Aug. 12, 1958 M. P. HNILICKA, JR 2,847,205

PRODUCTION OF METALS

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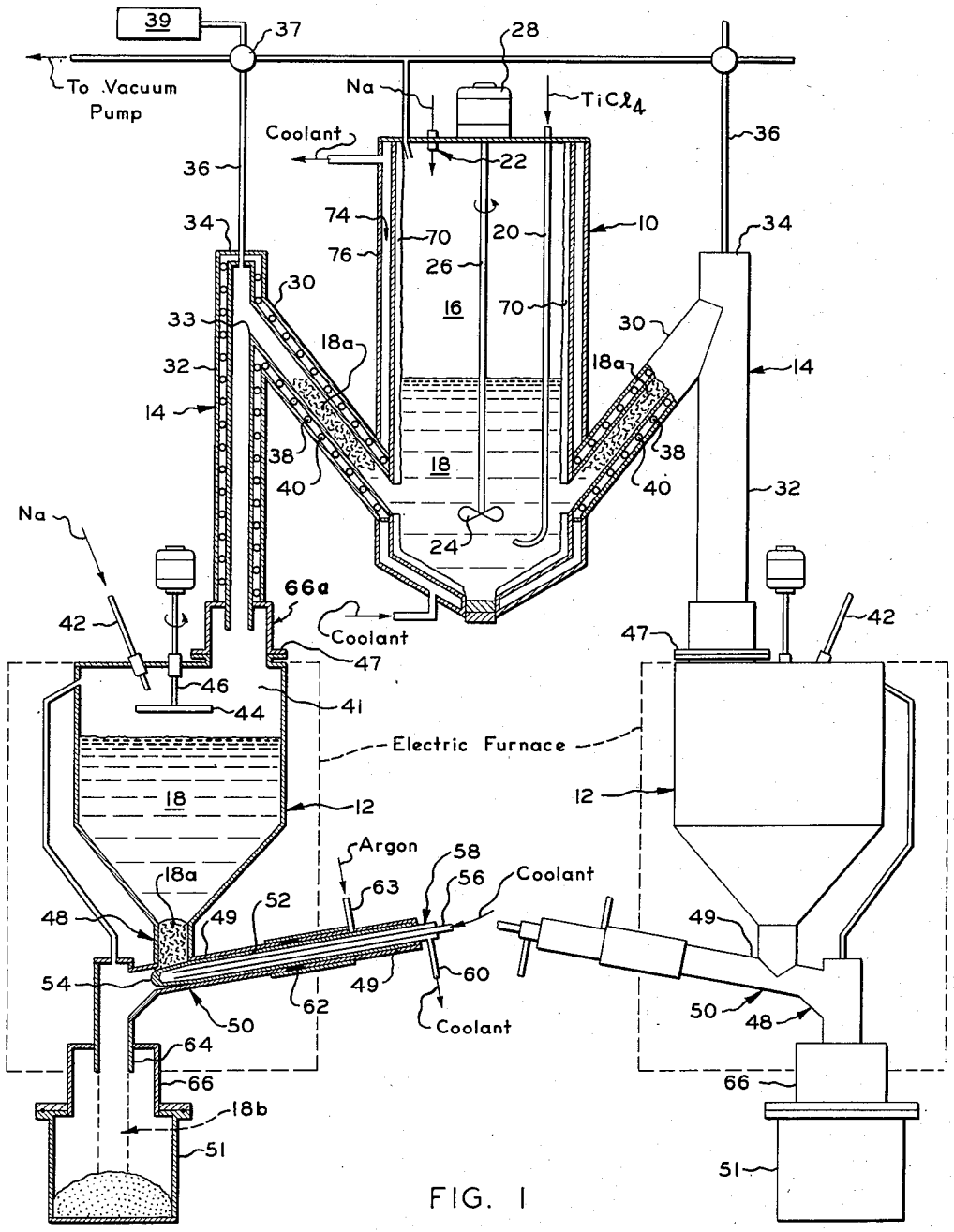



FIG. 1

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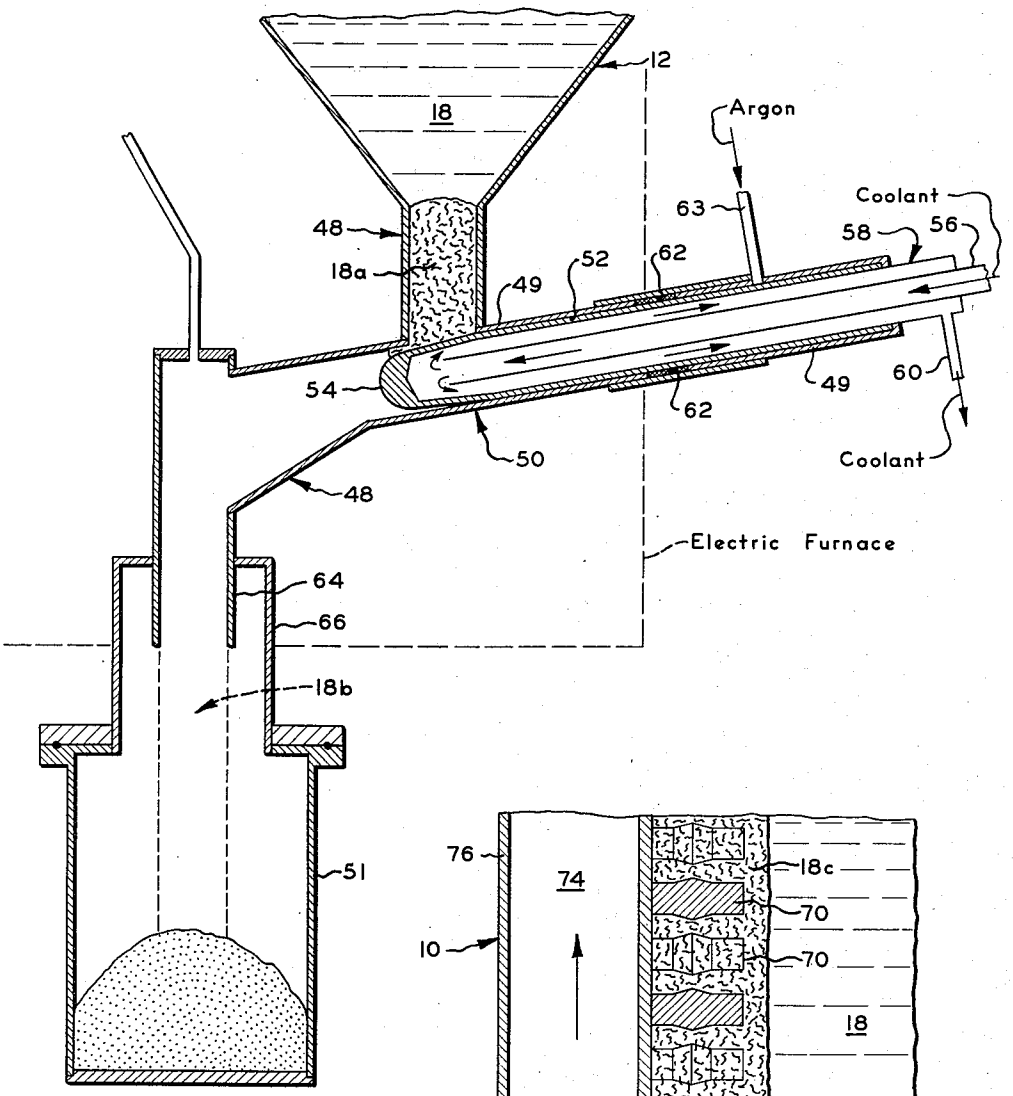



FIG. 2




FIG. 3

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2,847,205

# PRODUCTION OF METALS

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Application October 13, 1954, Serial No. 461,981

7 Claims. (Cl. 266—34)

This invention relates to the production of metals and more particularly to the production of refractory metals such as titanium and the like.

A principal object of the present invention is to provide an improved apparatus which is particularly adapted to the production of titanium and like metals by the reduction of a metal compound carried in a fused salt.

Another object of the invention is to provide an improved apparatus of the above type which is particularly adapted to large-scale operation with high rates of production.

Still another object of the present invention is to provide an improved apparatus of the above type which is particularly adapted for use with a process of the type described in the copending application of Keller et al., Serial No. 373,512, filed August 11, 1953.

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

The invention accordingly comprises the apparatus possessing the construction, combination of elements and arrangement of parts which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawings wherein:

Fig. 1 is a diagrammatic, schematic drawing illustrating one preferred embodiment of the invention;

Fig. 2 is a diagrammatic, enlarged detail of a portion of Fig. 1; and

Fig. 3 is a diagrammatic, enlarged detail of another portion of Fig. 1.

In the production of metals such as titanium, as described in the aforementioned copending application of Keller et al., it is preferred that the two-stage reduction of the titanium chloride be employed. In the first stage, sodium is preferably employed to reduce titanium tetrachloride to titanium dichloride which is dissolved in the by-product sodium chloride. In the second stage, this solution is reduced to titanium metal. It is also important that the second stage of the reduction be carried out gradually so that a relatively long time is involved in the reduction of mass of dissolved lower titanium chloride to titanium metal. It is also quite desirable that the two stages of the reduction be separated into two different pieces of equipment. Accordingly, each first stage reactor is preferably arranged so as to feed a number of second stage reactors. Since the second stage reactors are preferably sequentially filled from the first stage reactor and are sequentially removed from the system to provide for substantially continuous operation of the first stage reactor, it is necessary to provide for isolation of the various second stage reactors from the first stage reactor.

These objectives of the invention are achieved by providing a plurality of pipes which lead from the first stage reactor to the various second stage reactors, there being one such pipe for each second stage reactor. In a



preferred embodiment, a portion of each of these pipes is higher than the bottom of the first stage reactor so that the molten salt flowing from the first stage reactor to one of the second stage reactors must flow upwardly in this portion. The apparatus also preferably includes means for providing a sufficient gas pressure on the surface of the molten salt in the high portion of each pipe to overcome the hydrostatic salt pressure from the reactor and to thereby stop the flow of salt through the pipe. Associated with each pipe is a means for freezing the pipe which has thus been immobilized. This arrangement permits the formation of a solid salt plug which completely isolates the first stage reactor from that second stage reactor fed by the plugged pipe. This permits removal of the second stage reactor for emptying, cleaning and the like. When flow is to be resumed through the plugged pipe, the plug is melted by a suitable mechanism and the pressure-equalizing mechanism is adjusted so as to again permit flow of molten salt upwardly in the high portion of the connecting pipe. In one preferred embodiment of the invention, this pressure-equalizing mechanism comprises a vacuum-breaking vent line with necessary valving extending from the top of the first stage reactor to a high point in the syphon system, which includes the upwardly extending portion of the drain pipe and the following downwardly extending portion having its outlet port substantially lower than the intake port in the bottom of the first stage reactor.

Referring now to the drawings, there is shown in Fig. 1 one preferred arrangement of elements embodied in the present invention. In this Fig. 1, the first stage reactor is indicated at **10** as feeding a number of second stage reactors **12** by means of suitable pipes **14**. The first stage reactor comprises a reaction chamber **16** containing a charge of molten salt **18** within which there is achieved a partial reduction of titanium tetrachloride to a solution of titanium lower chlorides in sodium chloride by reaction of about two moles of sodium with one mole of titanium tetrachloride, as described more fully in the aforementioned copending application of Keller et al., Serial No. 373,512. In achieving this partial reduction, titanium tetrachloride is preferably introduced below the surface of the fused salt **18** by means of a tube **20**. The requisite amount of sodium is preferably introduced to the top of the fused salt by means of a pipe **22**. During this first stage reduction, the salt is preferably highly agitated by means of a stirrer **24** carried on a hollow rotating shaft **26** which is driven by a motor **28**. This shaft **26** is preferably provided with means for cooling by gas or liquid (not shown) and the stirring provides for a relatively uniform solution of titanium lower chloride in the by-product sodium chloride. The walls of the first stage reactor are preferably chilled so as to maintain a protective layer of frozen salt thereon (see Fig. 3).

Each of the connecting pipes **14** preferably constitutes a syphon fluid transfer system and includes an upwardly extending portion **30** and a downwardly extending portion **32**, the junction of these two portions including a lip **33** and a top portion **34** to which a pressure-equalizing line with provisions for opening or closing is connected. The pressure in the pressure-equalizing line is preferably controlled by means of a valve **37** which can either connect the line to the space above the level of the salt in the first stage reactor, or can connect the pipe **36** to an exhausting device such as a vacuum pump or to a supply **39** of a pressurized, inert gas such as argon. A heating coil **38** is provided around drain pipe sections **30—32**, and a cooling coil **40** is provided about one section of the upwardly extending pipe portion **30**.

The second stage reactor **12** preferably comprises a reaction chamber **41** adapted to carry a predetermined charge of molten salt **18** whose titanium chloride con-

tent is gradually reduced to titanium crystals by means of sodium added through a pipe 42 and uniformly distributed across the surface of the fused salt by means of a spinning disc 44 carried by a rotating shaft 46 of the type more fully described and claimed in the co-pending application of Hellier, Serial No. 442,525, filed July 12, 1954. Suitable flanges are provided as indicated at 47 for connecting the pipe 14 to the reactor 12. Each second stage reactor 12 is preferably arranged so that the salt charge therefrom can be drained through a passage 48 past a valve 50 into a sump 51.

This valve 50, as shown in greater detail in Fig. 2, preferably includes a cylindrical tube 49 which communicates with the side of the passage 48 and carries a hollow plug 52 which can be moved from a completely retracted position within tube 49 into a position where it nearly completely blocks the passage 48. In Fig. 2, the plug 52 is shown in its passage-blocking position. This hollow plug 52 has a tapered end 54 and preferably includes an internal refrigerant distribution passage 56 through which a refrigerant such as water or the like may be fed to refrigerate the plug and thus freeze the molten salt surrounding the plug in the unblocked portion of the passage 48. The coolant, which is either a gas or a suitable fluid such as water, Dowtherm or liquid metal, enters the hollow plug through a tube 58 and departs through a tube 60 so that the maximum chilling is achieved adjacent the tapered end 54. A packing 62 is preferably provided near the exterior end of the cylindrical tube 49 so as to prevent leakage of air into the system. A shown, this packing is preferably far removed from the molten salt 18. A positive pressure of an inert gas such as argon is provided by means of an inlet 63 so as to furnish an inert gas bleed inwardly through the packing 62. This prevents travel of the salt 18*a* up to the packing 62 and prevents damage to the packing by the high temperature of the salt and/or freezing up of the molten salt within the packing. An electric furnace (shown in dotted lines) is preferably provided around the cylindrical tube 49 and the adjacent portion of the tube 48 so as to permit remelting of the frozen salt plug when it is desired to empty the second stage reactor.

That portion of the passage 48 leading from the valve 50 to the sump 51 is so arranged that an effective heat barrier is provided which permits high temperature operation of this portion of the equipment to prevent unwanted freezing of the flowing salt while still providing for the use of gasketed connections near these high temperature portions. This heat barrier is formed of a downwardly extending pipe 64 communicating with the passage 48, this pipe 64 being inwardly spaced from the walls of a tube 66 communicating with the top of sump 51. Due to this arrangement, the pipe 64 guides the hot molten salt in a narrow stream indicated at 18*b* which is spaced from the tube 66. Accordingly, pipe 64 can be at the temperature of the molten salt (e. g., 850° C.) while the bottom of the tube 66 can be maintained at 100° C. or less, this being particularly true when tube 66 is made of thin-walled stainless steel tubing which has relatively poor heat conductivity.

As mentioned briefly above, the wall of the first stage reactor 10 is preferably protected from contact with titanium tetrachloride by means of a layer 18*c* of frozen salt. This layer of frozen salt is preferably maintained in position by means of anchoring studs 70 or other metallic protrusion made of thermally conductive material and attached to the cooled wall in such a manner that an efficient heat transfer furnishing a low temperature gradient between anchoring means and wall is secured. In one preferred embodiment, as shown more clearly in Fig. 3, these studs 70 can be on the order of ¼ inch to 1 inch in length and are welded to the inner wall 72 of the reactor 10. Because of the intimate heat transfer from the wall to the large surface of the studs 70, the frozen salt layer may be maintained by forced circulation of a cooling liquid, such as diphenyl or the like, in a suitable cooling channel 74 provided by means of an exterior wall 76. Because the heat conductivity of solidified salt is much lower than that of the metal wall and the anchoring studs, the frozen salt layer 18*c* represents an effective heat barrier which will consume the major part of the temperature drop between the molten salt bath and the cooling medium. At a given release of exothermic heat by the reaction within the molten salt medium, the frozen salt layer 18*c* will assume a definite thermal equilibrium thickness of frozen salt. If the released reaction heat and, consequently, the heat flux is high, the frozen salt heat barrier melts away until sufficiently thin to remove substantially all the heat. If the heat flux is low, the frozen salt regenerates its thickness until a new equilibrium is reached. This frozen salt layer constitutes not only an efficient means for reducing the operation temperature of the reactor wall (containing molten salt at a high temperature) to normal operating limits of construction, but it also provides a self-regenerating, non-contaminating refractory lining for the reactor.

In a preferred embodiment of the invention, when sodium chloride is utilized as the salt 18, an initial layer 18*c* of sodium chloride, in paste form, may be applied to the studs 70. The paste is then dried to bond the salt to the anchoring studs 70 and to remove any moisture. During operation of the first stage reactor, the exterior of wall 72 is preferably maintained at about 300° F. by the intensive heat exchange with the cooling fluid passing through channel 74. Meanwhile, the exothermic reaction taking place within the fused salt 18 will maintain the main body of this salt molten and will provide a relatively high flux through the frozen salt layer. This heat flux can be as high as 40,000 B. t. u. per hour per square foot while still maintaining a layer of frozen salt 18*c* of about 0.35 inch in thickness.

In the operation of the complete equipment illustrated in Figs. 1, 2 and 3, the apparatus is treated so as to remove all air and water vapor such as by evacuating and/or purging by an inert gas such as argon. A charge of molten anhydrous salt sufficient to fill all of the upwardly extending portions 30 of the tube 14 to the level indicated in Fig. 1 is then preferably poured into the reactor. Because the pressure-equalizing lines are open, the level in the reactor 10 and the risers 30 will be identical as in communicating vessels. If this initial level is below the overflow line 33, the riser or risers 30 are filled with stagnant molten salt. If desired, this initial salt charge may be a eutectic salt mixture having a melting point less than that of pure sodium chloride. The stagnant molten salt content in the riser can be used to form the various frozen salt plugs in the upwardly extending portions 38 by operating the cooling coils 40 so that all of the secondary reactors are isolated from the first stage reactor. Sodium and titanium tetrachloride are then fed into the first stage reactor, the titanium tetrachloride being preferably fed below the surface of the salt and the sodium being preferably fed above the surface of the salt. It is also preferred that slightly less than two moles of sodium be fed for each mole of titanium tetrachloride. During this feed, the salt is stirred by means of an agitator 24 so as to provide a uniform solution of titanium lower chloride in the salt. When the reaction has continued for a few hours so as to provide a relatively large mass of titanium lower chloride dissolved in sodium chloride within the molten salt inventory of the reactor 10, the melt level will have risen above syphon overflow 33. If one of the salt plugs 18*a* is then melted out by energizing the heating coil 38 in the upwardly extending pipe 30 and if the pressure-equalizing line 36 is closed, the syphoning effect will empty most of the salt solution from the reactor 10 into the secondary reactor 12, this solution passing through the heated line 14 and being stopped from further travel by means of frozen salt plug 18*a* in the

passage 48 at the bottom of the secondary reactor 12. When a sufficient charge of titanium lower chloride and sodium chloride has been fed to the secondary reactor 12, the upward flow of salt solution in the pipe 30 is stopped by breaking the vacuum in the upper section of the syphon venting pipe 36 to the top of the reactor by means of valve 37. If desired, at any time while the salt in pipe 30 is still molten, the syphoning action can be restored by application of suction to the space 34 by means of valve 37 and a vacuum pump (not shown). When the flow of molten salt is discontinued, reactor 10 can be sealed from reactor 12 by forming the frozen salt plug. Cooling fluid is then passed through the cooling coil 40 to freeze the immobilized salt solution in the pipe 30, thereby reestablishing the salt plug 18*a*. Operation of the first stage reactor is then continued to form another charge of titanium lower chloride dissolved in sodium chloride. When the predetermined charge has thus been formed and the level in the reactor 10 has risen above the overflow lip 33, the salt plug is melted and the charge is directed into another secondary reactor 12, as mentioned previously. Meanwhile, slow reduction of the titanium lower chloride contained in one or more of the secondary reactors 12 is being achieved by introducing sodium through the pipe 42 onto the spinning disc 44 so as to provide uniform distribution of the sodium across the surface of the fused salt mass. In a preferred embodiment of the invention, the secondary reduction takes place over a long period of time, on the order of a number of hours, so as to provide for the growth of relatively large crystals of titanium having low surface activity. When reduction has been substantially completed, the valve 50 at the bottom of the second stage reactor is preferably opened so as to dump the by-product salt into the sump 51. This is preferably achieved by stopping the flow of the cooling medium to the interior of the valve 50 so as to permit the melting of the salt surrounding the hollow plug 52. This melting may be speeded up by intensifying the heating in the furnace. The plug 52 can then be withdrawn so as to permit flow of the molten salt into sump 51 along the line 18*b* as illustrated in Fig. 2. The secondary reactor, drained of most of its salt, may then be removed from the system by breaking the downwardly extending pipe 32 at the flange 47, this flange being isolated from the hot salt by means of a heat barrier 66*a* similar to that illustrated in greater detail at 66 in Fig. 2. The contained titanium can be taken out, preferably by first water leaching with an acidified water spray jet. The secondary reactor is then preferably cleaned and a charge of molten salt is then poured into the tube 48 with the plugging means in the position shown in Fig. 2 and while water is circulated within the plug so as to freeze the molten salt running into contact with the plug 52. This reestablishes the frozen salt plug 18*a* at the bottom of the second stage reactor so that this reactor will be ready for another charge of lower chloride and molten salt.

The apparatus described above is preferably made of Inconel or nickel so as to be resistant to the corrosive action of titanium chlorides and sodium chloride or other halides employed. The apparatus is preferably run at atmospheric pressure or with a slight positive pressure of an inert gas such as argon. When the reaction mass comprises sodium chloride, a temperature on the order of 800° C. is preferred. A temperature somewhat lower than this may be maintained in the first stage reactor due to the eutectic formed by the titanium lower chlorides and sodium chloride. When halides of alkali metals and alkaline earth metals or mixtures thereof are used, numerous other temperature ranges can be employed. Quite low temperatures may be utilized when eutectic salt mixtures are provided. Numerous reducing agents other than the sodium or sodium-potassium alloy can be employed. For example, magnesium, calcium, lithium and various combinations of these elements may be utilized. From the standpoint of cheapness, sodium, sodium-potassium alloy or magnesium are preferred. Other halides of titanium may be utilized, although from the standpoint of cost, ease of handling, etc., the tetrachloride is preferred.

The present invention can be equally employed for the manufacture of other refractory metals by the reduction of suitable compounds carried in a fused salt. It can also be employed in the reduction of alloys, e. g., by the coreduction of several metallic compounds. Thus, if an alloy of titanium is to be formed, a chloride of a metal such as vanadium, chromium, manganese, iron and the like can be coreduced with the chloride of titanium. The same applies with respect to numerous other metallic elements. In this case, the alloy may be a binary alloy or it may be an alloy containing three, four or more constituents.

The salt mixture, as mentioned previously, can be formed of numerous halides of the alkali metals or alkaline earth metals and the salt can be a single halide or formed of a number of mixed halides. It can additionally include halides of materials other than the specific reducing agent or agents employed in the reaction. From the standpoint of simplicity of operation and ease of control, it is preferred, however, that the salt be the chloride of the reducing agent or agents employed.

It should be pointed out, in connection with a consideration of the various salts which can be employed, that these salts should be completely anhydrous and free of any contaminants such as carbon, nitrogen, oxygen or hydrogen, this being particularly true when titanium is to be formed, due to the tremendous reactivity of titanium metal at temperatures on the order of 800° C.–900° C. and above.

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

What is claimed is:

1. Apparatus for producing a refractory metal by the reduction of a compound thereof carried in a molten salt, said apparatus comprising a first stage reactor, a plurality of second stage reactors, a plurality of pipes leading from the first stage reactor, each of said pipes connecting a second stage reactor with the first stage reactor, a portion of each of said pipes extending upwardly, means for providing a sufficient gas pressure on the surface of the molten salt in the upwardly extending portion of each pipe to overcome the hydrostatic salt pressure in the reactor to thereby stop the flow of salt through the pipe, and cooling means associated with each pipe for freezing the stationary salt to create a frozen salt plug in each pipe.

2. Apparatus for producing a refractory metal by the reduction of a compound thereof carried in a molten salt, said system comprising a first chamber, a second chamber, means defining a passage for molten salt connecting said two chambers, means for partially plugging the passage, and means for feeding a refrigerant to the interior of the plugging means.

3. Apparatus for producing a refractory metal by the reduction of a soluble compound thereof carried in a molten salt, said system comprising a first stage reactor, a plurality of second stage reactors, a plurality of pipes leading from the first stage reactor, each of said pipes connecting a second stage reactor with the first stage reactor, a portion of each said pipe being higher than the bottom of the first stage reactor, means providing sufficient pressure on the surface of the salt in the high portion of each pipe to overcome salt pressure from the reactor and thereby stop flow of salt through the pipe, means associated with each pipe for freezing the thus immobilized salt in each pipe, and means associated with each pipe for melting frozen salt in each pipe.

4. Apparatus for producing a refractory metal by the reduction of a soluble compound thereof carried in a molten salt, said system comprising a first chamber, a second chamber, means defining a passage for molten salt connecting said two chambers, a hollow plug movable into a position where it at least partially plugs said passage, and means for circulating a refrigerant to the interior of said plug for freezing molten salt in the partially plugged passage.

5. Apparatus for producing a refractory metal by the reduction of a soluble compound thereof carried in a molten salt, said system comprising a first chamber, a second chamber, means defining a passage for molten salt connecting said two chambers, an elongated hollow plug carried by a side tube communicating with said passage, said plug being mounted for retraction into said side tube to permit free flow of molten salt through said passage, said plug being movable from its retracted position to a position where it at least partially plugs said passage, and means for circulating a refrigerant to the interior of said plug for freezing molten salt in the partially plugged passage.

6. Apparatus for producing a refractory metal by the reduction of a compound thereof carried in a molten salt, said system comprising a first chamber, a second chamber, means defining a passage for molten salt connecting said two chambers, means for preventing salt from flowing through the passage, means providing a flanged joint having a gasket, and means for maintaining the gasket at a temperature much below the melting point the molten salt, said last named means comprising a downwardly extending pipe for directing flowing salt in a downwardly extending predetermined path, a second pipe, serving as a heat barrier, surrounding and being spaced from said path,



the top of said second pipe being secured to said downwardly extending pipe and the bottom of said second pipe being secured to said flange joint.

7. Apparatus for producing a refractory metal by the reduction of a compound thereof carried in a molten salt, said system comprising a first chamber, a second chamber, means defining a passage for molten salt connecting said two chambers, means for preventing salt from flowing through the passage, means providing a flanged joint having a gasket, and means for maintaining the gasket at a temperature much below the melting point the molten salt, said last named means comprising a downwardly extending pipe for directing flowing salt in a free-flowing vertical path, a second pipe, serving as a heat barrier, surrounding and being spaced from said path, the top of said second pipe being secured to said downwardly extending pipe and the bottom of said second pipe terminating in an outwardly extending flange forming a part of said flanged joint.

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