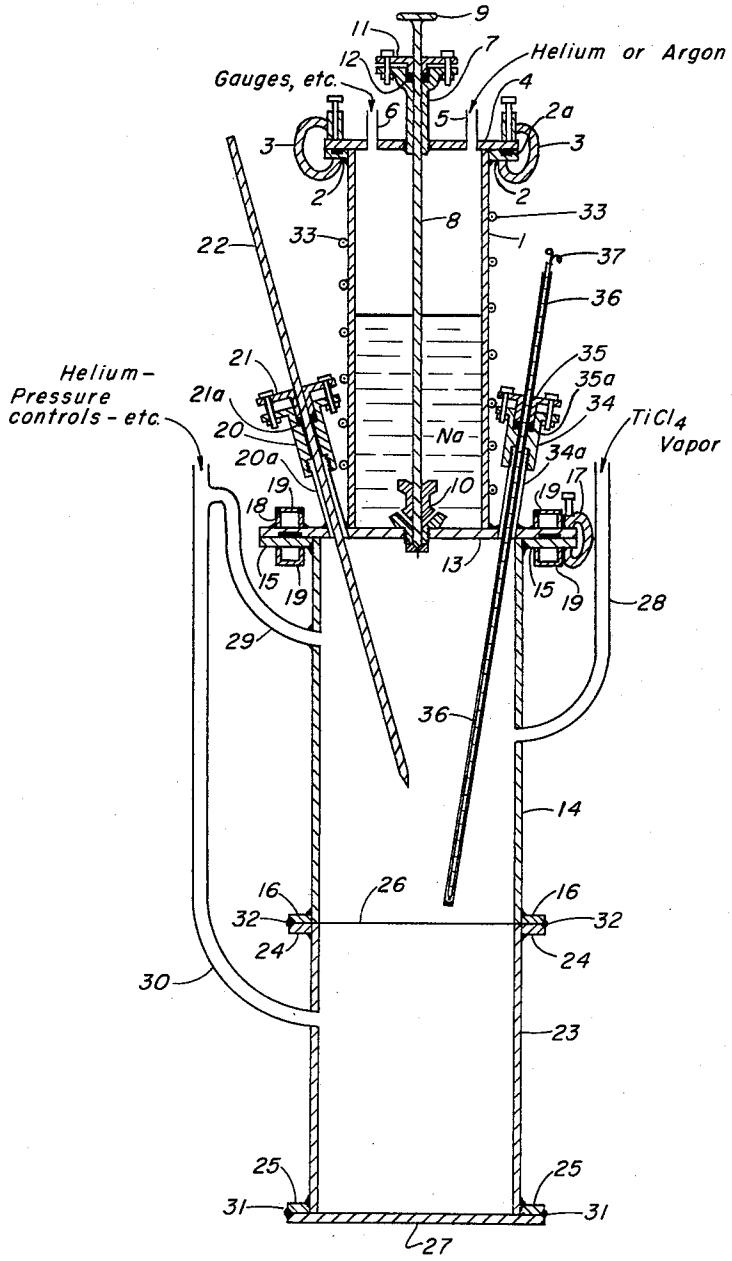
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PRODUCTION OF HIGH PURITY TITANIUM BY METALLIC SODIUM REDUCTION OF TITANIC HALIDE

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PRODUCTION OF HIGH PURITY TITANIUM BY METALLIC SODIUM REDUCTION OF TITANIC HALIDE

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The invention herein described and claimed may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of royalties thereon or therefor.

This invention concerns a process for the recovery of titanium metal in substantially pure crystalline form.

It has long been sought to produce titanium economically in a substantially pure homogenous form. Decomposition of titanium tetrachloride on a heated filament yields the pure metal directly, but the process is not suitable for production on more than a laboratory scale. The other methods in common use heretofore produce titanium contaminated in varying degrees by nitrogen, oxygen, etc. In order to obtain a purified metal, further refining steps must be employed. In the Kroll process, which is one of the most commonly employed methods for producing titanium, the metal produced is heterogeneous. Before use for most purposes it must undergo an expensive purification treatment. In addition, the titanium recovered from the Kroll process is a solidified mass, which must be bored out on a lathe, or otherwise removed from the reaction crucible—a time consuming and expensive operation.

It is an object of the present invention to provide an improved method for the preparation of titanium having a relatively low Brinell hardness number, in relatively pure crystalline form.

Another object of the invention is to provide an improved method for producing titanium by the reduction of titanium tetrachloride using sodium.

A further object of the invention is to provide a method for producing titanium wherein titanium tetrachloride is first reduced with sodium to lower valent chlorides, and then these latter are further reduced with additional sodium to titanium metal.

A further object is to separate crystalline titanium metal, produced by the sodium reduction of titanium chlorides, from molten salt by a simple drainage method. Other objects will appear hereinafter in the specification and claims.

These objects are achieved by first partially reducing titanium tetrachloride to the di- and trichlorides by dropping molten sodium through titanium tetrachloride vapors at a temperature of 400° to 750° C. This intermediate product is then converted to the desired form of crystalline titanium in a second stage treatment, as follows:

(1) To make a crystalline product that is predominantly composed of needle-type crystals, the reaction chamber is heated to 805°–875° C. and additional sodium added slowly to convert the lower chlorides of titanium to metal and salt. After the reaction is complete the molten salt is permitted to drain off from the titanium needle and granular crystal product, which can then be readily removed from the reactor. The slow reaction of the sodium with the titanium di- and trichlorides produces high purity titanium needles having a chlorine content as low as .01 percent and a Brinell hardness number as low as 60. Runs A to I in Table 1 illustrate this mode of operation.

(2) To make more dense crystals having a granular or dendritic shape, the reaction chamber is cooled to freeze the first-stage melt. The required amount of sodium is then added en masse and the reaction chamber heated gradually to the melting point of the first-stage product. An initial reaction takes place in the upper portion of the melt, but soon subsides. To obtain further reduction, the reaction chamber is heated to 750°–805° C. and maintained at this temperature until the reaction is complete. The molten salt is then permitted to drain from the reaction product and the crystals can then be readily removed from the reactor. A crystalline metal has been made having a Brinell hardness number as low as 49. Run J in Table 1 illustrates this mode of operation.

The FIGURE is a schematic sectional diagram of one form of apparatus which may be employed to carry out the invention.

In the drawing, 1 is a cylindrical chamber having an upper flange 2 and a lower sealing plate 13. Fastened to the upper flange by four C clamps 3 is an upper plate 4 having nipples 5 and 6 and gland 7 mounted therein. Gasket 2a acts as a seal between flange 2 and plate 4. Passing through gland 7 is a valve stem 8, having an upper handle 9, of a wire probe valve composed of seat number 10 threadably mounted in plate 13, and the stem 8. Compression cap 11 and packing 12 act to seal valve stem 8. An electrical heating coil 33 surrounds chamber 1.

Mounted below chamber 1 is a larger diameter cylindrical chamber 14 having upper and lower flanges 15 and 16. Chamber 14 is joined to chamber 1 by means of a plurality of clamps 17, of which only one is shown, which act to removably fasten plate 13 to flange 15. A gasket 18, of a suitable material, such as neoprene, is used as a seal. Water tubes 19 serve to cool the flanges and thereby prevent damage to the seal. Angularly mounted in plate 13 is nipple 20a, having threadably mounted thereon packing gland seal 20, having a compression cap member 21 fastened by bolts at its upper end. Passing through an opening in 21 and gasket 21a, and having a gas-tight sliding fit is pointed steel rod 22. Also angularly mounted in plate 13 is nipple 34a, having threadably mounted thereon packing gland seal 34, having a compression cap 35 fastened by bolts at its upper end. A pipe thermocouple well 36, sealed on the lower end passes through an opening in 35 and on through the packing 35a which provides a gas-tight sliding fit. A thermocouple 37 is inserted in well 36. Lower chamber 23 is of the same diameter as 14 and has upper and lower flanges 24 and 25. Sheet metal diaphragm 26, which is welded to flanges 16 and 24, separates chambers 14 and 23 in the manner shown, and plate 27 welded to flange 25 is the bottom closing member. Tubes 28, 29 and 30 permit access of reagents, purge gases, etc., into chambers 14 and 23. As shown, 29 and 30 are in communication with each other and act to equalize the pressures in 23 and 14. 31 and 32 are the beads resulting from the welding operation.

The lower portion of the apparatus, consisting of chambers 14 and 23, is mounted vertically in an electric furnace (not shown), such as one heated by silicon carbide resistance rods. By varying the power input to the furnace, the temperature of the reactor may be controlled.

In operation, sodium is introduced in chamber 1 and heated to melting under an atmosphere of argon, helium, or other inert gas introduced through nipple 5. Chambers 14 and 23 are evacuated through lines 29 and 30 and backfilled with an inert gas, preferably helium. Hot (200°–450° C.) titanium tetrachloride vapors are then introduced into the chamber 14. The valve stem 8 is then opened to permit molten sodium to fall dropwise through the titanium chloride vapors, the temperature of the chamber being maintained at 400°–750° C.

Here a sufficient amount of sodium reacts with titanium tetrachloride to form a complex or molten mixture of salt (NaCl) and lower valent titanium chlorides, which is supported on diaphragm **26**. This phase of the process depends on many variables including the size of the sodium feed orifice, length of drop through the hot zone, rate of titanium tetrachloride feed, and the temperature of the feed. During this first-stage reduction some titanium metal is formed along with the lower chlorides of titanium. Maintaining the stoichiometric balance for the reaction, $2Na+TiCl_4 \rightarrow TiCl_2+2NaCl$ then causes an excess of $TiCl_3$ in the melt. The melt is soaked at a temperature above its melting point to convert this $TiCl_3$ to $TiCl_2$ according to the reaction $2TiCl_3+Ti \rightarrow 3TiCl_2$. The titanium metal is thereby converted to titanous chloride.

After the first stage of the reduction is completed either of the two techniques described previously may be employed, depending on whether a predominantly needle titanium or a more dense granular and flat form is desired. Molten sodium is added from a relatively larger valve opening for this final stage of reduction. Since sodium is somewhat soluble in molten sodium chloride, the salt acts as a carrier in transferring sodium to the reaction zone slowly forming crystalline titanium.

When sufficient sodium has been added for a complete reduction, the reaction chamber is maintained at the reduction temperature for a period of time sufficient for the reaction to be completed, which varies with the depth of the melt. At the end of this period, pointed steel rod **22** is forced down and punctures diaphragm **26**. The molten salts then drain into the lower chamber **23** leaving the titanium needles and/or crystals on the diaphragm.

After cooling, the welding beads **31** and **32** are then ground off and the products removed.

After removal of the metal product from the reactor, the residual sodium chloride and unreacted lower chlorides of titanium (if present) are leached from the titanium with a cold dilute acid, such as HCl, H_2SO_4, etc. The pH of the leach solution is maintained below 2.0 to prevent hydrolysis of any titanium in the solution. After draining off the leach solution, the metal is washed in cold water and then dried. Fine metal, caused by a vapor reaction during reduction, contains most of the impurities and is removed by screening through an 80-mesh screen. If sized, pure crystalline metal products are desired, further screening can be used and a hydraulic classification made on each sized product to remove the granular agglomerations of fine metal associated with the crystalline metal.

While we have shown and described a form of apparatus which we have found suitable for carrying out the process, it is obvious that this equipment may be modified in a number of ways as desired. For example, instead of providing means for puncturing the diaphragm for salt drainage, valves, tap holes, or a siphon can be utilized, heating means other than the coils shown may be employed, etc. Aside from modificationns in the apparatus shown, other entirely different forms may be devised to conduct this step reaction under a blanket of inert gas. As an example, two separate heated reaction vessels could be employed for each of the reaction stages.

EXAMPLE

Various runs were made in the apparatus shown in the FIGURE. The following tables summarize the results obtained:

Table 1

RUN DATA FROM SEVERAL TWO-STAGE REDUCTIONS

Run No.	Feed Materials		Feed Temperatures		Furnace Temperatures, ° C.		Time of Reduction,[1] Hours	
	Sodium (lbs.)	$TiCl_4$ (lbs.)	Sodium, ° C.	$TiCl_4$, ° C.	1st Stage	2d Stage	1st Stage	2d Stage
A	19.38	40	105–175	210–435	700	875	1.33	1.67
B	19.38	40	110–170	240–385	700	805–875	1.42	1.50
C	29.07	60	120–175	270–360	700	820–875	1.63	1.13
D	38.76	80	120–165	210–380	600–700	850–875	6.11	1.75
E	29.16	60	122–144	246–524	700	875	3.30	1.41
F	29.16	60	114–146	214–466	700	875	2.82	1.83
G	29.16	64.5	124–152	258–438	700	875	3.17	1.75
H	29.07	60	122–159	256–575	700	875	2.67	1.67
I	29.16	60	121–146	230–466	700	875	2.33	1.41
J[2]	29.16	60	110–127	180–462	700	450–800	2.37	0.08

[1] Time of feeding.
[2] Use of technique for making dense granular and dendritic crystals.

Table 2

TWO-STAGE REDUCTION, METAL RECOVERY, AND METAL HARDNESS DATA

Run No.	Soaking				Metal Data			Average[1] BHN	Fraction <100 BHN (percent)
	First-Stage		Second-Stage		Ti Metal Recovery (percent)	Crystalline Titanium			
	Hours[2]	Temp., ° C.	Hours	Temp., ° C.		Pounds	BHN		
A	22.83	810–875	2.83	810–875	85.62	2.08	67–97	----------	22.0
B	3.50	750–835	1.08	875	65.64	1.59	83–95	----------	24.4
C	2.75	750–840	2.00	875	76.20	1.35	64–99	----------	11.7
D	16.30	750–850	4.50	850–875	54.30	2.70	74–91	----------	24.5
E	20.08	700–875	26.00	750–875	77.3	5.25	64–96	128	42.2
F	20.50	700–875	23.25	875	83.5	4.22	68–90	139	33.0
G	20.12	750–875	22.91	875	81.8	4.41	60–94	125	33.6
H	20.60	700–875	22.91	875	88.8	4.91	63–99	118	42.9
I	19.67	700–875	36.25	875	87.2	3.91	61–96	154	28.0
J	15.00	700–875	76.17	450–800	95.6	7.46	49–95	132	51.4

[1] The average Brinell hardness number was calculated from BHN values of all size fractions, not from an actual composite.
[2] The long periods of first-stage soaking are not necessary but were more convenient for single shift operation. Three to six hours is adequate for the melt depths and equipment used. This is also true of the second-stage soaking, except when using the technique employed for Run No. J.
The soaking periods for both steps do not include the time of reduction shown in Table 1.

Table 3

CHEMICAL ANALYSES OF TITANIUM METAL PRODUCTS

Reduction Number	Product	Mesh Size	BHN	Chemical Analyses, Percent								
				H_2	O_2	N_2	Fe	Na	S	Cl_2	C	Si
E	Needles	−4+14	68	0.011	0.034	0.001	0.005	0.006	0.002	0.02	0.049	0.008
F	do	−14+28	73	.012	.045	.001	.005	.012	.002	.01	.042	.010
G	do	−4+14	60			.001	.02	.005		.02	.020	
H	do	−14+28	68	.004	.017	.001	.03	.005	.001	.01	.018	.007
H	Fines	−80	224	.271	.180	.008	.86	.005	.003	.07	.040	.01
I	Needles	−14+28	61	.003	.004	.001	.005	.005	.002	.07	.031	.007
I	Fines	−80	152	.025	.050	.003	.09	.035	.002	.09	.021	.006
J	Coarse crystals	+4	49	.003	.008	.006	<.005		<.002		.019	.005
J	do	−28+14	57	.003	.012	.002	<.02		.001		.009	.005
J	do	−14+38	62	.002	.015	.002	<.02		<.001		.008	.02

It will be understood that various modifications and variations may be effected without departing from the spirit of this invention.

We claim:

1. The method of preparing titanium metal which comprises the steps of (1) reacting at an elevated temperature in a reaction zone completely blanketed with an inert gas, $TiCl_4$ in the vapor state initially received over the entirety of said reaction zone, with a quantity of molten sodium in an amount sufficient to reduce the $TiCl_4$ to lower chlorides, whereby a molten mixture comprising lower valent titanium chlorides, including $TiCl_3$, sodium chloride and some titanium metal is produced; (2) continuing the reaction for a time sufficient to react completely all the sodium present and to react all the titanium metal formed with $TiCl_3$ to produce $TiCl_2$; (3) increasing the temperature in the reaction zone; (4) adding molten sodium to the molten mixture in an amount at least sufficient to reduce the titanium chlorides to titanium; (5) continuing the reaction for a time sufficient to react the sodium present, whereby crystalline titanium is formed; and (6) draining off the molten material and recovering high purity crystalline titanium as a product of the process.

2. The method of preparing titanium metal which comprises the steps of introducing heated $TiCl_4$ vapor into the entirety of a hot reaction zone completely filled with inert gas, passing molten sodium downwardly through said zone receiving said heated $TiCl_4$ vapor in an amount sufficient to reduce the titanium tetrachloride to lower chlorides, whereby a molten mass of unreacted sodium, salt and lower valent titanium chlorides, including $TiCl_3$, is formed, together with some titanium metal and accumulates at the bottom of said reaction zone, continuing the reaction for a time sufficient to react completely the sodium present and to react the titanium metal formed with $TiCl_3$ to form $TiCl_2$, increasing the temperature in the reaction zone, adding additional molten sodium to the liquid mass at an increased rate in an amount at least sufficient to reduce the lower valent titanium chlorides to titanium, continuing the reaction until substantially all the titanium chlorides are completely reduced, draining off the molten material, and recovering high purity crystalline titanium as a product of the process.

3. The method of preparing titanium metal which comprises the steps of introducing titanium tetrachloride vapors at a temperature at about 200 to about 450° C. into the entirety of a reaction zone completely filled with inert gas, passing molten sodium, at a temperature not in excess of about 175° C., downwardly through said zone receiving said titanium tetrachloride vapors, maintaining the temperature of said zone at a temperature of from about 400 to about 750° C., said sodium being added in an amount sufficient to reduce the titanium tetrachloride to lower chlorides, whereby a molten mass of unreacted sodium, salt and lower valent titanium chlorides, including $TiCl_3$, is formed together with some titanium metal and accumulates at the bottom of said reaction zone, continuing the reaction for a time sufficient to react completely the sodium present and to cause all of the titanium forced to react with $TiCl_3$ to form $TiCl_2$, increasing the temperature of the reaction zone to within the range of about 805° C. to about 875° C., adding additional molten sodium to the liquid mass at an increased rate in an amount at least sufficient to reduce the lower valent titanium chlorides to titanium, continuing the reaction until substantially all the titanium chlorides are completely reduced, draining off the molten material, and recovering high purity crystalline titanium as a product of the process.

4. The method of claim 3, including, subsequently to draining off the molten material, the steps of leaching the remaining crystalline titanium mass with a dilute acid having a pH below about 2.0, draining off the leach solution, washing with cold water, drying, and then screening to remove any fines.

5. The method of preparing titanium metal which comprises the steps of introducing titanium tetrachloride vapors at a temperature of about 200° C. to about 450° C. into the entirety of a reaction zone completely filled with inert gas, passing molten sodium, at a temperature not in excess of about 175° C., downwardly through said zone, maintaining the temperature of said zone from about 400° C. to about 750° C., the sodium being added in an amount sufficient to reduce the titanium tetrachloride to lower chlorides, whereby a molten mass of unreacted sodium, salt and lower valent titanium chlorides, including $TiCl_3$, is formed together with some titanium metal and accumulates at the bottom of said reaction zone, continuing the reaction for a time sufficient to react completely the sodium present, and to cause all of the titanium present to react with $TiCl_3$ to form $TiCl_2$, cooling the reaction zone to freeze the melt, adding additional molten sodium en masse in an amount at least sufficient to reduce the lower valent titanium chlorides to titanium, increasing the temperature of the reaction zone to the melting point of the melt, whereby an initial reduction reaction occurs in the upper portion of the melt, then heating the reaction zone to a range of from about 750° to about 805° C., continuing the reaction until substantially all the titanium chlorides are completely reduced, draining off the molten material, and recovering crystalline titanium as a product of the process.

6. The method of claim 5, including, subsequently to draining off the molten material, the steps of leaching the remaining crystalline titanium mass with a dilute acid having a pH below about 2.0, draining off the leach solution, washing with cold water, drying, and then screening to remove any fines.

7. The method of preparing titanium metal which comprises the steps of (1) reacting, at an elevated temperature in a reaction zone completely blanketed with inert gas, $TiCl_4$ in the vapor state initially received over the entirety of said reaction zone, with a quantity of molten sodium in an amount sufficient to reduce the $TiCl_4$ to lower chlorides, whereby a molten mixture comprising lower valent titanium chlorides, including $TiCl_3$, sodium chloride and some titanium metal is produced; (2) con-

tinuing the reaction for a time sufficient to react completely all the sodium present, and to react all the titanium metal formed with $TiCl_3$ to produce $TiCl_2$; (3) cooling the reaction zone until the melt solidifies; (4) adding molten sodium en masse in an amount at least sufficient to reduce completely the titanium chlorides to titanium; (5) heating the reaction zones to from about 750° C. to about 805° C., until substantially all the titanium chlorides are completely reduced; (6) draining off the molten material and recovering high purity crystalline titanium as a product of the process.

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