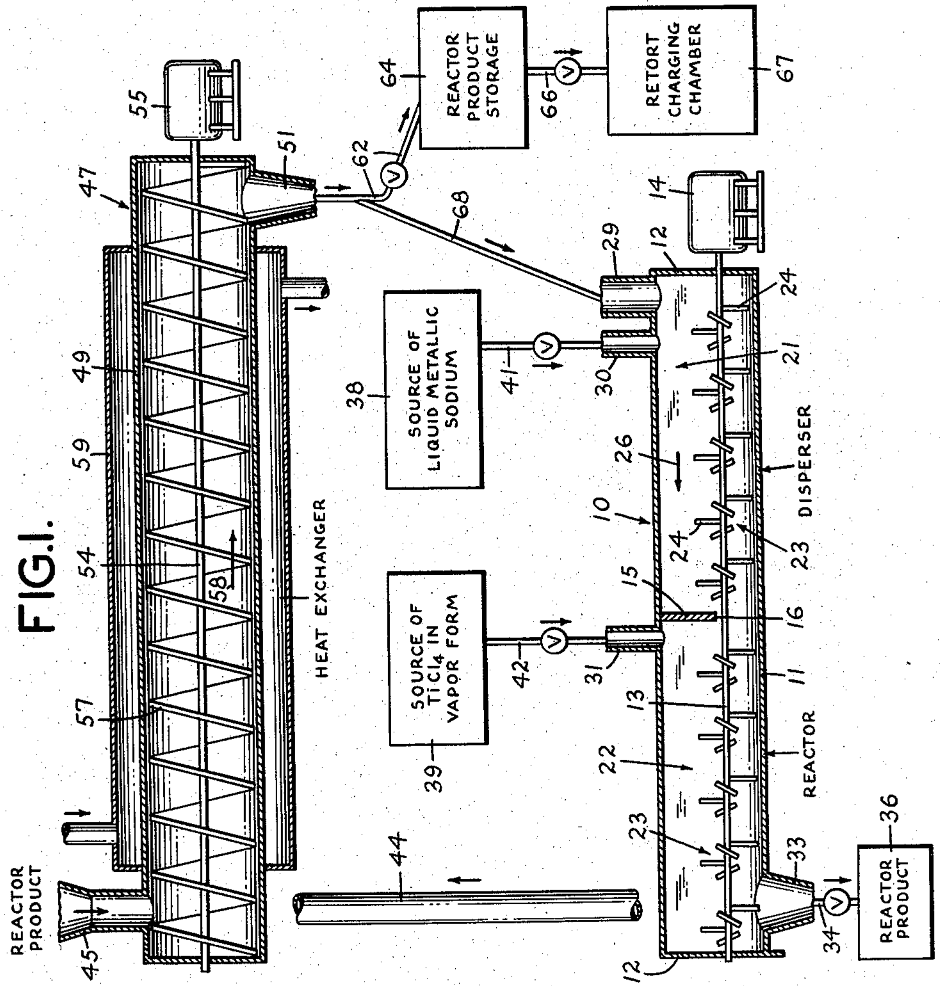
METHOD OF PRODUCING TITANIUM

Filed Aug. 22, 1955

2 Sheets-Sheet 1

FIG.1.



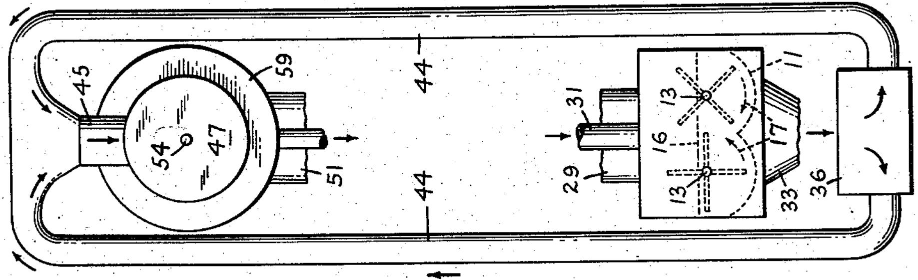


FIG.2.

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FIG.5.

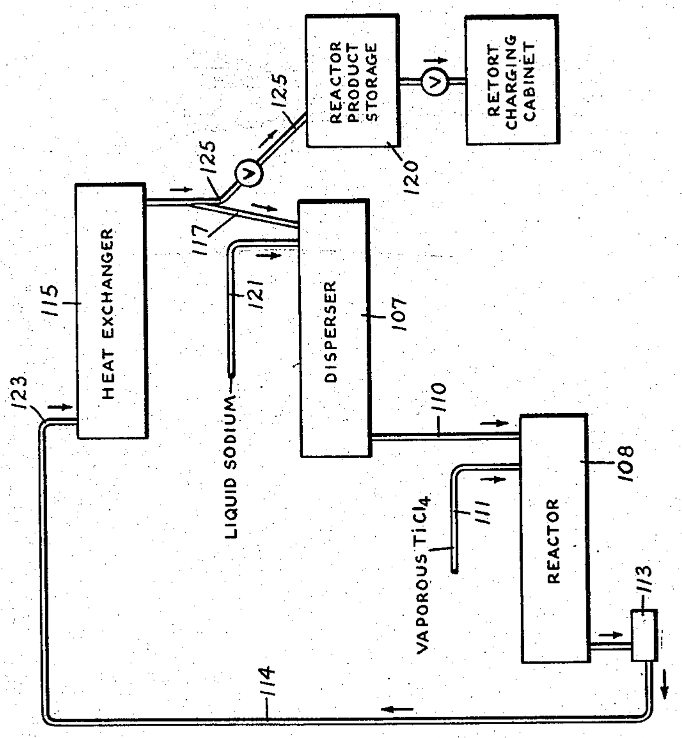


FIG.4.

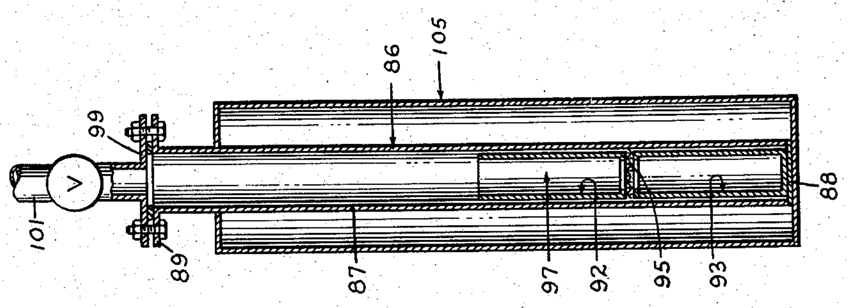
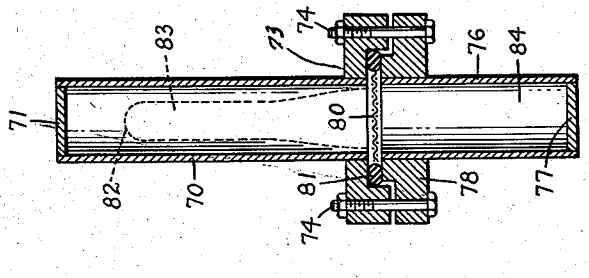


FIG.3.



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METHOD OF PRODUCING TITANIUM

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Application August 22, 1955, Serial No. 529,663
13 Claims. (Cl. 75—84.5)

This invention is directed to manufacture of metallic titanium.

It has been proposed to make metallic titanium by reducing titanium tetrachloride with an alkali metal e.g. elemental sodium. Known processes involve reaction at relatively low temperature of $TiCl_4$ with elemental alkali metal more or less dispersed on inert finely divided carrier material which may be alkali metal chloride or a portion of the reaction product of a previous cycle of operation. In the case of the use of elemental sodium, reaction products are sodium chloride, and metallic titanium which at this state exists in a finely divided, unstable more or less pyrophoric form. Subsequent to the reduction reaction, by procedures illustrated for example by Glasser et al. U.S. Patent 2,618,549 of November 18, 1952, the resulting reaction mass may be heated or furnaced at temperatures above about 800° C. primarily to convert the metallic titanium to a stable, ductile form which may be exposed to the air. Since this heating step is carried out at temperatures above the melting point of sodium chloride, the latter melts, and if desired at least some separation of sodium chloride and metallic titanium may be obtained for example by draining some of the molten sodium chloride away from the reaction mass while the latter is undergoing heating. In this situation, at the end of the heating operation, the furnaced material comprises a mixture of stabilized, ductile finely divided metallic titanium and some occluded sodium chloride. Following suitable cooling, the furnaced material, consisting of a solid, brittle mass more or less sponge-like in physical structure, may be ground and leached with water or weak hydrochloric acid to dissolve out the solidified residual sodium chloride. After leaching and drying of the resulting finely divided metallic titanium, the latter may be arc-melted and cast in ingot form. As known in the art, metallic titanium prior to stabilization is highly reactive with even very small amounts of elements such as oxygen and nitrogen, and therefore the entire operation up to completion of furnacing should be carried out in an inert atmosphere such as that formed by a blanket of relatively low positive pressure inert gas such as argon, krypton, or helium.

Heretofore, the advantages potentially possible by use of metallic alkali metal as reducing agent have not been fulfilled. A major object of the present improvement lies in provision of processes affording procedures which facilitate placing the $TiCl_4$-elemental alkali metal method for making metallic titanium on a continuous basis. Other objects include provision of processes which minimize formation of any substantial quantities of sub-quality titanium metal, and eliminate mechanical operational deficiencies, characterized by caking and balling up of solids, and plugging of the process dispersers, reactors, heat exchangers and connecting transfer lines, to such an extent that satisfactory continuous operation becomes possible. The invention is directed more particularly to provision of procedures for effecting manufacture, on a continuous basis, of reaction products consisting of

a mixture of alkali metal chloride and metallic titanium in the unstable form.

In accordance with one major feature of the invention, it has been found that manufacture of metallic titanium by the low temperature reduction of $TiCl_4$ by an alkali metal may be made continuous by effecting dispersion of the elemental alkali metal on the carrier material while in the absence of any significant amount of $TiCl_4$, and thereafter effecting the reaction of the thus dispersed alkali metal with $TiCl_4$ used in the vapor form. The invention includes other correlated operational factors which will appear from consideration of the following description taken in connection with the accompanying drawing, in which:

Figure 1 is a view, partly in longitudinal section and partly in diagrammatic elevation of apparatus which may be employed in accordance with the principles of the invention to effect formation of the metallic titanium-sodium chloride reaction product;

Fig. 2 is a diagrammatic end elevation of the apparatus of Fig. 1;

Fig. 3 is a longitudinal vertical section of one type of furnacing retort;

Fig. 4 is a longitudinal vertical section, partly diagrammatic, of a modified form of furnacing retort; and

Fig. 5 is a diagrammatic elevation of a modified form of the apparatus of Fig. 1.

Referring to Fig. 1, reference numeral **10** indicates generally a disperser-reactor comprising a horizontally elongated flat-topped, vertically-sided shell having a double U-shaped bottom **11** (Fig. 2), and supported in the position indicated by means not shown, and closed at either end by vertical end walls **12**. Conveyor-agitator shafts **13**, connected at one end to motor **14**, are rotatably mounted by suitable gas-tight bearings in end walls **12**. Attached to the under side of the shell top is a baffle **15** which is approximately rectangular in elevation as indicated by the dotted line **16** of Fig. 2. As shown in Fig. 1, the upper edge of baffle **15** is welded or otherwise connected in gas-tight relation to the contiguous portion of the shell top. The baffle extends downwardly to approximately the circumferences of shafts **13**, and in effect partitions the shell to form in one end thereof a dispersing zone **21** and in the opposite end a reaction zone **22**. In the embodiment illustrated, each shaft carries a multiplicity of groups **23** of radially disposed conveyor-agitator paddles **24**. Each group includes 4 paddles, and is axially spaced apart for adjacent groups on the same shaft, and is mounted in staggered relation with respect to adjacent groups on the other shaft. Paddles of a group are mounted in 90 degree relation to each other. Each paddle is adjustably attached to its shaft, and the paddles are formed and pitched so as to move solid material through the shell in the direction of the arrow **26**, and to effect, in conjunction with rate of rotation of the shafts, intense agitation of solids in the shell. Shafts **13** may be connected to rotate in the same or opposite directions.

The shell is provided at the dispersing zone end with an inlet **29** for recycled solids and with an inlet **30** for liquid alkali metal such as elemental sodium. $TiCl_4$ in vapor form may be introduced into the inlet end of the reaction zone **22** thru a feed pipe **31** placed close to the reaction zone side of baffle **15**. At the discharge end, shell **11** is equipped with a hopper-like outlet **33** which feeds reaction product thru a valved connection **34** into a reactor product chamber **36**. Numerals **38** and **39** respectively denote sources of liquid metallic sodium, and $TiCl_4$ in vapor form, which materials are conducted to shell inlets **30** and **31** thru suitable valve controlled pipe connections **41** and **42**.

As diagrammatically shown, particularly in Fig. 2, the interior of the reactor product chamber **36** is associated with an elevating conveyer, indicated generally by **44**, which transfers reactor product to the inlet **45** of a heat exchanger **47**. Structurally, exchanger **47** comprises an elongated cylindrical shell **49** having at the outlet end a discharge hopper **51**, and having rotatably mounted in gas-tight relation in the end walls a shaft **54** connected to motor **55** and carrying screw conveyor flight **57** rotated and pitched to move solid material in the direction of the arrow **58**. Shell **49** is jacketed as at **59** to provide for circulation of heat transfer medium ordinarily needed for cooling of solid material being passed thru shell **49**. The discharge hopper **51** of the heat exchanger is connected thru a valve controlled outlet conduit **62** with a product receiver **64** which in turn communicates thru a valve controlled transfer pipe **66** with a retort charging chamber **67**. A chute **68** affords means for feeding recycled solids to dispersing zone inlet **29**.

All of the equipment thus far described may be made of any suitable non-corrosive and non-product contaminating material such as mild steel. Further, as previously indicated, the processes which may be carried out in such equipment are effected preferably under a relatively low positive pressure (e.g. 2 to 10 inches of water) of an inert gas such as argon, helium and krypton. Hence, all of the apparatus described is equipped with various inert gas supply tanks under pressure of such gas, pipe connections, gauges, etc., not shown, arranged to maintain all of the materials being processed, from the control valves in sodium and $TiCl_4$ inlet pipes **41** and **42** thru and including the interior of retort charging chamber **67**, under the desired positive pressure of inert gas.

Fig. 3 illustrates one type of retort in which the metallic titanium-sodium chloride reactor product may be furnaced. This retort, which may be of stainless steel throughout, comprises a cylinder **70** one end of which is closed gas-tight by disk **71**. Welded to the lower end of cylinder **70** is a flange **73** drilled to accommodate bolts **74**. The bottom end of the retort comprises a similar cylinder **76** the bottom of which is closed by a disk **77**, and to the upper end of which is welded a flange **78**. Clearance and formation of contiguous faces of flanges **73** and **78** are sufficient to permit, in the assembled form, clamping of screen **80** between adjacent cylinder ends and the placing of an annular sealing gasket **81** between adjacent flange faces. Cylinder **70** above screen **80** provides a reactor product charge compartment **83**, and cylinder **76** below screen **80** affords a sodium chloride drainage and receiving compartment **84**. The furnace in which the retort of Fig. 3 may be placed is not shown.

Fig. 4 shows a modified type of furnacing retort **86** comprising an elongated cylinder **87**, gas-tight closed at the bottom by a disk **88** and provided with an integrally formed flange **89** at the top. Adapted to rest on the bottom of cylinder **87** is a second cylinder made in sections **92** and **93** in such a way that screen **95** may be securely clamped between such sections. Section **92** affords a reactor product charge chamber **97**, and section **93** provides a receiver for molten sodium chloride. The top of cylinder **87** may be closed by a disk **99** provided with a valved connection **101** for inert gas. The retort and accessories may be made of stainless steel. Numeral **105** designates a furnace shown diagrammatically into which retort **87** may be placed.

In the modified form of apparatus of Fig. 5, structurally the disperser **107** may duplicate substantially the reactor-disperser of Fig. 1 minus the partition **15** and the $TiCl_4$ inlet **31** of Fig. 1. The reactor **108** of Fig. 5 may be constructed substantially the same as the disperser **107** of Fig. 5 except that conduit **110** provides for transfer of the dispersion of sodium on recycled solids from disperser **107** to reactor **108** which is equipped with an inlet **111** for introduction of vaporous $TiCl_4$. Reactor product collector **113**, conveyer system **114**, and heat exchanger **115** of Fig. 5 may be substantially the same as corresponding apparatus units of Figs. 1 and 2.

Assuming use of elemental sodium as $TiCl_4$ reducing agent, the invention process involves low temperature reduction of titanium tetrachloride by means of elemental sodium dispensed throughout a great many times greater weight bulk of finely divided substantially free-flowing solid carrier material preferably consisting of a portion of the metallic titanium-sodium chloride reaction product of a previous reaction cycle. More particularly, but apart from certain hereinafter described operation factors, principal procedural features of the present improvements include continuously dispersing elemental sodium in liquid form on the carrier material in a dispersing zone in the substantial absence of titanium tetrachloride, preferably continuously transferring the thus dispersed elemental sodium and carrier material from the dispersing zone into a reaction zone while continuously feeding titanium tetrachloride in vapor form into the reaction zone to effect formation of a reaction mass comprising metallic titanium, sodium chloride and preferably a small amount of sodium, and continuously discharging such reaction mass from the reaction zone, it being understood that the entire foregoing operation is carried out in an inert atmosphere which, from a practical viewpoint, may be formed by a blanket of argon or other similar inert gas maintained under relatively low positive pressure.

Referring particularly to Fig. 1 of the drawing, practice of the invention includes provision of a source of feasibly pure titanium tetrachloride in vapor form, preferably held at temperature in the range of above the 136° C. vaporization point of $TiCl_4$ to 250° C. or higher, and at pressure high enough to facilitate charging vaporous $TiCl_4$ into the reaction chamber **22** against the back pressure of the argon gas blanket maintained therein. Operation also involves maintenance of a source of purified liquid metallic sodium. Storage tank **38** may be arranged to supply liquid sodium to dispersion zone inlet **30** at temperature in the range of say 110–225° C. Purified metallic sodium may be obtained by melting commercial metallic sodium, and filtering the molten material for example successively through 20 micron and 5 micron stainless steel filters.

In accordance with the invention, it has been found that the following additional principal procedural factors and control conditions interdependently contribute to the herein exemplified results: composition of the recycle, or sodium carrier, as introduced into the dispersion zone; physical nature and composition of the sodium-on-carrier dispersion, and the manner of making the same in the dispersion zone; reaction zone conditions including the carrying out of the Na—$TiCl_4$ reaction in the presence of a certain excess of sodium; relative and total amounts of Na and $TiCl_4$ fed into the process; weight ratio of recycled carrier to total weight of Na and $TiCl_4$ fed into the process; and formation of a reaction zone exit (which includes the "make" of a cycle) containing a certain amount of sodium.

The carrier of sodium or recycle used may be any relatively pure sodium chloride, or metallic titanium permissibly the unstabilized type, or any mixture of these materials. From practical standpoint, the carrier is finely divided substantially free-flowing solid material which is the metallic titanium-sodium chloride reaction product resulting from a previous reaction cycle. This material, usually sufficiently finely divided so that 100% passes a 10 mesh screen, may contain about 15–17% by weight of metallic titanium, although as shown by the herein appended examples, metallic titanium content is usually and preferably in the range of 16–17%. In the usual course of operations, such material contains small amounts of titanium subchlorides and corresponding small amounts of hereinafter more fully defined "unused reactant sodium." In accordance with one aspect of the invention, the recycle, as fed into the disperser, should contain some hereinafter more fully defined "stoichiometric excess sodium," at least 0.1% by weight, preferably 0.2–1.5%, and most desirably 0.2–1.0%, the purpose of which stoichiometric excess sodium content will hereinafter appear. Aside from the foregoing substances, the balance of the recycle material is NaCl.

A major feature constituting basis for successful continuous cyclic operation of the present process is formation of a thorough dispersion of metallic sodium on the carrier material. Because of high chemical activity of sodium, in order to satisfactorily control the course of reaction of $TiCl_4$ and sodium, it is necessary to distribute only a relatively small amount of metallic sodium throughout a relatively large body of carrier material which serves not only as a carrier for the "reactant sodium" reactable to produce cyclic "make" and other sodium not reactable to produce "make," but also functions as a reaction intensity and temperature control medium which smooths out temperature conditions in the reactor by taking up and distributing large quantities of heat. "Reactant sodium" is used herein to define the increment of metallic sodium which is fed into the process in amount substantially stoichiometrically equivalent to the total amount of introduced $TiCl_4$. In accordance with the invention, a finished dispersion as discharged from the dispersion zone contains not more than about 3.5%, preferably not more than 3.0%, by weight of total metallic sodium. Minimum total Na is not critical but is preferably 0.7% by weight. Further, it has been found that in order to put the $TiCl_4$—Na reaction on a successful continuous basis, the dispersion of sodium throughout the carrier should be effected in the substantial absence of $TiCl_4$. Development work shows that if formation of the dispersion is carried out in the absence of any significant amount of titanium tetrachloride, it is possible to bring about an even dispersion of sodium throughout the carrier, and more importantly, to effect formation of the dispersion in a dry and free-flowing physical condition which prevents balling and plugging-up in the dispersion zone and in subsequent apparatus units.

In view of ultimate teaching herein, starting-up procedure will be within the skill of the art, and hence for purpose of further delineation of details of the invention, it may be assumed that the process is under way, and that in addition to availability of vapor form $TiCl_4$ and liquid metallic sodium, there is also being discharged from the heat exchanger **47** a reactor exit of a previous cycle, part of which exit is process "make" and, by adjustment of the valve in exchanger outlet conduit **62**, is transferred to product collector **64**. The balance, constituting recycle of the above described composition, is passed thru chute **68** to the carrier material inlet **29** of the dispersing zone.

Operation effected in dispersion zone **21** is carried out at temperatures well above the 97.6° C. melting point of elemental sodium to insure absence of any solid sodium during formation of the dispersion. Ordinarily, overall temperatures in the dispersion zone should be held at not less than about 125° C., and in usual operation may lie in the range of about 140–200° C. Taking into account the size, capacity and normal radiation heat losses of a particular piece of apparatus, temperature control in the dispersion zone may be effected by regulating temperatures of incoming liquid sodium or carrier material or both. Primary purpose of heat exchanger **47** is to afford supply of carrier material to dispersion zone inlet **29** at temperature at least above the melting point of sodium. Usually, the heat exchanger functions as a cooler, but may under some circumstances be operated as a heater to bring up recycled reaction product to the required temperature prior to introduction into the zone **21**. Liquid sodium may be fed into the dispersion zone at temperature in the range of about 110–225° C., and recycled reaction product fed thereto at temperature in the range of about 140–200° C. It will be understood that for any given operation, temperature of incoming liquid sodium and recycle reaction product may be adjusted with respect to each other so as to maintain an effective minimum temperature in the dispersing zone.

Sodium fed into the dispersion zone thru supply pipe **41** should be such as to provide the preferred 0.7–3.0% total sodium to recycle weight values noted above.

Residence time and agitation in the dispersion zone are of importance. Residence time is a factor related mostly to particular apparatus. While in say a ten ton metallic titanium per day plant, residence time may vary from 2 to 8 minutes, because of permissible variability of overall operating conditions and of apparatus design, it is not possible to specify residence time suitable for all operations. As previously noted, conveyer-agitator design and permissible speed of rotation are such as to forward solids at the desired lineal rate while at the same time creating violent and intense agitating conditions. Preferably, the total volume of material in the dispersion zone and factors of agitator paddle design and rate of rotation are such that all during operation there is maintained in the dispersion zone a highly disseminated body of material occupying the lower two thirds or more of the dispersion zone. In the case of the particular apparatus of Fig. 1, the foregoing agitation conditions in conjunction with baffle **15** and the solids being discharged from the dispersion zone under the edge of the baffle and into the reaction zone form an effective vapor seal between the reaction zone and the dispersion zone in order to prevent the presence in the latter of any appreciable amount of $TiCl_4$. Hence, with the foregoing features in mind, for any particular design of apparatus, rate of conveyor-agitator rotation and optimum residence time in the dispersion zone may be determined by test runs.

Reduction of $TiCl_4$ effected in reaction zone **22** is exothermic. Reaction temperature therein may lie in the range of 150–350° C., but is more customarily and preferably in the range of about 175–300° C. Reaction zone temperatures below about 150° C. while useful are not conducive to best results. On the other hand, it is found that temperatures above about 350° C. are not required, this feature of the invention affording the advantage of use of conventionally constructed apparatus made of relatively inexpensive mild steel. Taking into account normal radiation heat losses from a given reaction zone, temperature control therein may be had by regulation of variables such as the amount of reactants present, temperature of dispersion fed into the reaction zone, and temperature of the $TiCl_4$ vapor charged thereto. Regulation of reaction zone temperature may be had primarily by adjustment of the temperature and to some extent quantity, of the recycled solids fed to the disperser. Such temperature may be selected with regard to other more or less fixed operating conditions so as to maintain temperature in the reaction zone at the desired levels.

In accordance with another feature of the invention, it has been found that $TiCl_4$ should be supplied to the reaction zone **22** in vapor form. This procedure appears to promote almost instantaneous reaction and minimization of subchloride formation. More importantly, vapor form supply of $TiCl_4$ avoids the presence of any liquid in the reaction zone, and experience indicates that this feature, in conjunction with the above described formation of the sodium dispersion on recycled solids, is a major contributing factor with regard to avoidance of apparatus plugging and placing the process on a successful continuous operation basis. $TiCl_4$ may be fed into the reaction zone at temperatures from slightly above the vaporization point up to 250° C. or higher if desired.

As shown by appended examples, the herein process is such that reduction of $TiCl_4$ to metallic titanium approaches theoretical. Nevertheless, from time to time the material exiting the Na—$TiCl_4$ reaction zone may contain variable relatively very small quantities of titanium subchlorides. In these instances, the reaction zone exit also contains "unused reactant sodium" which expression defines an increment of sodium which (*a*) was initially fed into the process as part of the "reactant sodium" and was unused because of incomplete reduction of $TiCl_4$ to Ti, and (*b*) exists in the reaction zone exit in amount corresponding with the titanium subchlorides content thereof, i.e. an amount which would have been used had all the subchlorides been fully reduced to Ti. It has been found that in order to insure the absence of titanium subchlorides in the final metallic titanium of the process, the material gathered in the reactor product collector **64** for preferred operation should contain a small amount of "stoichiometric excess sodium" which expression defines an increment of sodium over and above the quantity of sodium needed stoichiometrically to reduce all $TiCl_4$ to Ti. Thus, with respect to material gathered in collector **64**, "stoichiometric excess sodium" designates sodium over and above any "unused reactant sodium" which may be present. During a furnacing operation, subsequently to be described, stoichiometric excess sodium functions under the relatively rigorous furnacing conditions to drive to completion reaction of any titanium subchlorides and unused reactant sodium and thus clean up reduction of any subchlorides which possibly may be present. If not needed in the furnacing step to insure elimination of titanium subchlorides, the presence of stoichiometric excess sodium affords no disadvantages because of its ready separation from furnaced product by a leaching to be described. Thus, a feature of the invention comprises production of a $TiCl_4$—Na reaction zone exit containing the amount of stoichiometric excess sodium desired to be present in the cyclic make which may be continuously separated out of the circuit and fed into bin **64**. The stoichiometric excess sodium content of the reaction zone exit should be at least 0.1% by weight, may be as high as about 1.5%, and preferably is in the range of about 0.2–1.0%.

Another feature indicated by experience to be notably conducive to high reduction of $TiCl_4$ obtained in the reaction zone is maintenance therein of the presence of a substantial reaction zone excess of sodium over that theoretically required to completely reduce the $TiCl_4$ present. While any substantial reaction zone sodium excess is conducive to improvement of results, it has been found that the reaction zone operation should be such that there is constantly maintained therein preferably at least about 15% by weight excess sodium over that theoretically needed to reduce all $TiCl_4$ present to Ti. In most operations, such excess is well above the 15% indicated, but need not be above about 200%. In some practice, more desirable results are obtained when the excess is not less than about 20%. It is noted that the foregoing values do not include whatever relatively small quantities of unused reactant sodium which might possibly be present, i.e. brought into the reaction zone as a recycle constituent.

With regard to relative amounts of $TiCl_4$ and elemental sodium fed into the process circuit through supply pipes **42** and **41**, sodium is charged to provide a reactant sodium feed of at least and preferably just about a stoichiometric quantity of reactant Na on the basis of fed $TiCl_4$, i.e. at all times, $TiCl_4$ and at least an approximately stoichiometric quantity of reactant Na are continuously fed into the cyclic circuit. However, it will be noted that the "make" of each cycle is bled out of the circuit, and that the bled-out make takes out of the circuit the stoichiometric excess sodium content of such make. The thus lost stoichiometric excess sodium is referred to herein as "bleed loss sodium." Hence, continuously or intermittently there is introduced into the circuit, thru sodium supply conduit **41**, an additional amount of sodium, over stoichiometric Na requirements, approximately corresponding to the bleed loss sodium. Accordingly, it will be noted that all during operation, vaporous $TiCl_4$ is fed into the reaction zone in quantity which is less than that theoretically needed to react with all elemental sodium present, and also that, because of feed into the reaction zone of stoichiometric amounts of Na plus additional Na equivalent to bleed loss sodium, the above discussed reaction zone Na excess to be maintained present in the reaction zone always may be held constant at a chosen level, i.e. preferably not below the indicated 15% by weight.

The total weight of $TiCl_4$ and of "reactant Na" (which does not include the small amount of bleed loss sodium preferably used to offset Na loss in the make) fed into the circuit may be varied depending upon the quantity of carrier material recycled. A further feature of the invention comprises regulating the amount of recycle charged into the dispersion zone so as to provide in the reaction zone a preferred weight ratio of recycle to total weight of (*a*) fed $TiCl_4$ plus (*b*) an approximately stoichiometric equivalent of fed reactant Na, preferably approximately in the range of 60:1 to 25:1. Previous discussion shows that for best operation important process factors are (1) a dispersion zone exit containing not more than 3.5% by weight of total Na, preferably not more than 3%; (2) maintenance in the reaction zone of the presence of preferably at least a 15% excess of Na over that needed to theoretically react with all the $TiCl_4$ present; (3) and formation of a reaction zone exit containing stoichiometric excess sodium in amount preferably in the range of about 0.2–1.0% by weight. In accordance with the invention, it has been found that when $TiCl_4$ and the approximately stoichiometric quantity of reactant Na are fed into the circuit thru conduits **42** and **41**, and the recycle employed contains about 0.2–1.0% by weight of stoichiometric excess Na, if the preferred weight ratio range of 60:1 to 25:1 is utilized, operation is such that the three just previously named process factors are automatically maintained.

When, as preferred, the recycle employed contains 0.2–1.0% by weight of stoichiometric excess Na, the 25:1 weight ratio provides disperser zone exits containing about 1.5–2.3% by weight of Na; the presence in the reaction zone of a 15–75% by weight reaction zone excess of Na over that needed to react theoretically with all of the $TiCl_4$ fed (which reaction zone excess does not include whatever amount of Na may be introduced into the circuit to offset bleed loss sodium); and reaction zone exits containing about 0.2–1.0% by weight of stoichiometric excess Na. On the other hand, the 60:1 weight ratio provides dispersion zone exits containing about 0.7–1.5% by weight of Na; the presence in the reaction zone of about 36–180% by weight excess of Na over that needed to react theoretically with all the $TiCl_4$ fed; and reaction zone exits containing about 0.2–1.0% by weight of stoichiometric excess Na. When desired to insure the presence in the reaction zone of a greater minimum excess of sodium, operations may be conducted so that the described weight ratio is in the range of about 60:1 to 33:1. When using the 33:1 ratio and the preferred 0.2–1.0% by weight stoichiometric excess Na recycle, disperser zone exits may contain about 1.2–2.0% Na; the sodium excess in the reaction zone is in the range of about 20–100%, and reaction zone exits contain about 0.2–1.0% of stoichiometric excess Na. By way of further illustration, when employing apparatus similar to that shown in Figs. 1 and 5 of the drawing, assuming about 10 tons per day production of metallic titanium, substantially all heat removal from the system by means of heat exchanger **47**, a dispersion zone exit temperature of about 125° C., and use of a recycle containing about 0.2% by weight of stoichiometric excess Na, when working with a ratio of 33:1, the dispersion zone exit contains by weight about 1.2% Na, the reaction zone sodium excess present in the reaction zone is about 20% by weight, the reaction zone exit contains about 0.2% by weight of stoichiometric excess Na, and the reaction zone temperature sustains itself at about 250° C. or something a few degrees less. Herein given values as to Na content of dispersion zone exits do not include the whatever relatively small quantities of unused reactant Na which might possibly be present, i.e. brought into the disperser as a recycle constituent.

Agitation and residence time conditions in the reaction zone are generally comparable with those described in connection with the dispersing zone. Although in the reaction zone thorough agitation is equally important, residence time is not so much so since reaction for the most part appears to be instantaneous. Thus, residence time in the reaction zone approximately the same as that in the dispersion zone, while not necessary, beneficially promotes completion of reaction. Since volume of solids in the reaction zone increases in accordance with the make of any incremental portion of a reaction operation, the reaction zone solids volume runs higher than that of the dispersion zone. Accordingly, if desired, the paddles of the conveyer-agitator in the reaction zone may be more steeply pitched to effect more rapid passage of solids thru the reaction zone, this procedure being possible because residence time in the reaction zone may be appreciably less than optimum residence time in the dispersing zone.

By means of reactor exit product collecting and elevating apparatus indicated in Fig. 2, reactor product recovered in chamber **36**, ordinarily at temperature not much below the average temperature level existing in the reaction zone, may be introduced continuously into heat exchanger **47** via inlet **45**. Under practically all good operating conditions, the reactor exit as fed into the heat exchanger is at temperature above the temperature desired for recycled solids in chute **68** connected to dispersing zone inlet **29**. Rate of flow of cooling medium, such as a suitable oil, thru heat exchanger jacket **59**, and rate of movement of reactor product thru the heat exchanger are regulated primarily to facilitate feeding into chute **68**, at the proper temperature, that portion of reactor product to be recycled. The remainder of material discharged from the heat exchanger, corresponding to the process make, is transferred thru pipe **62** into the reactor product collecting bin **64**. As previously described, this material is dry, free-flowing and usually contains by weight about 16–17% titanium in the unstable form, small corresponding amounts of titanium subchlorides and unused reactant sodium, balance being NaCl plus preferably 0.2–1.0% of stoichiometric excess Na. The foregoing product, still blanketed by positive pressure argon, is then heat-treated at higher temperatures to convert the unstable metallic titanium to the stable, ductile form. Heat treatment may be effected in a retort such as shown in Fig. 3.

The retort is dismantled (bolts **74** removed) and placed in a retort charging chamber indicated at **67**. The chamber, communicating feed pipe and retort are air-evacuated and blanketed with positive pressure argon. The long end **70** of the retort is charged with solids from the reactor product storage bin **64** by transfer thru conduit **66**. The reactor is assembled with filter screen **80** and gasket **81** in place, the retort ends are bolted together, and the unit is removed from the argon atmosphere of the charging chamber to the air. The filter element **80** may be 0.04 inch wire cloth made of stainless steel. It will be understood that the solid material in the retort at this stage is still under the positive argon pressure existing in the charging chamber.

With the short end **76** of the retort down, the retort may be lowered into a gas-fired furnace (not shown) in which the material in the tube is heated for a substantial time at temperatures above the 804° C. melting point of sodium chloride and below the temperature at which metallic titanium begins to alloy with iron, i.e. about 975° C. More particularly, heating may be effected at temperature in the range of about 850 to 950° C. for from 2 to 4 hours. During heating, sodium chloride melts, and the metallic titanium is converted to the stable form. More or less sodium chloride drains thru filter **80** and collects in lower retort chamber **84**. In the course of furnacing, solids in the upper end of the retort shrink away from the side walls thereof, and on completion of heating the solid residue in compartment **83** is more or less rod-like in form approximated by the dotted line **82** shown in Fig. 3.

The tube is removed from the furnace, cooled and opened. The shrunk rod, easily shaken loose from the filter wire **80** and from any incidental points of contact with the lower periphery of the tube **70**, is a frangible, more or less sponge-like mass which in a typical operation as presently illustrated may contain by weight about equal parts of metallic titanium and solidified NaCl. This material is crushed to below ¼ inch, leached with about a 3% HCl solution, and then with water until chloride-free. The solid residue may be methyl alcohol washed and dried at about 60° C. in vacuum. The dried material is stabilized, ductile metallic titanium, i.e. so-called sponge, all of which passes about a 6 mesh screen. If desired, the product may be arc-melted and cast into ingots.

Furnacing of reactor product in the apparatus of Fig. 4 is approximately the same as in the retort of Fig. 3. Retort **86** is charged in retort charging chamber **67**, and then transferred to furnace **105**, after which the interior of retort **86** is kept under argon blanket by connecting an argon source to pipe **101** and opening the valve thereof. Subsequent operation may be substantially the same as noted in connection with the retort of Fig. 3.

Taking into consideration the 62.3° C. melting point of K, the 776° C. melting point of KCl, the 5° C. melting point of the equimolecular NaK alloy, and the approximately 660° C. melting point of the equimolecular NaCl—KCl mixture, it is within the skill of the art to use potassium or the NaK alloy in place of sodium in practice of the invention.

The following examples illustrate practice of the invention.

Example 1.—This operation was carried out in apparatus substantially the same as illustrated in Figs. 1 and 3 of the drawing. Internal axial length of the reactor disperser unit **10** was about 72 inches, internal vertical cross-sectional area about 1.25 sq. ft., and baffle **15** was located about midway of the unit. The unit was wrapped in a 1.5 inch layer of insulating material to reduce radiation losses. The interior of the entire apparatus thru and including the reactor product storage bin **64** was maintained all during operation at a positive pressure of argon of about 2 inches of water.

The following delineates average conditions over an approximately 3 day continuous run.

Reactor product from previous cycle, analyzing by weight about 0.5% stoichiometric excess Na, and with balance about 16.9% Ti and 82.6% NaCl (basis complete reduction of $TiCl_4$ to metallic Ti), was continuously fed thru chute **68** into disperser inlet **29** at temperature of a few degrees below 145° C. and at the rate of about 840 lbs./hr. Commercial metallic sodium was melted and purified by filtration successively thru 20 and 5 micron stainless steel filters. Purified liquid sodium (reactant sodium) was introduced into disperser inlet **30** thru conduit **41** at temperature of about 150° C. and at a rate of about 5 lbs./hr. The combined quantity of recycled solids and sodium fed provided about 40 lbs. of material in the dispersing zone during operation. Average temperature in the dispersing zone was of the order of 140°–160° C. Pitch of the conveyer paddles and the approximate 200 r.p.m. rotation of the conveyer shafts **13**, rotating in the opposite directions (arrows **17**, Fig. 2), maintained conditions of vigorous agitation and tumbling of material such that the dispersion zone was "flooded" to a level above the under edge of baffle **15** and provided residence time of incremental portions of the dispersion in the dispersion zone of about 3 minutes. Including the stoichiometric excess sodium contained in the recycled solids as fed into the dispersing zone, the Na content of the dispersion, as continuously discharged in a free-flowing condition into the reaction zone thru the relatively vapor-tight seal formed under the edge of baffle **15**, was about 1.1% by weight.

Vaporized $TiCl_4$ at temperature of above 140° C. was fed continuously into reaction zone inlet **31** thru inlet pipe **42** at rate of about 10 lbs./hr., i.e. substantially the amount of $TiCl_4$ theoretically needed to react with the reactant sodium fed in thru disperser inlet **30**. The total quantity of $TiCl_4$ introduced was such that, including the stoichiometric excess sodium content of the recycle and the reactant sodium fed into dispersed inlet **30**, there was present in the reaction zone about 4.2 lbs./hr. of Na in excess of that theoretically required to react with all the $TiCl_4$ charged, that is, the reaction as a whole was continuously carried out in the presence of not less than about an 84% by weight excess of sodium over theory. Exothermic reaction took place, and reaction zone temperature was within the range of about 200° to 230° C. Residence time and conditions of highly vigorous agitation of solids in the reaction zone were about the same as in the dispersion zone. Reactor product, which included "make" and recycled solids, was continuously discharged into reactor product receiver **36** at rate of about 855 lbs./hr. at temperature of approximately 220° C.

Such product was continuously fed into inlet **45** of heat exchanger **47** at a temperature of about 170° C. Heat transfer medium employed was conventional high temperature heat transfer oil. The particular heat exchanger employed was jacketed and equipped with a screw conveyer provided with means for circulation of cooling medium therethru. Inlet temperature and flow of cooling medium thru the jacket and thru the conveyer, and rate of rotation of the conveyer were such that solids were discharged continuously into heat exchanger outlet **51** at temperature of about 145° C. By suitable adjustment of the valve in transfer conduit **62**, about 840 lbs./hr. of solids were returned to the dispersing zone, the balance, constituting approximately the "make," was run into reactor product collecting bin **64** at the rate of about 15 lbs./hr. This product analyzed by weight 0.5% stoichiometric excess sodium, and with balance about 16.9% Ti and 82.6% NaCl (basis complete reduction of $TiCl_4$ to metallic Ti). Weight ratio of recycle to the total weight of fed $TiCl_4$ and fed reactant Na in this operation was about 56/1. During the course of the run, there was added a small but sufficient additional amount of sodium above overall theoretical requirements to offset the bleed loss sodium corresponding to the amount of stoichiometric excess sodium discharged into product collector bin **64** as a constituent of the make. In this manner, the presence of the above-noted 84% excess of sodium in the reaction zone **22** was maintained throughout the operation. The foregoing run was continuous without interruption, and no balling up of material or plugging of any of the apparatus was encountered.

A 5–6 pound sample of product collected in bin **64** was placed in a retort similar to that of Fig. 3 in the argon blanketed manner already described. The retort and the material contained therein were placed in a gas-fired furnace and heated therein at temperature in the range of about 850° to 950° C. for a period of about 4 hours. The retort was removed from the furnace, cooled, opened to the air, and the solid residue was found to be substantially all shrunk away from the retort walls and to be in the form approximately as indicated by the dotted line **82** in Fig. 3. The mass was easily shaken loose from screen **80** and the lower periphery of retort section **70**. Color was relatively light grey, and physical structure was cellular and more or less sponge-like. The quantity of sodium chloride which drained into retort bottom section **76** during furnacing was such that the solid residue recovered from retort section **70** contained about 50% by weight of metallic titanium and about 50% by weight of NaCl.

The foregoing material was crushed to pass 6 mesh, leached 3 times with a 3% HCl solution, and then water-washed about 4 times until filtrate was chloride-free. The water-washed material was then washed once with methyl alcohol and once with ether, and dried at about 60° C. in vacuum. Notwithstanding some known air leakage into the retort during furnacing, the dried material analyzed by weight not less than 99.5% Ti, and contained not more than 0.25% oxygen, 0.25% nitrogen, and 0.05% carbon. A sample of this sponge product was arc-melted under an argon blanket, and the resulting ingot had a Brinell hardness of 220.

Example 2.—This operation was carried out in apparatus substantially the same as illustrated in Figs. 5 and 4 of the drawing. Internal axial length of each of the disperser **107** and of the reactor **108** was about 72 inches, and internal vertical cross-sectional area of each about 1.25 sq. ft. Both units were wrapped in a 1.5 inch layer of insulating material to reduce radiation losses. The interior of the entire apparatus of Fig. 5 thru and including the reactor product storage bin **120** was maintained all during operation at a positive pressure of argon of about 9 inches of water.

The following delineates average conditions over an approximately two-week continuous run.

Reactor product from previous cycle, analyzing by weight about 1.0% stoichiometric excess Na, with balance about 16.8% Ti and 82.2% NaCl (basis complete reduction of $TiCl_4$ to metallic Ti), was continuously fed thru chute **117** into the inlet of disperser **107** at temperature of a few degrees below 170° C. and at the rate of about 1500 lbs./hr. Commercial metallic sodium was melted and purified by filtration successively thru 20 and 5 micron filters. Purified liquid sodium (reactant sodium) was introduced into the inlet of the disperser thru conduit **121** at temperature of about 180–200° C. and at a rate of about 10 lbs./hr. The combined quantity of recycled solids and sodium fed provided about 80 lbs. of material in the disperser all during operation. Average temperature in the disperser zone was about 165° C. Pitch of the conveyer paddles and the approximate 168 r.p.m. rotation of the conveyer shafts **13**, rotating in opposite directions as in Example 1, maintained conditions of vigorous agitation and tumbling of material such that the dispersion zone was "flooded" above the level of shafts **13** and provided residence time of incremental portions of the dispersion in the disperser **107** of about 3 minutes. Including the stoichiometric excess sodium contained in the recycled solids as fed into the disperser, the Na content of the dispersion, as continuously discharged in a free-flowing condition into transfer pipe **110** was about 1.7% by weight. The relatively small cross-section of conduit **110** and the downflow of solids into reactor **108** formed a seal which prevented the presence of any significant amount of $TiCl_4$ in the disperser **107**.

Vaporized $TiCl_4$ at temperature of about 220° C. was fed continuously into the reactor **108** thru inlet pipe **111** at rate of about 20 lbs./hr., i.e. substantially the amount of $TiCl_4$ theoretically needed to react with the reactant sodium fed into disperser inlet **30**. The total quantity of $TiCl_4$ introduced was such that, including the stoichiometric excess sodium content of the recycle and the reactant sodium fed into disperser inlet **121**, in the reactor there was present about 15 lbs./hr. of Na in excess of that theoretically required to react with all the $TiCl_4$ charged, that is, the reaction as a whole was carried out continuously in the presence of not less than about a 150% by weight excess of sodium over theory. Exothermic reaction took place, and reaction zone temperature was within the range of 200 to 250° C. Residence time and conditions of highly vigorous agitation of solids in the reaction zone were about the same as in the disperser. Reactor product, which included "make" and recycled solids, was continuously discharged into reactor product receiver **113** at rate of about 1530 lbs./hr. and at temperature of about 225° C.

Such product was continuously fed into inlet **123** of heat exchanger **115** at a temperature of about 185° C. Heat transfer medium employed was conventional high temperature heat transfer oil. As in Example 1, the heat exchanger was jacketed and equipped with a screw conveyer provided with means for circulation of cooling medium therethru. Inlet temperature and flow of cooling medium thru the jacket and thru the conveyer, and rate of rotation of the conveyer were such that solids were discharged continuously into heat exchanger outlet pipe **125** at temperature of about 170° C. By suitable adjustment of the valve in transfer conduit **125**, about 1500 lbs./hr. of solids were returned thru chute **117** to the disperser, the balance, constituting approximately the "make," was run into reactor product collecting bin **120** at the rate of about 30 lbs./hr. This product analyzed by weight about 1.0% stoichiometric excess Na, with balance about 16.8% Ti and 82.2% NaCl (basis complete reduction of $TiCl_4$ to metallic Ti). Weight ratio of recycle to total weight of fed $TiCl_4$ and fed reactant Na was about 50/1. During the course of the run, there was added a relatively small but sufficient additional amount of sodium above overall theoretical requirements to offset bleed loss sodium corresponding to the amount of stoichiometric excess sodium discharged into product collector bin **120** as a constituent of the make. By such procedure, the presence of the above noted 150% excess of sodium in the reaction zone **108** was maintained throughout the operation. The foregoing run was continuous without interruption, and no balling up of material or plugging of any of the apparatus occurred.

A 3 pound sample of product collected in bin **120** was placed in a retort similar to that of Fig. 4 in the argon blanketed manner already described. The retort and the material contained therein were placed in a gas-fired furnace and heated therein at temperature in the range of about 850 to 950° C. for a period of about 4 hours. The retort was removed from the furnace, cooled, opened to the air, and the solid residue was found to be substantially all shrunk away from the walls of compartment **97** and to be in the form approximately as indicated by the dotted line **82** in Fig. 3. The mass was easily shaken loose from screen **95** and the lower periphery of retort section **92**. Color was relatively light grey, and physical structure was cellular and more or less sponge-like. The quantity of sodium chloride which drained into retort bottom section **93** during furnacing was such that the solid residue recovered from retort chamber **97** contained about 50% by weight of metallic titanium and about 50% by weight of NaCl.

The foregoing material was crushed to pass 6 mesh, leached 3 times with a 3% HCl solution, and then water-washed about 4 times until filtrate was chloride-free. The water-washed material was then washed once with methyl alcohol and once with ether, and dried at about 60° C. in vacuum. The dried material analyzed by weight not less than 99.5% Ti, and contained not more than 0.2% oxygen, 0.05% nitrogen, and 0.05% carbon. Samples of this sponge product were arc-melted under an argon blanket, and the resulting ingots had a Brinell hardness in the range of 141–157, averaging 150.

Example 3.—Operation was continued under substantially the same conditions as given in Example 2, and at the end of about another week, a sample of "make" was processed as described to sponge which was converted to ingot form having a Brinell hardness of 134 and contained 0.036% nitrogen.

We claim:

1. In a substantially continuous multi-stage cyclic process for making metallic Ti involving a circuit comprising a dispersing zone for dispersing Na on solid finely divided carrier reaction product of a previous cycle, a separate reaction zone for reacting Na and $TiCl_4$ to form metallic Ti, a recycle of carrier reaction product thru said zones in the order named, and separation from the circuit of reaction product formed during a cycle, the steps comprising providing a recycle carrier consisting of reaction product of a previous cycle and containing metallic Ti, NaCl and about 0.2–1.0% by weight of stoichiometric excess Na, introducing said carrier into said dispersion zone, feeding elemental Na in liquid form into said zone and dispersing the fed Na on said carrier while at temperature high enough to insure absence of solid sodium but not higher than about 200° C. and while in the absence of $TiCl_4$, transferring the thus dispersed Na and carrier thereof into said reaction zone, feeding $TiCl_4$ in vapor form into said reaction zone while in the absence of sodium from source other than said dispersing zone and maintained at temperature in the range of about 175°–300° C. to effect formation of metallic Ti and NaCl from fed reactants, regulating relative amounts of Na and $TiCl_4$ charged to provide a Na feed of about a stoichiometric quantity of Na on the basis of fed $TiCl_4$ plus a Na excess approximately corresponding to the amount of bleed loss Na contained in hereinafter separated cyclic make, regulating the amount of recycle charged into the dispersion zone so as to provide in the reaction zone a weight ratio of recycle to total weight of fed $TiCl_4$ plus an approximately stoichiometric equivalent of fed Na substantially in the range of 60:1 to 33:1, discharging reaction mass from the reaction zone, separating from said mass reaction product in amount corresponding approximately to cyclic make, and recycling substantially the balance of said mass to the dispersion zone, the entire foregoing operation being carried out in an inert atmosphere.

2. In a multi-stage process for making metallic titanium involving low temperature reduction of titanium tetrachloride with elemental alkali metal, of the group consisting of sodium, potassium and NaK alloy, dispersed throughout a many times greater weight bulk of finely divided substantially free-flowing solid carrier material of the group consisting of alkali metal chloride, metallic titanium and mixtures thereof, the improvement comprising dispersing elemental alkali metal in liquid form on the carrier material in a dispersing zone while held at temperature such as to maintain alkali metal in liquid form and high enough to insure absence of solid alkali metal and while maintaining the absence of titanium tetrachloride, thereafter transferring the thus dispersed elemental alkali metal and carrier material thereof from said dispersing zone into a separate reaction zone while in the absence of alkali metal from source other than said dispersing zone and while feeding titanium tetrachloride in vapor form into said reaction zone and while maintaining therein moderately elevated temperature substantially below the fusion point of the chloride of the reducing alkali metal but high enough to effect production of a reaction mass comprising metallic titanium and alkali metal chloride, and discharging said reaction mass from said reaction zone, the entire foregoing operation being carried out in an inert atmosphere.

3. In a substantially continuous multi-stage cyclic process for making metallic Ti involving a circuit comprising a dispersing zone for dispersing alkali metal on solid finely divided carrier reaction product of a previous cycle, a separate reaction zone for low temperature reduction of $TiCl_4$ by alkali metal to form metallic Ti, a recycle of carrier reaction product thru said zones in the order named, and separation from the circuit of reaction product formed during a cycle, the steps comprising providing a recycle carrier consisting of reaction product of a pre-

vious cycle and containing metallic Ti and alkali metal chloride, introducing said carrier into said dispersion zone, feeding into said dispersion zone liquid elemental alkali metal, of the group consisting of Na, K and NaK alloy, the amount of metal being restricted so as to provide in the dispersion zone a many times greater weight bulk of carrier, passing thru said dispersion zone said alkali metal and said carrier while held at temperature such as to maintain alkali metal in liquid form and high enough to insure the absence of solid alkali metal, and while in the absence of $TiCl_4$ and while under conditions of residence and vigorous agitation both sufficient to effect dispersion of said metal on said carrier, thereafter discharging the mass of thus-dispersed elemental metal and carrier from said dispersing zone and introducing said mass into said separate reaction zone, feeding into said reaction zone vaporous $TiCl_4$ in quantity less than that theoretically needed to react with all the elemental alkali metal present, maintaining in said reaction zone moderately elevated temperature high enough to effect reduction of $TiCl_4$ to metallic titanium and substantially below the fusion point of the chloride of the reducing alkali metal, passing the reactants thru said reaction zone while in the absence of alkali metal from source other than said dispersing zone and while under conditions of temperature, residence and vigorous agitation all sufficient to effect formation of a reaction mass comprising metallic Ti, alkali metal chloride and elemental alkali metal, discharging said reaction mass from the reaction zone, separating from said mass reaction product in amount corresponding substantially to cyclic make, and recycling substantially the balance of said mass to the dispersion zone, the entire foregoing operation being carried out in an inert atmosphere.

4. In a substantially continuous multistage cyclic process for making metallic Ti involving a circuit comprising a dispersing zone for dispersing alkali metal on solid finely divided carrier reaction product of a previous cycle, a separate reaction zone for reacting alkali metal and $TiCl_4$ to form metallic Ti, a recycle of carrier reaction product thru said zones in the order named, and separation from the circuit of reaction product formed during a cycle, the steps comprising providing a recycle carrier consisting of reaction product of a previous cycle and containing metallic Ti and alkali metal chloride, introducing said carrier into said dispersion zone, feeding into said dispersion zone liquid elemental alkali metal, of the group consisting of Na, K and NaK alloy, the amount of metal being not substantially in excess of 3.5% by weight of total fed metal and carrier, passing thru said dispersion zone said alkali metal and said carrier while maintained at temperature not higher than about 200° C. but high enough to insure the abence of solid alkali metal, and while in the absence of $TiCl_4$ and while under conditions of residence and vigorous agitation both sufficient to effect dispersion of said metal on said carrier, thereafter discharging the mass of thus-dispersed elemental metal and carrier from said dispersing zone and introducing said mass into said separate reaction zone, feeding into said reaction zone vaporous $TiCl_4$ in quantity less than that theoretically needed to react with all the elemental alkali metal present, maintaining temperature in said reaction zone in the range of about 150–350° C., passing the reactants thru said reaction zone while in the absence of alkali metal from source other than said dispersing zone and while under conditions of residence and vigorous agitation both sufficient to effect formation of a reaction mass comprising metallic Ti, alkali metal chloride and elemental alkali metal, discharging said reaction mass from the reaction zone, separating from said mass reaction product in amount corresponding substantially to cyclic make, and recycling substantially the balance of said mass to the dispersion zone, the entire foregoing operation being carried out in an inert atmosphere.

5. In a substantially continuous multistage cyclic process for making metallic Ti involving a circuit comprising a dispersing zone for dispersing Na on solid finely divided carrier reaction product of a previous cycle, a separate reaction zone for reacting Na and $TiCl_4$ to form metallic Ti, a recycle of carrier reaction product thru said zones in the order named, and separation from the circuit of reaction product formed during a cycle, the steps comprising providing a recycle carrier consisting of reaction product of a previous cycle and containing metallic Ti and NaCl, introducing said carrier into said dispersion zone, feeding elemental Na in liquid form into said zone, the amount of Na being not substantially in excess of 3.5% by weight of total fed Na and carrier, passing thru said dispersion zone said Na and said carrier while maintained at temperature not higher than about 200° C. but high enough to insure the absence of solid Na, and while in the absence of $TiCl_4$ and while under conditions of residence and vigorous agitation both sufficient to effect dispersion of said Na on said carrier, thereafter discharging the mass of thus-dispersed elemental Na and carrier from said dispersing zone and introducing said mass into said separate reaction zone, feeding into said reaction zone vaporous $TiCl_4$ in quantity less than that theoretically needed to react with all the elemental Na present, maintaining temperature in said reaction zone in the range of about 150–350° C., passing the reactants thru said reaction zone while in the absence of sodium from source other than said dispersing zone and while under conditions of residence and vigorous agitation both sufficient to effect formation of a reaction mass comprising metallic Ti, NaCl and elemental Na, discharging said reaction mass from the reaction zone, separating from said mass reaction product in amount corresponding substantially to cyclic make, and recycling substantially the balance of said mass to the dispersion zone, the entire foregoing operation being carried out in an inert atmosphere.

6. The process of claim 5 in which the $TiCl_4$—Na reaction is effected in the presence of at least 15% by weight of sodium in excess of that theoretically needed to reduce all of the $TiCl_4$ fed to metallic Ti.

7. The process of claim 5 in which the solid carrier reaction product contains sufficient sodium so that, in conjunction with fed sodium, the $TiCl_4$—Na reaction is effected in the presence of about 15–200% by weight of sodium in excess of that theoretically needed to reduce all of the $TiCl_4$ fed to metallic Ti.

8. The process of claim 5 in which the dispersed elemental sodium and carrier material thereof are discharged into the reaction zone at temperature not less than 125° C., and reaction zone temperature is maintained in the range of about 175–300° C.

9. The process of claim 5 in which the solid carrier reaction product contains about 0.2–1.5% by weight of stoichiometric excess Na, the relative amounts of Na and $TiCl_4$ charged are regulated to provide an Na feed of at least about a stoichiometric quantity of Na on the basis of fed $TiCl_4$, and the amount of carrier charged into the dispersion zone is regulated so as to provide in the reaction zone a weight ratio of carrier to total weight of fed $TiCl_4$ plus an approximately stoichiometric equivalent of fed Na substantially in the range of 60:1 to 25:1.

10. In a substantially continuous multi-stage cyclic process for making metallic Ti involving a circuit comprising a dispersing zone for dispersing Na on solid finely divided carrier reaction product of a previous cycle, a separate reaction zone for reacting Na and $TiCl_4$ to form metallic Ti, a recycle of carrier reaction product thru said zones in the order named, and separation from the circuit of reaction product formed during a cycle, the steps comprising providing a recycle carrier consisting of reaction product of a previous cycle and containing metallic Ti, NaCl and about 0.2–1.0% by weight of stoichiometric excess Na, introducing said carrier into said dispersion zone, feeding elemental Na

in liquid form into said zone and dispersing the fed Na on said carrier while at temperature high enough to insure absence of solid sodium but not higher than about 200° C. and while in the absence of $TiCl_4$, transferring the thus dispersed Na and carrier thereof into said reaction zone, feeding $TiCl_4$ in vapor form into said reaction zone while in the absence of sodium from source other than said dispersing zone and maintained at temperature in the range of about 150–350° C. to effect formation of metallic Ti and NaCl from fed reactants, regulating relative amounts of Na and $TiCl_4$ charged to provide a Na feed of about a stoichiometric quantity of Na on the basis of fed $TiCl_4$, regulating the amount of recycle charged into the dispersion zone so as to provide in the reaction zone a weight ratio of recycle to total weight of fed $TiCl_4$ plus an approximately stoichiometric equivalent of fed Na substantially in the range of 60:1 to 25:1, discharging reaction mass from the reaction zone, separating from said mass reaction product in amount corresponding approximately to cyclic make, and recycling substantially the balance of said mass to the dispersion zone, the entire foregoing operation being carried out in an inert atmosphere.

11. The process of claim 10 in which the dispersed elemental sodium and carrier thereof are discharged into the reaction zone at temperature not less than 125° C., and reaction zone temperature is maintained in the range of about 175–300° C.

12. The process of claim 10 in which the total amount of Na introduced into the system is in excess of theoretical Na requirements to an extent approximately corresponding with the amount of the bleed loss Na contained in the cyclic make and cyclically discharged from the circuit.

13. The process of claim 10 in which sodium and carrier in the dispersion zone and solids in the reaction zone are maintained in the forms of vigorously mechanically agitated contiguously constituted beds of substantially dry, free-flowing materials.

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