

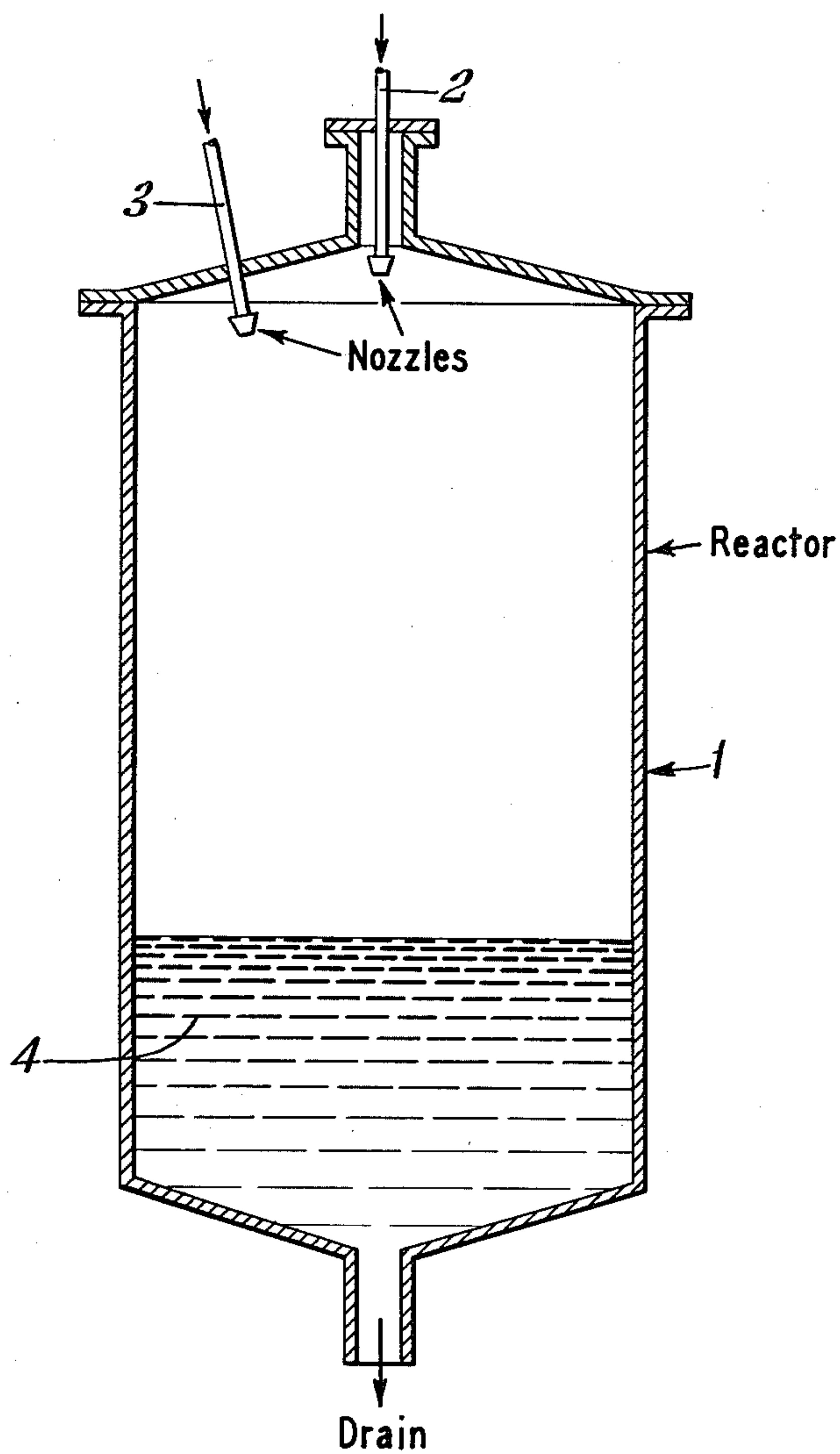
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PROCESS FOR PRODUCING REACTIVE METALS

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PROCESS FOR PRODUCING REACTIVE METALS
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This invention relates to a method for producing reactive metals selected from the group consisting of titanium, vanadium, columbium, molybdenum, and tantalum.

Titanium, vanadium, columbium, molybdenum, and tantalum have a great number of actual and potential uses. Titanium especially is of great interest at this time, for example, for use in the construction of aircraft. The many desirable properties of titanium metal and its abundant natural compounds have stimulated widespread searches for a practicable means of producing this metal.

It is the object of this invention to provide a method for producing metals selected from the group consisting of titanium, vanadium, columbium, molybdenum, and tantalum. It is a further object of this invention to provide a method for producing the above metals which results in relatively pure metal. Still another object of the invention is to provide a method for producing titanium of high purity on a commercial scale.

The objects of the invention are accomplished by reducing a halide of the metal to be produced, the reduction being effected by causing a solid stream of a liquid halide of the metal to be produced and a solid stream of molten alkali metal to intersect and intermix in a reaction chamber under an inert atmosphere. The materials are mixed in substantially stoichiometric proportions, some advantage being found in having a slight excess of the alkali metal present during the reaction.

The difficulties and obstacles encountered in the production of titanium metal are many and have thus far prevented the achievement of a fully satisfactory process for full scale commercial production. Both electrolytic and reduction processes have been investigated. The reduction process which perhaps has been used most widely involves the reduction of titanium tetrachloride with magnesium metal. Among the problems encountered in that process are those of separating magnesium chloride from the titanium and maintaining the magnesium in a molten condition during the reaction. The alkali metal, preferably sodium, used in the process of the invention, has a low melting point which facilitates its use in the molten state in a closed system. The use of such a metal also makes it easier to remove contaminants from the product of the reaction.

Some prior art methods have made use of amalgams of the reducing metal in order that the heat of reaction might be more carefully controlled and the temperature maintained at a lower value. These methods have the disadvantage of requiring a mercury removal step before a pure metal can be produced. By the method of the invention, the reaction is enabled to occur in one step at an elevated temperature.

One of the most serious problems involved in the reduction of a titanium halide is that of obtaining adequate agitation of the reactants. For a number of reasons mechanical agitation has proven unsatisfactory. To operate and properly lubricate bearings at high temperatures in the presence of corrosive materials is in itself a difficult undertaking. A long unsupported shaft with an impeller at its extended end loses strength and rigidity at high temperatures. Deposition of the solid products of the reaction further militates against mechanical agitation. The solution to the problem of mixing the reactants forms an important part of the present invention.

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The method of the invention will be described in more detail with respect to the reaction of titanium tetrachloride and sodium. The accompanying drawing is a schematic representation of apparatus in which the invention may be practiced.

The reaction is carried out in chamber 1 which is closed at both ends, preferably with its longitudinal axis vertical. Intersecting solid streams of liquid titanium tetrachloride and molten sodium are introduced into the chamber. The stream of titanium tetrachloride enters, for example, through inlet 2 and the molten sodium through inlet 3. The intersection of the streams provides for a rapid and thorough mixing of the reactants. The reaction to produce titanium metal and sodium chloride proceeds almost instantaneously and takes place in the liquid phase. The reduction reaction is highly exothermic and raises the temperature of the surrounding atmosphere to temperatures approximating 1300° C. to 1400° C. As the reactants are being introduced in stream form at very high velocity, the heat transfer from the surrounding atmosphere is very poor. For this reason, no difficulty is experienced in maintaining the liquid phase of the reactants up to the point of intersection. Titanium metal falls to the bottom of the vessel where it fuses as a sponge-like solid mass. The sodium chloride forms a molten pool. Very small percentages of the reactants fail to react immediately. When this occurs, the titanium tetrachloride vaporizes and the liquid sodium falls into the molten sodium chloride bath where it, too, is vaporized. A vapor phase reaction then takes place between the gaseous reactants. This vapor phase reaction is highly undesirable, however, as the titanium formed is deposited on the walls of the reaction vessel rather than with the main mass of sponge. By proper adjustment of velocities, applicants have been able to limit the titanium produced by vapor phase reactions to less than 1 percent of the total amount formed. The reaction proceeds in an inert atmosphere, preferably a monatomic gas such as argon, to prevent side reactions and contamination of the titanium metal.

To further minimize top and sidewall deposition, it is desirable to maintain the temperature of the chamber and of the reacting mass at the minimum practicable level. Maintaining the temperature of the outside walls of the reactor between about 800° C. and 1000° C. has been found to be eminently satisfactory.

In the preferred procedure, a small fraction, not more than about 10 percent, of the alkali metal is introduced into the reactor. The temperature of the reactor and its contents is adjusted to melt the metal. The remaining amounts of metal and halide are then introduced into the reactor as liquid streams through the nozzles 2 and 3 so that the mixing of the reactants is insured by the intersection of the two streams. The metal and halide are introduced in stoichiometric proportions until all of the metal is placed in the reactor at which time the remaining halide is added. The outer walls of the reactor are maintained at a temperature of below about 1000° C. during the addition of the reactants. This temperature is maintained by adjusting the amounts of reactants introduced and in some instances by cooling the outside of the reactor. For a time after the reactants are introduced the outer walls of the reactor are maintained at a temperature of between about 800° C. and 1000° C. to permit the completion of the reaction.

As alternatives to the preferred procedure, but still within the scope of the invention, the metal and halide may be introduced into the reactor in stoichiometric proportions without first providing a pool of metal in the reactor. Also, up to about ten percent of the metal may be placed in the reactor and the remainder of the reactants added at rates such that the last of one reactant is intro-

duced into the reactor at substantially the same time as the last of the other reactant.

To promote agitation and reaction, the reactants should be introduced into the reactor at substantial velocities. Satisfactory results have been obtained with nozzle velocities for the liquid reducing metal of between 2 and 100 feet per second and for the liquid halide of between 10 and 200 feet per second.

In one example of the invention one part by weight of sodium, 5 percent of the total sodium to be reacted, was charged into the reactor. The temperature of the sodium was maintained at about 100° C. The balance of the sodium, about 19 parts by weight, and the total amount of titanium tetrachloride, about 41 parts by weight, were introduced through the nozzles at a rate such that all of the sodium and all of the titanium tetrachloride were placed in the reactor at substantially the same time. The nozzles directed the solid streams of liquid sodium and liquid titanium tetrachloride along intersecting paths. Cooling was employed when necessary during the introduction of the reactants to maintain the temperature of the reactor below about 950° C. and above about 800° C. so that the sodium chloride formed by the reaction was maintained in a molten condition. Following the introduction of the reactants into the reactor, the reactor was held at a temperature of about 925° C. to complete the reaction.

In the example described above about 81 percent of the titanium introduced into the reactor was recovered in the form of titanium metal. The Brinell hardness of the metal was about 180.

In another example of the process of the invention about 41 parts by weight of titanium tetrachloride and a stoichiometric amount of sodium, about 20 parts by weight, were fed into the reactor. The feeding rates were such that the last of the sodium and the last of the titanium tetrachloride were fed into the reactor substantially simultaneously. Cooling was provided as before and the reactants held at 925° C. for about 5.5 hours to complete their reaction. In this example over 92 percent of the titanium was recovered in the form of metal. The Brinell hardness of the titanium product was about 127.

In still another example of the process of the invention about 958 pounds of sodium were fed into the reactor in a solid liquid stream at an average rate of 13.2 pounds per minute and at an average velocity of 50.3 feet per second. After about five percent of the sodium had been placed in the reactor, a solid stream of liquid titanium tetrachloride was directed into the reactor along a path such that it intersected the stream of sodium. The titanium tetrachloride was fed at a rate of about 13.2 pounds per minute and at an average nozzle velocity of about 50.3 feet per second until about 1980 pounds were introduced into the reactor. About five percent of the titanium tetrachloride was introduced after the last of the sodium had been placed in the reactor. The temperature of the reactor wall was maintained at a temperature of between about 700° C. and 900° C. After cooling, the product was removed and 98.5 percent of the titanium in the titanium tetrachloride was recovered in the form of titanium metal which had a Brinell hardness of approximately 158.5.

The metal produced may be removed from the reactor in any suitable way, as for example, by chipping or machining. The metal may be separated from the other reaction products by conventional techniques such as leaching.

This application is a continuation-in-part of application Serial No. 497,037, filed March 28, 1955, now abandoned.

What is claimed is:

1. A method for producing a metal selected from the group consisting of titanium, vanadium, columbium, molybdenum and tantalum which comprises introducing into a reactor containing an inert atmosphere a solid stream of liquid halide of said metal at a velocity in a range of from 10 to 200 feet per second and a solid stream of molten alkali metal at a velocity in a range of from 2 to

100 feet per second; intersecting, intermixing, and reacting said liquid halide and said molten alkali metal at their point of contact in a reaction consisting essentially of a liquid state reaction between said liquid halide and said molten alkali metal whereby top and side wall deposition is minimized; maintaining the temperature of the outer walls of said reactor below about 1000° C. during the introduction of said liquid halide of said metal and said molten alkali metal; and maintaining the outer walls of said reactor at a temperature between 800° C. and 1000° C. after said introduction of said liquid halide of said metal and said molten alkali metal and until the reaction is completed, whereby a molten halide of the alkali metal and a sponge-like solid mass of the product metal are formed.

2. A method for producing titanium which comprises introducing into a reactor containing an inert atmosphere in substantially stoichiometric quantities a solid stream of a liquid halide of titanium at a velocity in a range of from 10 to 200 feet per second and a solid stream of molten sodium at a velocity in a range of from 2 to 100 feet per second; directing said streams along intersecting paths to effect the intermixture and reaction of said liquid halide of titanium and said molten sodium at their point of contact in a reaction consisting essentially of a liquid state reaction between said liquid halide of titanium and said molten sodium whereby top and side wall deposition is minimized; maintaining the temperature of the outer walls of said reactor below about 1000° C. during the introduction of said liquid halide of titanium and said molten sodium; and maintaining the outer walls of said reactor at a temperature between about 800° C. and 1000° C. after said introduction of said liquid halide of titanium and said molten sodium and until the reaction is completed, whereby molten sodium chloride and a sponge-like solid mass of titanium are formed.

3. A method for producing titanium which comprises providing a pool of molten sodium in a reactor, containing an inert atmosphere, introducing into said reactor a solid stream of molten sodium at a velocity in a range of from 12 to 100 feet per second and a solid stream of liquid titanium tetrachloride at a velocity in a range of from 10 to 200 feet per second, said streams being directed along intersecting paths and towards said pool of molten sodium, said streams intersecting and intermixing and said liquid titanium tetrachloride reacting with said molten sodium; stopping the introduction of molten sodium into said reactor and continuing the flow of liquid titanium tetrachloride until the amount of titanium tetrachloride in said reactor is sufficient to react stoichiometrically with the molten sodium in said reactor; said reactions consisting essentially of liquid state reactions between said liquid titanium tetrachloride and said molten sodium whereby top and side wall deposition is minimized; maintaining the temperature of the outer walls of said reactor below about 1000° C. during the introduction of said liquid titanium tetrachloride; and maintaining the outer walls of said reactor at a temperature between 800° C. and 1000° C. after the introduction of said molten sodium and said liquid titanium tetrachloride and until the reaction is completed, whereby molten sodium chloride and a sponge-like solid mass of titanium are formed.

4. A method for producing titanium which comprises providing in a reactor, containing an inert atmosphere, a quantity of molten sodium, introducing into said reactor a solid stream of liquid titanium tetrachloride at a velocity in a range of from 10 to 200 feet per second and a solid stream of molten sodium at a velocity in a range of from 2 to 100 feet per second, the total sodium in said reactor being in stoichiometric proportions to the product metal and the initial quantity of sodium in said reactor being up to 10 percent of said sodium to be reacted; directing said streams along intersecting paths to effect the intermixture and reaction of said molten sodium and said

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liquid titanium tetrachloride in a reaction consisting essentially of a liquid state reaction between said liquid titanium tetrachloride and said molten sodium whereby top and side wall deposition is minimized; said stream of molten sodium and said stream of titanium tetrachloride being introduced at rates such that the introduction of the two materials into said reactor is accomplished substantially simultaneously; maintaining the temperature of the outer walls of said reactor below about 1000° C. during the introduction of said molten sodium and said liquid titanium tetrachloride; maintaining the outer walls of said reactor at a temperature of between about 800° C. and 1000° C. after said introduction of said molten sodium and said liquid titanium tetrachloride and until the reaction is completed, whereby molten sodium chloride and

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a sponge-like solid mass of titanium are formed; removing at least a part of the sodium chloride formed in a molten state and separating the remainder of said sodium chloride from the titanium formed.

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