(54) Title: THERMAL AND ELECTROCHEMICAL PROCESS FOR METAL PRODUCTION

THERMODYNAMIC EQUILIBRIUM CALCULATION
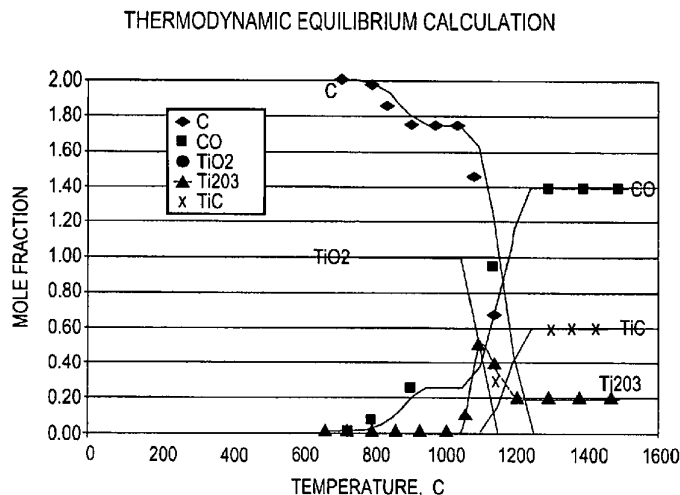
(57) Abstract: A method of winning a metal from its oxide ore by heating the ore in a partial vacuum or under an inert atmosphere in the presence of a reductant. The resulting product may be further reduced electrochemically to produce a purer metal. The ore is preferably a titanium oxide ore and the reductant carbon or graphite.

1   **THERMAL AND ELECTROCHEMICAL PROCESS**

2   **FOR METAL PRODUCTION**

3   The present invention relates to the production of metals. The invention has

4   particular utility in connection with the production of titanium and will be described in

5   connection with such utility, although other utilities are contemplated, e.g., production of

6   other high value multi-valence and high (2 or more) valance metals, in particular

7   refractory metals such as chromium, hafnium, molybdenum, niobium, tantalum,

8   tungsten, vanadium and zirconium which are given as exemplary.

9   The properties of titanium have long been recognized as a light, strong, and

10   corrosion resistant metal, which has lead to many different approaches over the past few

11   decades to extract titanium from its ore. These methods were summarized by Henrie [1].

12   Despite the many methods investigated to produce titanium, the only methods currently

13   utilized commercially are the Kroll and Hunter processes [2, 3]. These processes utilize

14   titanium tetrachloride ($TiCl_4$) which is produced from the carbo-chlorination of a refined

15   titanium dioxide (TiO_2) according to the reaction:

16              $TiO_2(s) + 2Cl_2(g) + 2C(s) \rightarrow TiCl_4(g) + 2CO(g).$
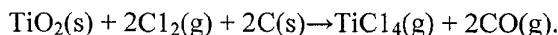
17   In the Kroll process [2] $TiCl_4$ is reduced with molten magnesium at $\approx 800°C$ in an

18   atmosphere of argon. This produces metallic titanium as a spongy mass according to the

19   reaction:

20              $2Mg(l) + TiCl_4(g) \rightarrow Ti(s) + 2MgCl_2(l)$
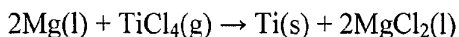
21   from which the excess Mg and $MgCl_2$ is removed by volatilization, under vacuum at $\approx$

22   1000°C. The $MgCl_2$ is then separated and recycled electrolytically to produce Mg as the

23   reductant to further reduce the $TiCl_4$. In the Hunter process [3,4] sodium is used as a

24   reductant according to the reaction:

25              $4Na(l) + TiCl_4(g) \rightarrow Ti(s) + 4NaCl(l)$
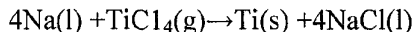
26   The titanium produced by either the Kroll or Hunter processes must not only be

27   separated from the reductant halide by vacuum distillation and/or leaching in acidified

28   solution to free the titanium sponge for further processing to useful titanium forms, but

29   also require the recycling of the reductant by electrolysis. Because of these multiple

30   steps the resultant titanium is quite expensive which limits its use to cost insensitive

31   applications.

32   The high cost of the Kroll process results in a high cost of titanium products

33   limiting their widespread utilization in spite of their exceptionally desirable properties.

1   Since titanium's discovery, investigations have been conducted to produce titanium by

2   more economical processing other than the metalothermic reduction such as magnesium

3   or sodium reduction of TiCl$_4$, but without sufficient success to replace the high cost Kroll

4   process. The intensive interest to develop low cost processing to produce titanium has

5   recently spun several published processes. Since titanium primarily appears as the oxide

6   (TiO$_2$), it can be conceived that an oxide feed to produce titanium could be more

7   economical than making the chloride (TiCl$_4$) by carbo-chlorination of the oxide as the

8   feed (TiCl$_4$) which is used in the Kroll process.

9   The US Bureau of Mines performed extensive additional investigations [1,5-8] to

10 improve the Kroll and Hunter processes. Many other processes have been investigated

11 that include plasma techniques [9-13], molten chloride salt electrolytic processes [14],

12 molten fluoride methods [15], the Goldschmidt approach [16], and alkali metal-calcium

13 techniques [17]. Other processes investigated have included aluminum, magnesium,

14 carbothermic and carbo-nitrothermic reduction of TiO$_2$ and plasma reduction of

15 TiCl$_4$[18] without measurable success. Direct reduction of TiO$_2$ or TiCl$_4$ using

16 mechanochemical processing of ball milling with appropriate reductants of Mg or

17 calcium hydride (CaH$_2$) also have been investigated [19] without measurable success.

18 Kroll, who is considered as the father of the titanium industry [20] predicted that

19 titanium will be made competitively by fusion electrolysis but to date, this has not been

20 realized.

21   An electrolytic process has been reported [21] that utilizes TiO$_2$ as a cathode and

22 carbon or graphite as the anode in a calcium chloride electrolyte operated at 900°C. By

23 this process, calcium is deposited on the TiO$_2$ cathode, which reduces the TiO$_2$ to

24 titanium and calcium oxide. However, this process is limited by diffusion of calcium

25 into the TiO$_2$ cathode and the build-up of calcium oxide in the cell, which limits

26 operating time to remove the calcium oxide or replacement of the electrolyte. Also the

27 TiO$_2$ cathode is not fully reduced which leaves contamination of TiO$_2$ or reduced oxides

28 such as TiO, mixed oxides such as calcium titanante as well as titanium carbide being

29 formed on the surface of the cathode thus also contaminating the titanium.

30   In the Fray-Farthing-Chen (FFC) Cambridge process, or simply, the Fray process,

31 titanium dioxide (TiO$_2$) is utilized as a cathode and electrolyzed with a graphite anode in

32 molten calcium chloride (CaCl$_2$) which allegedly removes the oxygen from the TiO$_2$ in

33 pellet form leaving titanium and with the graphite anode produces CO$_2$ at the anode. A

1   fundamental teaching is that the oxygen ionized from the TiO_2 in the cathode must be

2   dissolved in the electrolyte which is $CaCl_2$ for transport to the anode. In addition, it is

3   stated that calcium titanites $(Ca_xTi_yO_z)$ are formed as well as toxic chlorine is also given

4   off initially at the anode. In technical public symposium, presenters of the FFC process

5   have noted that the formation of calcium titanite is a problem to producing titanium

6   metal and that the Columbic efficiency is very low at under 20% thus making the process

7   expensive. Independent analysis, US Dept. of Energy Contract 4000013062 report,

8   implies the cost of the FFC process is more expensive than the Kroll process and the

9   product does not meet the purity of the standard Kroll material.

10   International patent publications WO 02/066711 Al, WO 02/083993 Al, WO

11   03/002785 A1 and US 6,663,763 B2 also utilize TiO_2 as a cathode feed to

12   electrolytically extract oxygen to produce titanium metal remaining at the cathode with

13   oxygen discharged at the anode. Each of these publications state the Fray/FFC process

14   produces titanium with residual oxygen, carbon and calcium titanite which is unsuitable

15   for commercial use. International patent publication WO 02/066711 Al to Strezov et al.,

16   assigned to BHP Steel, Ltd., reports that the Fray et al. process consist of ionizing

17   oxygen at the titania (TiO_2) cathode under applied potential which oxygen removed or

18   ionized from the TiO_2 cathode is dissolved in the $CaCl_2$ electrolyte and is transported to a

19   graphite anode to be discharged as CO_2. The first aspect of the teachings of WO

20   02/066711 Al is that the electrical contact to the TiO_2 cathode influences the reduction

21   process and that a high resistive electrical conductor to the cathode is made part of the

22   cathode. It is further reported the oxygen removed from the TiO_2 cathode in a pellet

23   form passes onto solution and/or chemically reacts with the electrolyte cation. The

24   teaching is that deposition of the cation at the cathode is prevented through controlled

25   potential at under 3.0V in the $CaCl_2$ electrolyte. It is stated Al_2O_3 in the cathode with

26   TiO_2 can also be reduced but non-uniformly with the only reduction taking place where

27   the Al_2O_3 touches the cathode conductor. The publication WO 02/066711 Al teaches the

28   TiO_2 must be made into a pellet and presintered before use as a cathode and states the

29   Fray et al. application mechanism is incorrect, produces 18 wt% carbon in the final

30   titanium pellet as well as calcium titanites and silicates if silica is in the titania (TiO_2)

31   pellets. This publication claims to avoid or prevent anode material (graphite/carbon)

32   from transport into the cathode, but provides no teaching of how this is accomplished.

1   International publication WO 02/083993 Al to Stresov et al. assigned to

2   BlueScope Steel, Ltd., formerly BHP Steel, Ltd., teaches that the electrolyte to

3   cathodically reduce pelletized TiO_2 must be calcium chloride containing CaO. This

4   publication states that the $CaCl_2$ electrolyte is operated to produce Ca^{++} cations which

5   provide the driving force that facilitate extraction of O^{--} anions produced by the

6   electrolytic reduction of titania (TiO_2) at the cathode. It is reported that Ca metal exist in

7   the electrolyte and that it is responsible for the chemical reduction of titania (TiO_2). It is

8   also reported that significant amounts of carbon are transferred from the anode to the

9   cathode thus contaminating the titanium and was responsible for low energy efficiency

10 of the cell. This publication teaches replacing the carbon anode with a molten metal

11 anode of silver or copper to eliminate carbon contamination of the reduced TiO_2. The

12 teaching is that the cell potential be at least 1.5V but less than 3.0V with a cell potential

13 above the decomposition potential of CaO. Again the titania (TiO_2) cathode is in the

14 form of a solid such as a plate.

15 International publication WO 03/002785 Al to Strezov, et al., also assigned to

16 BHP Steel, Ltd., teaches the oxygen contained in the solid form of titantia (TiO_2) is

17 ionized under electrolysis which dissolves in the $CaCl_2$ electrolyte. It is taught that the

18 operating cell potential is above a potential at which cations are produced which

19 chemically reduce the cathode metal oxide/TiO_2. It is further stated that chlorine (Cl_2)

20 gas is removed at the anode at potentials well below the theoretical deposition, that

21 $Ca_xTi_yO_z$ is present at the TiO_2 cathode and that CaO is formed in the molten electrolyte

22 bath which is $CaCl_2$ containing oxygen ions. It is also stated the potential of the cell

23 must vary with the concentration of oxygen in the titanium requiring higher potentials at

24 lower concentrations of oxygen to remove the lower concentrations of oxygen. It is

25 unlikely to remove the oxygen from TiO_2 to low concentrations (i.e., 500ppm) in a single

26 stage operation. It is again taught that cations must be produced to chemically reduce the

27 cathodic TiO_2 requiring refreshing the electrolyte and/or changing/increasing the cell

28 potential. The method teaches carrying out the reduction of TiO_2 in a series of

29 electrolytic cells of successively transferring the partially reduced titanium oxide to each

30 of the cells in the series. The cell potential is above the potential at which Ca metal can

31 be deposited via the decomposition of CaO wherein the Ca metal is dissolved in the

32 electrolyte which migrates to the vicinity of the cathode TiO_2.

1   In U.S. Patent 6,663,763 B2 which is substantially the same as international

2   publication WO 02/066711 Al, it is taught that CaO must be electrolyzed to produce

3   calcium metal and Ca^{++} ions which reduce the titania (TiO_2) in the cathode with oxygen

4   (O^-) migrating to the anode. This is very unlikely the mechanism. If Ca in metallic

5   (Ca^0) or ionic (Ca^{++}) form reduces the TiO_2 the product of reduction will be CaO i.e.,

6    $TiO_2 + 2Ca = Ti + 2CaO$. The produced calcium from electrolysis must diffuse into the

7   titania (TiO_2) pellet to achieve chemical reduction as claimed and the formed CaO will

8   then have to diffuse out of the Ti/TiO_2 which has been preformed and sintered into a

9   pellet. If calcium metal (Ca^0) or ions (Ca^{++}) are produced by electrolysis, the oxygen

10   ions (O^-) produced from that electrolysis can diffuse to the anode. The calcium

11   produced at the cathode and diffused into the bulk of the cathode thus chemically

12   reducing the TiO_2, will form CaO which must become soluble in the electrolyte ($CaCl_2$)

13   and diffuse out of the cathode before additional calcium can diffuse into the inner portion

14   of the cathode for the chemical reduction.

15   It is also known from x-ray diffraction of the cathode that calcium titanite

16   ($CaTiO_3$) forms as the TiO_2 is reduced. A possible reaction is $O^{2-} + Ca^{2+} + TiO_2 =$

17   $CaTiO_3$ which remains as a contaminate in the cathodically reduced TiO_2 to Ti.

18   US Patent 6,540,902 Bl to Redey teaches that a dissolved oxide in the electrolyte

19   is required to cathodically reduce a metal oxide such as UO_2. The example is Li_2O in

20   LiCl and the oxygen-ion species is dissolved in the electrolyte for transport to the anode

21   which is shrouded with a MgO tube to prevent back diffusion of oxygen. It is reported

22   the cathodic reduction of the oxide (examples UO_2 and Nb_2O_3) may not take place if the

23   cathode is maintained at a less negative potential than that which lithium deposition will

24   occur. The electrolyte (LiCl) should contain mobile oxide ions which may compress

25   titanium oxide whose concentration of the dissolved oxide species are controlled during

26   the process by controlled additions of soluble oxides. Which titanium oxide is not

27   defined, however, as there are a plethora of different titanium oxides. It is generally

28   known titanium oxides are not soluble in molten salts which accounts for the fact

29   titanium is not electrowon from an oxide feed analogous to aluminum being electrowon

30   from the solubility of Al_2O_3 in cryolite/sodium fluoride. While the Redey patent teaches

31   cathodic reduction of UO_2 and Nb_2O_3 in a $LiCl/Li_2O$ electrolyte, no residual oxygen

32   concentrations are given in the cathode but it was estimated the reduction was 90%

33   complete and no teaching is suggested TiO_2 would be reduced to very low oxygen levels.

1   International publication WO 03/046258 A2 to Cardarelli, assigned to Quebec

2   Iron and Titanium Inc. (QIT) provides a review of electrolysis processes to produce

3   titanium including Fray et al. This patent publication teaches a process analogous to

4   Fray et al. except the process is carried out at a temperature above the melting point of

5   titanium which is approximately 1670°C. A liquid slag containing titantia is used as a

6   cathode on a cell bottom with an electrolyte such as CaF_2 floating on top and in contact

7   with anodes such as graphite. Under electrolysis, the impure metals such as iron are

8   deposited at the molten electrolyte titania slag interface and sink to the bottom of the slag

9   since the iron is heavier. After the iron and/or other impurities are removed, titanium is

10   reportedly deposited at the molten slag electrolyte interface and also sinks through the

11   slag settling to the bottom of the cell for subsequent tapping. Oxygen ions diffuse

12   through the electrolyte to an upper anode of graphite. It is suggested the overall reaction

13   is TiO_2 (liquid) + C (solid) = Ti (liquid)$\downarrow$ + CO_2 (gas)$\uparrow$.

14   No specific oxygen residual in the harvested titanium is provided.

15   Thus, current TiO_2 cathode electrolytic processes are no more commercially

16   viable than the electrolytic processes before them.

17   It is known that metals can be won from their oxide ores by heating with a

18   reductant which typically is carbon. Carbothermic reduction has been established as the

19   most economical process to produce a metal in its pure metallic form. However,

20   carbothermic reduction is not always possible to win a metal from its ore due to not

21   sufficiently reducing impurities within the ore and/or not fully reducing the oxide which

22   may lead to forming the carbide versus complete reduction of the metal oxide. Thus,

23   oxides such as alumina (Al_2O_3) have not produced pure aluminum by carbothermic

24   reduction. Similarly TiO_2 heretofore has not been carbothermically reduced to produce

25   pure titanium. However, in our co-pending parent application, U.S. Serial No.

26   10/828,641, filed April 21, 2004, we describe how TiO_2 could be carbothermically

27   reduced to TiO. Further investigations have shown it is possible to carbothermically

28   remove more oxygen from the TiO to produce a suboxide of titanium, i.e., having a ratio

29   of oxygen to titanium less than one. The more oxygen removed by the highly efficient

30   and low cost carbothermic reduction, the less required to be removed by electrons in

31   electrolytic reduction which frequently is quite inefficient. Thus the carbothermic

32   reduction of TiO_2 as the first process step of producing titanium from TiO_2 is enabling.

1   Titanium is the fourth most abundant metal in the Earths' crust in several mineral

2   forms. The most common utilized minerals are rutile (TiO_2) and ilmenite ($FeTiO_3$).

3   Calcium titanates are also an abundant source which contains the element titanium.

4   Utilized as mined or purified through various leaching and/or thermal processing's TiO_2

5   is the most utilized compound which has applications as pigment and for carbo

6   chlorination to produce $TiCl_4$ which is reduced with metals such as magnesium (Kroll

7   Process) or sodium (Hunter Process) that produces titanium metal or the chloride is

8   oxidized to produce a highly purified pigment.

9   Titanium exists in multivalent species of Ti^{+4}, Ti^{+3}, and Ti^{+2} in various anionic

10   compositions such as the oxide or chloride. Except for the oxide those compounds are

11   typically unstable in the ambient atmosphere. In general there has been limited

12   application of these subvalent compounds which has not generated processing to produce

13   the subvalent oxides or others compounds.

14   The high cost of titanium metal has limited its usage to critical aerospace where

15   weight reduction over rides cost sensitivity. Because of the high cost of producing

16   titanium by the Kroll or Hunter processes the cost volume ratio of titanium has tended to

17   be inelastic. The holy grail of titanium is to reduce the cost of the primary metal as well

18   as down stream processing cost. Initiatives are known to be underway to improve

19   efficiency and reduce cost of the basic Kroll and Hunter processes as well as alternative

20   processing involving electrolytic processing. It is known as stated above the FFC

21   Cambridge process which cathodically reduces TiO_2 in a calcium chloride process is

22   under development to reduce the cost of primary titanium. It is also known that calcium

23   titanate also forms in this process which limits the process commercial viability. It is

24   also known if cathodic reduction were conducted with a titanium suboxide such as TiO

25   the calcium titanate problem would be eliminated as there is insufficient oxygen to

26   straight forwardly form calcium titanate. It is also generally known that thermal

27   reduction of metal oxides is more economical than using electrons produced by

28   electrolysis which is why iron and many other metals are won by thermal reduction

29   processes.

30   Since the initiation of the Kroll process to produce titanium in the mid twentieth

31   century, it has been predicted titanium would be produced by an electrolytic process and

32   that process would be similar to the Hall process to produce aluminum. The latter

33   process consist of alumina (Al_2O_3) exhibiting solubility in fused cryolite (Na_3AlF_6)

1 which is electrolyzed with a carbon anode that produces CO_2 with some CO and the

2 metal aluminum. However, no equivalent process has been developed for solubalizing

3 TiO_2. It is possible; however, that the suboxides of titanium can exhibit solubility in

4 some fused salts that may include the alkali, alkaline earth and rare earth halides.

5 However, no reliable low cost process has been available to produce the titanium

6 suboxides that could be used as a feed to electrolytically produce titanium. The titanium

7 suboxide could be utilized cathodically and electrolytically reduced to titanium metal

8 without the calcium titanate problem when using TiO_2, and the titanium suboxide could

9 be dissolved in fused salts with electrolysis with a carbon or inert anode to produce

10 titanium. Either processing extreme can produce titanium more economically then the

11 Kroll or Hunter processes. The enabling requirement to produce titanium by these

12 electrolytic processes is a low cost source of titanium suboxides.

13   It is known that titanium suboxides as well as most metal suboxides can be

14 produced by the metal reducing the highest valent oxide. For example silicon monoxide

15 (SiO) can be produced by reducing SiO_2 with silicon (Si). That is $SiO_2 + Si + heat =$

16 2SiO. The SiO_2 can be reduced with other reductants but the product is contaminated

17 with the reductant as well as unwanted other compounds can be produced. For example

18 $SiO_2 + C + heat = SiO$ and $SiC + CO$. Producing a titanium suboxide by reducing TiO_2

19 with titanium metal is uneconomical since titanium metal must first be produced. Also if

20 carbon is utilized as the reducing agent, titanium carbide is typically a contaminate.

21 Titanium carbide has a very high free energy of formation which is exceeded only by

22 zirconium and hafnium carbide. The free energy of formation of TiC is approximately

23 183 KJ/mole which makes it formation prominent in any carbon reduction process. As

24 used herein the term "carbon" is meant to include carbon in any of its several crystalline

25 forms including, for example, graphite. However, because of the economics of carbon

26 and thermal reduction, the carbo-thermic reduction of TiO_2 would be ideal to produce

27 titanium suboxides if the formation of TiC can be prevented and only one suboxide

28 produced such as Ti_2O_3 or TiO.

29   Further features and advantages of the present invention will be seen from the

30 following detailed description, taken in conjunction with the accompanying drawings

31 wherein:

32   Figs. 1-3 show the XRD patterns of stoichiometric TiO_2-C heat treated in argon

33 at 1300°C, 1400°C and 1750°C for one hour, respectively;

1   Fig. 4 shows thermodynamic equilibrium patterns thereof;

2   Fig. 5 shows the XRD patterns of stoichiometric TiO_2-C heat treated to 1450°C

3   in one step followed by heat treatment at 2100°C in vacuum;

4   Fig. 6 shows the XRD patterns of 1:1:TiO_2-Ti heat treated to 1760°C in vacuum;

5   Fig. 7 shows the XRD patterns of stoichiometric TiO_2-C heat treated to 1450°C

6   with a second heat treatment to 1800°C in high vacuum;

7   Fig. 8 shows the XRD patterns of stoichiometric TiO_2-C from phenolic in a pre-

8   mix heat to 1450°C at one atmosphere pressure in argon;

9   Fig. 9 shows the XRD patterns of stoichiometric TiO_2-C from a 110°C softening

10   point coal tar pitch mixed at 190°C and heat treated at 1650°C at atmospheric pressure in

11   argon;

12   Fig. 10 shows the XRD patterns of slag-C from a 110°C softening point coal tar

13   pitch mixed at 190°C and heat treated at 1650°C at atmospheric pressure in argon;

14   Fig. 11 shows the XRD patterns for Ilmenite ore treated with an intimate carbon

15   coating on ore particles with heat treatment to 1650°C in argon;

16   Fig. 12 shows the XRD patterns for Ilmenite ore treated with an intimate carbon

17   coating on ore particles with heat treatment to 1650°C in argon plus 1800°C in a vacuum

18   lower than 10^{-3} Torr;

19   Fig. 13 shows the XRD patterns of TiO_2 treated with an intimate mixture of

20   carbon with heat treatment to 2100°C at atmospheric pressure in argon; and

21   Fig. 14 shows the XRD patterns for Anatase TiO_2 with an intimate mixture of

22   carbon with heat treatment to 2100°C under argon at atmospheric pressure.

23   To establish if a suboxide of titanium could be carbothermically produced several

24   trials of mixing various carbon sources such as coke and carbon black, and heating to

25   various temperatures at various pressures was performed.

26   Stoichiometric amounts of TiO_2 powder and a source of carbon as finely ground

27   coke or carbon black were mixed in a ball mill for periods up to 24 hours. The

28   thoroughly mixed TiO_2 and carbon were then heat treated in a graphite element furnace

29   purged with argon. The initial heat treatment was performed at 1300°C for one hour.

30   The heat treated mixed powder was subjected to x-ray diffraction (XRD) with the results

31   showed in Fig. 1. As can be seen, the major product is TiC with a minor amount of

32   Ti_3O_5. A sample of the TiO_2-C was heat treated to 1400°C with the results shown in Fig.

1   2. A sample was heated to 1750°C which also produced major amounts of TiC as shown

2   in Fig. 3. The heating container was a graphite crucial which it was thought may be

3   contributing carbon to the TiC formation.

4   Duplicate experiments were run in a magnesium oxide (MgO) crucible with the

5   following results:

Compound	Graphite Crucible	MgO Crucible
TiC%	63	54
TiO%	22	46
Ti_2O_3%	15	0

6

7   The small variation in compositions suggests the graphite crucible is not the

8   major contribution to the formation of TiC.

9   Duplicate experiments were run but instead of atmospheric argon, a vacuum was

10 generated with a fore pump to about 0.1 atmosphere. The TiC concentration was

11 reduced to approximately 20%, with 30% TiO and 50% Ti_2O_3. The TiC composition

12 was reduced with an increase in Ti_2O_3. The TiC is in a +4 valence state and

13 unacceptable as a reduced valence state feed for electrolytic producing titanium. A

14 thermodynamic equilibrium calculation was performed as shown in Fig. 4 which

15 indicates that TiC is a major product component above about 1100°C.

16   A two step heat treatment was performed which consisted of first heating to

17 1450°C and then in a second step heating to 2100°C in vacuum of approximately 0.1

18 atmosphere. In this case only TiO was formed as shown in Fig. 5. Desirably TiO which

19 is in a +2 valence is produced and serves as a feed to electrolytically produce titanium.

20 However, heating to 2100°C in vacuum is an expensive batch operation not conducive to

21 commercial production of titanium at low cost, consequently less severe heat treatments

22 were investigated to produce TiO.

23   First it was decided to define a base line using titanium metal to reduce TiO_2.

24 Different ratios of TiO_2 to Ti were investigated. The best was a 1:1 ratio heat treated at

25 1760°C also in vacuum which is shown in Fig. 6. As seen some higher oxides of Ti_3O_5

26 and Ti_2O_3 remained and pure TiO was not formed at these process conditions.

27   To avoid the high temperature treatment of 2100°C to produce the TiO as shown

28 in Fig. 5, the two stage treatment of first heating to 1450°C to expel most of the CO

29 followed by heating to 1800°C in high vacuum was run. The result is shown in Fig. 7

1   which shows that TiO was indeed formed and some product desirably contained less

2   oxygen than a 1:1 ratio to titanium. As desirable as this may be, the 1800°C high

3   vacuum treatment may be too costly to produce low cost titanium commercially. It is

4   therefore desirable to develop less expensive processing to produce TiO.

5   The process given above was the through mixing of a carbon powder source and

6   TiO_2 powder followed by the heat treatment steps discussed. A different approach to

7   producing carbon and TiO_2 is to utilize a liquid which when pyrolized will provide a

8   high yield of carbon. The TiO_2 particles can be uniformly mixed into the liquid

9   precursor and then pyrolized. The precursor will produce a carbon film uniformly and

10 intimately in contact with the individual TiO_2 particles. Example liquid precursors that

11 have a high yield of carbon when pyrolized are furfural alcohol, resins such as phenyol

12 formalide (phenolics) and pitches (coal and petroleum tars). Sugars and other materials

13 can be used but their carbon char yield is low. Pitches have melting points from under

14 100°C up to nearly 400°C. TiO_2 was mixed with phenolic resin such as Borden B1008

15 and heated to form a solid at approximately 110°C. TiO_2 was mixed with a 110°C

16 softening point coal tar pitch at a mixing temperature of 190°C. The char yield on the

17 phenolic or coal tar pitch is approximately 50%. A stoichiometric mixture of each type

18 of precursor was heated to temperatures of 1300°C to 1650°C with the results subjected

19 to XRD analysis. The lower temperature, the 1450°C example is shown in Fig. 8. As

20 can be seen the major portion is TiO but some higher oxide of Ti_2O_3 remains; however,

21 the amount of TiO produced is greater than when only particles of carbon and TiO_2 were

22 heated together, and importantly no TiC was formed. The XRD of the sample heated to

23 1650°C is shown in Fig. 9. At this temperature of 1650°C heating at atmospheric

24 pressure pure TiO is produced. The atmospheric pressure treatment is quite economical

25 and the pure TiO produced can be used to electrolytically produce low cost titanium,

26 e.g., by the electrochemical reduction method described in our aforementioned parent

27 application.

28   The intimate mixing of the carbon precursor with the metal oxide can also be

29 used to purify titania type ores. For example rutile ore, titania slag or ilmenite ore can be

30 purified to a higher purity titanium oxide utilizing the intimate mixing of the carbon

31 reductant. Titania slag which is a by product of pig iron production from ilmenite ore,

32 obtained through QIT in Canada which has the composition shown in Table 1 was mixed

1   with a 110°C softening point coal tar pitch at 190°C to obtain an intimate mixture of the

2   carbon precursor and the slag particulate.

3   **Table 1-Composition of TiO$_2$ slag, a byproduct of pig iron production from**

4   **Ilmenite.**

Compound	Elemental composition in parts per million (ppm)
Al	2500
Ba	<100
Be	<100
Ca	<100
Cd	<100
Co	<100
Cr	<100
Cu	<100
Fe	7500
Hf	<100
K	<100
Mg	1500
Mn	<100
Mo	<100
Na	<100
Nb	<100
Ni	<100
P	<100
Pb	<100
Si	10,000
Sn	<100
Ta	<100
Ti	510,000
V	2000
W	2700
T	<100
Zn	<100
Zr	<100

5

6   The mixture was heated to 1650°C in an argon inert atmosphere wherein the coal tar

7   pitch was pyrolized with the heat treatment producing carbon in intimate contact with the

8   titania slag particulate. The intimate carbon contact with the slag particulate produced

9   TiO with the composition shown in Table 2.

10

1   **Table 2-Composition of TiO₂ slag from Ilmenite after the intimate mixture with**

2   **pitch and heating to 1650°C in an inert atmosphere.**

Compound	Elemental composition in parts per million (ppm)
Al	5500
Ba	<100
Be	<100
Ca	<100
Cd	<100
Co	<100
Cr	<100
Cu	<100
Fe	1200
Hf	<100
K	<100
Mg	<100
Mn	<100
Mo	<100
Na	<100
Nb	<100
Ni	<100
P	<100
Pb	<100
Si	1800
Sn	<100
Ta	<100
Ti	745,000
V	2800
W	3200
T	<100
Zn	<100
Zr	<100

3

4   As can be seen in the carbothermic reduction, slag is purified from approximately

5   95% purity to 99+% purity utilizing the intimate carbon pretreatment before the heat

6   treatment to 1650°C. The XRD after the 1650°C treatment with the carbon in intimate

7   contact with the TiO₂ slag is shown in Fig. 10.

8   Ilmenite which is iron titanite $FeTiO_3$ with a variety of impurities consists

9   typically of the composition shown in Table 3.

10

1 **Table 3-Composition of Ilmenite ore.**

Element	ElementalComposition Parts per million (ppm)
Al	4400
B	<100
Ba	<100
Be	<100
Ca	200
Cd	<100
Co	<100
Cr	500
Cu	<100
Fe	19.5%
HF	<100
K	<100
Li	<100
Mg	1400
Mn	9400
Mo	<100
Na	400
Nb	500
Ni	<100
P	800
Pb	<100
Si	1500
Sn	100
Ta	<100
Ti	38.5%
V	650
W	<100
Y	<100
Zn	200
Zr	<100

2

3   The ilmenite ore was mixed with 110°C softening point coal tar pitch heated to

4   190°C to provide intimate mixture of stoichiometric carbon and the ilmenite ore

5   particles. The mixture was heated to 1650°C heat treatment in an inert atmosphere which

6   pyrolized the pitch providing intimate contact of the carbon on metal oxide particles.

7   The chemical composition after the 1650°C in an inert atmosphere which pyrolized the

8   pitch providing intimate contact of the carbon on the metal oxide particles is shown in

9   Table 4 and the XRD in Fig. 11.

10

1   Table 4-Composition of product after heating Ilmenite ore with an intimate mixture
2   of carbon to 1650°C.

Element	Elemental Composition Parts per million (ppm)
Al	7100
B	<100
Ba	<100
Be	<100
Ca	<100
Cd	<100
Co	100
Cr	<100
Cu	<100
Fe	300
Hf	<100
K	<100
Li	<100
Mg	<100
Mn	<100
Mo	300
Na	<100
Nb	200
Ni	<100
P	<100
Pb	<100
Si	<100
Sn	100
Ta	<100
Ti	76.0%
V	<100
W	<100
Y	<100
Zn	<100
Zr	<100

3
4   Note the XRD pattern in Fig. 11 shows iron metal is present. The iron metal can
5   be removed by leaching and/or complexing in an aqueous solution at ambient
6   temperature. The iron and other impurities can be removed by heating in a vacuum less
7   than 10^{-3} Torr to 1800°C after or instead of the 1650°C heat treatment. The purity of the
8   high vacuum 1800°C treated material is shown in Table 5 and the XRD in Fig. 12.
9
10
11

1   Table 5-Composition of product after heating Ilmenite ore with an intimate mixture
2   of carbon to 1650°C with a second heat treatment to 1800°C in a vacuum less than
3   10^{-3} Torr.

Elements	Composition Parts per million (ppm)
Al	6300
B	<100
Ba	<100
Be	<100
Ca	<100
Cd	<100
Co	<100
Cr	<100
Cu	<100
Fe	100
HF	<100
K	<100
Li	<100
Mg	<100
Mn	<100
Mo	300
Na	<100
Nb	200
Ni	<100
P	<100
Pb	<100
Si	<100
Sn	100
Ta	<100
Ti	85%
V	<100
W	<100
Y	<100
Zn	<100
Zr	<100

4

5   Examples of producing titanium metal with a starting feed of TiO_2 or impure ore
6   are given in the following working examples:

7   Example 1 - Preparation:

8   1.   A TiO_2 pigment type feed obtained from the DuPont Company was mixed with
9   powdered coal tar pitch (CTP) and a solvent of normal methyl pyrrolidone (NMP). The
10   ratio was 80 parts TiO_2 and 30 parts of a 110°C CTP and 80 parts of NMP. The NMP
11   provides good fluidity of the mix and dissolves a portion of the CTP. After mixing by

1   stirring, signal blade mixing, ball milling, attrition milling, etc. the mix is heated to

2   evaporate the NMP for collection and reuse. The TiO_2 particulate is fully coated and

3   intimately mixed with the pitch which chars or cokes to about 50% carbon with continued

4   heating. The mixture was heated to 1700°C under atmosphere pressure in a non-oxidizing

5   atmosphere which is typically argon, CO_2, CO, etc. Nitrogen atmosphere is avoided to

6   prevent the formation of titanium nitride. After the 1700°C treatment the product was

7   pure TiO with an XRD pattern analogous to that shown in Fig. 9. The produced TiO was

8   utilized in four different trials to electrolytically produce titanium particulate. The trials

9   were as follows:

10   **Trial 1**-The TiO was mixed with a 110°C coal tar pitch which served as a binder and

11   carbon black particulate to provide a stoichiometric mixture of TiO and carbon based

12   on an off gas of 1:1 CO_2/CO. The mixture was pressed in a steel die at 190°C to

13   provide a solid on cooling. The composite anode was heated in an inert atmosphere

14   to 1200°C which pyrolized/carbonized the pitch binder. Resin or other precursors

15   which yield carbon on heating in an inert atmosphere are satisfactory binders for

16   producing a solid anode. The composite anode was utilized in a fused salt electrolyte

17   consisting of the tri-eutectic of Li-K-Na chlorides. Virtually any fused salt mixture

18   of the alkali and/or alkali halides are satisfactory as an electrolyte. A stainless

19   cathode was used in a cell maintained in an inert atmosphere with electrolysis at 1

20   amp/cm² which produced titanium metal particulate in the size range of 10-500

21   microns.

22   **Trial 2**-The TiO was used as a cathode in a salt composition of 80% $CaCl_2$-20% LiCl

23   operated at 850°C. The TiO was ground to minus 100 mesh (147 microns). The TiO

24   particles were placed in a stainless steel mesh and placed in the salt electrolyte as a

25   cathode with a graphite anode. A potential of 3.0V was applied between the graphite

26   anode and TiO particles contained in the stainless mesh cathode. After 30 hours of

27   electrolysis the cathodic particles were analyzed as titanium metal with a residual

28   oxygen content of 2500 parts per million. During the electrolysis the anode gas was

29   analyzed with a mass spectrometer to be primarily CO_2 with traces of CO.

30   **Trial 3**-The same electrolyte as in Trial 2 was utilized at the same temperature of

31   850°C. In this trial the TiO was ground to a minus 325 mesh (less than 44microns).

1   Two weight percent TiO was added to the electrolyte with stirring. After one hour

2   stirring a stainless tube cathode was used with a 600 mesh stainless screen covering

3   the bottom of the tube. A graphite rod was placed in the center of the stainless tube.

4   Electrolysis was performed with the stainless tube as the cathode and the graphite rod

5   as the anode. A cathode current density of 1 amp/cm^2 was utilized. After two hours

6   electrolysis of the cathode anode assembly was removed from the salt electrolyte and

7   water washed. Titanium metal particulate was produced in the size range of

8   approximately 1 to 200 microns which demonstrates the TiO had solubility in the

9   electrolyte in order to yield titanium metal on electrolysis.

10   **Trials 4A and 4B**-A closed cell inert atmosphere system was utilized that had

11   tungsten coil resistors between two electrodes in the bottom of the reactor. Calcium

12   fluoride (CAF$_2$) was used as the electrolyte and power applied to the tungsten

13   resistors that brought the CaF$_2$ to a molten state and 1700°C. In Trial 4A, a TiO

14   particle as given in Trial 2 was placed in a molybdenum screen and electrolyzed at

15   3.0V as a cathode with a graphite anode. Titanium was produced as a molten glob in

16   the molybdenum screen. In Trial 4B, TiO-325 mesh was added to the CaF$_2$

17   electrolyte and electrolysis performed between a molybdenum cathode and a graphite

18   anode. Molten droplets of titanium metal were produced at the molybdenum cathode

19   which shows the TiO had solubility in the CaF$_2$ electrolyte at 1700°C producing

20   titanium metal in the molten state due to the electrolysis.

21   Example 2 - Preparation

22   Ilmenite ore obtained from QIT – Fer et Titane, Inc., of Quebec, Canada, which

23   had the composition shown in Table 3 was mixed at room temperature with 110°C

24   softening point powdered coal tar pitch (CTP) in a ratio of 100 grams of ilmenite ore to

25   40 grams of CTP and 100 grams of toluene. The mixture was ball milled for four hours

26   at room temperature to achieve good mixing and then heated to evaporate the toluene

27   which was collected for reuse. The mixture was further heated to 1700°C under an inert

28   atmosphere at atmospheric pressure followed by reducing the pressure to 10^{-3} Torr or

29   less and the temperature raised to 1800°C and held for one hour. After cooling the

30   treated ilmenite ore had the composition shown in Table 5. The purified TiO product

31   was subjected to the same electrolysis trials listed in Trials 1, 2 and 5 producing purified

32   titanium metal from an impure ore.

1   **Trial 5**-The same set-up was used as given in Trial 2. In this case hydrogen gas was

2   bubbled over the TiO in the cathode. After electrolysis at 3V for 30 hours the

3   titanium particles were subjected to vacuum evaporation of the residual salt at

4   1200°C and 10^{-5} Torr vacuum. The residual oxygen content was 300ppm.

5   It should be noted that since TiO is an electronic conductor with a conductivity

6   superior to graphite, electrical contact is easily made which eliminates the necessity to

7   form a partially sintered porous body to serve as a cathode for the electrolytic reduction

8   to Ti metal particles. In the case of cathodic reduction of TiO_2 to the metal it is

9   necessary to produce a porous perform in order that current can flow to the TiO_2 body

10   whereas with the high electrolytic conduction of TiO particles are easily contacted to

11   achieve cathodic reduction and making it possible for the continuous cathodic reduction

12   as compared to batch processing of porous TiO_2 preforms.

13   The concentrations of titanium and oxygen in TiO are 74.96% titanium and

14   25.04% oxygen. This composition of TiO is typical of the material such as shown in

15   Fig. 9. However, it is possible to further reduce the oxygen content to produce up to

16   approximately 92% titanium. The higher titanium content is desirably obtained

17   carbothermically which results in less electronic reduction in a second electrolysis step to

18   obtain pure metallic titanium with very low oxygen contents of less than 500ppm.

19   Greater carbothermic reduction can be achieved by heating to higher temperatures than

20   the 1650-1700°C as above described.

21   Samples of TiO_2 (the ores of ilmenite, rutile, slag, etc can also be used), and

22   carbon when intimately mixed and heated to higher temperatures, produces a higher

23   titanium content in the remaining product. TiO_2 was intimately mixed at 190°C with

24   coal tar pitch in stoichiometric ratio to produce low oxygen content titanium and was

25   heated to 2100°C in a non-oxidizing atmosphere. The XRD of the product is shown in

26   Fig. 13. The analysis of the product obtained from an outside laboratory, Wah Chang,

27   showed a residual oxygen content of 5.4%. Residual carbon content is quite low in the

28   range of 0.7 to 2%.

29   A sample was heated to 2800°C in a non-oxidizing atmosphere in a graphite

30   container. The XRD of that product showed primarily TiC which is believed the graphite

31   crucible contributed to the TiC formation. A TiC crucible was fabricated and a TiO_2-C

32   sample was heat treated to 2800°C which resulted in little TiC and a reduced oxygen

33   content of less than TiO in the residual titanium.

1   It is known that when TiO_2 and carbon are heated above about 1200°C the

2   product is a mixture of TiO and TiC. It is noted here that TiO_2 when heated at

3   atmospheric pressure and/or at reduced pressure only TiO is produced as exemplified in

4   the XRD patterns shown in Figs. 10, 12 and 13 and verified from carbon and oxygen

5   analysis which showed less than 1% carbon thus ruling out any appreciable amount of

6   TiC formation with a remaining oxygen content depending on the heat treatment

7   temperature of down to about 5% oxygen at 2100°C. It was also noted there was some

8   difference in reactivity between the crystal forms of TiO_2 in rutile and anatase. The

9   qualative results showed that anatase was more likely than rutile to produce a slight

10   amount of TiC at 2100°C than rutile as shown in the XRD pattern in Fig. 14. To produce

11   TiO_x $X \leq 1$ at atmospheric pressure and/or vacuum an enabling step is the intimate

12   mixing of the TiO_2/ore source with the carbon source as a pitch, resin or other carbon

13   source in the liquid state.

14   The metal oxide produced by carbothermic reduction as above-described may

15   then be formed into a feed electrode or used as a solute in the electrochemical reduction

16   system described in our above parent application, Serial No. 10/828,641.

17   The above embodiments and examples are given to illustrate the scope and spirit

18   of the instant invention. These embodiments and examples are within the contemplation

19   of the present invention. Therefore, the present invention should be limited only by the

20   appended claims.

21

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group

5   of integers or steps.

The reference to any prior art in this specification is not, and should not be taken as, an acknowledgment or any form or suggestion that the prior art forms part of the common general knowledge in Australia.

10

The claims defining the invention are as follows:

1.	A method for winning a metal from its oxide ore, which comprises heating the ore under an inert atmosphere in the presence of a reductant.

2.	The method of claim 1, wherein the reductant comprises carbon or graphite.

5	3.	The method of claim 1, wherein the reductant comprises a coal tar pitch, carbon derived from furfural alcohol, or carbon derived from a resin.

4.	The method of claim 1, wherein the reductant comprises a phenolic resin.

5.	The method of claim any one of claims 1 to 4, wherein the heating is conducted at a temperature in excess of 1100°C.

10	6.	The method of any one of claims 1 to 5, wherein the heating is conducted at a temperature of 1100-2100°C.

7.	The method of any one of claims 1 to 6, wherein the heating is conducted at a temperature of 1400-1800°C.

8.	The method of any one of claims 1-7, wherein the heating is conducted in two steps.

15	two steps.

9.	The method of any one of claims 1-8, wherein the ore comprises titanium oxide.

10.	The method of any one of claims 1-9, wherein said ore is heated under an inert atmosphere, under a partial vacuum, in the presence of a reductant.

20	11.	A method for the production of a metal from its oxide ore, comprising the steps of:

(a)	heating the ore under an inert atmosphere in the presence of a reductant, whereby to produce a lower oxide of said metal; and

(b)	subjecting the lower oxide of said metal produced in step (a) to an
25	electrochemical reduction.

12.	The method of claim 11, wherein the metal oxide from step (a) is mixed with carbon and formed into an anode for use in the electrochemical reduction of step (b).

13.	The method of claim 11 or claim 12, wherein one or more of the following
30	features:

(a)	wherein the ore comprises titanium oxide;

- 22 -

(b)   wherein the ore is heated in step (a) under an inert atmosphere, under a partial vacuum, in the presence of a reductant;

(c)   wherein the lower oxide of said metal produced in step (a) is employed as a solute in the electrochemical reduction in step (b); and

5   (d)   wherein the lower oxide of said metal produced in step (a) is formed into an electrode and employed as a feed electrode in the electrochemical reduction in step (b).

14.   A method for the production of a metal from its oxide ore, substantially as herein described with reference to Example 1 or Example 2.

10   15.   TiO and Ti_2O_3 when produced by the method of any one of claims 1 to 10.

16.   Titanium when produced by the method of any one of claims 11 to 13.

FIG. 1

XRD OF STOICHIOMETRIC TiO_2 -C HEAT TREATED
IN ARGON AT 1300°C FOR ONE HOUR
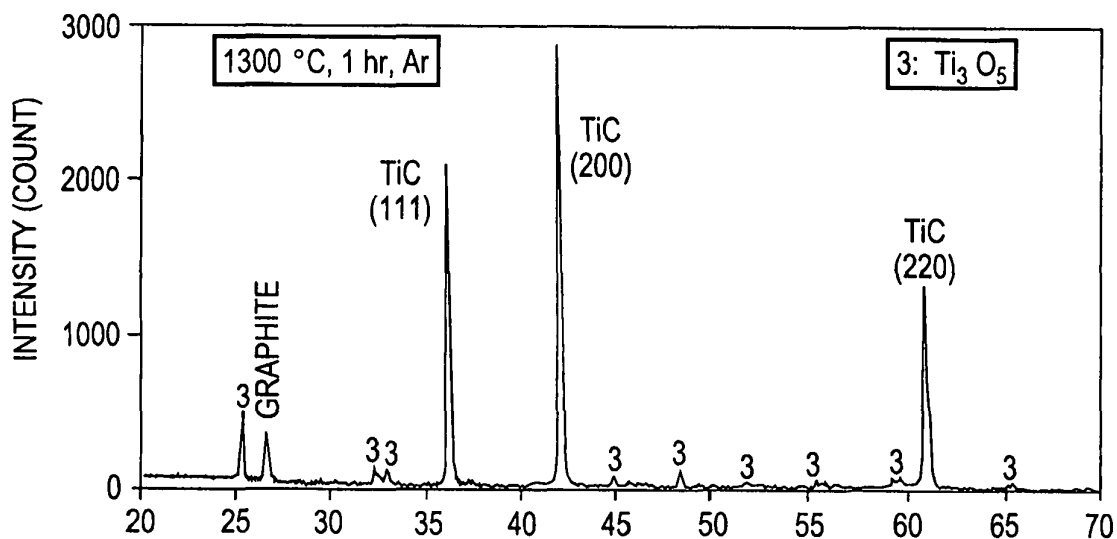
FIG. 2

XRD OF STOICHIOMETRIC TiO_2 -C HEAT TREATED
IN ARGON AT 1400°C FOR ONE HOUR
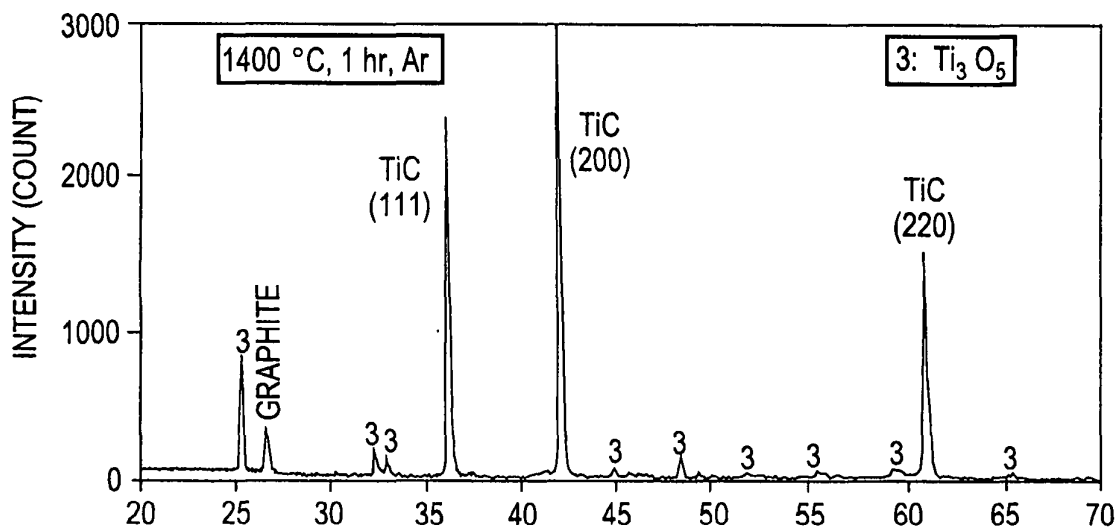
FIG. 3

XRD OF STOICHIOMETRIC TiO₂ -C HEAT TREATED
IN ARGON AT 1750°C FOR ONE HOUR
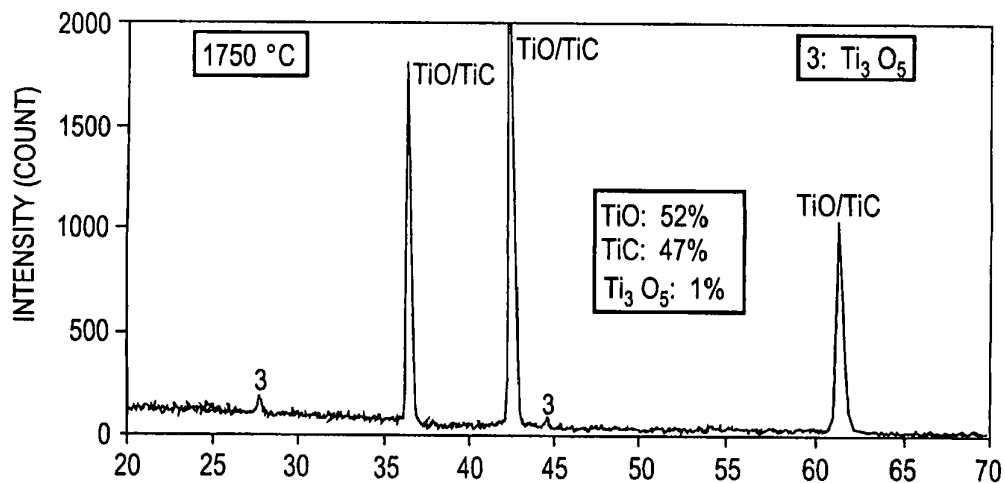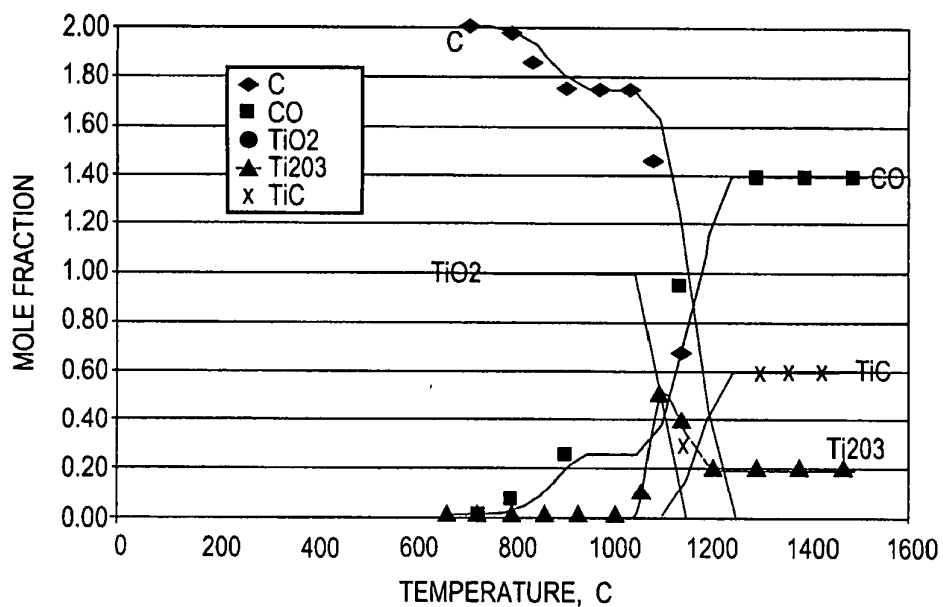

FIG. 4

THERMODYNAMIC EQUILIBRIUM CALCULATION

FIG. 5

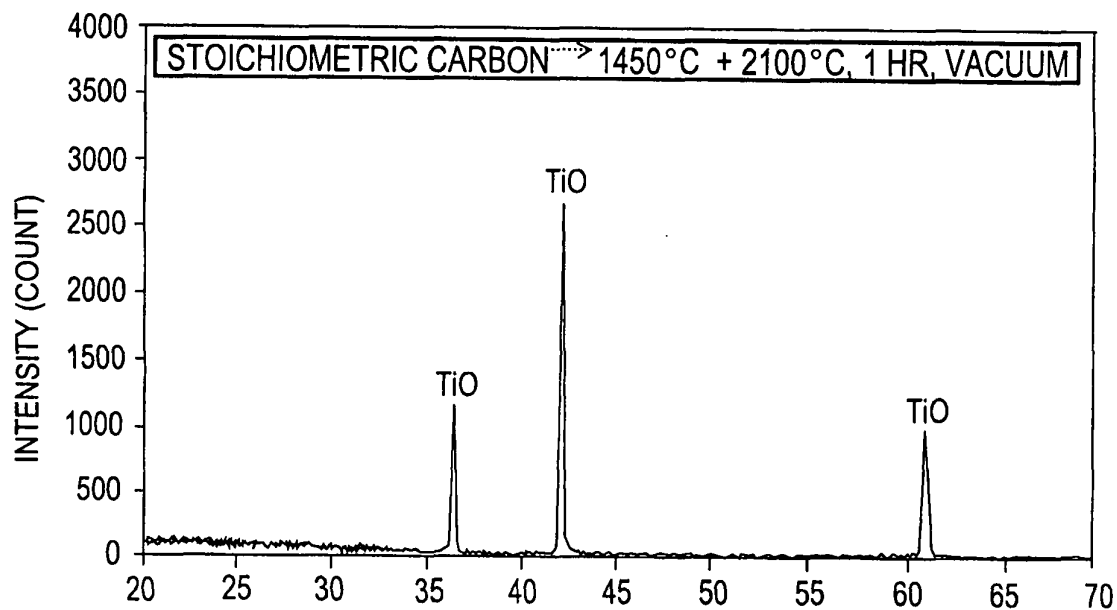### XRD OF STOICHIOMETRIC TiO$_2$-C HEAT TREATED TO 1450°C IN ONE STEP FOLLOWED BY HEAT TREATMENT AT 2100°C IN VACUUM

FIG. 6

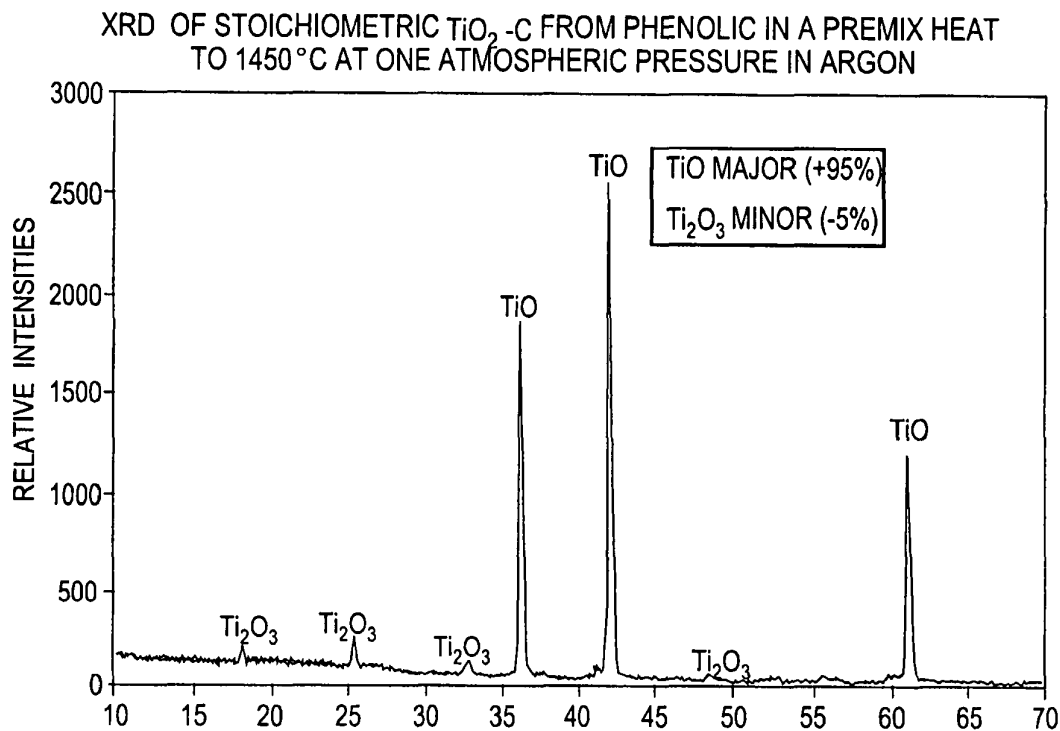### XRD OF 1:1 TiO$_2$-Ti HEAT TREATED TO 1760°C IN VACUUM

FIG. 7

XRD OF STOICHIOMETRIC TiO_2 -C HEAT TREATED TO 1450°C
WITH A SECOND HEAT TREATMENT TO 1800°C IN HIGH VACUUM

1 (TiO MAJOR (95%)

2 (TiO) MINOR (-5%)

FIG. 8

XRD OF STOICHIOMETRIC TiO_2 -C FROM PHENOLIC IN A PREMIX HEAT
TO 1450°C AT ONE ATMOSPHERIC PRESSURE IN ARGON

TiO MAJOR (+95%)

Ti_2O_3 MINOR (-5%)
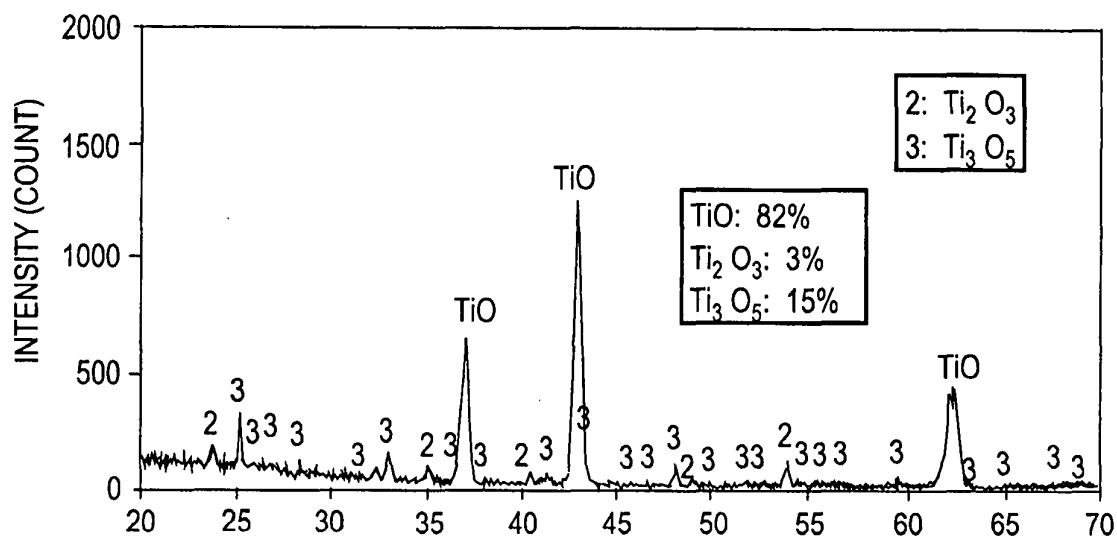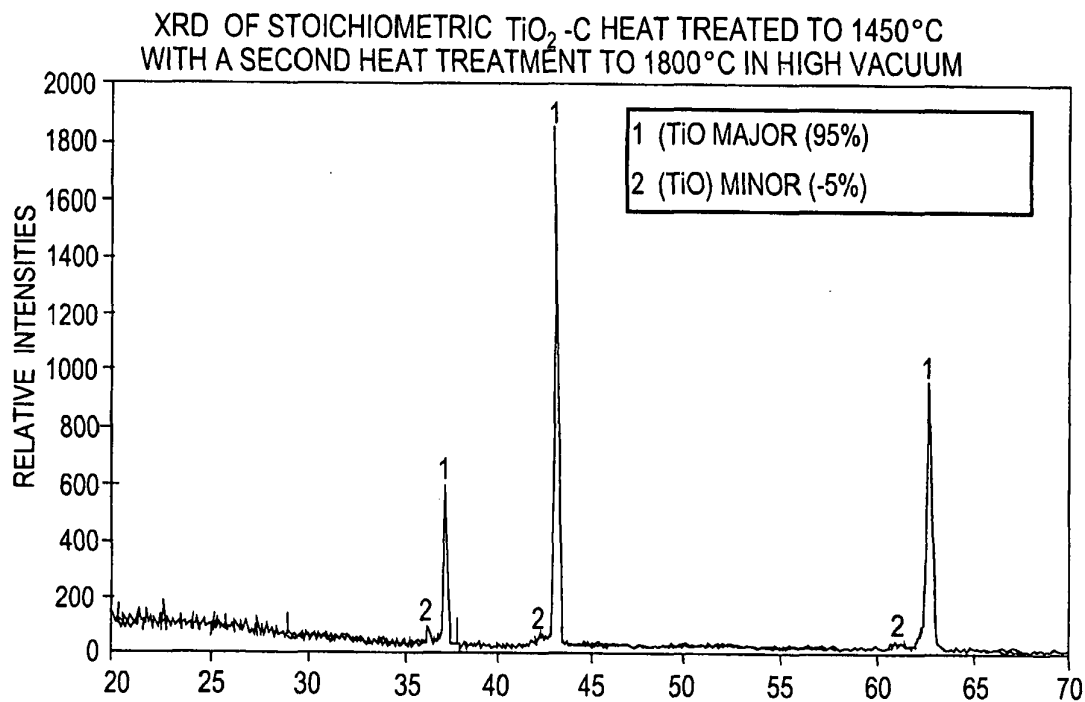
FIG. 9

XRD OF STOICHIOMETRIC TiO$_2$ -C FROM A 110°C SOFTENING POINT COAL TAR
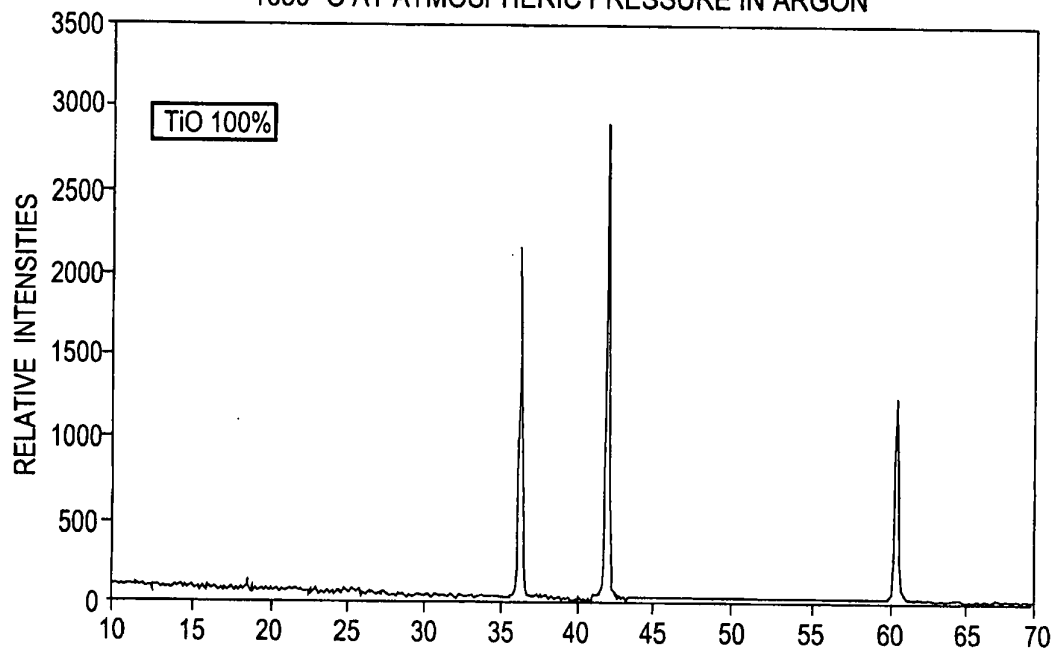PITCH MIXED AT 190°C AND HEAT TREATED AT
1650°C AT ATMOSPHERIC PRESSURE IN ARGON

FIG. 10

XRD OF SLAG-C FROM A 110°C SOFTENING POINT COAL TAR
PITCH MIXED AT 190°C AND HEAT TREATED AT
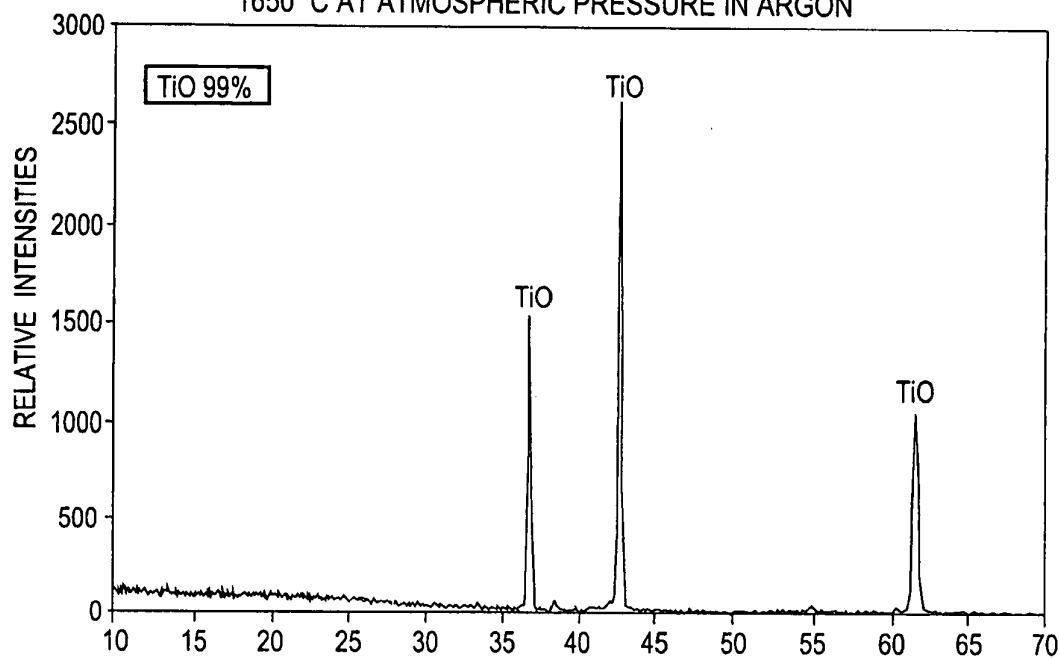1650°C AT ATMOSPHERIC PRESSURE IN ARGON

FIG. 11

ILMENITE ORE TREATED WITH AN INTIMATE CARBON COATING ON ORE PARTICLES WITH HEAT TREATMENT TO 1650°C IN ARGON
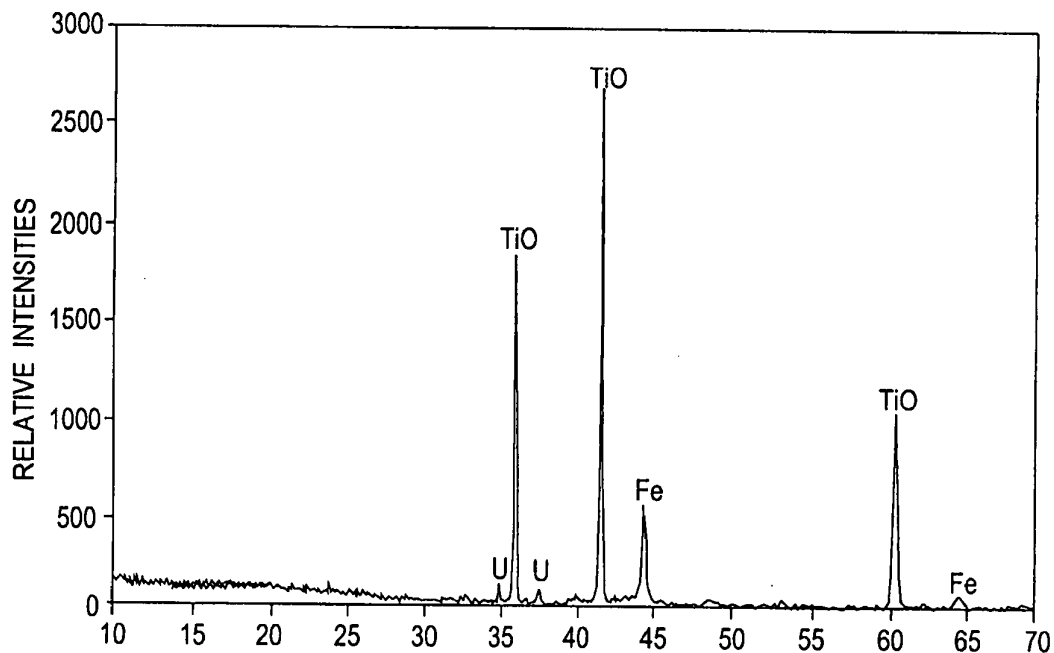

FIG. 12

ILMENITE ORE TREATED WITH AN INTIMATE CARBON COATING ON ORE PARTICLES WITH HEAT TREATMENT TO 1650°C IN ARGON PLUS 1800°C IN A VACUUM LOWER THAN 10^{-3} Torr
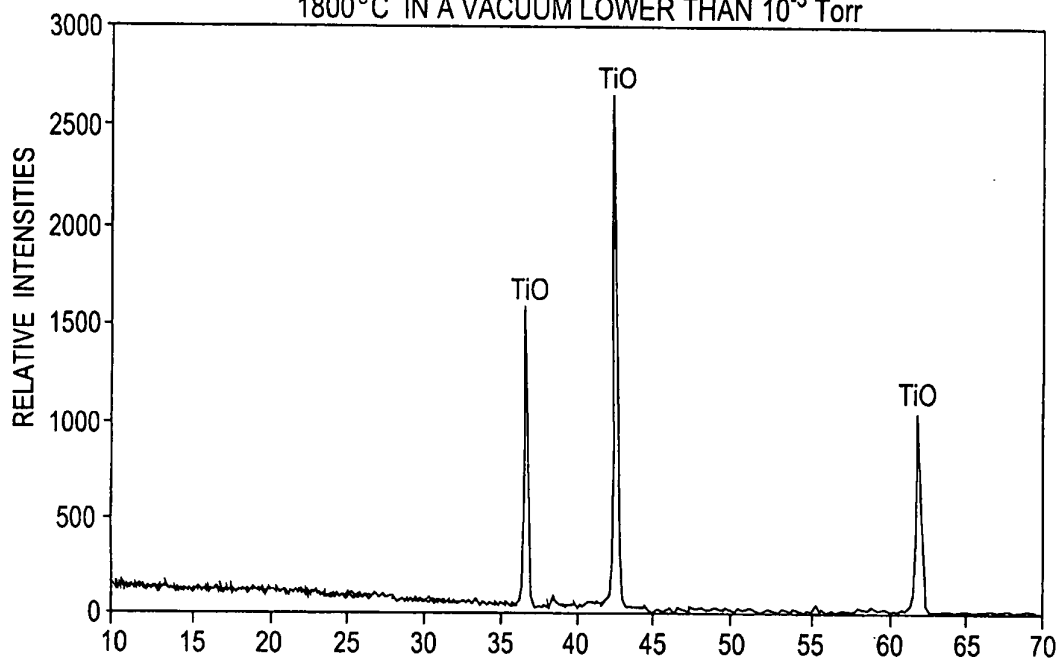
FIG. 13

XRD OF TiO$_2$ TREATED WITH AN INTIMATE MIXTURE OF CARBON
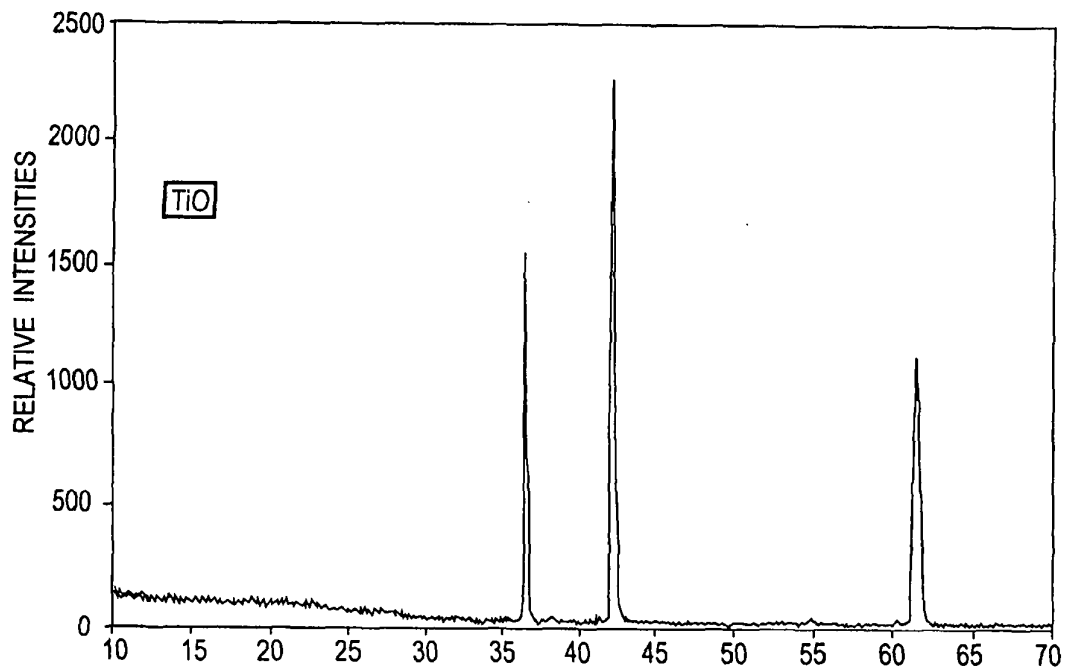WITH HEAT TREATMENT TO 2100°C AT ATMOSPHERIC PRESSURE IN ARGON

FIG. 14

XRD OF ANATASE TiO$_2$ WITH AN INTIMATE MIXTURE OF CARBON
WITH HEAT TREATMENT TO 2100°C UNDER ARGON AT ATMOSPHERIC PRESSURE