METHOD OF MINIMIZING PRODUCT BUILDUP IN THE PRODUCTION OF METAL INCLUDING TITANIUM AND ZIRCONIUM

Filed Sept. 29, 1953
METHOD OF MINIMIZING PRODUCT BUILDUP IN THE PRODUCTION OF METAL INCLUDING TITANIUM AND ZIRCONIUM

Christian E. Rick, Wilmington, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

Application September 29, 1953, Serial No. 383,077

9 Claims. (Cl. 75—84.5)

This invention relates to the production of metals, especially the group IV-A metals, titanium and zirconium. More particularly, this invention relates to an improvement in processes for the reduction of metal halides, especially titanium halides, by a fluid reducing metal.

My invention may be described by considering the commercial adaptation of known methods for the production of titanium metal wherein a reducing metal is added in the fluid state, i.e., in the liquid or vapor state, to an atmosphere of a titanium halide. In such processes, serve clogging of the nozzle introducing the fluid metal to the reaction space is encountered. My invention is directed to relief from this problem and provides an improved method for the addition of the fluid reducing agent. Prior processes illustrating types in which my invention may be advantageously employed are disclosed by Maddex in U. S. Patent 2,556,763 in which liquid magnesium is added to an atmosphere of titanium tetrachloride and by Weintraub in U. S. Patent 1,306,568 in which reducing metal vapors are introduced into a reaction zone containing vapors of the metal halide to be reduced.

These are illustrative of the types of processes in which a serious amount of difficulty will be encountered with clogging of the nozzle for introducing the fluid reducing metal.

My invention has as one object an improved method for introducing fluid reducing metals into a reaction zone. Another object of my invention is to provide a method which will minimize the clogging of inlet nozzles for fluid reactants. Further objects are to provide an improved method for the addition of the fluid reducing metal in which the clogging will be minimized thereby permitting continuous reduction operations for extended operating periods.

These and other objects are accomplished by my invention which is an improved method for the introduction of a fluid reducing metal into a reactor, wherein a metal halide is to be reduced, and which comprises shielding the inlet flow of the fluid reducing metal with a sheath of molten metal halide salt, selected from the class of alkali and alkaline earth metal halides.

My invention is most applicable to continuous reduction processes for preparing the group IV-A metals. In this type of reaction, the fluid reducing metal and the halide of the fourth group metal must be added to the reaction zone in a regulated manner, usually with a slight excess of reducing metal, so that the product metal will be produced continuously. This requires that the flow of the reducing metal must not be interrupted or hindered in any manner. It has been found that soon after the introduction of the reducing metal through the plain pipe nozzle inlet shown in prior art methods that the reducing metal "wets" the feed pipe and a reactive surface of the reducing metal coats the inlet nozzle surface. This coating of reducing metal then reacts with the metal halide and produces a growth of the product metal on the nozzle structure. Soon after the initial portion is produced, further amounts of the metal are formed because of clogging disturbances on the inlet stream and the process proceeds rapidly to a state where the nozzle is completely clogged or where the direction and the amount of reducing metal cannot easily be controlled.

My invention protects the incoming fluid stream of reducing metal with a sheath or protective layer of molten alkali or alkaline earth metal halide salt. The molten salt prevents contact of the reducing metal with the inlet nozzle portion that is within the reactor vessel and in contact with the metal halide vapor. By preventing the contact of the reducing metal with this portion of the apparatus and presenting a barrier between the reducing metal and the metal halide in portions of the apparatus which are liable to clog, the primary causes of clogging and formation of reducing metal in that portion of the apparatus are overcome.

It is apparent from discussions in the prior art that certain advantages accrue from the simultaneous addition of the reducing metal and metal halides into the reactor. In Kroll U. S. Patent 2,206,854 such an operation is disclosed with the comment that certain advantages occur because from the beginning always the proper mixture is caused to react. If such an operation is attempted, using an ordinary inlet for feeding the fluid reducing metal into the reaction zone it will be found that the reaction will be terminated very quickly by clogging of the inlet port.

The simplicity of my improved method is revealed by reference to the drawing showing a suitable inlet or nozzle for admission of fluid reactants into reaction chambers maintained at high temperature. Two fluids are fed through the two concentric tubes or pipes, 1 and 3. The fluid metal reactant, e.g., molten magnesium, is fed through the inner pipe 1 and an inert molten salt e.g. molten magnesium chloride, is allowed to flow or is forced through the outer pipe 3 and through the annular space 2 thereby producing a stream of the metal reactant surrounded by a film or sheath of inert molten salt at the point where the metal reactant enters the hot reaction chamber and encounters the reactive gas within the said chamber. The sheath serves to prevent direct contact of the molten metal with the walls of the chamber which is suitably constructed of metal. This type co-axial nozzle permits the molten metal reactant to enter the reactor practically into the reactor as stream 4 and surrounded by molten salt sheath 5.

My invention may be illustrated by its application to the reduction process described in U. S. Patent 2,556,763, with additional details given in the Journal of Metals for April 1950, page 634, by Maddex and Eastwood. In this process molten magnesium is fed into an atmosphere of titanium halide. The magnesium inlet nozzle will become coated with titanium particles which will cause the magnesium stream to be deflected towards the wall and rapidly causes complete plugging and cessation of magnesium flow. The difficulty is revealed in the journal article and a proposed solution disclosed. A probe pin of the proper size is periodically pushed into and through the orifice used to admit the magnesium to the reaction chamber. The authors state that this operation "freees the orifice of any solid material" but complete removal of titanium metal is not realized in practise and at best the operation becomes intermittent. However, the operation of this prior art process when modified by insertion of an inlet nozzle similar to that shown in the drawing using magnesium with a protective sheath of molten magnesium chloride allows controlled and uninterrupted addition of the reducing metal.

My improved process is revealed in more detail by the following example which is given as illustrative of a simple embodiment of the invention and with the understanding that many variations of the same are possible.
Example

Molten magnesium at a temperature of 750° C. and at a rate of 100 pounds per hour was admitted to a large closed steel reaction chamber having an internal temperature in excess of 900° C. through a nozzle assembly such as that shown in the drawing and having a 0.5 inch central pipe. The outer pipe was so arranged that there was a 0.10 inch annular opening between it and the inner pipe and through this opening was forced a circumferential sheath of magnesium chloride having a temperature of about 800° C. The reaction chamber was filled with a gaseous mixture of titanium tetrachloride and argon with the internal pressure being maintained substantially constant by the addition of approximately 360 pounds of gaseous titanium tetrachloride per hour, i.e. the rate at which it is consumed by reaction with the reducing agent. The reaction continues smoothly without clogging of the reactor and as long as the reaction vessel can accommodate the reaction product mass.

My invention as exemplified above in its preferred embodiment is directed to the addition of a molten metal reducing agent to a reaction chamber having present therein a gaseous reactant. These molten metals, such as magnesium, wet the walls of the reaction vessel and there is a tendency for the metal reactant to creep over the surfaces of the vessel. The magnesium film in the case of a steel reaction vessel reacts with the titanium tetrachloride atmosphere and deposits titanium metal thereon. This titanium metal deposit is also wetted by the magnesium and, as a result, the mass of titanium adhering to the steel structure grows adjacent to the magnesium inlet and in course of time there is plugging of the magnesium inlet. The protective sheath of molten magnesium chloride surrounding the incoming stream of molten magnesium prevents the spreading of the magnesium reactant over the surface of the steel structure and it is believed that this is the explanation of my ability to operate for indefinite periods without plugging of the magnesiu inlet and without having to resort to the probe pin technique of the prior art.

It is obvious that the sheathing method herein described may be applied to many operations which produce various metals, such as titanium, zirconium, chromium, vanadium and the like. It may also be applied to the production of reduced chemical compounds of metals from volatile compounds of the same metal. An example of this is the production of titanium subchlorides from vaporized titanium tetrachloride, this being possible if a large excess of the tetrachloride in conjunction with a reducing metal such as sodium, potassium or magnesium. In any event, the molten metal reducing agent is kept out of contact of the walls of the reaction vessel by the film or sheet of molten salt admitted through an annular opening adjacent to the inlet for the molten metal. The temperatures at the metal inlet should be such that the metal is in a fluid state and the salt is above its melting point, but below its vaporization temperature.

In another process disclosed in Weintraub U. S. Patent 1,306,588 to an operable metal production unit having means equivalent in results to the elements illustrated in the drawing of the patent, it will be found that an inlet pipe for the reducing metal equivalent to feed tube of said drawing will present severe clogging difficulties in the reducing metal vapor, such as sodium, reacts with the metal halide vapor, such as titanium tetrachloride, deposing crystalline metal particles adjacent to the feed pipe inlet. This causes deflection of the inlet stream, recirculation of the reactants back toward the inlet feed pipe, and very rapid build-up around the feed pipe. My improved method of feeding the reducing metal, using sodium protected by a sheath of molten sodium chloride, minimizes this build-up tendency, prevents deposition of the product metal on the inlet nozzle, and allows controlled and uninterrupted addition of the fluid reducing metal.

In the operation of my invention the sheathing effect of the molten salt on the fluid reducing metal stream is necessary only for a short distance beyond the structure of the inlet. The inlet nozzle may be spaced some distance from the reaction zone and the stream may break up into drops of metal or it may be closely adjacent to the reaction zone. Although my invention may be operated most advantageously when the nozzle inlet is positioned so that the flow is downwardly it may be operated also in substantially horizontal positions. In the latter case, the protection of the metal stream will not continue as far from the nozzle as in the vertical position, but a very great advantage may be obtained over an unshielded nozzle inlet.

My invention is particularly successful in processes using as the reducing metal the alkali metals, especially lithium, sodium, and potassium, and the alkaline earth metals, magnesium, calcium, strontium and barium. The reducing metals of commercial interest are sodium and magnesium and calcium. The reducing metal may be added as a fluid in the liquid or vapor state.

The melting and boiling points of the various materials suitable for use in my invention are known from such references as L. L. Quill, "The Chemistry and Metallurgy of Miscellaneous Materials," pp. 28, 30, 196, 197; McGraw-Hill (1950). Mixtures of metal reducing agents or of sheathing halides are contemplated such as Na-K alloys with NaCl-KCl shielding fluid. Materials of construction for handling molten reducing metals are discussed in "Liquid-Metals Handbook," A. E. C., Department of the Navy, June 1, 1950, Washington, D. C.

The molten salt utilized as the shield or sheathing means may be selected from the group of alkali and alkaline earth metal halide salts. Most advantageously the shielding fluid is obtained by draining from the reaction zone the by-product halide produced by the reduction reaction. A portion of the drained by-product halide is utilized as the molten salt shielding fluid. The use of a shielding fluid having elements not present in the reducing metal or metal halide reactants is contemplated in certain cases. Such an instance may occur with the reduction of titanium tetrachloride by magnesium in which the molten salt shielding fluid may contain sodium chloride. In this instance the mixed salt from the reaction will have a lower melting point than magnesium chloride thereby making the drainage of the by-product salt from the reactor much easier.

It is contemplated to utilize as the metal halide to be reduced, the halides, that is the fluorides, chlorides bromides and iodides of the metal, especially those halides of titanium, zirconium and hafnium. Other metal halides may be utilized in my invention, such as the halides of iron, chromium, vanadium, etc.

When it is found in certain reaction systems that clogging of the reducing metal inlet port is prevented by my invention, but that the metal halide inlet port presents a clogging problem, the method of my invention may be utilized to prevent clogging at this entrance port. Many modifications of the nozzle inlet structure may be made. If it is desired to protect the outer surfaces of the inlet nozzle illustrated in the drawing the molten salt may be allowed to flow over the exterior of this by drilling small holes from the outer surface of the nozzle. The droplets of molten salt from these surfaces is especially useful when the temperature of the reaction is high enough to allow vaporization of some of the reducing metal which then may condense on some of the exposed colder surfaces of the nozzle. The presence of the molten salt flow will prevent the accumulation of large amounts of this
condensate, it will return the reducing metal to the reaction zone and it may prevent condensation of pyrophoric reducing metal.

Preferred molten salt compositions have as their metallic element, the same element as the reducing metal or metals higher in the electromotive series, the nonmetallic element is preferably the same halogen as is present in the metal halide to be reduced. However, other salts may be employed, as for example when the molten salt removed from the reactor is to be used as the electrolyte for recovery of the reducing metal by electrolysis. For this purpose the molten salt composition is selected so as to produce an acceptable cell feed, such as the use of sodium chloride molten salt protection of magnesium and subsequent electrolysis of the sodium and magnesium chlorides to recover magnesium. The temperature of the molten salt employed as a protective sheath should be about the melting point of the reactant but below the vaporization temperature of the molten salt and preferably about the same temperature as the fluid reactant being fed to the reactor.

In the operation of a metal process such as described in U.S. Patent 2,556,763, the molten salt shielding fluid may be obtained as the by-product salt from the reaction by draining as described. The molten salt is recovered and a portion retained in the molten state in a head tank for this purpose. If small particles of metal are contained in the melt a screen or porous filter in the line to the shielding nozzle is advantageous. If by inadvertence the molten salt contains lower halides of the metal to be reduced, a preliminary step to remove them by treatment with reducing metal and then filtering to remove the product metal before flowing to the nozzle is advisable. In adoptions of my invention where the molten salt used as the protection sheath is not a by-product, salt mixing equipment suitable for use in the molten salt art may be utilized to provide the supply of shielding fluid. The thickness of the protective layer of molten salt is a variant in the operation and is best determined by experiment, but good results are obtained with thin layers of less than one sixteenth of an inch with thicker layers being operable although larger amounts of molten salt must be handled.

My invention achieves a useful improvement in processes for the reduction of metal halides by a fluid reducing metal by minimizing the feeding difficulties and permitting continuous operation of such processes for lengthy periods.

I claim as my invention:
1. A method for preventing reactor inlet clogging during introduction in molten state of a metal reducing agent selected from the group consisting of alkali and alkaline earth metals into said reactor for reaction therein at an elevated temperature with a vaporized reducible halide of a metal selected from the group consisting of titanium, zirconium, hafnium, iron, chromium and vanadium, comprising effecting said reducing metal introduction through a reactor inlet in the form of a stream and out of direct contact with the metal halide present in said reactor by sheathing said metal reducing agent for a short distance on its discharge into said reactor from said inlet within an annular, encircling layer of an inert molten halide salt selected from the group consisting of alkali and alkaline earth metal halides and mixtures thereof concurrently charged through said inlet with said molten metal reducing agent.

2. A method for preventing reactor inlet clogging during introduction of a magnesium in fluid state into said reactor for reaction wherein with vaporous titanium tetrachloride present therein to produce titanium metal, comprising effecting said introduction out of direct contact with the surfaces of said inlet and that portion thereof which would contact the titanium tetrachloride reactant by enclosing said magnesium metal reactant during its passage through said inlet and for a short distance beyond the structure of the latter within an inert molten metal salt selected from the group consisting of alkali and alkaline earth metal halides and mixtures thereof concurrently charged through said inlet with said metal salt.

3. An improved method for minimizing reaction product build up on and introducing a fluid reactant through an inlet into a reaction chamber wherein a vaporous halide of a metal selected from the group consisting of titanium, zirconium, hafnium, iron, chromium and vanadium, is maintained and reacted for reduction with a molten reducing metal selected from the group consisting of alkali and alkaline earth metals being charged as a stream through said inlet, comprising sheathing said stream at its point of introduction into said chamber against contact and reaction with the vaporous metal halide reactant present in said chamber by sheathing said stream at said point within a protective, surrounding molten metal halide salt selected from the group consisting of alkali and alkaline earth metal halides and mixtures thereof concurrently charged through said inlet with said stream.

4. An improved method for minimizing reaction product build up on and introducing a fluid reactant through an inlet into a reaction chamber wherein a vaporous chloride of a metal selected from the group consisting of titanium, zirconium, hafnium, iron, chromium and vanadium, is maintained and reacted for reduction with a stream of a molten reducing metal selected from the group consisting of alkali and alkaline earth metals being charged as a stream through said inlet, comprising sheathing said stream at its point of introduction into said chamber against contact and reaction with the vaporous metal chloride reactant present in said chamber by sheathing said stream at said point within a protective, surrounding molten metal chloride salt selected from the group consisting of alkali and alkaline earth metal chlorides and mixtures thereof concurrently charged through said inlet with said stream.

5. An improved method for introducing a fluid reactant into a reaction chamber wherein a vaporous chloride of a metal selected from the group consisting of titanium, zirconium, hafnium, iron, chromium and vanadium, is maintained and reacted for reduction with a stream of fluid reducing metal selected from the group consisting of alkali and alkaline earth metals being charged to said chamber from an inlet thereof, which comprises sheathing said stream from contact with said vaporous metal chloride reactant at its point of introduction into said chamber and for a short distance beyond the structure of said inlet within an enclosing protective sheath of an inert chloride of a metal selected from the group consisting of alkali and alkaline earth metals and mixtures thereof which is concurrently charged through said inlet with said stream, said inert chloride being at a temperature above the melting point thereof but below its vaporization temperature.

6. An improved method for introducing molten magnesium into a reaction chamber for reaction therein with vaporous titanium tetrachloride to effect reduction of the latter which comprises sheathing said molten magnesium from contact with said vaporous TiCl₄ at its point of introduction into said chamber and for a short distance beyond the reaction chamber inlet therefore within a protective, surrounding sheath of molten magnesium chloride which is concurrently charged through said inlet with said molten magnesium.

7. An improved method for introducing vaporous titanium tetrachloride with a molten alkaline earth reducing metal which comprises charging said metal reducing metal in the form of a stream into a reaction chamber containing the vaporous titanium tetrachloride reactant, and preventing contact of said reducing metal with the surfaces of the reducing metal inlet to said reactor and with said tetrachloride reactant at said inlet by encircling said stream
with a surrounding sheath of a molten chloride salt of said reducing metal being concurrently charged with said reducing metal through said inlet.

8. An improved method for introducing reactants for the production of titanium by reduction within a reaction zone of a vaporous titanium halide with a molten reducing metal selected from the group consisting of alkali and alkaline earth metals which comprises separately charging a stream of said vaporous titanium halide and a stream of said molten reducing metal into said reaction zone and preventing contact of said reactants at their point of introduction into and for a short distance beyond the structure of the reactor inlet therefor within a sheath of a molten chloride of a metal selected from the group consisting of alkali and alkaline earth metals and mixtures, thereof concurrently charged through said inlet with said stream.

9. An improved method for introducing a fluid reducing metal selected from the group consisting of alkali and alkaline earth metals into a reactor wherein vaporous titanium halide is being reduced by reaction with said reducing metal, comprising shielding said reducing metal from contact with said vaporous titanium tetrachloride at its point of introduction into and for a short distance beyond the structure of the reactor inlet therefor within a sheath of a molten chloride of a metal selected from the group consisting of alkali and alkaline earth metals being concurrently charged to said inlet with said reducing metal, said molten chloride being at a temperature above the melting point of said reducing metal but below its vaporization temperature.

References Cited in the file of this patent

UNITED STATES PATENTS

1,306,568 Weintraub June 10, 1919
1,536,176 Aldrich May 5, 1925
2,564,337 Maddex Aug. 14, 1951
2,607,674 Winter Aug. 19, 1952
2,618,549 Glasser et al. Nov. 18, 1952
2,647,826 Jordan Aug. 4, 1953
2,732,292 Jordan Jan. 24, 1956

FOREIGN PATENTS

296,867 Germany Mar. 13, 1917
827,315 France Jan. 24, 1938

OTHER REFERENCES