July 31, 1962 J. R. SPRAUL ETAL 3,047,477

REDUCTION OF TITANIUM DIOXIDE

Filed Oct. 30. 1957 2 Sheets-Sheet 1

FIG. 1

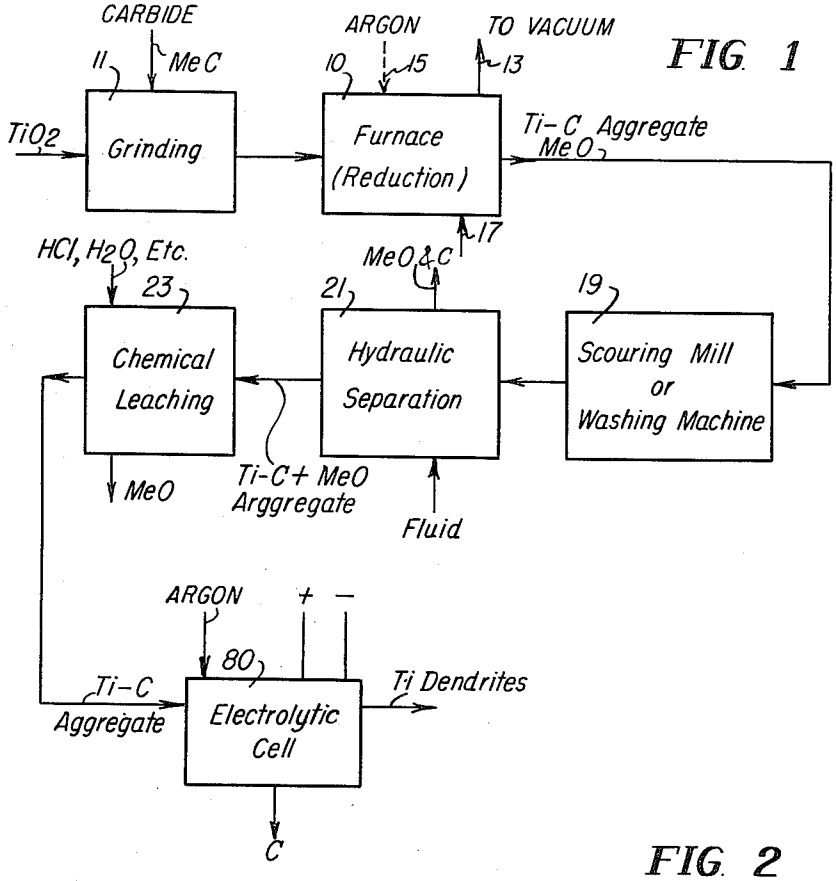
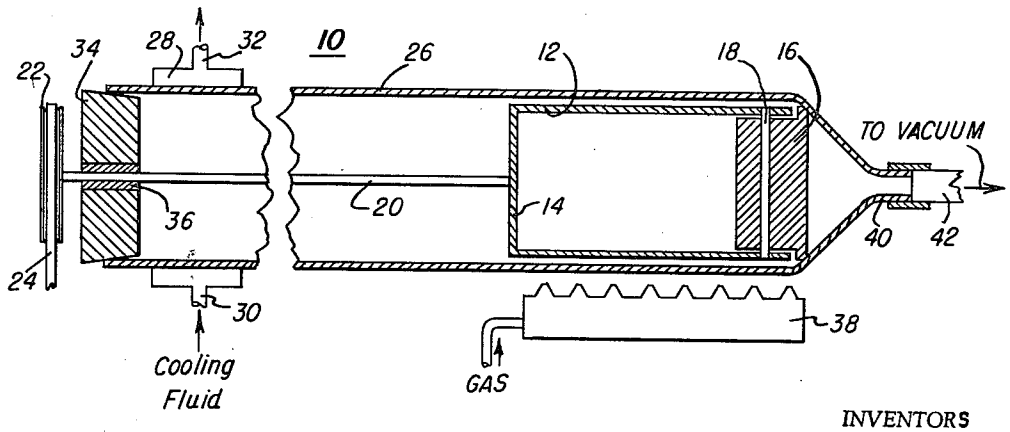


FIG. 2



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FIG 3

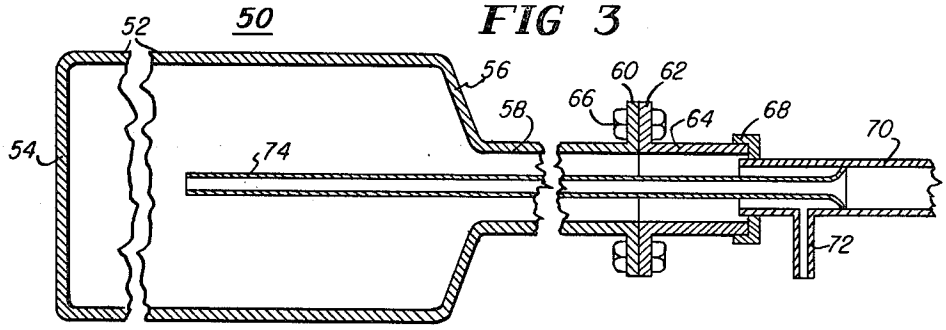
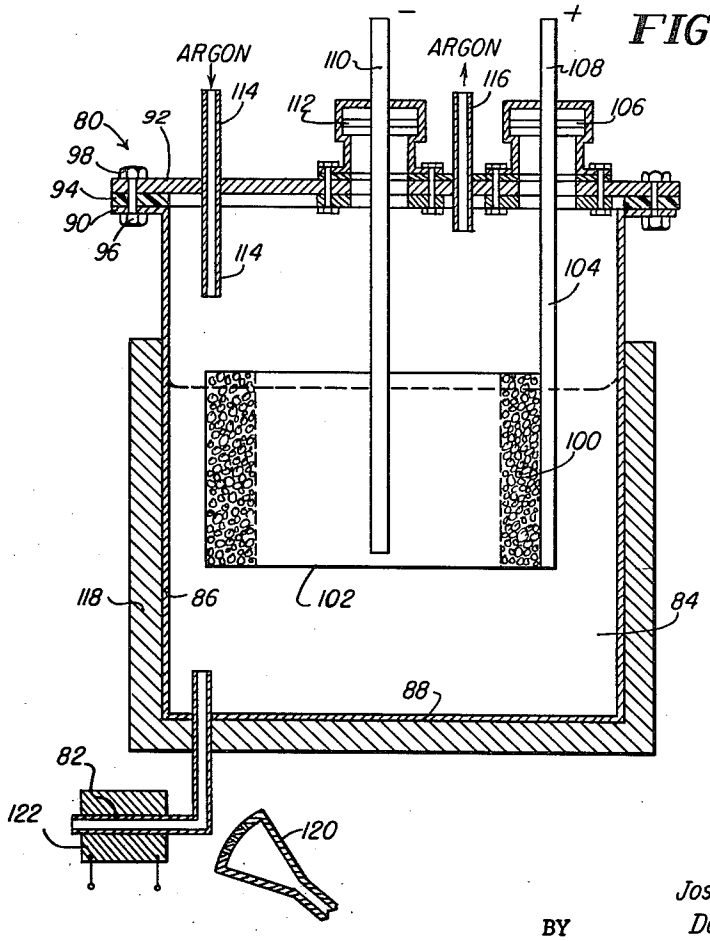


FIG. 4



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REDUCTION OF TITANIUM DIOXIDE

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26 Claims. (Cl. 204—64)

This invention relates to the reduction of titanium dioxide to form free titanium metal, and particularly to producing aggregates comprising free titanium metal intermixed with and adhering to particles of carbon and other reaction products and to electrorefining of the aggregates to produce titanium metal dendrites.

The processes used heretofore to reduce titanium dioxide to produce free titanium metal have been indirect and expensive. The titanium dioxide in these prior processes is first converted to halogen compounds which are in turn reduced to free titanium metal. These prior processes have been thought necessary to produce titanium metal sufficiently free of impurities and alloying agents to render the titanium metal ductile and generally useful.

Accordingly, it is an important object of the present invention to provide improved processes of reducing titanium dioxide to produce free titanium metal.

Another object of the invention is to provide an improved process to produce free titanium metal which is less expensive than processes known heretofore and which yields a satisfactory product.

Still another object of the invention is to provide an improved process for reducing titanium dioxide at relatively low temperatures with metal carbides to produce free titanium metal, and particularly such a process in which free titanium metal is obtained directly from the carbide reduction reaction.

Still another object of the invention is to provide an improved method of reducing titanium dioxide utilizing metallic carbides as the reducing agent followed by electrorefining to produce free titanium metal dendrites.

These and other objects and advantages of the invention will be better understood from the following description when taken in conjunction with the accompanying drawings. In the drawings, wherein like reference numerals have been utilized to designate like parts throughout:

FIG. 1 is a schematic flow diagram of the process of the present invention;

FIG. 2 is a view in vertical section through one form of furnace useful in carrying out the process of the present invention;

FIG. 3 is a view in vertical section through a second form of furnace useful in carrying out the process of the present invention; and

FIG. 4 is a view in vertical section through an electric cell suitable for carrying out one step in the process of the present invention.

It has now been found that the objects and advantages of the present invention can be obtained by reacting in the solid state titanium dioxide and the carbide of a metal seletced from the class consisting of aluminum and alkaline earth metals by preparing an intimate mixture of the ingredients in finely divided form, and heating the mixture to an elevated temperature below about 1200° C. throughout a time interval sufficiently long to effect a substantially complete reaction whereby to produce free titanium metal. The product of the reaction is an aggregate comprising fine particles of titanium metal intimately adhering to small particles of carbon. The titanium metal can be separated from the aggregate by immersing the aggregate in a fused salt bath including a small amount of soluble titanium dichloride and passing a direct electric current between the aggregate connected as an anode and

a cathode whereby to produce on the cathode dendrites of free titanium metal. Any of the various forms of titanium dioxide can be utilized in the present invention including without limitation those forms generally designated as anatase, brookite and rutile. Refined titanium dioxide such as that utilized in paints and designated "pigment grade" as well as naturally occurring commercial or technical grades available in bulk form may be used.

Various metallic carbides have been successfully used in carrying out the present invention. In general it has been found that any carbide selected from the class consisting of aluminum and alkaline earth metals may be used. A preferred carbide for use in this invention is calcium carbide because of its availability and moderate cost. Mixtures of metal carbides can also be used advantageously.

The ratio between the titanium dioxide and the metallic carbide is at least such as to give equimolecular amounts and preferably an excess of metallic carbide is utilized such as, for example, 25% excess.

It has been found that the reaction can be carried to substantial completion within a reasonable time. With the preferred calcium carbide, conditions can be chosen so that the reaction is substantially complete in about 15 to 90 minutes.

The particle size of the reactants was also found to be of importance in successfully carrying out the process. In general the particle size of the titanium dioxide and the metallic carbide should be less than 60 microns and may be as small as less than 1 micron. A preferred range of particle size is from about 5 to 60 microns, although larger particle sizes may be utilized in which case the reaction time and yield may be adversely affected.

Because of the affinity of free titanium metal for oxygen and certain other gases such as nitrogen, it has been found desirable to carry out the reduction reaction between the titanium dioxide and the metal carbide substantially in the absence of atmospheric oxygen and nitrogen. In one practical form of the invention the reaction is carried out in a vacuum of approximately 2 mm. of mercury, absolute pressure. Alternatively, the reaction may be carried out in an atmosphere of gas which is inert to free titanium metal. Examples of such gases are argon and the other noble gases. It is believed that the reaction is carried out in the solid state with the reactants being in the solid state and the reaction products being in the solid state, although the reaction is carried out at relatively high temperatures. Accordingly, it is desirable that complete and continuous intermixing of the products be obtained at all times during the reaction. This can be achieved by utilizing rotary type furnaces or stirring and scraping devices in the reaction vessel, or a combination thereof.

The product from the reduction of titanium dioxide with metal carbides is an aggregate comprising small particles of free titanium metal intermixed with and intimately adhered to small particles of carbon. The particle size of free titanium metal in the aggregate depends upon the screen analysis of the original titanium dioxide employed in the reduction, but in the usual case, the particle size is such that it has a miximum dimension in any direction of about 10 microns. The particles of carbon are ordinarily larger than those of the titanium metal and in many cases completely surround the titanium metal particles whereby to embed the titanium particles in the carbon. The metal oxides corresponding to the metal carbide utilized as a reducing agent will also be present in the aggregate. Because of the relatively low temperature of the reaction very little titanium carbide is present, but small quantities of titanium carbide are present, as well as traces of other reaction products derived from impurities contained in the titanium dioxide, etc.

It has been found that the larger part of the metallic oxides and part of the carbon present in the aggregate product can be separated therefrom. Specifically, the aggregate is first treated in a scouring mill or washing machine, and is thereafter subjected to fluid separation processes such as hydroseparations, air separations and flotation processes. Such separations are made possible because of the higher specific gravity of the titanium particles and the physical admixtures of the titanium metal embedded in carbon as compared with the specific gravity of the metal oxides and free carbon. Further removal of the metal oxides can be achieved by leaching. For example, in the case of calcium oxide, any dilute acid such as sulfuric acid or hydrochloric acid may be utilized, as can also certain salt solutions such as ammonium acetate, or even water in large amounts.

The aggregate product either before separation of the metal oxides therefrom or after such separation can be utilized advantageously in electrorefining processes to recover the titanium metal therefrom in the form of useful, ductile titanium metal dendrites. More specifically, the aggregate can be successfully utilized in the electrorefining process developed by the Chicago Development Corporation of Riverdale, Maryland, which is described in the booklet entitled "Electrolytic Titanium" published by that company, edited by R. S. Dean and bearing an issue date of January 23, 1957. When separating the free titanium metal from the aggregate utilizing the electrorefining method of the Chicago Development Corporation, the aggregate is placed in a foraminous basket which is immersed in a molten salt solution that contains a small amount of soluble titanium dichloride. The refining process is carried out under an inert atmosphere such as, for example, argon with a low voltage applied so as to render the aggregate the anode and a suitable support rod as the cathode. The titanium metal is leached from the aggregate and deposited as free metal in the form of dendrites on the cathode.

Referring to FIG. 1 of the drawings there is schematically illustrated a flow diagram illustrating the process of the present invention for producing titanium metal from titanium dioxide. The titanium dioxide and the metallic carbide may be ground together as at **11** after which the reactants are charged into a furnace **10**. Furnace **10** is provided with a vacuum connection **13** and in certain forms is also provided with a connection **15** for an inert gas such as argon and also may be provided with a cooling connection **17**. The product from furnace **10** is an aggregate which may include titanium metal, free carbon, titanium carbide, a metallic oxide derived from the reducing agent, and unreacted titanium dioxide and metallic carbide. The aggregate is then processed to separate the titanium metal bearing portions from the other materials. In the process illustrated in FIG. 1, the first step in the separation process is to treat the aggregate in a scouring mill **19**. The liberated particles of the aggregate can then be treated by hydraulic separation as at **21** to remove therefrom certain of the oxides and a portion of the carbon. The product from the hydraulic separation can have the larger portion of the remaining metallic oxide removed by a chemical leaching step **23**. Next the product which now comprises essentially titanium metal and carbon is then electrically refined in a cell **80** to produce titanium metal dendrites as a final product.

Several examples of the present invention will be given for purposes of illustration. It is to be understood that these examples are illustrative only and are not to be considered to impose limitations upon the scope of the invention.

EXAMPLE 1

Pigment grade titanium dioxide having a titanium dioxide content of more than 98% by weight and a commercial grade of calcium carbide having a purity of 80% by weight were utilized as the reactants. There was mixed together a sample consisting of 2.30 grams of titanium dioxide and 5.75 grams of calcium carbide. The reactants were ground to a fine powder in a mortar and pestle.

The reduction reaction was carried out in a rotary vacuum furnace of the type illustrated in FIG. 2 of the drawings and generally designated by a numeral **10**. Furnace **10** includes a rotating cylindrical tube **12** approximately 6 inches long and formed of ¾ inch stainless steel pipe. One end of tube **12** is closed by means of a transverse wall **14** and the other end receives a plug **16** loosely fitted in the end of tube **12** and held in plugging position by means of a removable transverse pin **18** passing through aligned apertures in tube **12** and plug **16**. The loose fit of plug **16** permits the loss of gas from tube **12** with a negligible loss of reacting materials. The capacity of tube **12** was slightly greater than 8 grams. Extending to the left from wall **14** is a shaft **20** passing out of the furnace **10** and having affixed thereto a pulley **22**. A suitable drive belt **24** engages pulley **22** and is driven by a prime mover (not shown). Belt **24** and pulley **22** were arranged to rotate tube **12** thirty revolutions per minute. A cylindrical stationary outer furnace wall **26** is provided and has a length several times the length of tube **12**. The left hand end of wall **26** as in FIG. 2 is provided with a cooling jacket **28** having a cooling fluid inlet **30** and a cooling fluid outlet **32**. A plug **34** tightly seals the left-hand end of wall **26** with shaft **20** passing through a suitable pressure tight seal **36**. Cooling jacket **28** provides a cold section for furnace **10**. A hot section for furnace **10** is provided at the right-hand end thereof as in FIG. 2. Suitable means such as a gas burner **38** is provided to heat wall **26** and the contents thereof. The adjacent end of wall **26** is tapered inwardly to provide a connecting portion **40** which can be coupled to a line **42** connecting with a vacuum pump (not shown) to exhaust air from the interior of furnace **10** and from the interior of tube **12**.

In carrying out the present invention, furnace **10** is brought up to operating temperature by means of the heater **38** after which the rotating tube **12** is inserted into the cold portion adjacent to the cooling jacket **28**. Vacuum is then drawn through line **42** whereby to exhaust the air from within furnace **10** including the reaction tube **12**. Preferably the pressure within furnace **10** was reduced to a value of 2 mm. of mercury, absolute pressure, and held at this value throughout the reaction. After evacuation of furnace **10**, the reaction tube **12** is advanced while rotating into the heated zone at the right-hand end of wall **26**. Reaction tube **12** is rotated at thirty revolutions per minute throughout the reaction time. At the end of the reaction time the rotating tube **12** is moved to the cold section of the furnace **10** where it is cooled rapidly by the use of the cooling jacket **28**. Atmospheric pressure is then admitted to furnace **10** and reaction tube **12** is withdrawn for recovery of the product.

In Example 1, the reaction was carried out at 1038° C. for a period of 60 minutes. The gram-molecular raito of calcium carbide to titanium dioxide was approximately 1.25:1 which, using the purity of reactants described above, results in a gross weight raito of 2.5 grams of calcium carbide to 1.0 gram of titanium dioxide.

The product was analyzed and was found to contain substantially 100% yield of free titanium metal based on the titanium available in the titanium dioxide starting material. The product was in the form of an aggregate of very fine particles of titanium metal embedded in and intimately adhered to carbon. Using a metalloscope, it was determined that the titanium metal had a particle size of from about 2 to about 10 microns in the greatest dimension thereof and the titanium metal particles were embedded in larger particles of carbon. Also present in the aggregate was calcium oxide and some unreacted calcium

carbide. In general the titanium metal carbon encrusted particles were in clusters having an average diameter of 40 microns. The clusters fracture easily and the material can be readily reduced in particle size in a scouring mill.

In Example 1 above, an excess of calcium carbide over and above that required theoretically to react all of the titanium dioxide was provided assuming that the reaction which takes place is as follows:

$$TiO_2+2CaC_2 \rightarrow Ti+2CaO+4C$$

The ratio of reactants given for Example 1 provides an excess of calcium carbide of substantially 25% of the minimum amount required theoretically to complete the reaction. It is highly advantageous to provide an excess of calcium carbide to insure completion of the reaction at a convenient reaction temperature. If only the minimum amount of calcium carbide theoretically required for complete reaction is utilized, a reduced yield of titanium metal is obtained, see Example 2 below.

EXAMPLE 2

Five grams of calcium carbide (80% purity) and 2.5 grams of pigment grade titanium dioxide were ground to a fine powder in a mortar and pestle. The reactants were charged into furnace 10 and heated therein at 1038° C. for 60 minutes. After cooling and analysis, the product showed a 43% yield of free titanium metal by weight aggregated with calcium oxide, free carbon and unreacted titanium dioxide and calcium carbide.

The temperature of reaction is also functional and directly affects the yield of free titanium metal. Example 3 was run with all the parameters of the reaction the same as Example 1 above, except that the temperature was lowered to 927° C. The percent yield of titanium metal on a weight basis was only 32% as compared with substantially 100% in Example 1 which was reacted at 1038° C.

It has also been found that the time of reaction is critical. The reactants when placed in the heated zone of furnace 10 arrive at the temperature of reaction in approximately 12 minutes. For convenience, however, the reaction time is measured from the time of insertion of the reactants into the hot zone of furnace 10. The following is a table illustrating the effect of time on the reaction, all of the reaction parameters being maintained constant except time.

Table I

Example No.	Ratio of CaC_2 to TiO_2 by weight	Temp., ° C.	Time, minutes	Percent Yield Ti
4	2.5	1,038	15	14
5	2.5	1,038	30	85
1	2.5	1,038	60	100

From the above it will be seen that the yield increases with an increase in reaction time with the optimum reaction time being approximately 60 minutes or one hour.

The ratio of the reactants, i.e., the ratio of calcium carbide to titanium oxide also affects the reaction and has been found to be critical. In general at least equimolecular amounts of calcium carbide and titanium dioxide must be present as has been described above. When utilizing 80% pure calcium carbide and pigment grade titanium dioxide, the ratio by gross weight of calcium carbide to titanium dioxide to obtain equimolecular proportions is 2:1. It further has been found that increased yields are produced for a given set of reaction conditions if an excess of calcium carbide is utilized. When the optimum temperature of approximately 1000° C. and the optimum reaction time of 60 minutes are utilized, it has been found that it is desirable to provide approximately a 25% molecular excess of calcium carbide over that theoretically required to complete the reaction. When utilizing the commercial grade of calcium carbide and the pigment grade of titanium dioxide, a ratio by weight between the calcium carbide and the titanium dioxide of 2.5:1 is required. When other than the optimum reaction time and temperature are utilized, it has been found that the reaction can be driven toward completion by utilizing even higher excesses of calcium carbide and it is possible to utilize an excess of seven or more times that required to complete the theoretical reaction. A series of reactions were carried out at 816° C. for 60 minutes to demonstrate the effect of changes of the ratio of calcium carbide to titanium dioxide upon the yield of free titanium metal. This series of reactions was carried out in a Sentry Model V electric tube furnace. After the reacting materials were ground to a fine powder in a mortar and pestle, they were pressed into a pill and then placed in an Alundum boat and heated in the furnace under a reduced atmosphere of less than 2 mm. of mercury, absolute pressure. The following table summarizes the results of this series of reactions.

Table II

Example No.	Ratio of CaC_2 to TiO_2 by weight	Percent Yield Ti
6	1	7
7	2.5	11
8	4	38
9	7	65

Example 6 in Table II is exemplary of the yields produced when less than equimolecular proportions of calcium carbide and titanium dioxide are utilized. Actually the ratio of reactants of Example 6 is such that there is insufficient calcium carbide present to react all of the titanium dioxide available for reduction to titanium metal. Example 7 represents a 25% excess of calcium carbide over that theoretically required to react all the titanium dioxide available. Examples 8 and 9 represent molecular ratios of 2:1 and 3.5:1, respectively, of calcium carbide to titanium dioxide. The examples in Table II demonstrate that even if less than optimum temperature conditions are utilized, the reaction can be driven toward completion utilizing a large excess of calcium carbide. By slightly raising the temperature above that utilized in Example 9 it is possible to obtain substantially 100% yield of free titanium metal by using the substantial excess of calcium carbide demonstrated therein.

Example 10 was a reaction carried out utilizing the same reaction conditions including the ratio of calcium carbide to titanium dioxide as those utilized in Example 9. The temperature, however, was elevated to 942° C. The yield from Example 10 was substantially 100%. Accordingly, a good yield was obtained at a temperature substantially below the optimum temperature of 1000° C. by using a ratio of calcium carbide to titanium dioxide of 7:1 by weight of the commercial products or 3.5:1 calculated on a molecular basis. When utilizing the optimum reaction conditions, however, it has been found that approximately 25% excess of calcium carbide provides satisfactory and economic operation of the reaction.

Even higher temperatures than the optimum reaction temperature of approximately 1000° C. can be utilized and still obtain good yields of titanium metal as is illustrated in Example 11 below.

EXAMPLE 11

A charge including five parts by weight of commercial grade calcium carbide and one part by weight of pigment grade titanium dioxide were ground and formed into a pill. The pill was placed in an Alundum boat and heated in the Sentry Model V furnace for 60 minues at a temperature of 1120° C. The yield of free titanium metal was substantially 100% of the titanium available in the reaction materials.

For the purpose of producing larger samples, a rotary furnace of the type illustrated in FIG. 3 may be utilized.

This furnace, generally designated by the numeral 50, includes a large tube 52 mounted for rotation (by a mechanism not shown). Tube 52 is made from a 12-inch length of pipe having a 3½-inch diameter. One end of tube 52 is closed by a transverse wall 54 and on the other end is provided an inturned shoulder 56 which joins a tube 58 of smaller diameter. Formed on the outer end of tube 58 is an outwardly directed flange 60 which is adapted to cooperate with a flange 62 formed on a tube 64. Nuts and bolts 66 connect flanges 60 and 62 for ready separation thereof so that material to be reacted can be charged into tube 52 through tube 58 and the reaction products withdrawn therefrom.

The other end of tube 64 is provided with a rotary vacuum seal 68 which interconnects tube 64 which is rotated and a stationary tube 70. A gas outlet 72 is provided on pipe 70 to permit evacuation of the reaction portion of tube 52. Also mounted within tube 70 is a gas inlet 74 extending from a point disposed outwardly with respect to outlet 72 and extending inwardly to substantially the center of tube 52. The inlet 74 permits an inert gas such as argon to be admitted into tube 52. The capacity of furnace 50 is about one kilogram.

For the purpose of carrying out a commercial reaction, it is desirable to use grades of titanium dioxide other than the pigment grade. For example, it would be desirable to utilize naturally occurring deposits of titanium dioxide such as rutile. For example, an experiment was conducted with such material in the form of an airfloated concentrate obtained from the Foote Mineral Company and derived from the Australian deposits. This natural airfloated rutile concentrate consisted of approximately 92% of titanium dioxide by weight as compared with the better than 98% titanium dioxide by weight contained in pigment grade materials. It also was noted that the particle size of the commercial material was substantially greater than that of the pigment grade material.

Table III is a comparison of the yields obtained when utilizing pigment grade material and the above described commercial material under the same reaction conditions. The calcium carbide was also the commercial form. The reactants were ball milled under toluene and then reacted in furnace 50.

Table III

Example No.	Percent by weight CaC_2	Percent by weight TiO_2	Temp., ° C.	Time, min.	Grade of TiO_2	Percent Yield Ti
12	72	28	1,000	60	pigment.	92.0
13	72	28	1,000	60	commercial.	34.5
14	72	28	1,000	180	do.	21.5

In example 14, it was attempted to increase the yield of titanium metal by increasing the reaction time. The results indicated that increasing the time did not increase the yield of titanium metal in this instance.

An examination of certain of the products in the above examples indicated the presence of titanium carbide. It is believed that in addition to the pricipal reaction discussed above, two other reactions probably are taking place whereby there are present the following three competing reactions:

$$TiO_2+2CaC_2 \rightarrow Ti+CaO+4C \quad (I)$$
$$TiO_2+2CaC_2 \rightarrow TiC+2CaO+3C \quad (II)$$
$$Ti+C \rightarrow TiC \quad (III)$$

Reaction I is slightly less endothermic than reactions II and III. A series of reactions were carried out to determine the amount of free titanium metal and the amount of titanium carbide present at the end of certain specified reaction times. In these reactions, a calcium carbide material was utilized containing 89% calcium carbide and the commercial grade of titanium dioxide containing approximately 92% titanium dioxide was used. The reactants were ball milled under toluene to an average particle size of less than 2 microns. The results of these experiments are set forth in Table IV below.

Table IV

Example No.	Ratio by weight, CaC_2:TiO_2	Temp., ° C.	Time, min.	Percent Ti	Percent TiC	Percent Total Ti Available Reacted
15	2.5	1,000	30	14	58	72
16	2.5	1,000	40	13	74	87
17	2.5	1,000	60	77	20	97

Because of the small particle size used in Examples 15, 16 and 17, the furnace 50 was also provided with a combination stainless steel scraper blade and knocker to minimize caking of the reactants.

The yield of titanium was determined by an approximate method described more fully below; which approximate method has been confirmed as being satisfactory by an accurate X-ray diffraction method. In this approximate method, the yield of titanium was determined by leaching the product with hydrochloric acid and determining the titanium removed by the hydrochloric acid. The titanium carbide was determined by treating the residue from the hydrochloric acid extract with nitric acid and determining the amount of titanium extracted by the nitric acid.

It has also been found that the particle size of the reactants and particularly the particle size of the titanium dioxide has an important influence on the reduction reaction. There is shown in Table V the results of utilizing different particle sizes of titanium dioxide. The natural airfloated rutile ore as received was separated by settling rate into the following fractions:

(1) 0–2 microns (average 1 micron)
(2) 1–6 microns (average 3 microns)
(3) 4–15 microns (average 7 microns)
(4) 15–50 microns (average 30 microns)

The calcium carbide utilized contained 89% CaC_2 and was ball milled under toluene to a particle size of approximately 4 microns. The reactants were mixed in the ratio of 2.5 parts by weight of the calcium carbide material to 1 part by weight of the titanium dioxide concentrate. The reaction was conducted at 1000° C. for 60 minutes in furnace 50 under an argon atmosphere.

Table V

Example No.	Average Particle Size of TiO_2, microns	Percent Yield of Ti	Percent Yield of TiC	Total Percent of Available Ti Reacted
19	1	55.5	37.3	92.8
20	3	69.0	24.8	93.8
21	7	71.5	21.0	92.5
22	30	82.5	11.0	93.5

From Table V it is apparent that the optimum yield of the desired free titanium metal is obtained when the titanium dioxide has a particle range in the size of 15 to 50 microns and with the average of approximately 30 microns.

Other metallic carbides were successfully utilized in reducing titanium dioxide in addition to calcium carbide. For example, it was found that aluminum carbide having the empirical formula Al_4C_3 can be successfully utilized to reduce titanium dioxide. The aluminum carbide used in the following examples contained approximately 85% Al_4C_3 by weight as determined by methane evolution. The titanium dioxide utilized was the pigment grade. The ratio by weight of the reactants was 50 parts of titanium dioxide to 40 parts of aluminum carbide which provides approximately 28% excess aluminum car-

bide over that theoretically required, assuming that the products react in accordance with the following formula:

$$3TiO_2+Al_4C_3\rightarrow 3Ti+2Al_2O_3+3C$$

The aluminum carbide and the titanium dioxide were ground by hand in a mortar and pestle and the reaction was carried out in the rotary furnace **50**. Table VI summarizes the results of these reactions.

Table VI

Example No.	Temp., ° C.	Time, hours	Percent Yield Ti	Percent Yield TiC
23	800	5	4.7	1.0
24	1,000	3	21.6	1.9
25	1,000	5	78.0	9.7

From Table VI it is seen that a good yield of titanium metal can be obtained using aluminum carbide as the reducing agent. Higher temperatures and longer reaction times provide improved yields of the titanium metal.

Other alkaline earth metal carbides can also be utilized to reduce titanium dioxide. There are given in Table VII below examples of the use of barium carbide and magnesium carbide as reducing agents for titanium dioxide.

Table VII

Example No.	Type of Carbide	Type of Weight of Carbide	Percent by Weight TiO_2	Temp., ° C.	Time, Hours	Percent Yield Ti	Percent Yield TiC
26	BaC_2	42	8	1,000	1	34.5	7.6
27	BaC_2	42	8	1,000	3	21.5	15.0
28	Mg_2C_3	36.4	28.6	730	1	94	6

The titanium dioxide utilized in Examples 26, 27 and 28 was the pigment grade and was dried in vacuum at 120° C. for 48 hours before use. The barium carbide utilized in Examples 26 and 27 was prepared by the following reaction:

$$BaCO_3+C+3Mg\rightarrow BaC_2+3MgO$$

The product was used without purification and contained 47% barium carbide and less than 1% magnesium metal. The magnesium carbide utilized in Example 28 was prepared by reacting magnesium metal powder with acetylene and propane and had a purity of 51%.

The reactants in each of Examples 26, 27 and 28 were ball milled under toluene and reacted in furnace **50**. In Examples 26 and 27, a 25% excess of barium carbide was utilized above that theoretically required to react the titanium dioxide present, assuming that the reaction takes place as follows:

$$TiO_2+2BaC_2\rightarrow Ti+2BaO+4C$$

A 20% excess of magnesium carbide was utilized in Example 28 assuming that the reaction proceeds as follows:

$$TiO_2+Mg_2C_3\rightarrow Ti+2MgO+3C$$

The reaction with magnesium carbide gives good yields of the desired free titanium metal.

In the examples heretofore disclosed, the particle size of the TiO_2 employed had a fine particle size (less than 60 microns); however, it is feasible to use TiO_2 having a coarse particle size (50 x 200 mesh) in the presence of a small amount of sodium fluoride as an accelerator. Specifically, it has been discovered that the reduction reaction may be substantially accelerated by the presence of a small amount of sodium fluoride, normally about 10% by weight with respect to the titanium dioxide; and in the furnace **50**, runs were made employing the reactants calcium carbide and titanium dioxide, both with and without sodium fluoride. In these runs, the reactants (CaC_2—25 gms. and TiO_2—10 gms.) were thoroughly intermixed; and also the accelerator (NaF—1 gm.) was thoroughly intermixed, when it was present.

Two comparative runs were made, each at 1000° C. and for 60 minutes, employing coarse rutile concentrate (50 x 200 mesh) as received from the Foote Mineral Company, with the following results:

Table VIII

Example No.	Reactants by weight, gms.	Percent Yield Ti	Percent Yield TiC	Percent Total
29	CaC_2—25, TiO_2—10	3.5	1.0	4.5
30	CaC_2—25, TiO_2—10, NaF—1	43	6	49

Moreover in the furnace **50**, comparative runs were made, each at 1000° C., employing pigment grade TiO_2, having a fine particle size (less than 60 microns) and variable time intervals. In each of these runs the ratios of the reactants by weights were fixed: CaC_2—25; TiO_2—10; NaF—1. The results of these runs are set forth below:

Table IX

Example No.	Time	Percent Yield Ti	Percent Yield TiC	Percent Yield Total
31	10	68	23	91
32	20	53	36	89
33	35	17.5	57.0	74.5

In each of these Examples 29 to 33, inclusive, the CaC_2 was ball-milled; the percent free Ti was established by the solubility in HCl and the percent of Ti as TiC by the solubility of the residual Ti in HnO_3; all as previously explained.

Accordingly, it is apparent that the NaF substantially reduces the reaction time to obtain a satisfactory yield of free Ti metals and accommodates the use of coarse TiO_2 in the reaction; whereby the NaF constitutes an accelerator for the reduction reaction.

The product from each of Examples 1 through 33 is an aggregate of titanium metal particles intimately adhered to and in most instances embedded in free carbon. Also admixed physically in the aggregate may be a metallic oxide derived from the reducing agent, such as calcium oxide, aluminum oxide, barium oxide, magnesium oxide and the like. There also may be present titanium carbide as well as unreacted titanium dioxide and unreacted metal carbide. It is possible directly to refine such aggregates in the electric cell **80**. However, in most instances it is more desirable and economical to remove the various metallic oxides and a portion of the carbon and the metallic carbide if any is present from the aggregate before electrical refining in cell **80**.

In the process illustrated in FIG. 1 in the drawings, a portion of the metallic oxide and part of the carbon can be removed mechanically by the grinding operation **19** followed by some suitable separation as, for example, the hydraulic separation **21**. In one preferred example, the aggregate as obtained from the furnace **10** or **50** is ball milled 24 hours in the dry condition. The ground product is then washed with water to remove excess metallic carbide. The product can then be dried and washed with cold concentrated nitric acid to remove titanium carbide.

Instead of scour milling in the dry condition, it has also been found desirable in certain instances to scour mill in an ammonium chloride solution, in which case 0.1% by weight of sodium carboxymethylcellulose may be added as a suspending agent.

After scour milling by one of the methods described above, the scoured product may be subjected to hydroseparation to remove the major portion of the metallic oxides present. Other hydraulic separations such as air separations may be used to remove the major portion of the metallic oxides.

After the hydraulic separation, the metallic oxides still remaining in the ground product can be largely removed by leaching with dilute acid solutions such, for example, as sulfuric acid and hydrochloric acid. Certain solutions such as a solution of ammonium acetate can also be used advantageously to remove the metallic oxides.

After refining the aggregate as directed above, the titanium metal can be removed from the product and converted to the form of dendrites which are substantially free of contaminating materials including carbon. A suitable method and apparatus are disclosed in the publication of the Chicago Development Corporation referred to above. That electrorefining process utilizes an electric cell of the type illustrated in FIG. 4 of the drawings and designated by the numeral **80**. In a complete installation, it is preferred that two electric cells **80** be connected through a one-inch stainless steel pipe **82** connecting the cells at the bottom. Such interconnection of two cells **80** permits substantially continuous operation and substantially continuous use of the salt bath **84** contained therein, one cell being operating while the product of the other cell is being cooled. For purposes of illustration, only one electric cell **80** has been shown.

The electric cell **80** includes a stainless steel pot **86** which is cylindrical in form and has the bottom thereof closed by a transverse wall **88**. The upper end of pot **86** is provided with an outwardly extending flange **90** which is used to bolt a cover **92** thereto. A suitable gasket material **94** is provided between flange **90** and cover **92** and the parts are held in operative position by bolts **96** and cooperative nuts **98**. Preferably cover **92** is water cooled by apparatus (not shown).

The aggregate containing the free titanium metal embedded in carbon is generally designated by the numeral **100** and is confined within a suitable foraminous container such as a steel basket **102**. Basket **102** is supported upon a steel rod **104** which extends upwardly through a suitable pressure-tight seal **106** in cover **92** whereby to provide a free end **108** extending upwardly from cell **80**. A cathode in the form of steel rod **110** is provided. Rod **110** passes upwardly through cover **92** and through a suitable pressure-tight seal **112**. The lower end of cathode **110** extends downwardly into the center of the annular basket **102** and the upper end of the rod **110** extends outwardly from the cell **80** for ready connection to a source of electrical power.

Means is provided to place an inert gas atmosphere within cell **80** completely to occupy the area above the surface of the molten salt bath **84**. To this end a gas inlet tube **114** is provided on cover **92** and a gas outlet pipe **116** is also provided. Suitable connection (not shown) is made to a source of inert gas under pressure such as, for example, argon.

The molten salt bath **84** comprises principally sodium chloride and contains approximately 4.5% titanium as soluble chlorides of titanium. The titanium ions present in the electrolyte **84** have an average valence of 2.4 and there is present dissolved free sodium corresponding to the equilibrium:

$$TiCl_3 + Na \rightleftarrows TiCl_2 + NaCl$$

The dissolved free sodium amounts to approximately 15 mg. per gram of electrolyte. A voltage is applied to rods **108** and **110** such that the rod **108** and attached basket **102** containing the aggregate provide an anode and the center rod **110** provides a cathode. The applied voltage is approximately 0.8 volt. Currents up to 500 amps. have been used in cells such as cell **80** and produce up to five pounds of titanium dendrites per run. The instantaneous open circuit voltage is about 40 millivolts.

To begin a run in electrolytic cell **80**, the aggregate **100** is placed in the basket **102**, the basket **102** placed within the pot **86** and the cover **92** placed in position upon the pot **86**. The electrolyte **84** is then heated by means of a heating jacket **118** to raise the temperature of the electrolyte **84** to approximately 850° C. Pipe **82** is cold whereby to hold the electrolyte **84** within pot **86**. If necessary, pipe **82** can be cooled by means of a water spray from a spray head **120**. The potential described above is then applied between rods **108** and **110** whereby to make the basket **102** the anode and the center rod **110** the cathode. The titanium in the aggregate **100** moves to the cathode **110** and builds thereon in the form of dendrites of free titanium metal substantially free of all other materials.

At the end of the electrorefining in cell **80**, the connecting pipe **82** is heated by means of an electrical heater **122** and the gas pressure on the surface of electrolyte **84** is increased whereby to move the electrolyte **84** into the adjacent companion cell, not shown, through the pipe **82**. At the completion of the electrolyte transfer, the pipe **82** is again sealed by spraying cold water thereon from the spray head **120**. The potential is removed from the rods **108** and **110** and the pot **86** is permitted to cool. After cooling, the cover **92** is removed whereby to recover the dendrites of titanium metal formed on the rod **110**. Any of the larger impurities are trapped in basket **102** and are removed therefrom. Smaller impurities are dropped into the electrolyte **84** and are trapped therein.

The final product resulting from the electro-refining of the aggregate in cell **80** is in the form of substantially pure free titanium metal. The metal is present on the rod **110** as dendrites. The product is extremely soft and ductile with a Brinell (3000 kg.) hardness falling below values which can be reliably measured (i.e., 90 BHN). Elements such as iron, chromium, aluminum, carbon, silicon, nitrogen and oxygen are not transferred from basket **102** to the dendrites on cathode rod **110**.

It is to be understood that there are other operating conditions and other types of cells such as those described in the booklet published by the Chicago Development Corporation referred to above which may be used. In general, any electrorefining process of the general type disclosed therein can be advantageously utilized to obtain titanium metal in the form of dendrites from the aggregate **100**.

It will be seen that there has been provided an improved method for reducing titanium dioxide to form free titanium metal which fulfills all of the objects and advantages set forth above. More specifically, a less expensive and more direct process yielding a satisfactory product has been provided. This is accomplished by reducing titanium dioxide with metal carbides at temperatures much below the melting points of the reactants to obtain directly from the reduction reaction free titanium metal. A new product is also obtained from the reduction reaction in the form of an aggregate comprising free titanium metal intermingled with and intimately adhered to carbon and other reaction products. The products so obtained can be converted to free titanium metal dendrites by an electrorefining process, or to titanium compounds by well known chemical methods.

Although certain preferred forms of the invention have been described and shown in the drawings for purposes of illustration, it is to be understood that various changes and modifications can be made therein without departing from the spirit and scope of the invention. Accordingly, the invention is to be limited only as set forth in the following claims.

What is claimed is:

1. The process of reacting in the solid state titanium dioxide and the carbide of a metal selected from the class consisting of aluminum and alkaline earth metals to produce free titanium metal, comprising preparing an intimate mixture of said ingredients in finely divided form, and heating said mixture to an elevated temperature below about 1200° C. throughout a time interval sufficiently long to effect a substantially complete reaction to produce particles of free titanium metal and of carbon and of the oxide of said class metal.

2. The process of reacting in the solid state titanium dioxide and the carbide of a metal selected from the class consisting of aluminum and alkaline earth metals to produce free titanium metal, comprising preparing an intimate mixture of said ingredients in finely divided form, and heating said mixture in the substatnial absence of oxygen and nitrogen gases to a temperature in the general range of 700° C. to 1200° throughout a time interval sufficiently long to effect a substantially complete reaction to produce particles of free titanium metal and of carbon and of the oxide of said class metal.

3. The process of reacting in the solid state titanium dioxide and the carbide of a metal selected from the class consisting of aluminum and alkaline earth metals to produce free titanium metal, comprising preparing an intimate mixture of said ingredients in finely divided form in which the molecular ratio of the carbide to the dioxide is at least about 2:1, and heating said mixture to a temperature in the general range of 700° C. to 1200° C. throughout a time interval sufficiently long to effect a substantially complete reaction to produce particles of free titanium metal and of carbon and of the oxide of said class metal.

4. The process of reacting in the solid state titanium dioxide and the carbide of a metal selected from the class consisting of aluminum and alkaline earth metals to produce free titanium metal, comprising preparing an intimate mixture of said ingredients in finely divided form in which at least 25% excess of carbide is provided, and heating said mixture in the substantial absence of oxygen and nitrogen gases to a temperature in the general range of 700° C. to 1200° C. throughout a time interval sufficiently long to effect a substantially complete reaction to produce particles of free titanium metal and of carbon and of the oxide of said class metal.

5. The process of reacting in the solid state titanium dioxide and the carbide of a metal selected from the class consisting of aluminum and alkaline earth metals to produce free titanium metal, comprising preparing an intimate mixture of said ingredients in finely divided form, and heating said mixture to a temperature in the general range of 700° C. to 1200° C. throughout a time interval of about 15 to 90 minutes to effect a substantially complete reaction to produce particles of free titanium metal and of carbon and of the oxide of said class metal.

6. The process of reacting in the solid state titanium dioxide and the carbide of a metal selected from the class consisting of aluminum and alkaline earth metals to produce free titanium metal, comprising preparing an intimate mixture of said ingredients in finely divided form in which the particle size of the ingredients is less than about 60 microns, and heating said mixture to a temperature in the general range of 700° C. to 1200° C. throughout a time interval sufficiently long to effect a substantially complete reaction to produce particles of free titanium metal and of carbon and of the oxide of said class metal.

7. The process of reacting in the solid state titanium dioxide and the carbide of a metal selected from the class consisting of aluminum and alkaline earth metals to produce free titanium metal, comprising preparing an intimate and finely divided mixture of said ingredients in which there is present at least a 25% excess of the carbide and in which the titanium dioxide has a particle size of about 10 to about 60 microns, and heating said mixture in the substantial absence of oxygen and nitrogen gases to a temperature in the general range of 700° C. to 1200° C. throughout a time interval of about 15 to 90 minutes to effect a substantially complete reaction to produce particles of free titanium metal and of carbon and of the oxide of said class metal.

8. The process of reacting in the solid state titanium dioxide and calcium carbide to produce free titanium metal, comprising preparing an intimate mixture of said ingredients in finely divided form, and heating said mixture to an elevated temperature below about 1200° C. throughout a time interval sufficiently long to effect a substantially complete reaction to produce particles of free titanium metal and of carbon and of calcium oxide.

9. The process of reacting in the solid state titanium dioxide and calcium carbide to produce free titanium metal, comprising preparing an intimate mixture of said ingredients in finely divided form in which at least a 25% excess of carbide is provided, and heating said mixture to a temperature in the general range of 800° C. to 1200° C. throughout a time interval sufficiently long to effect a substantially complete reaction to produce particles of free titanium metal and of carbon and of calcium oxide.

10. The process of reacting in the solid state titanium dioxide and calcium carbide to produce free titanium metal, comprising preparing an intimate mixture of said ingredients in finely divided form in which the titanium dioxide has a particle size of less than about 60 microns, and heating said mixture to a temperature in the general range of 800° C. to 1200° C. throughout a time interval sufficiently long to effect a substantially complete reaction to produce particles of free titanium metal and of carbon and of calcium oxide.

11. The process of reacting in the solid state titanium dioxide and calcium carbide to produce free titanium metal, comprising preparing an intimate mixture of said ingredients in which at least a 25% excess of carbide is provided and in which the dioxide has a particle size of less than about 60 microns, and heating said mixture in the substantial absence of atmospheric oxygen and nitrogen to a temperature of about 1000° C. for a time interval of about 15 to 90 minutes to effect a substantially complete reaction to produce particles of free titanium metal and of carbon and of calcium oxide.

12. The process of reacting in the solid state titanium dioxide and aluminum carbide to produce free titanium metal, comprising preparing an intimate mixture of said ingredients in finely divided form, and heating said mixture to a temperature in the general range of 800° C. to about 1200° C. throughout a time interval sufficiently long to effect a substantially complete reaction to produce particles of free titanium metal and of carbon and of aluminum oxide.

13. The process of reacting in the solid state titanium dioxide and barium carbide to produce free titanium metal, comprising preparing an intimate mixture of said engredients in finely divided form, and heating said mixture to a temperature in the general range of 800° C. to 1200° C. throughout a time interval sufficiently long to effect a substantially complete reaction to produce particles of free titanium metal and of carbon and of barium oxide.

14. The process of reacting in the solid state titanium dioxide and magnesium carbide to produce free titanium metal, comprising preparing an intimate mixture of said ingredients in finely divided form, and heating said mixture to a temperature below about 1200° C. throughout a time interval sufficiently long to effect a substantially complete reaction to produce particles of free titanium metal and of carbon and of magnesium oxide.

15. The process of reacting in the solid state titanium dioxide and magnesium carbide to produce free titanium metal, comprising preparing an intimate mixture of said ingredients in finely divided form, and heating said mixture to about 730° C. throughout a time interval of approximately one hour to effect a substantially complete reaction to produce particles of free titanium metal and of carbon and of magnesium oxide.

16. The process of reacting in the solid state titanium dioxide and the carbide of a metal selected from the class consisting of aluminum and alkaline earth metals to produce free titanium metal, comprising preparing an intimate mixture of said ingredients in finely divided form, and heating said mixture to an elevated tempera-

ture below about 1200° C. throughout a time interval sufficiently long to effect a substantially complete reaction while continuously and intimately intermixing said ingredients to produce particles of free titanium metal and of carbon and of the oxide of said class metal.

17. The process comprising preparing an intimate mixture in finely divided form of titanium dioxide and the carbide of a metal selected from the class consisting of aluminum and alkaline earth metals, and reacting said ingredients in the solid state by heating said mixture in the substantial absence of oxygen and nitrogen gases to an elevated temperature below about 1200° C. throughout a time interval sufficiently long to produce an aggregate comprising finely divided particles of titanium metal intimately adhered to small particles of carbon and mixed with oxides of said class metal.

18. The process comprising preparing an intimate mixture in finely divided form of titanium dioxide and the carbide of a metal selected from the class consisting of aluminum and alkaline earth metals, reacting said ingredients in the solid state by heating said mixture in the absence of the atmosphere to an elevated temperature below about 1200° C. throughout a time interval sufficiently long to produce an aggregate comprising finely divided particles of titanium metal intimately adhered to small particles of carbon and mixed with oxides of said class metal, and thereafter treating the aggregate to recover the titanium metal therefrom.

19. The process comprising preparing an intimate mixture in finely divided form of titanium dioxide and the carbide of a metal selected from the class consisting of aluminum and alkaline earth metals, reacting said ingredients in the solid state by heating said mixture in the absence of the atmosphere to an elevated temperature below about 1200° C. throughout a time interval sufficiently long to produce an aggregate comprising finely divided particles of titanium metal intimately adhered to small particles of carbon and mixed with oxides of said class metal, and thereafter treating the aggregate to separate at least a substantial proportion of the carbon and the class metal oxides from the titanium metal therein.

20. The process comprising preparing an intimate mixture in finely divided form of titanium dioxide and the carbide of a metal selected from the class consisting of aluminum and alkaline earth metals, reacting said ingredients in the solid state by heating said mixture in the substantial absence of oxygen and nitrogen gases to an elevated temperature below about 1200° C. throughout a time interval sufficiently long to produce an aggregate comprising finely divided particles of titanium metal intimately adhered to small particles of carbon and mixed with oxides of said class metal, scouring the aggregate, and then subjecting the scoured product to hydraulic treatment to separate therefrom at least a part of the carbon and the class metal oxides.

21. The process comprising preparing an intimate mixture in finely divided form of titanium dioxide and the carbide of a metal selected from the class consisting of aluminum and alkaline earth metals, reacting said ingredients in the solid state by heating said mixture in the substantial absence of oxygen and nitrogen gases to an elevated temperature below about 1200° C. throughout a time interval sufficiently long to produce an aggregate comprising finely divided particles of titanium metal intimately adhered to small particles of carbon and mixed with oxides of said class metal, scouring the aggregate, and then leaching from the scoured product the class metal oxides.

22. The process comprising preparing an intimate mixture in finely divided form of titanium dioxide and the carbide of a metal selected from the class consisting of aluminum and alkaline earth metals, reacting said ingredients in the solid state by heating said mixture in the substantial absence of oxygen and nitrogen gases to an elevated temperature below about 1200° C. throughout a time interval sufficiently long to produce an aggregate comprising finely divided particles of titanium metal intimately adhered to small particles of carbon and mixed with oxides of said class metal, scouring the aggregate, thereafter separating out part of the class metal oxides and the carbon of hydraulic treatment, and then leaching the separation product containing the titanium metal to remove substantially the remaining portion of the class metal oxides.

23. The process set forth in claim 18, wherein said treatment of the aggregate to recover the titanium metal therefrom includes subjecting the same to an electrolytic separation in a fused salt bath.

24. The process of reacting in the solid state titanium dioxide and calcium carbide to produce free titanium metal, comprising preparing an intimate mixture of titanium dioxide and calcium carbide and sodium fluoride in finely divided form, and heating said mixture in the substantial absence of oxygen and nitrogen gases to an elevated temperature below about 1000° C. throughout a time interval sufficiently long to effect a substantially complete reaction to produce particles of free titanium metal and of carbon and of calcium oxide.

25. The process set forth in claim 24, wherein said mixture comprises the ingredients CaC_2; TiO_2; NaF in the approximate ratios 25:10:1 by weight.

26. The process set forth in claim 24, wherein said time interval is in the range 10 to 30 minutes.

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CERTIFICATE OF CORRECTION

Patent No. 3,047,477 July 31, 1962

Joseph R. Spraul et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 13, line 6, for "substatnial" read -- substantial --; column 14, line 41, strike out "about"; column 16, line 22, for "of" read -- by --.

Signed and sealed this 4th day of December 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents