Oct. 13, 1964 B. B. RANEY 3,152,885

TITANIUM GROUP METALS

Filed April 22, 1959 2 Sheets-Sheet 1

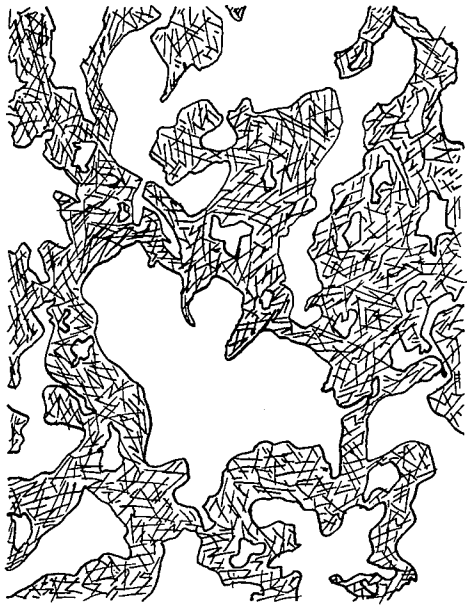


Fig. 1

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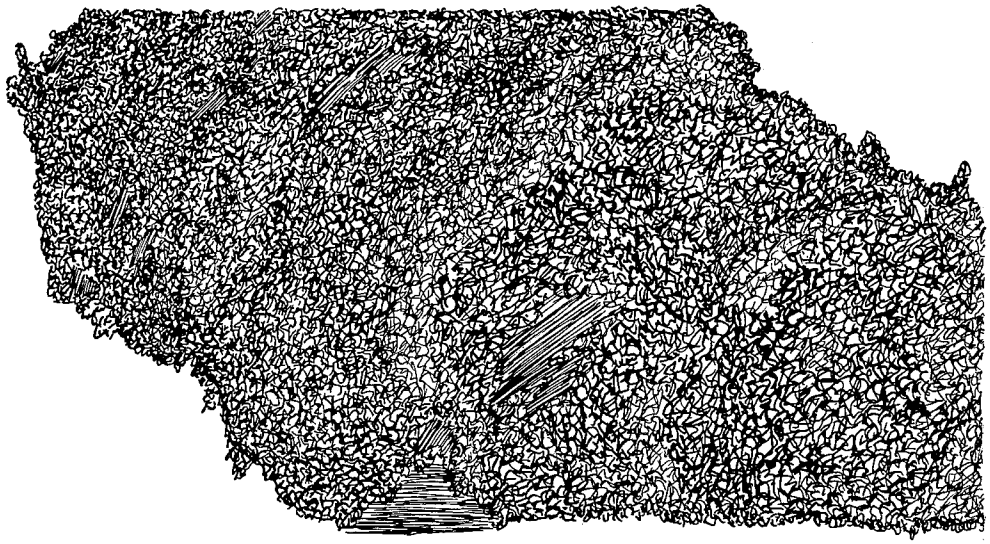


Fig. 2

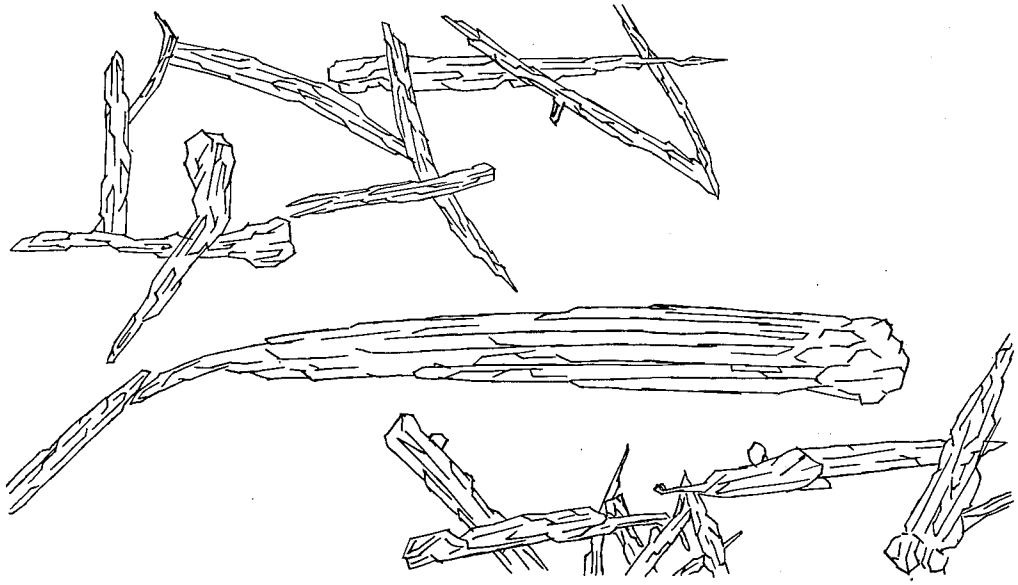


Fig. 3

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3,152,885

TITANIUM GROUP METALS

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Filed Apr. 22, 1959, Ser. No. 808,279
1 Claim. (Cl. 75—84)

This invention relates to the production of metals of the titanium group in subdivided form. It relates particularly to processes for the reduction of compounds of metals of the titanium group to metallic particles by reacting these compounds with solutions of alkalinous metals in fused chlorides of alkalinous metals to the products of such reactions, and to the treatment of such reaction products whereby to produce the metals in very pure form. I have found that such reduction is more rapid than is reduction by alkali or alkaline earth metals in other forms such as the massive and vapor states; also, it produces the titanium group metals in the form of characteristic particles. If the metal compound is soluble in the melt, the resulting metal particles will be filamentary.

This application is a continuation-in-part of my copending application Serial No. 567,706, filed February 24, 1956, now abandoned.

In carrying out my invention, the alkalinous metal chlorides are fused and saturated with alkalinous metal, and the resulting solution of the alkalinous metal, in the absence of undissolved alkalinous metal, is reacted with a compound of metal of the titanium group which is soluble in the fused alkalinous metal chlorides. The compound to be reduced must, however, be introduced at a rate no greater than the fused salt solution is replenished with reducing alkalinous metal. This is conveniently done, for example, by introducing the alkalinous metal into the bath only as rapidly as it dissolved, and introducing the titanium group compound into the solution, at the same rate, in another portion of the bath.

I have found that in order to dissolve the alkalinous metal in the fused alkalinous metal chlorides, the same must be substantially free from dissolved oxide. The process of my invention is inoperative if there is a substantial amount of oxide dissolved in the bath.

A preferred form of carrying out my invention consists in the reduction of titanium group metal chlorides to filamentary metal particles by bringing them into the solution of alkalinous metal in fused chloride produced by electrolysis of oxide-free alkalinous metal chlorides at a suitable rate so that the alkalinous metal solution is always in excess, but no undissolved alkalinous metal is present at the place of reaction.

The anode in this embodiment of my process may be graphite, in which case chlorine is evolved adjacent the anode and removed from the cell by suitable means. It is frequently convenient, however, to provide the titanium group metal chloride by anodic reaction. In the simplest instance, these compounds may be merely the chlorides of the anode metal or metals. The anode may advantageously be made, however, of partially reduced metal, in which case oxides and chlorides are provided by the anode. The oxides separate as anode slime. It is necessary that there be enough metal in such partially reduced material that the anode, formed therefrom, be electrically conducting. Other conducting heavy metal compounds which form chlorides when used as anodes in the molten alkalinous metal chloride bath may be used as anodes. Anodes which react with chlorine to form chlorides such as mixtures of the heavy metal oxides and carbon may also be used.

The shape and form of the metal produced by my process is important because in the production of pure metals I may make use of this shape factor to separate the reduced metal from anode fragments of the original metal

and from non-metallic anode slime or other non-metallic materials. The methods of separation of solids based on shape factors are well known and include gravity and electrostatic methods. For example, the bundles which form from the filamentary particles are easily washed over the riffles of a shaking table, whereas the more symmetral particles fall into the riffles of the table. The bundles of filamentary particles produced by my process are quite advantageous from the standpoint of draining and dissolving salt from them, and also because they may be, if desired, readily disintegrated by mulling to provide more rigorous washing.

In the drawing I have illustrated the nature of the bundles produced by the several procedures described, and which I desire to claim. In order to fully illustrate the article of my invention, I have included in the drawing photolithographic reproductions of several photomicrographs which illustrate my invention. These include:

FIG. 1, a sectional view of one of the bundles, at about 35 diameters;

FIG. 2, a representation of a bundle from which salt has been in part removed in order to show the individual filamentary crystals, at about 10 diameters; and

FIG. 3, individual filamentary crystals from the above bundle at higher magnification, at about 75 diameters.

The conditions of electrolysis are not particularly critical as regards current densities. Current densities at the anode may be 100–5,000 amperes per square foot, and cathode current density may be 100–1,000 amperes per square foot. The anode may be of the impure metal it is desired to produce in pure filamentary crystalline form. The cathode may be any unattacked metal or conducting material. When the anode is of the impure metal which it is desired to produce in pure form, the cathode may be the same metal and the current reversed from time to time in order to produce subdivided metal from both electrodes. In this case, the vessel holding the bath may be any unattacked metal or ceramic. When using a carbon anode, the cathode may be conveniently the electrically conductive metal vessel which contains the salt.

I have described my invention with the use of chlorides of the alkali and alkaline earth metals and magnesium (the alkalinous metals) because these chlorides are practically advantageous. Bromides, or mixtures of bromides and chlorides, of alkalinous metals may be used without departing from the spirit of my invention and are considered the chemical equivalent of their chlorides.

It will be recognized that the procedures which are set forth here are all embodiments of the invention of the application of which this is a continuation and which can be described in general terms as reducing a solution of titanium chloride in a fused alkalinous metal chloride by bringing such a solution together with a solution of alkalinous metal in fused alkalinous metal chloride at the rate of which the titanium is formed. An essential feature of the invention is maintaining the reaction zone at a low concentration of both reactants. Under these conditions the reaction produces bundles of filamentary titanium particles.

The present invention is concerned with the maintenance of conditions which affect the precise nature of these bundles. These conditions are basically the same whether the reactants are produced in an electrolytic cell or in a chemical reaction vessel.

The titanium bundles produced may be described in terms of the following parameters:

(1) Shape and size of the individual particles
(2) Degree of orientation of the particles
(3) Packing density of particles
(4) Degree of salt retention
(5) Composition of individual particles

The particles of this invention are all filamentary, that is, one dimension is considerably longer than the others. The size of the particles depends on their rate of formation which in turn is a function of the concentration of the titanium salt in the reaction zone in which they are grown. It is one of the parameters of this invention that the reactants are brought together at the rate at which titanium metal is formed and therefore the concentration of the reactants in the reaction zone is maintained at a low level.

In general, when the concentration of titanium chloride is low, simple filamentary crystals haivng a maximum dimension of from 0.15 to 1.0 mm. are formed. When a very low concentration is maintained in the reaction zone the filamentary particles tend to branch and are of shorter length.

It is difficult to determine the exact concentrations of the reactants in the reaction zone since this is clearly a dynamic function. Since the alkalinous metal diffuses into the reaction zone much more rapidly than does the titanium chloride, the position of the reaction zone with relation to the sources of the reactants is largely a function of titanium chloride content of the bath adjacent the reaction zone.

If the concentration is from 0.5% to 2% titanium as chloride, the titanium will be formed in bundles of unoriented simple filamentary crystals. When the concentration of titanium as chloride is below 0.5% the filamentary crystals are smaller then .15 mm. maximum diameter and tend to become branched and twinned.

In the embodiment of my invention in which the titanium chloride in the bath is provided by the anodic solution of titanium in an electrolytic cell, the concentration in the body of the electrolyte remains constant and is that initially provided. Concentrations from 0.5–3% provide bundles of simple filamentary particles adherent to the cathode at 95% or better current efficiency.

Example I

In this example I take a fused bath of 98% NaCl–2% $BaCl_2$ maintained in an argon atmosphere. This bath is held at 825° C., and to it I add sodium to produce and maintain a layer of molten sodium over the top of the bath, the bath being held in an iron pot. I then add $TiCl_4$ to a bell having an opening under the surface of the bath. The $TiCl_4$ is dissolved in the salt in the bell by reduction or direct solution. I add the $TiCl_4$ at such a rate that about 1% Ti is dissolved in the body of the bath as titanium chloride. A reaction zone is formed just below the sodium layer and bundles of simple filamentary crystals, each having a maximum dimension up to 1 inch and particles up to 1" length and 2 mm. diameter, are formed and fall to the bottom of the bath. There is no orientation of the particles in the bundles.

Example II

In this example I take a fused bath of 98% NaCl–2% $SrCl_2$ maintained in an argon atmosphere. I place a titanium cathode and a graphite anode in the bath each surrounded with a sillimanite bell.

The cathode bell which serves as a source of sodium dissolved in the fused bath is connected below the bath surface with another bell into which $TiCl_4$ is passed. The bells may conveniently be concentric.

The $TiCl_4$ enters the bath by physical or chemical solution and diffuses to the bottom of the bell where it meets the diffusing sodium and, in accordance with the basic disclosure of my invention, forms bundles of filamentary titanium particles which fall to the bottom of the bath. The $TiCl_4$ is added at such a rate as to form in the body of fused salt in the outer bell a concentration of about 1% Ti as chloride.

The operating data for this example are as follows:

$TiCl_4$	188 grams/hour.
Amperes	108.
Current density, anode	400 amps./sq. ft.
Current density, cathode	100 amps./sq. ft.
Titanium recovered, g./hour	46.
Applied voltage	2.3 volts.

Inst. open circuit cell voltage 1.75–1.95 volts which indicates that the cathode potential is 0.2 v. or less more electropositive than pure titanium. Conc. Ti chloride as Ti in outer bell—0.5%. Current efficiency at cathode for Ti—96%.

Nature of titanium formed: Bundles approximately ¼" average diameter consisting of particles each about 0.5 mm. maximum dimension and 0.05 mm. diameter, in an unoriented position in a mat or "felted" organization which when drained at 850° C. contained 11.0% salt. Leached with 1% HCl and washed, it contained 0.02% Cl as salt residue.

Analysis of titanium:

Fe	0.08%.
O_2	0.03%.
N_2	0.001%.
Other impurities	Traces.
Ti	Balance.
Brinell hardness of button melted in argon	92.

Example III

In this example I provide the titanium chloride to be reduced by using a crude titanium anode. This anode may be titanium scrap or may be crude titanium produced by methods known in the art. In this particular example I use an anode of the following analysis:

Fe	0.5%.
O_2	1.2%.
Cu	3.6%.
N_2	0.4%.
C	0.3%.
Ti	Balance, except for traces of other impurities.

The procedure consists in placing the anode in the center of a cylindrical iron pot which serves as the cathode as well as the cell for containing the electrolyte. The cell is provided with a bottom drain for removing the salt at the end of the experiment. The pot is 8" in diameter, the anode 2" in diameter. The depth of the bath is 12". The electrolyte is 2% $BaCl_2$, 3% Ti as chloride, balance NaCl. An inert atmosphere (argon) is maintained above the electrolyte.

The operating data for this example follow:

Temperature of operation	850° C.
Cathode current density	100 amps./sq. ft.
Anode current density	800 amps./sq. ft.
Amperes	150.
Time of operation	10 hours.
Anode loss	1550 grams.
Anode slime	85 grams.
Ti bundles produced on cathode	1450 g.
Operating voltage	.7 v.
OC cell voltage	.1 v.
Current efficiency cathode	95%.

Nature of metal adhering to cathode: The titanium is formed in a mat of simple filamentary particles adherent the cathode. Each particle has a maximum dimension of about 10 mm. and an average diameter of about 0.50 mm. The drained mat contains 12.0% salt and has a density of 1.0 gram titanium per cubic centimeter. The analysis of the washed titanium particles is as follows: Cl, .02%; Fe, .06%; Ca, .01%; oxygen, .05%; nitrogen .003%; other impurities, traces; hardness of melted button—101 Brinell.

Example IV

In this example I proceed exactly as in Example III except that the electrolyte composition is .25% Ti as chloride 1/ $BaCl_2$, balance NaCl. The operating data for this example are as follows:

Temperature of operation	850° C.
Cathode CD	100 amps./sq. ft.
Anode CD	800 amps./sq. ft.
Amperes	150.
Time of operation	10 hours.
Anode loss	1550 grams.
Anode slime	120 grams.
Ti bundles produced on cathode	1400 g.
Operating voltage	.7 v.
OC cell voltage	.2 v.
Current efficiency	88%.

Nature of metal: The titanium is in bundles adherent to the cathode. The particles of the bundles are branched filamentary crystals of 0.15–0.20 mm. maximum dimension and 0.10 mm. average diameter. The bundles after draining have a salt content of 35% and a packing density of 1.4 grams titanium per cc. The analysis of the washed particles is as follows: Cl, .03%; Fe, .08%; Cu, .01%; oxygen, .05%; nitrogen, .003%; other impurities, traces only. Hardness of melted button is 110 Brinell.

Example V

I make a fused bath of oxygen-free calcium and sodium chlorides in the proportion 66% $CaCl_2$, 34% NaCl. I heat this bath in a ceramic pot to 750° C., at which temperature it is fused. I introduce into this bath metallic sodium in the form of a ribbon near one side of the pot. The metallic sodium reacts with the calcium chloride to form metallic calcium which dissolves in the bath. I introduce titanium trichloride, dissolved in the salt mixture, on the other side of the pot. The sodium is introduced at such a rate that no undissolved alkalinous metal is formed in the pot, and the titanium chloride is introduced at the rate that bundles of filamentary crystals are formed at the reaction zone.

The use of sodium in a calcium chloride-containing bath is for the purpose of utilizing the greater solubility of metallic calcium. Since calcium is soluble in the fused bath up to about 30 mol percent, it will be seen that calcium in low concentration has a lower negative free energy than the more nearly saturated solution of sodium; hence, as the sodium is in introduced calcium is formed and diffuses into the bath. The calcium diffuses much more rapidly than does the $TiCl_3$, so that the reaction zone locates itself near the point of sodium introduction and is fed by the titanium chloride solution formed in the body of the bath.

The formation of filamentary crystals depends on a low concentration of titanium chloride reaching the reaction zone. The rate at which it reaches the reaction zone is determined by the concentration maintained in the body of the bath.

Operating data for this example are as follows:

Rate of sodium addition g./hr.	23.
Concentration of Ca in bath	.5% by wt.
Concentration of Ti as chloride in bath	.75% by wt.
Rate of titanium formation	11.8 g./hr.

Nature of titanium bundles: The titanium bundles formed are composed of filamentary particles about 0.5 mm. maximum diameter and .06 mm. average diameter. The salt content of the drained bundles is 12.0% and the packing density 1.1 grams titanium per cc. Analysis of the disintegrated and washed bundles is: Cl, .02%; Fe, .03%; O_2, .04%; other impurities traces only; balance Ti.

Example VI

I take a molten electrolytic bath composed of 90% NaCl, 10% $BaCl_2$, and pass a unidirectional current through the bath between a graphite anode, partially enclosed in a bell to collect and remove Cl_2 and a titanium cathode until the bath is saturated with alkalinous metal; I then continue electrolysis and add titanium tetrachloride at the rate of 188 grams per hour, which is the electrochemical equivalent of the current passed if all the tetrachloride is reduced to metal. In this example the titanium chloride is added beneath the surface of the bath in the cathode zone, and the entire cathode zone may be regarded as the reaction zone.

The operating data for this example follow:

Temperature of operation	850° C.
Cathode Cd	300 amps/sq. ft.
Anode Cd	800 amps/per sq. ft.
Amperes	130.
$TiCl_4$ added per hour	188 grams.
Ti produced per hour	47 grams.
OC voltage of cell	1.85.

Nature of titanium produced: The titanium produced in this example is in the form of small bundles 1/16" average diameter, which bundles consist of branched filamentary particles having an average maximum dimension .15–20 mm. and average diameter .08 mm. The salt content after draining is 50%, and the packing density of the bundles is 1.4 grams per cc. After disintegration and washing, the titanium particles have an analysis of .04% Cl; .03% Fe; .03% O_2; .002% N_2, balance titanium except for traces of other impurities.

Example VII

I make a fused bath of 50% lithium chloride and 50% potassium chloride by weight. I heat this bath to 600° C. in an iron pot. In the center of this pot I place a graphite electrode provided with a ceramic sleeve dipping into the fused bath. The sleeve is provided with an outlet for chlorine. The remainder of the bath is protected by an atmosphere of argon. I pass a unidirectional current through the bath so that the pot is the cathode and the graphite the anode. When the bath is saturated with alkalinous metal but contains no undissolved alkalinous metal, I introduce anhydrous zirconium tetrachloride into the bath between the electrodes. There are formed bundles of filamentary particles of zirconium in the fused bath. I continue the addition of finely divided zirconium tetrachloride at the rate the metal is formed at the reaction zone. I then dicontinue the electrolysis and allow the bath to solidify. I remove the solidified bath from the pot, dissolve the salts in water and recover the subdivided metal.

The operating data for this example follow:

Temperature of bath	600° C.
Cathode Cd	200 amps/sq. ft.
Anode Cd	2,000 amps/sq. ft.
Amperes	130.
$ZrCl_4$ introduced per hour	90 g.

Nature of zirconium produced: The zirconium metal is formed as bundles of filamentary particles. The bundles are 1/16" in diameter, and the particles forming the bundles are branched with a maximum dimension of .15–20 mm. and an average diameter of .06 mm. The salt content of the drained bundles is 42% and the packing density 2.4 grams per cc. The zirconium is pure except for traces of impurities.

Example VIII

I make a fused bath of 67% KCl, 33% $CaCl_2$. I place this bath in a ceramic pot and heat to 700° C. In this bath I place two electrodes of titanium which contain about 0.5% oxygen. An argon atmosphere is maintained above the bath. I pass a unidirectional current at 2,500 amperes per square foot between the electrodes, the direction of the current being reversed every 30 seconds. There is formed at the electrode, which is the anode, titanium dichloride. This titanium dichloride is reduced in situ by calcium, formed at the same electrode and dissolved

in the electrolytic bath when the current is reversed, to form filamentary particles of titanium. The calcium chloride formed by this reduction replenishes the bath. The oxide in the electrodes forms TiO_2. It will be clear that in this process no undissolved alkalinous metal is formed in the bath, and that the dissolved titanium salt is reduced at the reaction zone at the same rate it is formed. I continue the electrolysis with periodic reversals of the current until both electrodes are consumed. I then allow the bath to solidify, and dissolve the salts in dilute hydrochloric acid which also dissolves the calcium oxide formed. I recover the pure oxygen-free titanium as aggregates of filamentary particles. I find that this process is highly efficient electrically; there is produced almost exactly 24 grams of subdivided metal per ampere hour.

The operating data for this example follow:

Temperature	700° C.
Electrode current density	2,500 amps/sq. ft.
Amperes	130.
Ti produced per hour	47 grams.

The titanium bundles produced are 1/64" in diameter and are made up of branched filamentary particles about .25 mm. maximum dimension.

The bundles are disintegrated into individual particles and washed free of salt and included TiO_2.

The titanium product thus prepared analyzed: Cl, .01%; Fe, .02%; O_2, .04%; N_2, .002%; other impurities traces; balance Ti.

Example IX

In this example, I proceed as in Example VIII except that I reverse the current at 10 minute intervals. Bundles of filamentary particles are formed in the fused bath as in Example VIII. These bundles are larger than in Example VIII and may be up to an inch or more in diameter and individual filamentary particles may be up to 3/4" long.

Example X

In this example I take a cylindrical steel pot, which I use both as a container and as a cathode in an electrolytic cell. I provide this pot with a cover having an inlet and outlet for maintaining an atmosphere of pure argon in the cell. As an anode, I provide in the center of the cell a cylindrical rod of impure titanium containing oxygen which is in solid solution in the titanium. I also provide an auxiliary circuit in the cell, consisting of a graphite anode near the bottom of the pot, and a foraminous cylindrical cathode between the main anode and the pot wall, which is also the main cathode. The purpose of this auxiliary circuit is to provide some chlorination of the electrolyte and thus reduce the concentration of the alkalinous metal solution formed at the cathode. At the same time, any more noble impurities dissolved at the anode, due to open circuit cell voltage between anode and cathode, are deposited on the auxiliary cathode which is maintained anodic to the main cathode by a few hundredths of a volt, but cathodic to the main anode.

I use an electrolyte of 83% NaCl, 2% $TiCl_2$ and 15% $BaCl_2$. The cell is operated at 250 amperes per square foot of cathode and 750 amperes per square foot of anode. The temperature is 815° C. The titanium, which is formed adjacent the cathode, and adherent thereto, consists of bundles of interlaced filamentary crystals of pure titanium containing in their interstices the electrolyte and some included very fine TiO_2 which is formed at the anode and finds its way by convection to the cathode. The bundles of primarily filamentary particles were up to 15 mm. in length and 0.75 mm. in diameter. The electrolysis is terminated at a stage at which the residual anode, although rendered spongy by removal of titanium, still is substantially self-supporting. I drain the salt from the cell and cool the contents of the cell in argon.

Example XI

In this example I produce the zirconium bundles for treatment, according to my invention, by the operation of a compartment cell having a catholyte of 80% $CaBr_2$, 10% BaBr and 10% $ZrBr_2$, and an anolyte $CaBr_2$. $ZrBr_4$ is passed into the cathode area, which is maintained at 750° C. The anode is graphite, the cathode zirconium. An inert atmosphere is maintained above the catholyte and anolyte. Direct current is passed through the cell at 250 amperes per square foot cathode current density, and 500 amperes per square foot anode current density. The rate of addition of $ZrBr_4$ is so controlled that the open circuit voltage of the cell an instant after operation is 1.7 volts. Zirconium is produced adjacent the cathode in bundles of interlaced filamentary crystals. I remove the zirconium metal from the cell, and cool it in an inert atmosphere. The zirconium bundles are disintegrated in a multiple hammer mill with titanium surfaces, then thoroughly washed on a 100 mesh screen.

The product obtained in this way is similar in appearance to that produced in Example V, and is found on analysis to be 99.99+% zirconium.

Example XII

I make a fused bath of oxygen-free calcium and sodium chlorides in the proportion 66% $CaCl_2$, 34% NaCl. I heat this bath in a ceramic pot to 750° C., at which temperature it is fused. I introduce into this bath metallic sodium in the form of a ribbon near one side of the pot. The metallic sodium reacts to form metallic calcium, which dissolves in the bath. I introduce titanium tetrachloride as a liquid at the other side of the pot, being sure that the rate of introduction of the sodium on the one hand and the titanium chloride on the other are equivalent. An atmosphere of argon is maintained over the bath. Metallic titanium particles, filamentary in form, are formed in the bath. I recover pure oxygen-free titanium as aggregates of filamentary particles. The titanium tetrachloride is added by forcing the same under the surface of the fused salts. The rate of addition is adjusted so that neither the metal chloride to be reduced, nor dissolved alkalinous metal is in excess.

What is claimed is:

A new composition suitable for the production of pure metals of the titanium group by aqueous leaching, said composition consisting of bundles of macroscopic particles, primarily filamentary in shape, of one of the above group of metals having their interstices at least partially filled with an alkalinous metal chloride substantially free from chloride of the filamentary metal and from undissolved alkinous metal.

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