten reducing metal and then to continue to react to completion without the benefit of externally supplied heat or agitation.

Another important feature of the present invention, is that after the reduction reaction is completed, the product, the zero valence state of the reduced metal, is substantially separated from the by-product salt and can be easily recovered from the reaction vessel.

THE DRAWINGS

FIG. 1 is a side elevation of an apparatus, including a reaction vessel, which can be used in the practice of this invention on a laboratory scale.

FIG. 2 is a cross-sectional view of the reaction vessel shown in FIG. 1. This view is taken along the lines 2—2 in the direction of the arrows in FIG. 1.

DETAILED DESCRIPTION

THE REDUCIBLE METAL COMPOUND

The process of the present invention is applicable to any metal compound which can be reduced with a molten reducing metal. Such reducible compounds include the halides, oxides and sulfides of titanium, zirconium, hafnium, vanadium, niobiom, tantalum, silicon, germanium, tin, lead, thorium, uranium, boron, beryllium, and the like. Among the various compounds of these metals, the metal salts of the common inorganic acids are preferred. The metal halides are particularly preferred, especially the halides of the metals found in groups IVA, IVB, VA, VB, VIA, and VIB of the Periodic Chart. To a somewhat lesser extent, the halides of metals of groups IIIA, IIIB and the actinoid Series can be used to advantage in the present process.

Illustrative reducible metal compounds are $TiCl_4$, $TiBr_4$, TiF_4, $ZrCl_4$, $BeCl_2$, $SnCl_4$, $NbCl_5$, VCl_4, $TaCl_5$, UCl_4, UF_6, $ThCl_4Fe_2O_3$, Nb_2O_5, CoO and MoS_2.

Reducible metal compounds of the transition metals are very useful in this invention. Of the transition metals, titanium and zirconium are preferred. The present

invention is usually well suited for the production of titanium from titanium tetrachloride and zirconium from zirconium tetrachloride.

Further, alloys of the various metals discussed above can be produced by the process of the present invention. For example, a titanium-tin alloy can be formed by reacting a reducible metal compound of titanium, such as $TiCl_4$, and a reducible metal compound of tin, such as $SnCl_4$, in the presence of a suitable reducing metal, such as sodium, within the conditions of the present method.

The metals which can be used as reducing agents in the present invention include any metal which is capable of reducing the selected reducible metal compound. As is known in the art, metals which will reduce certain compounds will not reduce all compounds. However, the selection of a suitable reducing metal is within the skill of the art once the reducible metal compound is identified or selected.

The reducing metals used in the practice of this invention can be selected from the group consisting of alkali metals, such as lithium, sodium, and potassium; the alkaline earth metals, such as magnesium, barium, and calcium; aluminum; and the rare earth misch metals.

Preferred reducing metals include sodium, magnesium, potassium, lithium, barium, calcium and mixtures thereof. Sodium, mixtures of sodium with barium, sodium with calcium and sodium with potassium are particularly useful as reducing metals for reducible metal halide compounds, such as $TiCl_4$, $BeCl_2$, $ZrCl_4$, VCl_4, $NbCl_5$, TiB_4, TiF_4, and UF_6.

Although aluminum is not a good reducing metal for producing metals from reducible metal halide compounds, it does function satisfactorily as a reducing metal for other reducible metal compounds, such as Fe_2O_3, Cr_2O_3, TiO_2, ZnO_2, and mixtures of FeO and TiO_2.

Selection of Suitable Reactants

In many instances, the selection of the reducible metal compound is limited by the availability in commercial quantities of reducible compounds of the selected metal. For example, titanium tetrachloride is commercially available or can be prepared from commercially available raw materials. Accordingly, titanium tetrachloride is one primary source of titanium metal.

The selection of a suitable reducing metal is within the skill of the art when aided by this disclosure. Factors to be considered in selecting a reducing metal for use in the process of this invention include the following:

1. The ability of the reducing metal to react with the reducible metal compound under the anticipated conditions of use.
2. The melting point and boiling point of the reducing metal compared to those of the reducible metal compound.
3. The cost and commercial availability of the reducing metal.
4. The relationship between the melting point of the reducing metal and the thermal initiation temperature for the reduction reaction for the selected combination of reducible metal compound and reducing metal.
5. The type of by-products produced during the reduction process.

As previously indicated, particularly effective combinations of reducible metal compound and reducing metal are the combination of titanium tetrachloride and sodium metal, and the combination of zirconium tetrachloride and sodium metal.

Relative Amounts of the Reactants

When possible, the relative amounts of reducing metal and reducible metal compound which are used in the practice of this invention should be substantially stoichiometric. Ordinarily it is not necessary to use any significant excess of either of the reactants, and the use of substantial excesses, for example, over 25 percent excess of either reactant, should be avoided. Ordinarily, the process of this invention requires less than 10 percent excess of either reactant, and desirably less than 5 percent excess of either reactant. Preferably, less than 1 percent excess of either reactant is most desirable.

The Temperature

The temperature at which the reaction of the present invention is initiated, by the sudden disruption of the surface of the molten reducing metal, is below the boiling point of the reducing metal and can range from the melting point of the reducing metal up to within about 50° C. of the "thermal initiation temperature" for the reduction reaction.

By "thermal initiation temperature," I mean the temperature to which the reactants must be heated at rest in a sealed reaction vessel to cause the reactants to react spontaneously without disrupting the surface of the molten reducing metal and then to continue to react to completion without the benefit of externally supplied heat or agitation.

By contrast, initiation of the process of the present invention is characteristically induced at temperatures significantly below the thermal initiation temperature. Thus, if one heats the reactants to an initiation temperature as taught herein (i.e., significantly below the thermal initiation temperature), and either does not mechanically initiate the reduction reaction by intentionally disrupting or proliferating the surface and body of the molten metal, or inadequately manipulates the reactants in mechanically initiating the reduction reaction, little or no reaction will occur and the reaction will not proceed to completion.

Desirably, the temperature at which the process of the present invention is initiated will be the minimum required to achieve an acceptable rate of reaction when the surface of the molten reducing metal is sharply disrupted in the presence of the reducible metal compound. In the present invention the preferred temperature of initiation is more than 100° C. and usually more than 200° C. below the thermal initiation temperature.

Frequently, a combination of reducible metal compound and reducing metal can be selected so that there is a broad temperature range, for example, several hundred centigrade degrees, over which the reaction could be induced or mechanically initiated. However, once initiated, the reducing reaction is exothermic and the temperature will rise above the calculated thermal initiation temperature. With this in mind, it is advantageous in the present invention to select the lowest initiation temperature that meets many or all of the following objectives:

a. The temperature should provide an acceptable rate of reaction when the reaction is initiated;

b. The temperature should be at or above the boiling point of the reducible metal compound; and

c. The temperature should be high enough to cause the exothermic temperature reached during the reaction to be sufficient enough to maintain the reduced metal and the by-product salt above their melting points.

When using magnesium or sodium as the reducing metal, and using titanium tetrachloride as the reducible metal compound, the thermal initiation temperature for the reduction reaction is ordinarily in excess of 600° C. and thermally initiated reduction processes, such as the Kroll process, are typically carried out within the temperature range of from 700°–850° C. By contrast, the present process can be carried out at temperatures as low as the melting point of sodium (about 98° C.). A very useful initiation temperature for the present process, using sodium metal as the reducing metal and titanium tetrachloride as the reducible metal compound, is from 120°–400° C.

Initiating the Reaction

The reduction process of the present invention is initiated by disrupting the surface of the molten reducing metal after it has been heated to the temperature previously indicated. This can be accomplished by abruptly shaking or jarring the reaction vessel or zone, by rapid agitation of the reactants, or by any other means which produces a sudden material change in the shape or area of the surface of the molten metal which is exposed to or in contact with the titanium tetrachloride.

Disrupting the surface of the molten metal results in a proliferation or dispersion of freshly exposed reducing metal into initmate contact with the reducible metal compound. this disruption or proliferation of the molten metal serves to initiate the reduction reaction in the present invention. Another way of viewing this phenomenon is to consider that the thermal initiation temperature under quiescent conditions, that is the "thermal initiation temperature" of the prior art, is higher than the initiation temperature under conditions wherein molten reducing metal is being dispersed or proliferated as in the present invention.

Although a variety of means can be used to disrupt or proliferate the molten reducing metal, vertical agitation, that is agitation in a direction perpendicular to the surface of the molten metal, is much more effective than, for example, side to side shaking or rotary mixing in vertically oriented cylindrical reaction vessels. Thus, the direction of agitation can be important and should ordinarily be performed in the direction or manner which results in the best or most efficient proliferation of the molten reducing metal. With cylindrical reaction vessels, agitation in the direction of the axis is preferred. For example, end-on-end mixing against the flattened ends of the reaction vessel is particularly beneficial.

Once initiated, heat is produced by the reduction process and desirably the external heat should be removed from the reactor and, if necessary, cooling means should be provided for controlling the temperature within the reaction zone.

Reaction Vessel and Related Equipment

The reaction vessel can take any of a variety of shapes. Apparatus suitable for practicing this invention on a laboratory scale is shown in the drawings.

In FIG. **1**, a reaction pot or vessel, generally designated by the numeral **1**, is attached to a supporting arm **2** which is bolted to an extension arm **3**. Extension arm **3** extends over a block **4** which serves as fulcrum. Block **4** rests on floor **5**.

Reaction vessel **1** comprises a cylindrical body **6**, the upper end of which is closed. The open end of cylindrical body **6** is provided with an outwardly extending annular flange **7** which is provided with means, such as bolts, for fastening gasket **8** and cover **9** to cylindrical body **6**. Reaction vessel **1** is further adapted for attachment to supporting arm **2**.

The details of construction of reaction vessel **1** are shown more clearly in FIG. **2**.

In operation, the reaction vessel which in FIG. **1** is disassembled and evacuated and/or purged with an inert gas, such as argon, as is known in the art. Then, while operating within an inert atmosphere, the reducing metal and the reducible metal compound, in stoichiometric proportions, are placed in cylindrical shell **6** in quantities sufficient to, for example, fill approximately 40–80 percent of the volume of reaction vessel **1**. The reaction vessel is then sealed by attaching the cover **9** to the cylindrical body **6** with suitable bolts and a copper gasket **8**. Reaction vessel **1** is then attached to supporting arm **2**. The contents of the reaction vessel **1** are then heated to the desired temperature. This heating can be accomplished by various means including the use of a heating mantle encircling the body of reaction vessel **1** and/or by means of a heater placed between floor **5** and supporting arm **2** immediately below reaction vessel **1**. After the desired temperature has been obtained, heating is discontinued.

Next, the reduction reaction is initiated by quickly or sharply disrupting the surface of the molten metal within reaction vessel **1**. Although various means can be used to accomplish this purpose, a convenient laboratory method is to suddenly depress or rotate extension arm **3** about fulcrum **4** one or more times in rapid succession to provide sharp vertical agitation.

While not wishing to be bound by any theory, it has been observed that a coating forms on the surface of the molten metal which is in contact with the reducible metal compound and it is believed that this coating or surface layer inhibits the reduction reaction until either the temperature is raised high enough to thermally initiate the reaction, for example, by causing the molten metal to boil, or until the surface of the molten metal is sharply disrupted to thereby expose fresh molten metal. By initiating the reaction in the latter manner, such as by mechanically disrupting the surface of the molten metal, the reaction can be started at a lower temperature and the enormous pressures associated with the prior art processes can be avoided. In the case of reducible compounds of polyvalent metals, this may be the result of a shift in the reaction mechanism and/or the reaction kinetics.

For example, once the reaction between titanium tetrachloride and sodium is initiated by disrputing or proliferating the surface of the molten sodium, the reaction proceeds spontaneously. The reaction is exothermic and it has been observed that some or all of the reaction vessel **1** will take on a red glow as the reaction proceeds. With small reaction vessels up to 10 liter capacity, the reduction reaction can be allowed to proceed without external heat and without external cooling means. After the reaction has completed, the reaction vessel and its contents can then be permitted to cool to room temperature. The reaction vessel is then

detached from supporting arm 2 and cover 9 is removed. The interior of the reaction vessel 1 will typically appear as shown in FIG. 2. At the bottom of reaction vessel 1 will be a disc or plaque 10 of titanium metal. Above this will be a salt deposit 11 of sodium chloride. The top and side walls of cylindrical body 6 will be covered with a thin layer of material 12 which may be salt, excess sodium metal, and small particles or nodules of titanium which adhere to the reactor walls.

It has been found that although small particles of titanium have been found along the upper side walls and top of reaction vessel 1, there are very few readily identifiable titanium particles within salt block 11. Excess sodium, when present, tends to deposit along the top wall or upper end of reaction vessel 1. For some reason, the titanium nodules or particles which are sometimes found along the upper walls of reaction vessel 1, within deposit layer 12 are more ductile or softer than the titanium disc or plug 10.

The present invention is further illustrated by the following specific examples which evidence the applicability of the present invention to reducible metal compounds of titanium, zirconium, hafnium uranium, vanadium, niobium, thorium, beryllium, and molybdenum. As can be seen from the following examples, the process of the present invention is particularly useful in the production of titanium, zirconium, hafnium, uranium, vanadium, niobium and thorium from reducible halide compounds of these metals.

Unless otherwise indicated in the following examples, all parts and percentages are by weight.

EXAMPLE 1

This example illustrates the improved reduction process of this invention using titanium tetrachloride as the reducible metal compound and sodium as the reducing metal. It further illustrates how other metals (such as copper) can be placed in the reaction zone to be melted and combined with or alloyed with the metal being produced by the reduction process.

The apparatus used in this example was of the type shown in FIG. 1. The reaction vessel was constructed from a section of a mild steel casing approximately 3/8 inch thick. A 3/8 inch steel plate was welded across one end of the casing and an annular 3/4 inch steel flange was welded to the opposite end of the casing to provide a reaction vessel of the configuration shown in FIGS. 1 and 2. The interior dimensions of this reaction vessel were 6 inches in diameter and 8 inches high. A steel cover was made from 3/4 inch steel. 510 grams of sodium metal from a sodium brick and 615 ml. of titanium tetrachloride were placed in the reaction vessel after first inverting it. A solid copper gasket (0.05 inches thick) was placed over the flange and the cover plate was then bolted to the flange using eight equally spaced 5/8 inch bolts. The gasket was disc-shaped and was within the inside bolt circle. Consequently, much of the gasket was exposed to the contents of the reaction vessel.

Next, the sealed reaction vessel was heated in an oven for approximately 2–3 hours until the temperature of the reaction vessel reached approximately 175° C.

The reaction vessel was then removed from the oven and immediately attached to a steel supporting arm. A wooden plank approximately 10 feet long was used as the extension arm. A block of wood nominally 4 inches by 6 inches in cross sections was used as the fulcrum. The surface of the molten sodium was sharply disrupted by rapidly depressing the left end of extension arm 3 as shown in FIG. 1 several times in rapid succession. The movement of the extension arm about the fulcrum was sufficient to cause the reaction vessel to rise approximately 6–8 inches from the floor before falling back to the floor. This sharp agitation was sufficient to initiate the reduction process.

Shortly after the reaction was initiated, the lower one-third of the reaction vessel became red. The vessel was set level and the reaction was immediate and complete. After completion of the reaction, the reaction vessel was permitted to cool to room temperature. The reaction vessel was then removed from its supporting arm, inverted and opened. The contents of the reaction vessel were substantially identical to that shown in FIG. 2.

A well consolidated lump of titanium metal and copper, as hereinafter explained, weighing approximately 128 grams was obtained from the bottom of the reaction vessel. See FIG. 2, element 10. 791 grams of sodium chloride crystals, containing no discernible particulate metal were removed from the reactor. See element 11 of FIG. 2. The outside of the reactor was pounded with a mallet to loosen material which had adhered to the inner walls of the reaction vessel. In this manner, 526 grams of a mixture of small nodules and particles of ductile metal admixed with sodium chloride particles, were recovered. Of this amount, 197 grams were titanium. Very little material remained within the reaction vessel.

Essentially no un-reacted sodium or titanium tetrachloride was found in the reaction vessel.

Total metal recovery (as the lump and as small nodules) was in excess of the theoretical yield of titanium metal. Subsequent examination of the reaction vessel and of the titanium plaque revealed that a portion of the copper gasket which was exposed to the interior of the reaction vessel had melted during the reaction and was co-mingled or alloyed with the titanium metal that was recovered from the cover of the reaction vessel.

The estimated temperature range at which the reaction would be initiated by only heating, the thermal initiation temperature, is from 500° to 600° C. The reaction is this Example was initiated at about 175° C.

EXAMPLE 2

In this example, titanium metal was again produced from titanium tetrachloride using sodium as the reducing metal.

The experimental apparatus of Example 1 was modified to the extent that the cover 9 was welded to the body of the reaction vessel after it was loaded with the reactants.

In Example 2, the reaction vessel was loaded with 1.8 Kg. of sodium in the form of two commercial two pound sodium bricks each measuring approximately 8 inches by 2½ inches by 2½ inches. A stoichiometric amount (2,190 ml.) of titanium tetrachloride was then added and the reaction vessel was sealed. It was then attached to the supporting arm. The contents of the reaction vessel were heated over a period of several hours until the temperature as measured externally along the top of the reaction vessel had reached approximately 180° C. Heating was accomplished by lifting the reac-

tion vessel from the floor sufficiently high to permit an electric heating element to be placed on the floor underneath the reaction vessel. An electric heating element or mantle was also placed around the reaction vessel. A cover of insulating board was then placed over the reaction vessel to prevent massive heat losses. When the temperature reached approximately 180° C., the heating elements and insulated cover were removed. The contents of the reaction vessel were then agitated by rapidly raising the reaction vessel about 8 inches from the floor (using the extension arm for this purpose) and allowing it to drop under its own weight. This procedure was repeated three times in rapid succession, that is, in less than 5 seconds. The reaction between the molten sodium and the titanium tetrachloride was thereby initiated and immediately the lower one-half of the reaction vessel turned red. The reaction was immediate and complete. After the completion of the reaction, the reaction vessel was allowed to cool to room temperature as the reaction subsided. After the reaction vessel had cooled to substantially room temperature, the reaction vessel was opened and the contents appeared substantially as shown in FIG. 2.

425 grams of titanium metal was recovered in a consolidated mass or lump. See element 10 of FIG. 2. This represents approximately 44 percent of the theoretical yield of titanium metal. In addition to this consolidated mass of titanium metal, nodules of titanium metal were found along the upper side walls of the reaction vessel and along the top of the reaction vessel. The combined weight of these nodules and the lump was in excess of 95 percent of the theoretical yield of titanium.

The nodules of titanium metal attached loosely to the wall were substantially softer than the consolidated mass of titanium found in the bottom of the reaction vessel. No discernible particles of titanium metal were found in the crystalline mass of sodium chloride which was located immediately above the lump of titanium. See element 11 of FIG. 2.

The estimated temperature range at which this reaction would be initiated by only heating, the thermal initiation temperature, is from 500° to 600° C. The reaction in this Example was initiated at about 180° C.

EXAMPLE 3

In this Example, titanium metal was produced from titanium tetrachloride using a mixture of sodium and calcium as the reducing metal.

In this embodiment 100 ml. of titanium tetrachloride, 61 grams of sodium and 21.5 grams of calcium were placed in the 300 ml. reactor. The reactor was sealed and heated in an oil bath to an oil bath temperature of 230° C. Upon shaking of the reactor at this temperature, a very vigorous reaction occurred. After the completion of the reaction 41.56 grams of titanium were recovered for a yield of 95.4 percent. The reduction reaction of this Example was initiated at 230° C., whereas the thermal initiation temperature for this reaction lies in the range from 500° to 600° C.

EXAMPLE 4

In this Example, titanium metal was produced from titanium tetrachloride using a mixture of sodium and barium as the reducing metal.

In this embodiment of the present invention, 100 ml. of titanium tetrachloride, 45 grams of sodium, and 125 grams of barium were placed in the 300 ml. reactor. The reactor was then shaken for about 60 seconds, which shaking produced a very vigorous reaction. After the completion of the reaction, 43.08 grams of titanium were recovered for a yield of 98.8 percent.

The reduction reaction of this Example was initiated at 230° C., whereas the thermal initiation temperature for this reaction lies in the range of from 500° to 600° C.

EXAMPLE 5

In this Example, an alloy of titanium and tin is produced from a mixture of $SnCl_4$ and $TiCl_4$ using sodium as the reducing metal.

In this embodiment, 5 ml. of $SnCl_4$ and 95 ml. of $TiCl_4$ were placed in the 500 ml. reactor with 85 grams sodium. The reactor was put in an oil bath which was heated to 160° C. and held at from 140° to 160° C. for 40 minutes. The reactor was then shaken end to end in a laboratory hydrogenation shaker for 20 seconds. It was noticed that immediately after the start of the shaking the residual oil smoked and the bottom of the reactor became red hot. After completion of the reaction, 45 grams of powder and nodules were recovered for a yield of 97 percent. In a subsequent laboratory investigation, the recovered material was found to be an alloy of 90 percent titanium and 10 percent tin.

The reduction reaction of this Example was initiated at from 140° to 160° C., whereas the thermal initiation temperature for this reaction lies in the range of from 500° to 600° C.

EXAMPLE 6

In this Example, titanium was produced from titanium tetrabromide using sodium as the reducing metal.

In this embodiment, 105.4 grams of $TiBr_4$ and 28 grams of sodium were placed in the 300 ml. reactor and sealed with a copper gasket as well as an eight bolt flange. The sealed reactor was heated in an oil bath at a bath temperature in the range of from 208° to 230° C. for a period of 25 minutes. The disruption of the reducing metal surface was accomplished by shaking the reactor in a laboratory shaker for 20 seconds. Upon completion of the reaction, 14.0 grams of powder, lumps, and spherules were recovered. Since all the sodium was reacted, this was used as a basis for a 100 percent theoretical yield of 14.58 grams of titanium metal. Accordingly, the actual yield was 96 percent of the theoretical yield.

The reduction reaction of this Example was initiated at a temperature in the range of from 208° to 320° C., whereas the thermal initiation temperature for the reaction lies in the range of from 500° to 600° C.

EXAMPLE 7

In this Example, titanium metal was produced from titanium tetrafluoride using sodium as the reducing metal.

In this embodiment, 108.6 grams of TiF_4 and 81.6 grams sodium were placed in a 300 ml. cylindrical reactor which was sealed with a solid copper gasket which was, in turn, secured by a bolted blank flange. The reactor was then placed in an oil bath which was heated in the range of from 225° to 240° 25 C. for 251minutes after which the reactor was shaken for 60 seconds. 18 seconds after the start of the shaking, the residual oil left on the outside of the reactor began smoking,

thereby indicating that the reaction had been initiated. Upon the realization that only a partial reaction had taken place, the reactor was again heated in asalt bath at a final temperature of 385° C. No indication of a further reaction was noted, nor did additional shaking give any evidence of a further reaction.

After the reactor was opened, the reactor was heat-soaked for 4½ hours at from 760°–790° C. in a crucible furnace. After extensive leaching of the end-product in isopropyl alcohol to kill the residual sodium, followed by a water and a concentrated nitric acid treatment to remove the residual fluoride, 17.8 grams of powdered and granular titanium were recovered for a recovery of 42.5 percent of the theoretical amount.

The relatively low recovery is believed to be caused by the lumpy and powdered nature of the TiF_4 starting material which was hydroscopic and which possessed an inherently low heat of reaction, certainly lower than that for the reduction of the bromide or chloride of titanium.

Nonetheless, titanium was recovered in appreciable amounts from the TiF_4 starting material in accordance with the procedure of this invention. The reduction reaction of this Example was initiated at from 225° to 240° C., whereas the thermal initiation temperature is from 500° to 700° C.

EXAMPLE 8

In this Example, zirconium metal was produced from zirconium tetrachloride using sodium as the reducing metal.

A large reactor was charged with about 9 kilograms of zirconium tetrachloride powder before the contents of the reactor were evacuated through an opening therein; such as, for example, a 3/8 inch nipple welded into the middle of one side of the reactor. A vacuum of 682 mm. (Hg) was maintained over a period of 5 hours during which time argon was admitted twice to encourage the removal of HCl and other gases. After a final addition of argon, the nipple was sealed off and the reactor was heated over a gas flame to a temperature on the top of the reactor of about 450° to 470° F. then the reactor was shaken end on end for a period of 70 seconds. After 40 seconds, the reactor was red over most of its area indicating that the reduction reaction was taking place.

After the completion of the reduction reaction, the reactor was opened and the contents thereof examined. The contents consisted of a large amount of salt (NaCl) substantially free of zirconium metal, and porous fused zirconium metal lying along the side of the reactor. Almost 70 kilograms of salt were segregated. The metal and the remaining salts were leached with isopropyl alcohol to remove traces of sodium, then sequentially with 0.1N HCl, 1N H_2SO_4, water and finally methyl alcohol. The yield of coarse zirconium metal was 7,569 grams for a recovery of 85 percent while the yield of fine zirconium metal amounted to 1,240 grams or 14 percent, for a total yield of 99 percent of the theoretical yield.

The reduction reaction of this Example was initiated at about 470° F., whereas the thermal initiation temperature for this reduction reaction is in the range of from 500° to 600° C.

EXAMPLE 9

In this Example, zirconium metal was produced from zirconium tetrachloride using a mixture of sodium and calcium as the reducing metal.

In this embodiment, 55.5 grams (0.238 moles) of zirconium tetrachloride powder, 12 grams (0.522 moles) of clean sodium and 10 grams (0.250 moles) of calcium were placed in a 300 ml. reactor. The reactor was closed with a solid copper gasket and an eight bolt blank flange as in Example 1 before the reactor was immersed in a mineral oil bath where the oil was held for 25 minutes at from 230° to 235° C. Immediately thereafter, the reactor was shaken vigorously for 20 seconds resulting in a pronounced smoking of the residual oil on the reactor surface after about 6 seconds. This smoking was considered as an indication that an exothermic reaction had been initiated shortly after the start of the agitation.

The resulting reaction mixture was treated with excess isopropyl alcohol to destroy the unreacted sodium and calcium. The alcohol was increasingly diluted with water as the hydrogen evolution subsided. After heating the residue on the steam bath for 4 hours with concentrated HNO_3, the yield was 20.7 grams (95.4 percent recovery) of a black powder and sponge mixture of zirconium.

The reduction reaction of this Example was initiated in the temperature range of from 230° to 235° C., whereas the thermal initiation temperature is from 500° to 600° C.

EXAMPLE 10

In this Example, vanadium was produced from vanadium tetrachloride using sodium as the reducing metal.

In this embodiment, 77 ml. of VCl_4 (containing some VCl_3 contaminant) was placed in a 300 ml. reactor with 70 grams of sodium. The reactor was immersed in an oil bath which was heated to 145° C. and held in a temperature range of from 140° to 163° C. for 27 minutes. The reactor was then shaken for about 23 seconds, during which shaking, smoke became evident and the bottom of the reactor became red hot. After leaching in 1/8N HCl overnight, 32.7 grams of vanadium powder and vanadium nodules were recovered for a yield of 86.7 percent.

The reduction reaction in this Example was initiated in the temperature range of from 140° to 163° C., whereas the thermal initiation temperature for this reaction is from 500° to 600° C.

EXAMPLE 11

In this Example, niobium was produced from niobium pentachloride using sodium as the reducing metal.

In this embodiment, 100 grams of $NbCl_5$ and 41.7 grams of sodium were placed in the 300 ml. reactor and sealed with a solid copper gasket and a bolted flange. The reactor was then placed in an oil bath heated in the temperature range of from 225° to 230° C. for 22 minutes after which the reactor was removed from the bath and shaken for 60 seconds with no evidence of heat development. The reactor was then placed in a salt bath and reheated with the bath temperature rising continuously over a period of 39 minutes from 229° to 366° C. After the heat treatment in the salt bath, the reactor was shaken in the laboratory shaker for 60 seconds during which time smoke appeared (at 40 seconds) and the residual oil on the shaking sleeve caught

fire (at 60 seconds). After the completion of the reduction reaction, 31.3 grams of fine black niobium powder and small niobium metal particles were recovered. The recovery was 91 percent of the theoretical value.

In this Example, the reduction reaction was initiated at under 366° C., whereas the thermal initiation temperature is in the range of from 500° to 700° C.

EXAMPLE 12

In this Example, beryllium is produced from $BeCl_2$ using sodium as the reducing metal.

In this Example, 50 grams of powdered, anhydrous beryllium chloride and 30 grams of sodium were charged to the 300 ml. reactor and the reactor was heated in an oil bath to a temperature of 230° C. Thereafter, the reactor was shaken for 30 seconds and vigorous reaction resulted. Upon the completion of the reaction 2.9 grams of beryllium were recovered for a yield of 52 percent.

This reduction reaction was initiated at 230° C., whereas the estimated thermal initiation temperature is from 500° to 600° C.

EXAMPLE 13

In this Example, molybdenum was produced from molybdenum sulphide using lithium as the reducing metal.

In this embodiment, a quantity of MoS_2 (natural molybdenite) was ground to −150 mesh and heated under vacuum for several hours. 30.8 grams of this treated molybdenite and 8.6 grams of lithium were placed in the 300 ml. reactor and heated to an oil bath temperature slightly in excess of 230° C. Upon end to end agitation in a laboratory shaker, a moderate reaction occurred. After cooling, 15.6 grams of molybdenum were recovered for a yield of 85 percent.

This reduction reaction was initiated at about 230° C, whereas the thermal initiation temperature for this reaction is in the range of from 500° to 700° C.

The following is a brief discussion of some other exemplary metals which may be produced by the procedure of the present invention.

Hafnium can be produced in the same manner as zirconium, see Examples 8 and 9 above, by treating hafnium tetrachloride with sodium or a sodium mixture as the reducing metal. The following data taken from Metallurgical Thermochemistry; Kubaschewski, Evans, and Alcock; Pergamon Press; Third Edition (1967), shows the similarities between the important properties of zirconium tetrachloride and hafnium tetrachloride essential to the performance of this invention:

	$HfCl_4$	$ZrCl_4$
Boiling Point	316°C. (sublimes)	331°C. (sublimes)
Melting Point	437°C.	432°C.
Heat of Formation	−236.7 Kcal.	−234.7 Kcal.

Uranium can be produced by the reduction of UF_6 with a sodium reducing metal according to the procedure of this invention, since the heat of reaction for $UF_6 + 6Na = U + 6NaF$ is −175.8 Kcal. Further, UF_6 melts at 64° C. with a vapor pressure of about 1.5 atmospheres and mixes quickly and completely with the reducing metal at low temperatures of about 140° to 240° C. Further still, an USAEC Document (ORNL-3012, C. D. Scott, May 24, 1961) clearly shows that UF_6 and sodium react when they are heated together.

Thorium has been produced by the thermally initiated reduction of $ThCl_4$ with sodium metal at a temperature of about 500° C. according to Z. anorg. allgem. Chem., C. Lely and L. Hamburger at 87,209 (1914). Accordingly, it is evident from the preceding Examples that the procedure of the present invention can produce thorium at temperatures significantly below 500° C.

Reducible metal compounds, other than the reducible metal halides, may be used as a source of the metal to be recovered. See, for instance, Example 13 above in which MoS_2 is reduced by lithium metal according to the procedure of the present invention. Further, British Pat. Nos. 729,503 and 729,504 indicate that TiO_2, Li_2TiO_3, V_2O_5, Cb_2O_5, Ta_2O_5, Cr_2O_3, MoO_3, WO_3, MnTe, FeS, and U_3O_8 may be reduced to form their respective metals.

Though the present invention has been illustrated above in a number of specific examples, the procedure of this invention may obviously be applied to reducible metal compounds not specifically mentioned above in view of the broader aspects of this procedure.

What is claimed is:

1. A reduction process for the production of metal, which process includes the steps of

a. introducing into a reaction zone without premixing a halide selected from the group consisting of halides of titanium, zirconium, hafnium, uranium, vanadium, niobium, thorium, beryllium, molybdenum and mixtures thereof and a reducing metal selected from the group consisting of sodium, potassium, calcium, barium, magnesium, lithium and mixtures thereof, said reducible metal compound and said reducing metal being introduced in amounts providing not more than 10 percent excess of either reactant over stoichimetric requirements for complete reduction of the reducible metal halide to reduced metal,

b. sealing the reaction zone,

c. heating the reactants without substantial agitation from a temperature below the melting point of the reducing metal to a temperature which is both above the melting point of the reducing metal and below the temperature at which a reduction reaction between the metal halide and the molten reducing metal will proceed spontaneously,

d. initiating a reduction reaction between the metal halide and the molten reducing metal by suddenly disrupting the surface of the molten reducing metal by means of a mechanical force sufficient to provide a dispersion of the reducing metal in intimate contact with the reducible metal compound,

e. permitting the reduction reaction to continue to thereby produce a reduced metal in a zero-valence state; and

f. thereafter removing said reduced metal from the reaction zone.

2. The process of claim 1 wherein the reducing metal is an alkali metal selected from the group consisting of sodium, potassium and lithium.

3. The process of claim 1 wherein the reducing metal is selected from the group consisting of sodium, potassium, sodium mixed with barium, and sodium mixed with calcium.

4. The process of claim 1 wherein the reducible metal halide is selected from the group consisting of halide of titanium and zirconium.

5. The process of claim 4 wherein the reducing metal is an alkali metal selected from the group consisting of sodium, potassium and lithium.

6. The process of claim 4 wherein the reducing metal is selected from the group consisting of sodium, potassium, sodium mixed with barium, and sodium mixed with calcium.

7. The process of claim 6 wherein the reducible metal halide is selected from the group consisting of titanium tetrachloride and zirconium tetrachloride.

8. A reduction process for the production of metal, which process includes the steps of

a. introducing into a reaction zone without premixing molybdenum sulfide and a reducing metal selected from the group consisting of sodium, potassium and lithium and mixtures thereof, said molybdenum sulfide and said reducing metal being introduced in amounts providing not more than 10 percent excess of either reactant over stoichiometric requirements for complete reduction of the molybdenum sulfide to molybdenum metal,

b. sealing the reaction zone,

c. heating the reactants without substantial agitation from a temperature below the melting point of the reducing metal to a temperature which is both above the melting point of the reducing metal and below the temperature at which a reduction reaction between the molybdenum sulfide and the molten reducing metal will proceed spontaneously,

d. initiating a reducing reaction between the molybdenum sulfide and the molten reducing metal by suddenly disrupting the surface of the molten reducing metal by means of a mechanical force sufficient to provide a dispersion of the reducing metal in initmate contact with the molybdenum sulfide,

e. permitting the reduction reaction to continue to thereby produce molybdenum metal,

f. thereafter removing said molybdenum metal from the reduction zone.

9. The process of producing titanium metal which comprises:

a. introducing titanium halide and sodium into a reaction zone without pre-mixing and in amounts providing not more than 10 percent excess of either reactant over stoichiometric requirements for complete reduction of the titanium halide to titanium metal;

b. sealing the reaction zone;

c. heating the reactants without substantial agitation from a temperature below the melting point of sodium to a temperature which is both above the melting point of sodium and below the temperature at which a reduction reaction between the titanium halide and molten sodium will proceed spontaneously;

d. initiating a reduction reaction between the titanium halide and molten sodium by suddenly disrupting the surface of the molten sodium;

e. permitting the reduction reaction to continue to thereby produce titanium metal; and

f. thereafter removing consolidated titanium metal from the reaction zone.

10. The process of claim 9 wherein the titanium halide comprises titanium tetrachloride and wherein the titanium halide and sodium are present in amounts providing not more than 5 percent excess of either reactant.

11. The process of claim 9 wherein the titanium halide comprises titanium tetrachloride and wherein the titanium halide and sodium are present in substantially stoichiometric proportions.

12. The process of claim 11 wherein the maximum temperature of step (*c*) is between 120° and 400° C.

13. The process of claim 11 wherein the disruption of step (*d*) is caused by sudden vertical shaking of the molten sodium.

14. The process of producing zirconium metal which comprises:

a. introducing zirconium halide and sodium or mixtures of sodium and calcium into a reaction zone without pre-mixing and in amounts providing not more than 10 percent excess of either reactnat over stoichiometric requirements for compelte reduction of the zirconium halide to zirconium metal;

b. sealing the reaction zone;

c. heating the reactants without substantial agitation from a temperature below the melting point of sodium or the mixture of sodium and calcium to a temperature which is both above the melting point of sodium or the mixture of sodium and calcium and below the temperature at which a reduction reaction between the zirconium halide and molten sodium or mixture of sodium and calcium will proceed spontaneously;

d. initiating a reduction reaction between the zirconium halide and molten sodium or the mixture of sodium and calcium by suddenly disrupting the surface of the molten sodium or the mixture of sodium and calcium;

e. permitting the reduction reaction to continue to thereby produce zirconium metal; and

f. thereafter removing consolidated zirconium metal from the reaction zone.

15. The process of claim 9 wherein the zirconium halide comprises zirconium tetrachloride and wherein the zirconium halide and sodium or mixtures of sodium and calcium are present in amounts providing not more than 5 percent excess of either reactant.

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