



Office de la Propriété
Intellectuelle
du Canada

Un organisme
d'Industrie Canada

Canadian
Intellectual Property
Office

An agency of
Industry Canada

CA 2621464 C 2016/06/14

(11)(21) 2 621 464

(12) BREVET CANADIEN
CANADIAN PATENT

(13) C

(86) Date de dépôt PCT/PCT Filing Date: 2006/12/01
(87) Date publication PCT/PCT Publication Date: 2007/08/30
(45) Date de délivrance/Issue Date: 2016/06/14
(85) Entrée phase nationale/National Entry: 2008/03/05
(86) N° demande PCT/PCT Application No.: US 2006/061461
(87) N° publication PCT/PCT Publication No.: 2007/097823
(30) Priorité/Priority: 2005/12/06 (US11/294,872)

(51) Cl.Int./Int.Cl. C22B 5/10 (2006.01),
C22B 34/12 (2006.01)

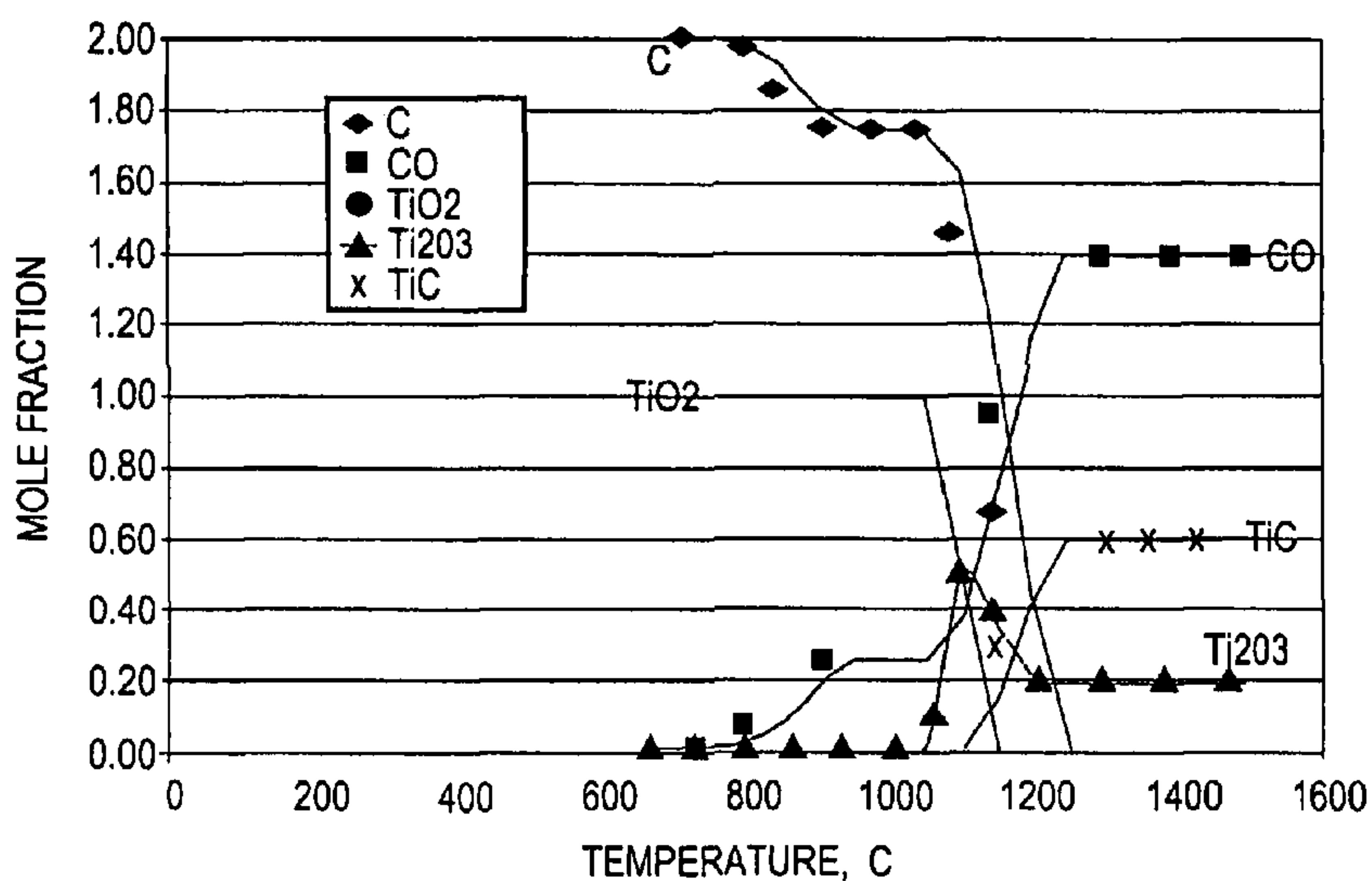
(72) Inventeurs/Inventors:
WITHERS, JAMES C., US;
LOUTFY, RAOUF O., US

(73) Propriétaire/Owner:
MATERIALS & ELECTROCHEMICAL RESEARCH
CORP., US

(74) Agent: OSLER, HOSKIN & HARCOURT LLP

(54) Titre : PROCEDE THERMIQUE ET ELECTROCHIMIQUE POUR PRODUIRE UN METAL
(54) Title: THERMAL AND ELECTROCHEMICAL PROCESS FOR METAL PRODUCTION

THERMODYNAMIC EQUILIBRIUM CALCULATION



(57) Abrégé/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.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
30 August 2007 (30.08.2007)

PCT

(10) International Publication Number
WO 2007/097823 A3(51) International Patent Classification:
C22B 5/10 (2006.01) C22B 34/12 (2006.01)

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(21) International Application Number:
PCT/US2006/061461(22) International Filing Date:
1 December 2006 (01.12.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
11/294,872 6 December 2005 (06.12.2005) US

(71) Applicant (for all designated States except US): MATERIALS & ELECTROCHEMICAL RESEARCH CORP. [US/US]; 7960 South Kolb Road, Tucson, Arizona 85706 (US).

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(72) Inventors; and

Published:

(75) Inventors/Applicants (for US only): WITHERS, James, C. [US/US]; Materials & Electrochemical Research Corp., 7960 South Kolb Road, Tucson, Arizona 85706 (US). LOUTFY, Raouf, O. [US/US]; Materials & Electrochemical Research Corp., 7960 South Kolb Road, Tucson, Arizona 85706 (US).

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

(74) Agents: SOLOWAY, Norman, P. et al.; Hayes Soloway P.C., 3450 E. Sunrise Drive, Suite 140, Tucson, Arizona 85718 (US).

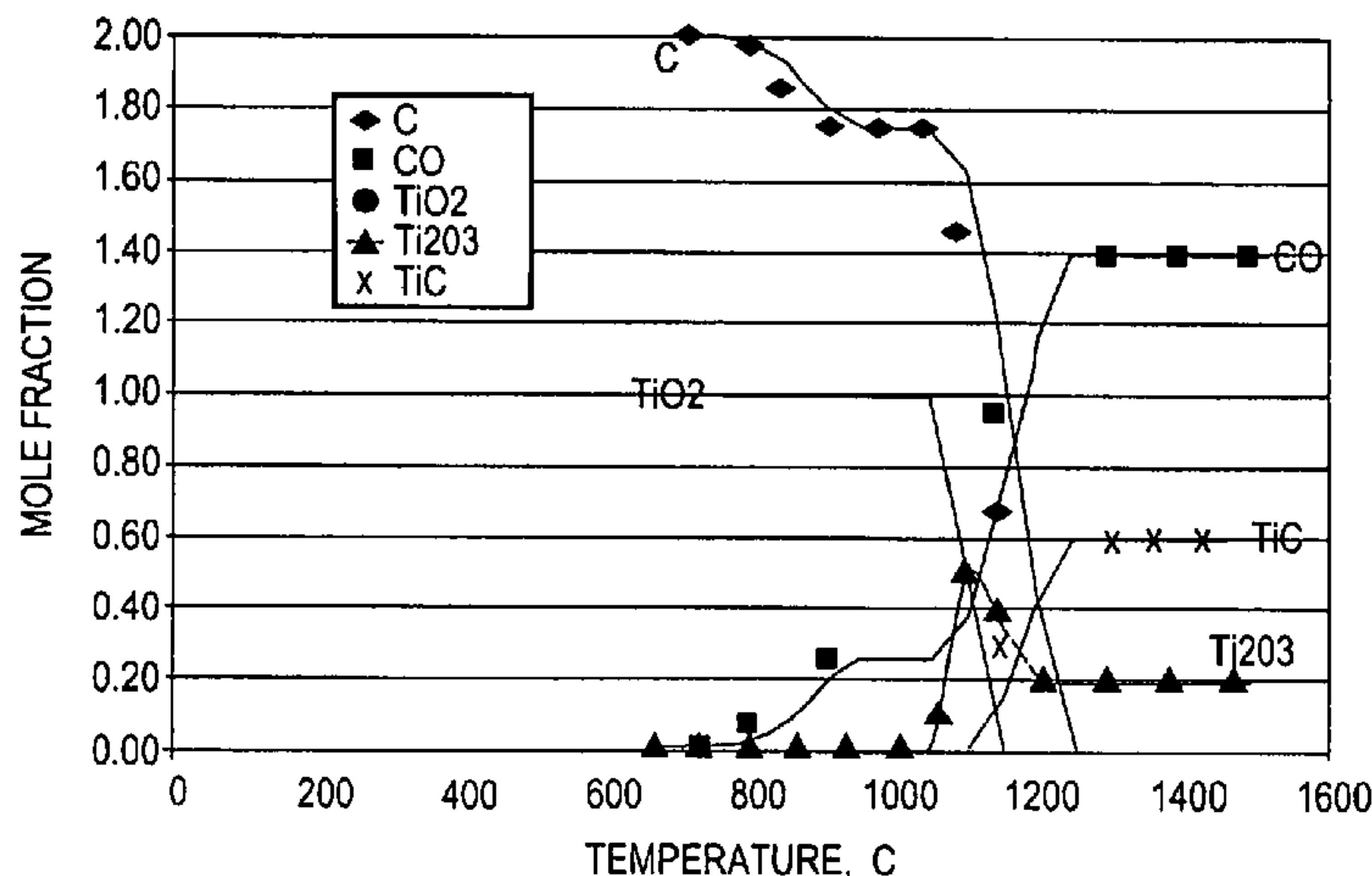
(88) Date of publication of the international search report:

15 November 2007

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(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.

WO 2007/097823 A3

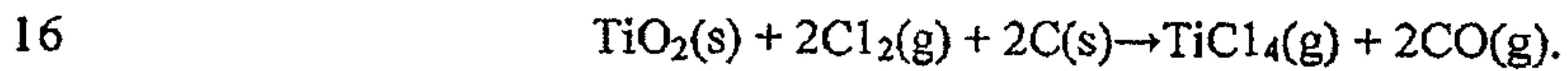
1 THERMAL AND ELECTROCHEMICAL PROCESS

2 FOR METAL PRODUCTION

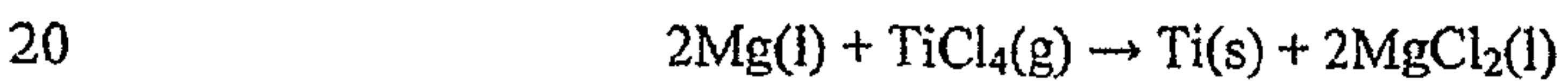
3 The present invention relates to the production of metals. The invention has
4 particular utility in connection with the production of titanium and will be described in
5 connection with such utility, although other utilities are contemplated, e.g., production of
6 other high value multi-valence and 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.

12 Despite the many methods investigated to produce titanium, the only methods currently
13 utilized commercially are the Kroll and Hunter processes. 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:



17 In the Kroll process $TiCl_4$ is reduced with molten magnesium at $\approx 800^\circ C$ in an
18 atmosphere of argon. This produces metallic titanium as a spongy mass according to the
19 reaction:



from which the excess Mg and MgCl₂ is removed by volatilization, under vacuum at \approx 1000°C. The MgCl₂ is then separated and recycled electrolytically to produce Mg as the reductant to further reduce the TiCl₄. In the Hunter process sodium is used as a reductant according to the reaction:



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 to
10 improve the Kroll and Hunter processes. Many other processes have been investigated
11 that include plasma techniques, molten chloride salt electrolytic processes
12 molten fluoride methods, the Goldschmidt approach, and alkali metal-calcium
13 techniques. Other processes investigated have included aluminum, magnesium,
14 carbothermic and carbo-nitrothermic reduction of TiO_2 and plasma reduction of
15 $TiCl_4$ 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 without measurable success.
18 Kroll, who is considered as the father of the titanium industry 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 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 A1, WO 02/083993 A1, 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 A1 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 A1 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 A1 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 A1 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 A1 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 A1, it is taught that CaO must be electrolyzed to produce
3 calcium metal and Ca⁺⁺ ions which reduce the titania (TiO₂) in the cathode with oxygen
4 (O⁼) migrating to the anode. This is very unlikely the mechanism. If Ca in metallic
5 (Ca⁰) or ionic (Ca⁺⁺) form reduces the TiO₂ the product of reduction will be CaO i.e.,
6 TiO₂ + 2Ca = Ti + 2CaO. The produced calcium from electrolysis must diffuse into the
7 titania (TiO₂) pellet to achieve chemical reduction as claimed and the formed CaO will
8 then have to diffuse out of the Ti/TiO₂ which has been preformed and sintered into a
9 pellet. If calcium metal (Ca⁰) 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 TiO₂, will form CaO which must become soluble in the electrolyte (CaCl₂)
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 (CaTiO₃) forms as the TiO₂ is reduced. A possible reaction is O²⁻ + Ca²⁺ + TiO₂ =
17 CaTiO₃ which remains as a contaminant in the cathodically reduced TiO₂ to Ti.

18 US Patent 6,540,902 B1 to Redey teaches that a dissolved oxide in the electrolyte
19 is required to cathodically reduce a metal oxide such as UO₂. The example is Li₂O 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 UO₂ and Nb₂O₃) 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 Al₂O₃ in cryolite/sodium fluoride. While the Redey patent teaches
31 cathodic reduction of UO₂ and Nb₂O₃ in a LiCl/Li₂O 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 TiO₂ 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 titania is used as a
6 cathode on a cell bottom with an electrolyte such as CaF₂ 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 TiO₂ (liquid) + C (solid) = Ti (liquid)↓ + CO₂ (gas)↑.

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

15 Thus, current TiO₂ 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 (Al₂O₃) have not produced pure aluminum by carbothermic
24 reduction. Similarly TiO₂ heretofore has not been carbothermically reduced to produce
25 pure titanium. However, in our co-pending parent application, U.S. Application Publication
26 No. 2005-0166706, we describe how TiO₂ 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 TiO₂ as the first process step of producing titanium from TiO₂ 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 CO₂ with some CO and the
2 metal aluminum. However, no equivalent process has been developed for solubalizing
3 TiO₂. 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 TiO₂, 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 SiO₂ with silicon (Si). That is SiO₂ + Si + heat =
16 2SiO. The SiO₂ 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 SiO₂ + C + heat = SiO and SiC + CO. Producing a titanium suboxide by reducing TiO₂
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 contaminant.
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 TiO₂ would be ideal to produce
27 titanium suboxides if the formation of TiC can be prevented and only one suboxide
28 produced such as Ti₂O₃ 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 TiO₂-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 crucible 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 ₂ O 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% Ti₂O₃. The TiC composition
 12 was reduced with an increase in Ti₂O₃. 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 TiO₂.
 24 Different ratios of TiO₂ 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 Ti₃O₅
 26 and Ti₂O₃ 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 pyrolyzed will provide a
8 high yield of carbon. The TiO_2 particles can be uniformly mixed into the liquid
9 precursor and then pyrolyzed. 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 pyrolyzed are furfural alcohol, resins such as phenol
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 TiO₂ 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 pyrolyzed 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 FeTiO₃ with a variety of impurities consists
 9 typically of the composition shown in Table 3.

10

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

Element	Elemental Composition 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 pyrolyzed 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 pyrolyzed 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 1650⁰C.**

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 1800⁰C after or instead of the 1650⁰C heat treatment. The purity of the
 8 high vacuum 1800⁰C 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 TiO₂ or impure ore
 6 are given in the following working examples:

7 Example 1 - Preparation:

8 1. A TiO₂ 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 TiO₂ 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 TiO₂ 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, CO₂, 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 CO₂/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 pyrolyzed/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% CaCl₂-20% 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 CO₂ 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 44 microns).

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/cm² 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 (CaF₂) was used as the electrolyte and power applied to the tungsten
13 resistors that brought the CaF₂ 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 CaF₂
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 CaF₂ 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 TiO₂ to the metal it is
9 necessary to produce a porous perform in order that current can flow to the TiO₂ 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 TiO₂ 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 TiO₂ (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. TiO₂ 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 TiO₂-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 qualitative 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, U.S. Application Publication
No. 2005-0166706.

The embodiments of the present invention for which an exclusive property or privilege is claimed are defined as follows:

1. A method for the production of titanium from its oxide ore, which comprises the steps of:
 - (a) mixing the oxide ore with a carbon-containing reductant;
 - (b) heating the oxide ore under an inert atmosphere in the presence of the carbon-containing reductant to produce a lower oxide of titanium; and
 - (c) subjecting the lower oxide of titanium to an electrochemical reduction characterized in that the heating is conducted at a temperature of 1300 to 1700°C.
2. The method of claim 1, wherein the carbon-containing reductant is a liquid which is furfural alcohol, a resin, or a pitch.
3. The method of claim 2, wherein the carbon-containing reductant comprises a coal tar pitch.
4. The method of claim 1, wherein the resin comprises a phenolic resin.
5. The method of claim 1, wherein the lower oxide of titanium from step (b) is mixed with carbon and formed into an anode for use in the electrochemical reduction of step (c).
6. The method of claim 1, wherein the lower oxide of titanium produced in step (b) is employed as a solute in the electrochemical reduction in step (c), or is formed into an electrode and employed as a feed electrode in the electrochemical reduction in step (c).

FIG. 1

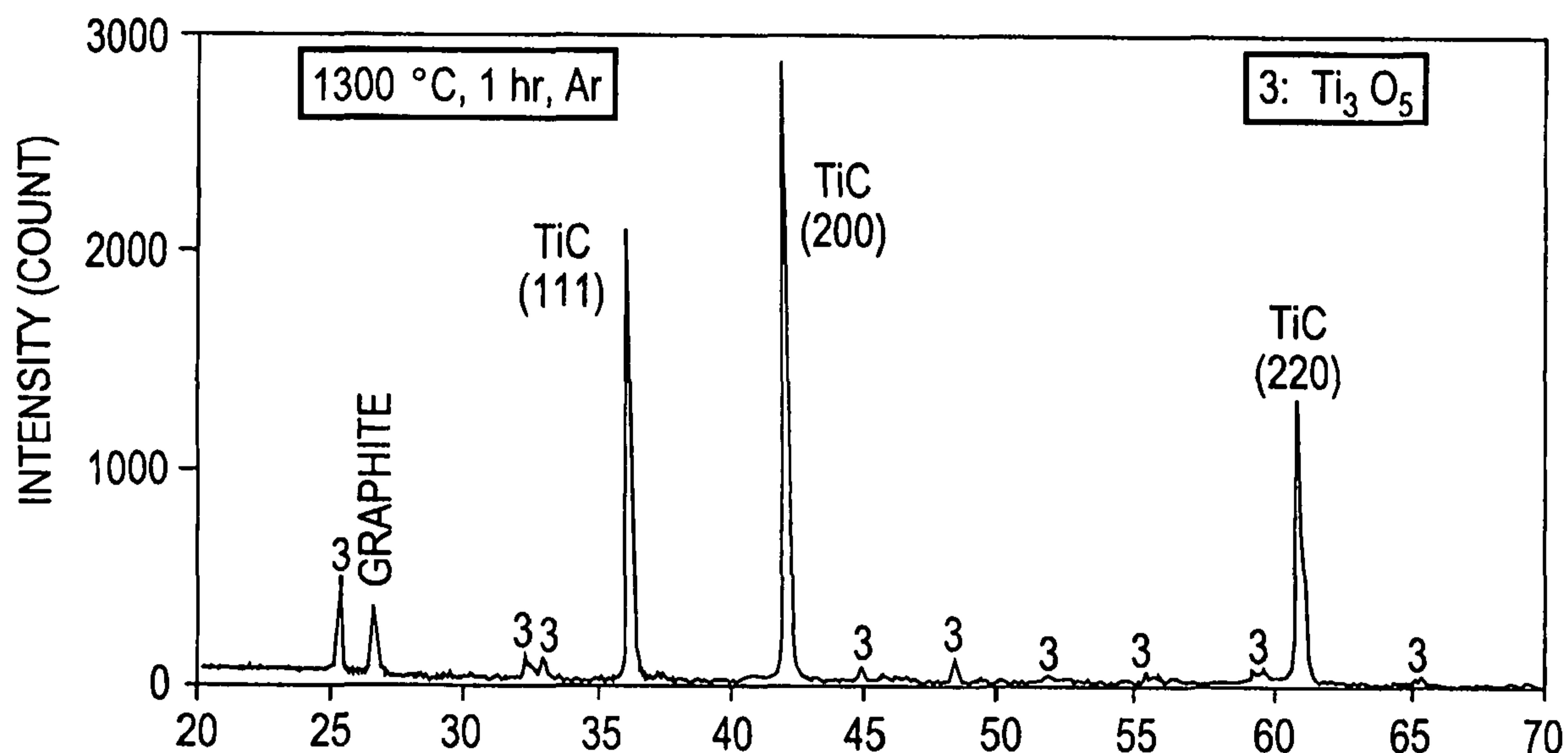
XRD OF STOICHIOMETRIC TiO_2 -C HEAT TREATED
IN ARGON AT 1300°C FOR ONE HOUR

FIG. 2

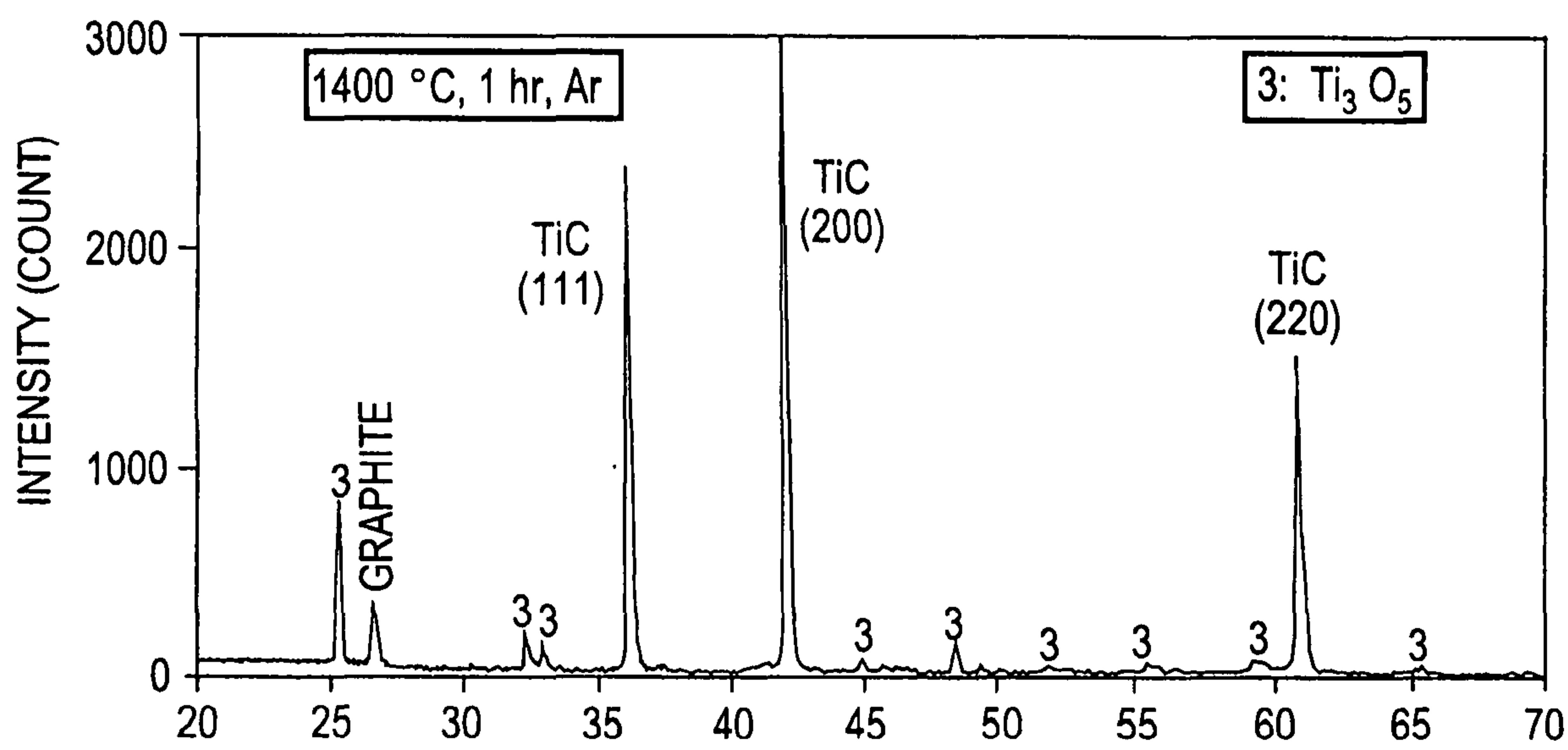
XRD OF STOICHIOMETRIC TiO_2 -C HEAT TREATED
IN ARGON AT 1400°C FOR ONE HOUR

FIG. 3

XRD OF STOICHIOMETRIC TiO_2 -C HEAT TREATED
IN ARGON AT 1750°C FOR ONE HOUR

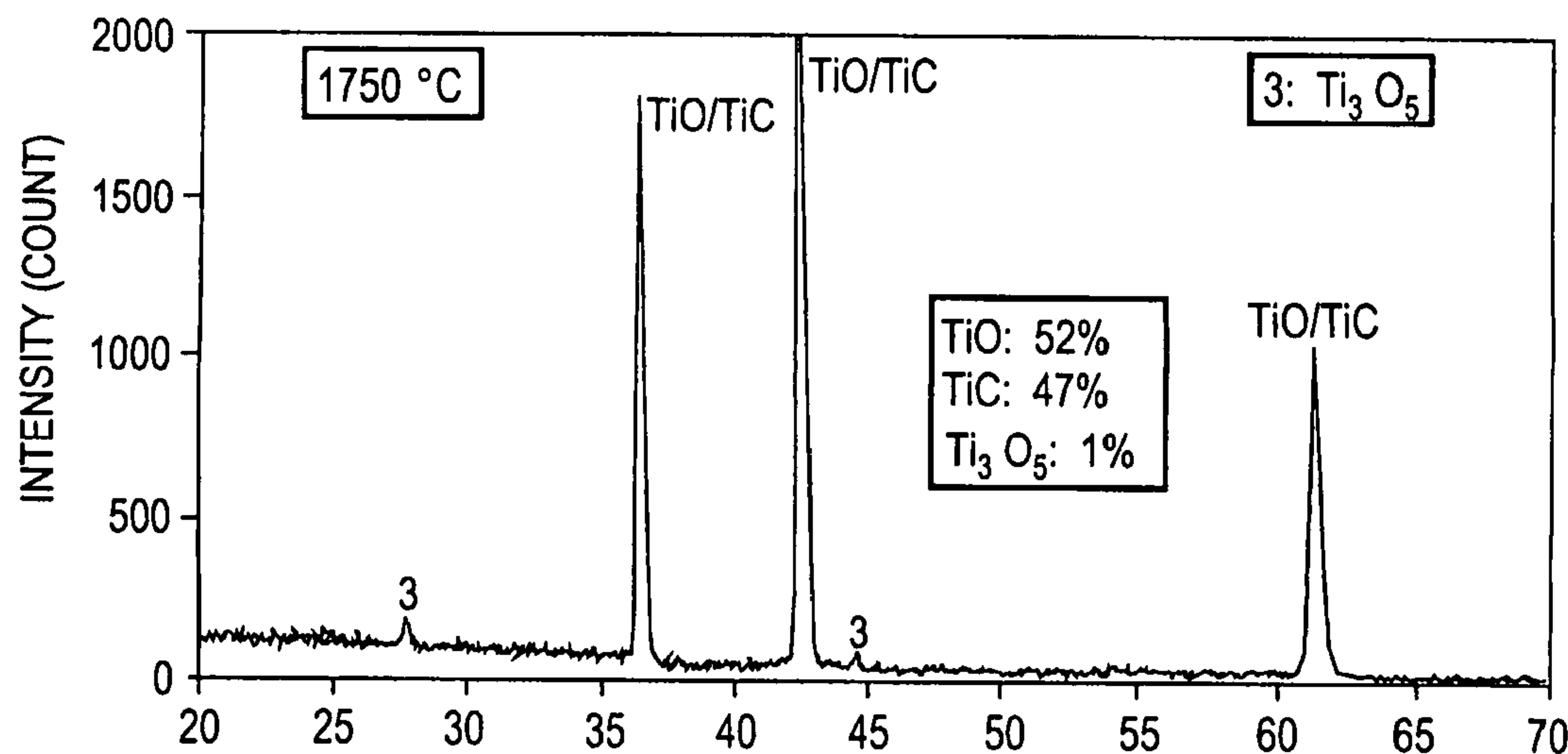


FIG. 4

THERMODYNAMIC EQUILIBRIUM CALCULATION

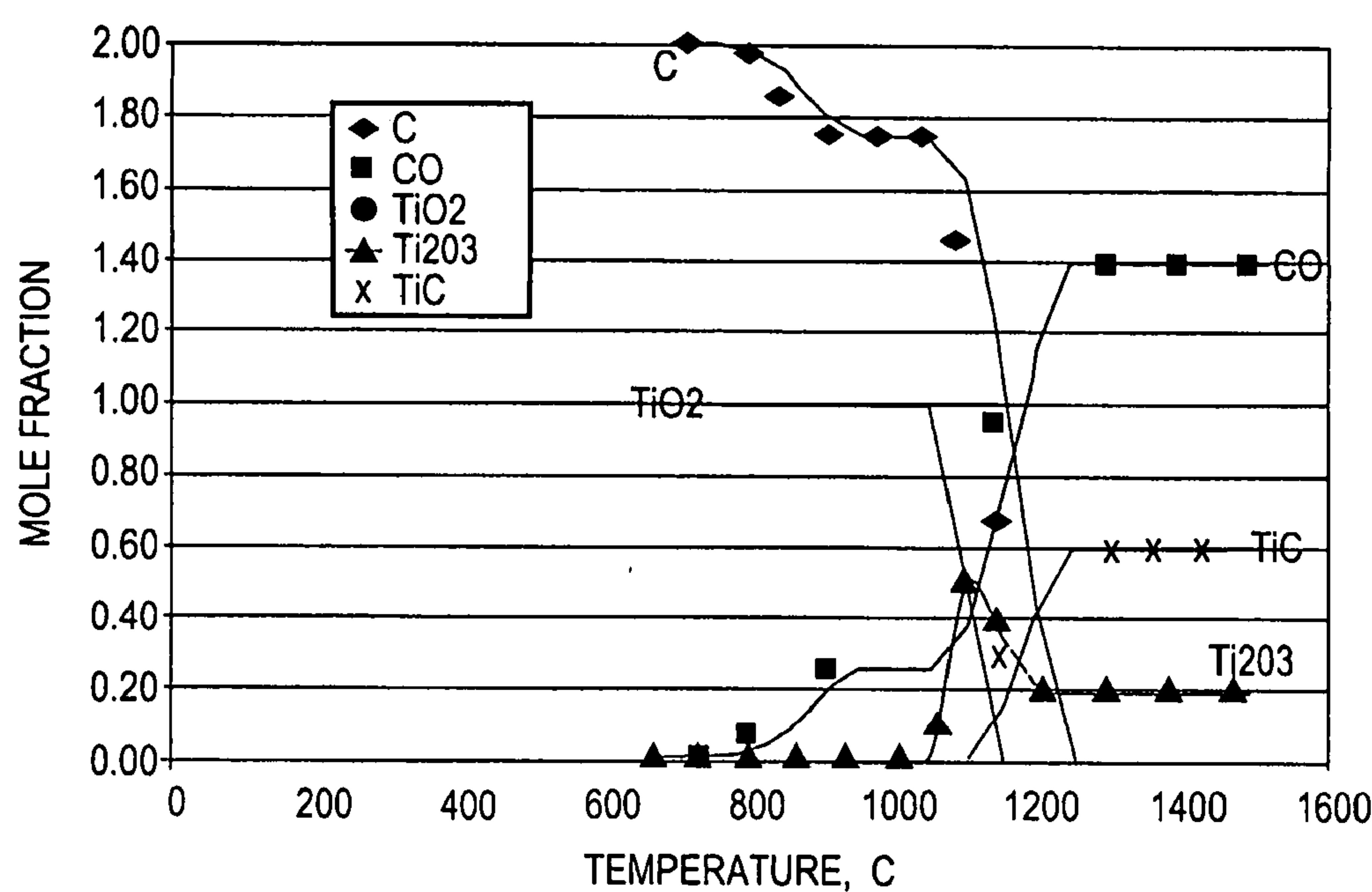
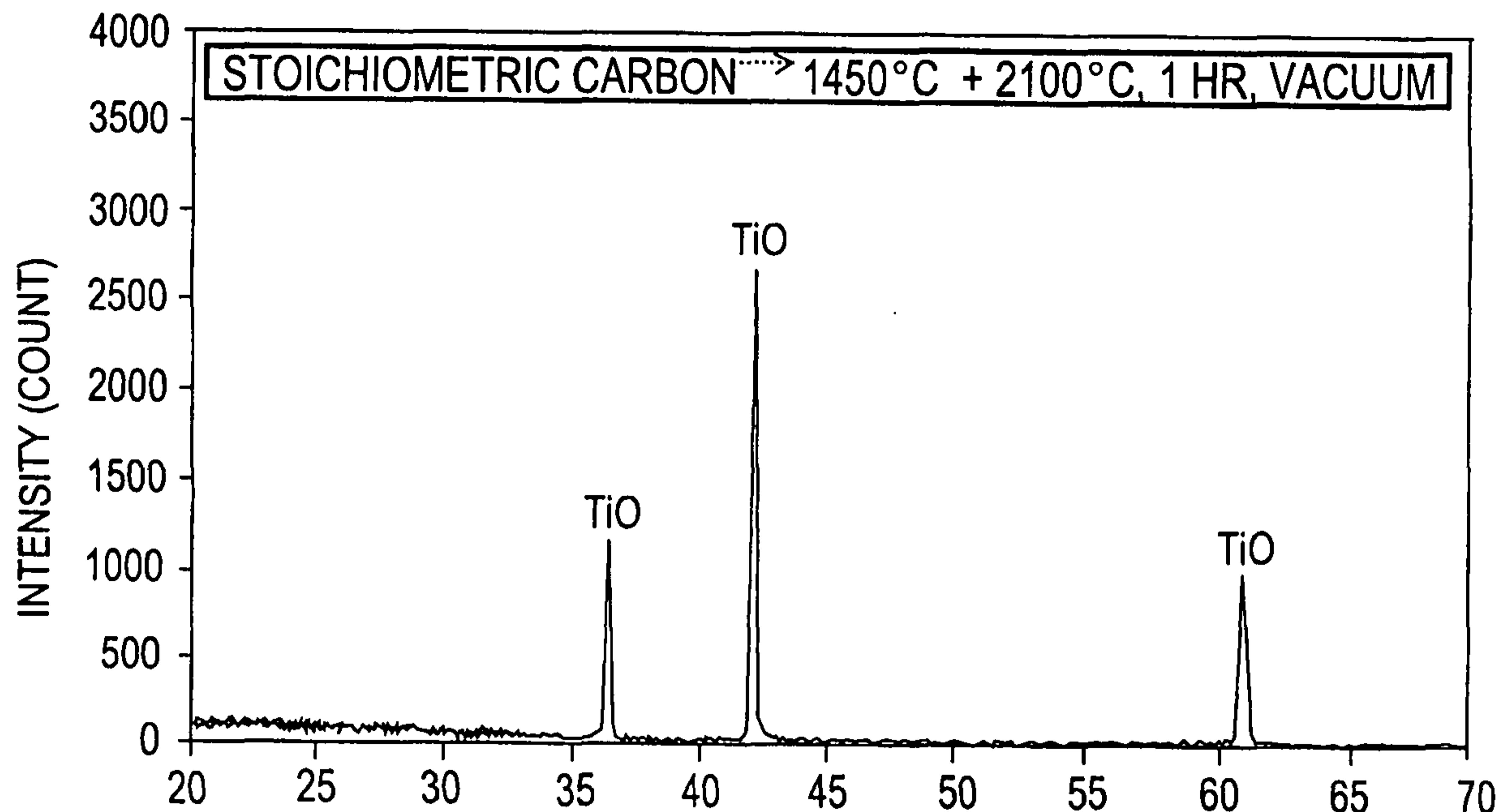


FIG. 5

XRD OF STOICHIOMETRIC TiO_2 -C HEAT TREATED TO 1450°C IN ONE STEP FOLLOWED BY HEAT TREATMENT AT 2100°C IN VACUUM



XRD OF 1:1 TiO_2 - Ti HEAT TREATED TO 1760°C IN VACUUM

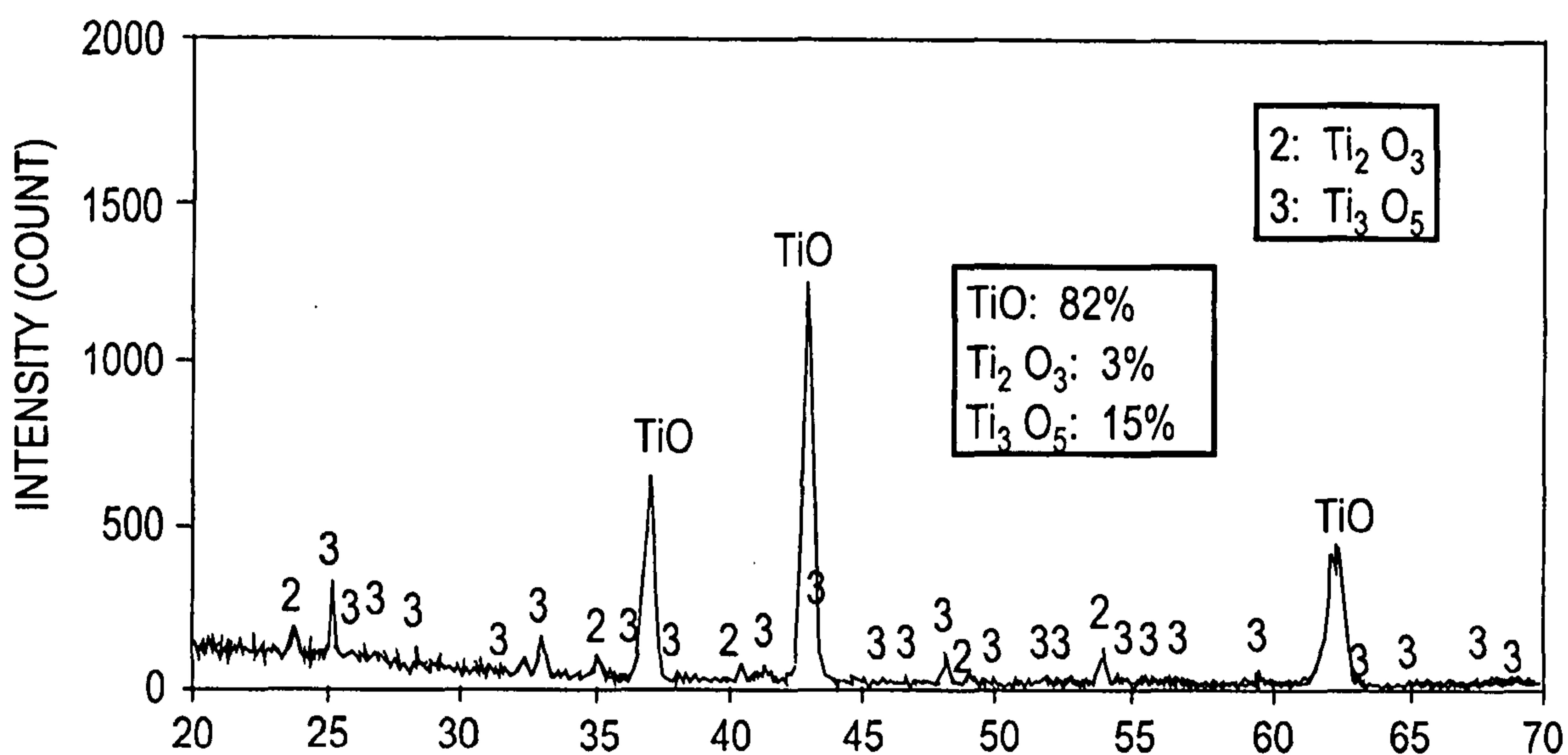


FIG. 7

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

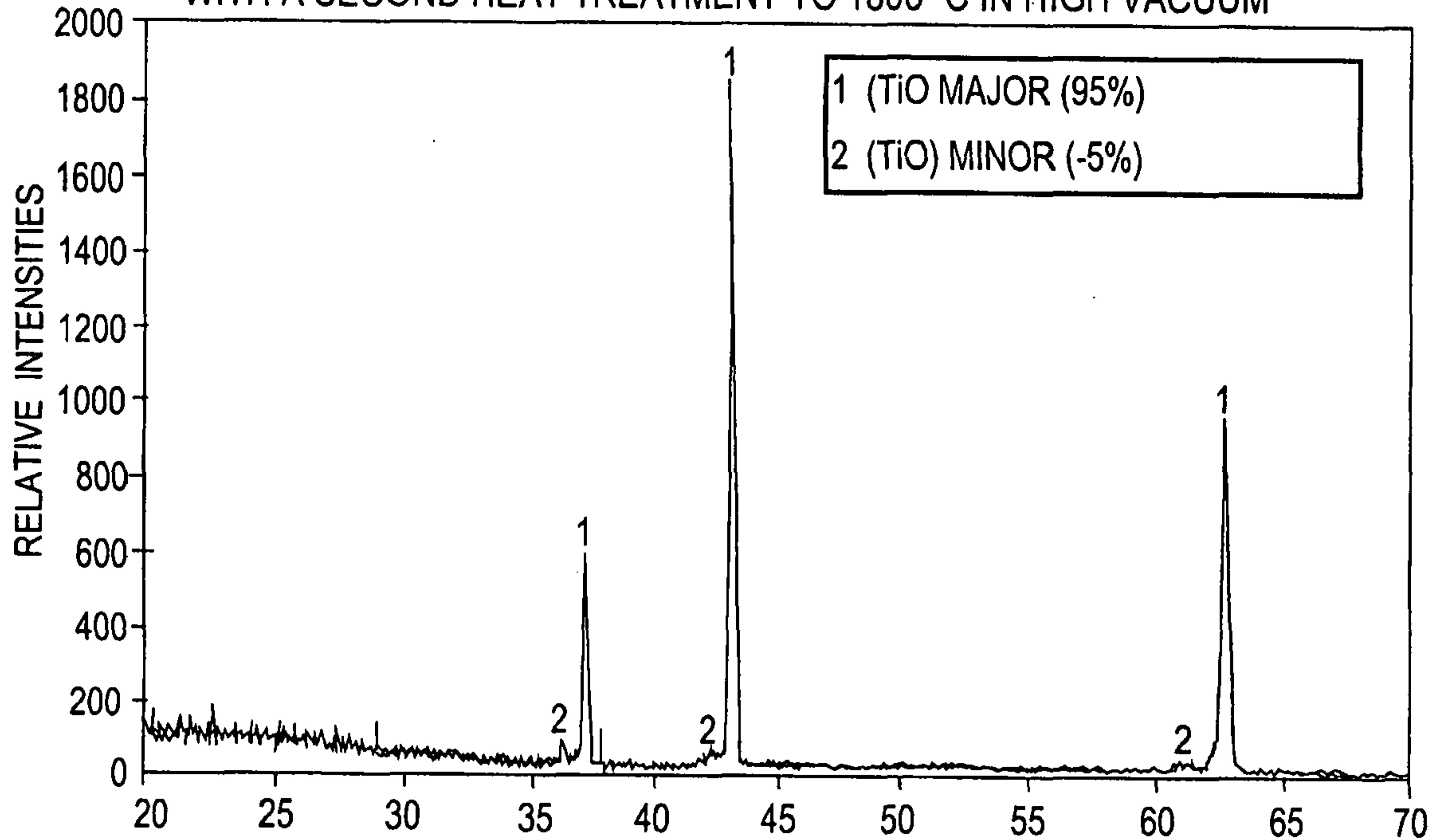


FIG. 8

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

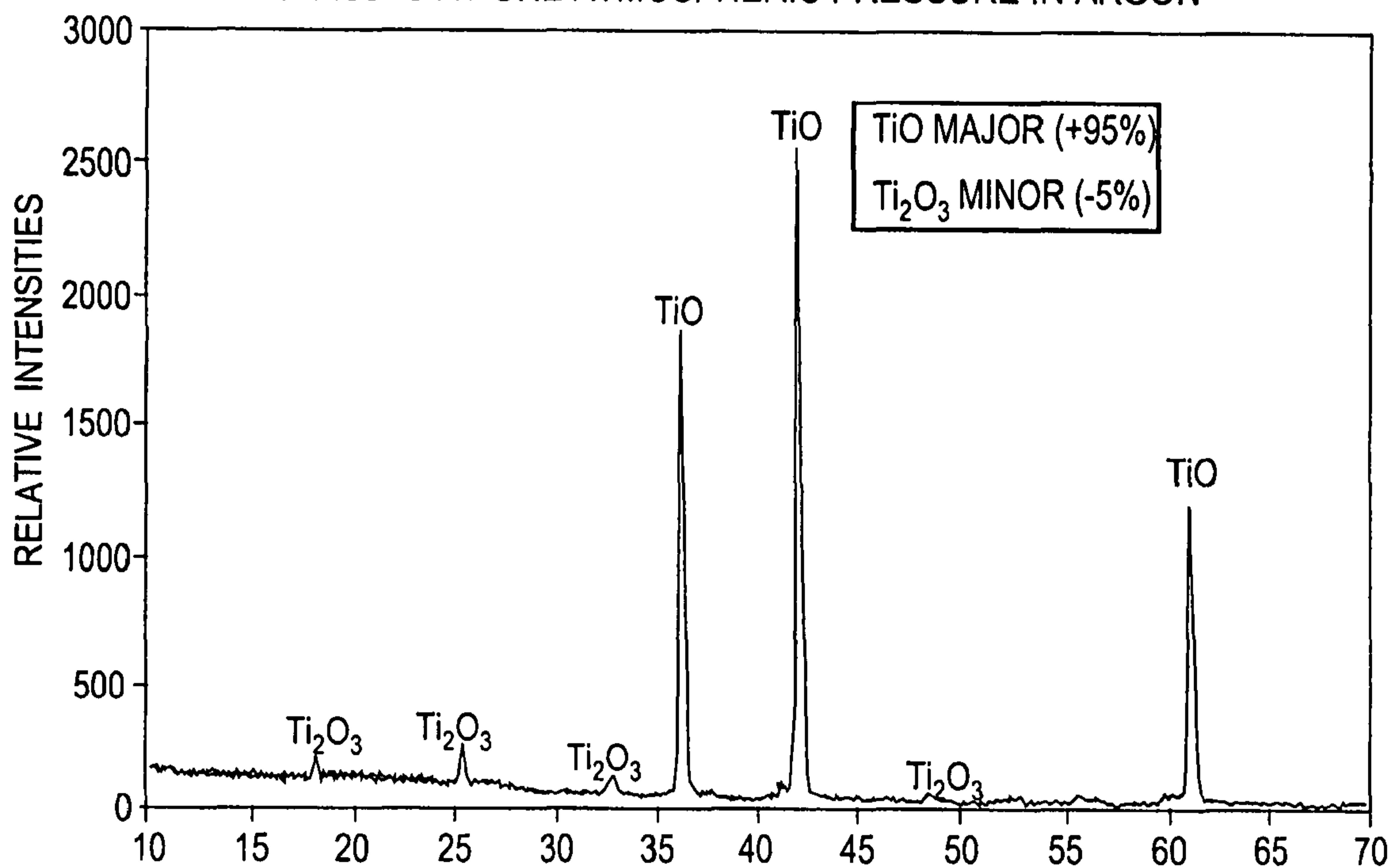


FIG. 9

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

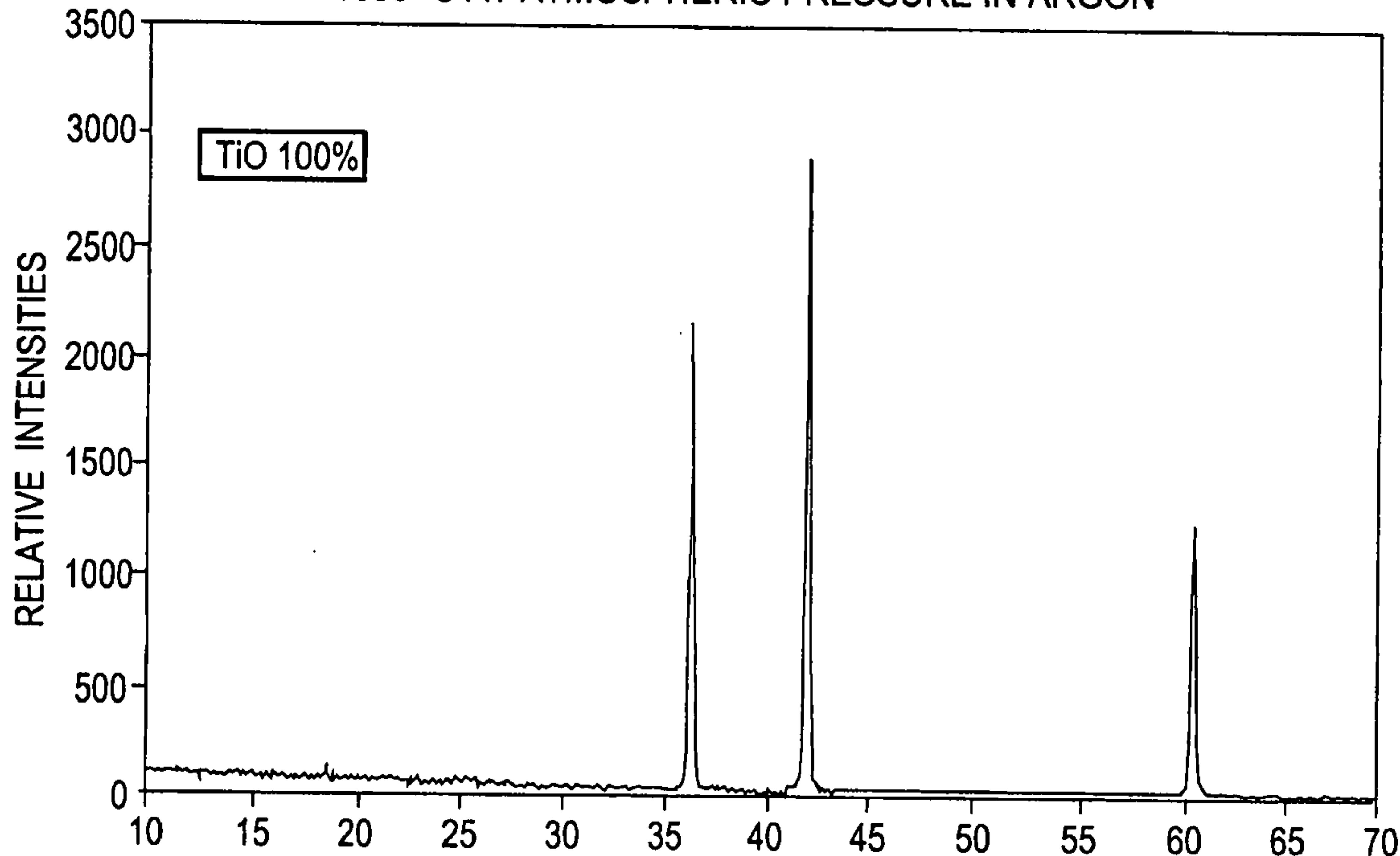


FIG. 10

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

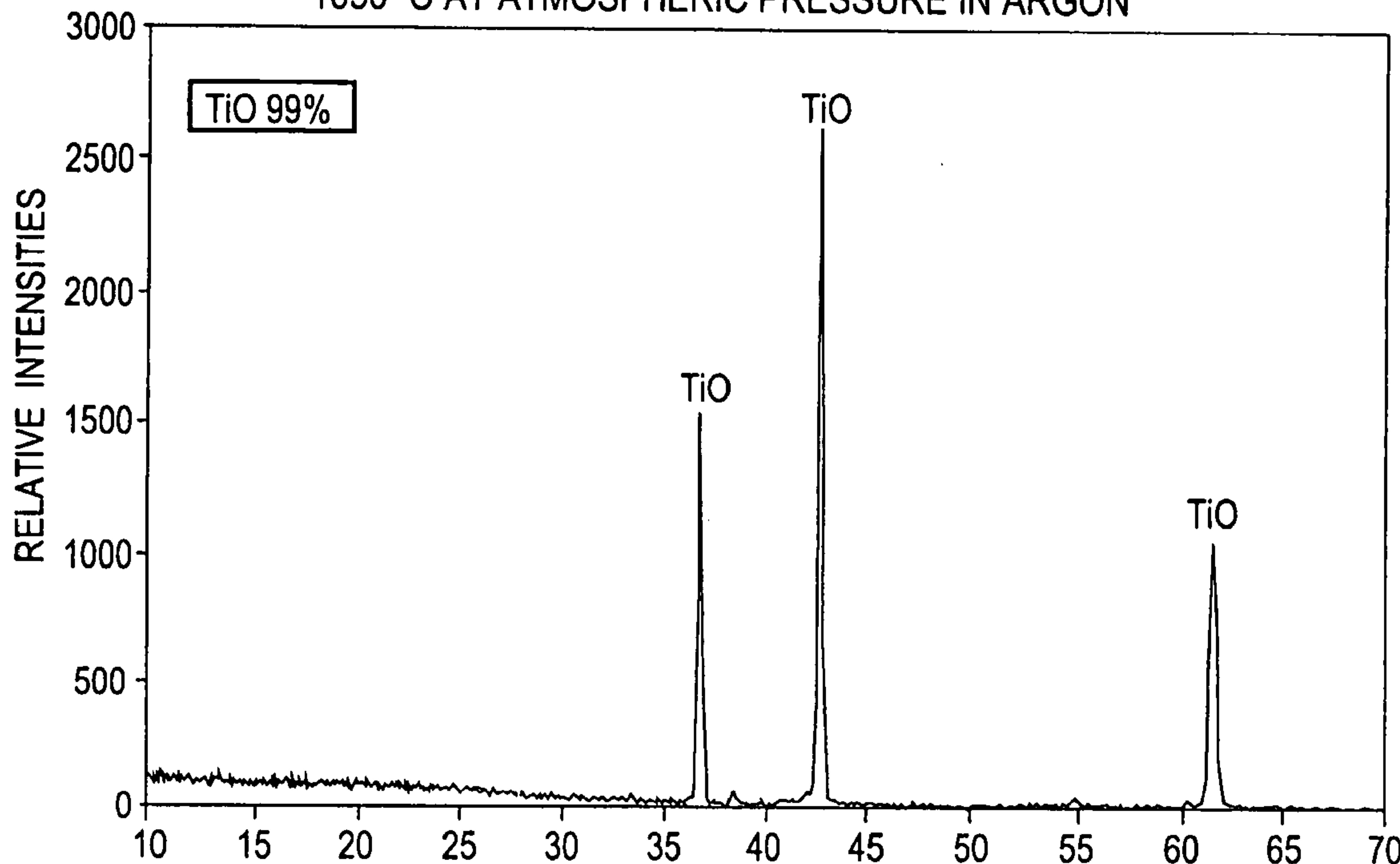


FIG. 11

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

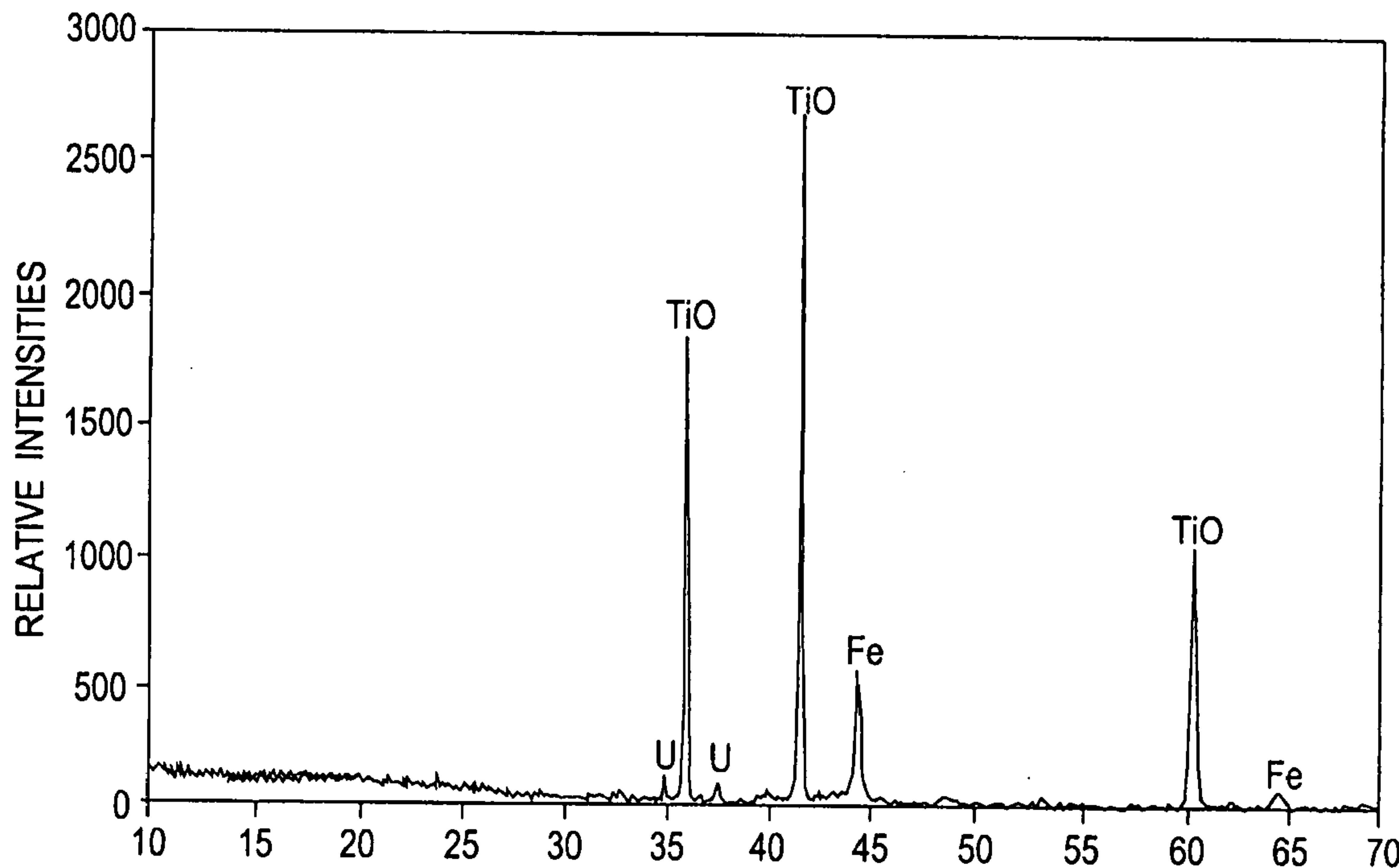


FIG. 12

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

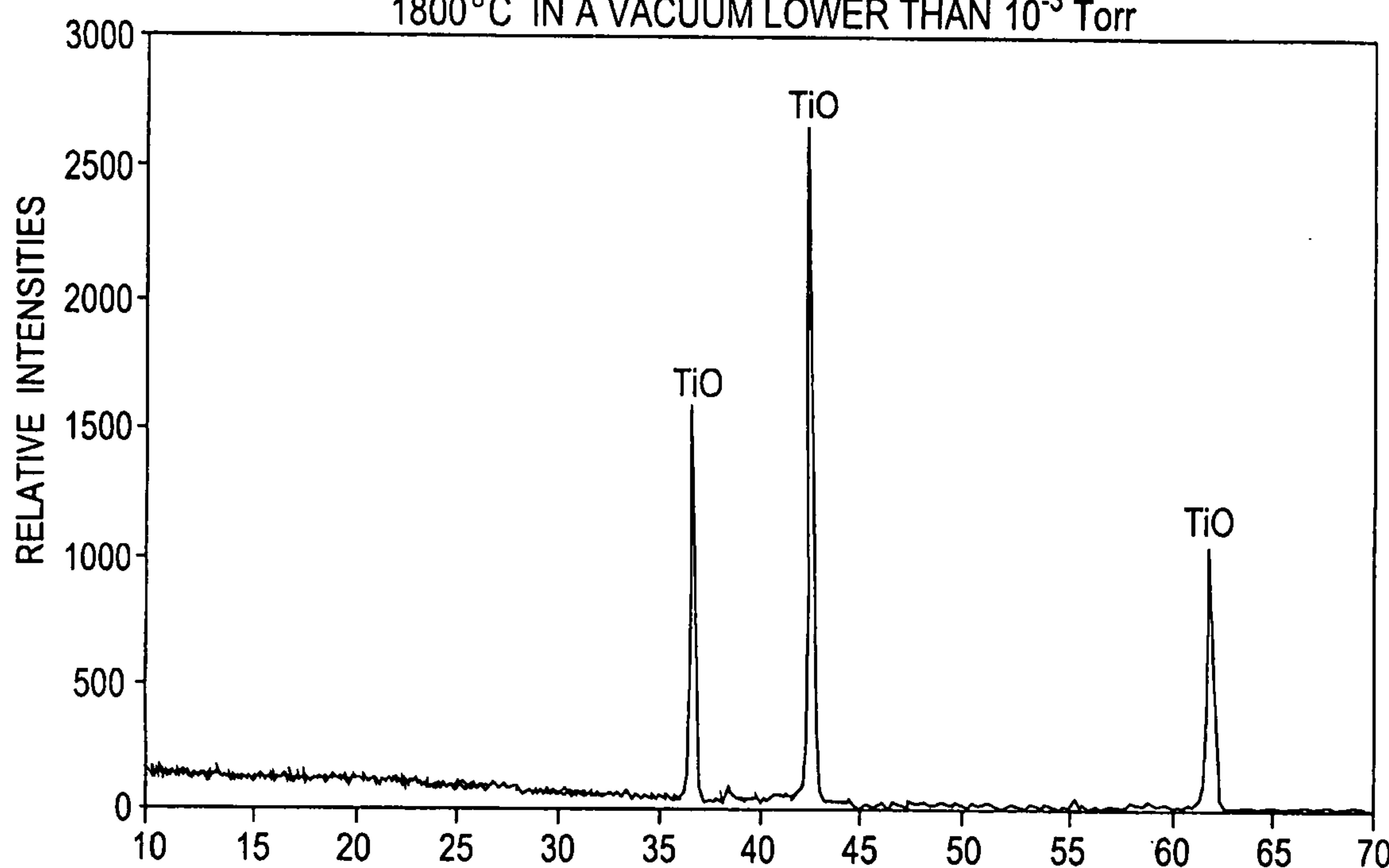


FIG. 13

XRD OF TiO_2 TREATED WITH AN INTIMATE MIXTURE OF CARBON
WITH HEAT TREATMENT TO 2100°C AT ATMOSPHERIC PRESSURE IN ARGON

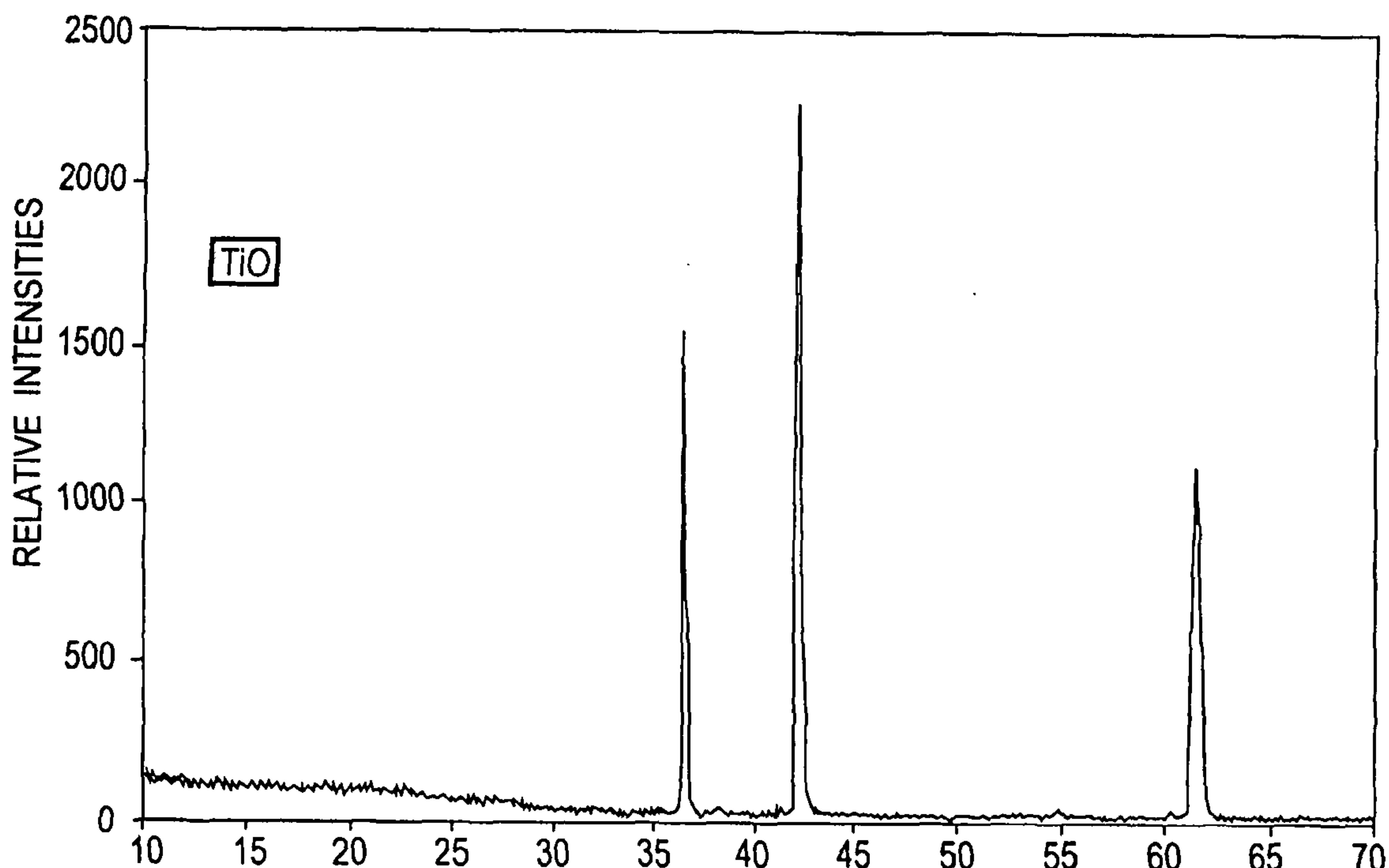
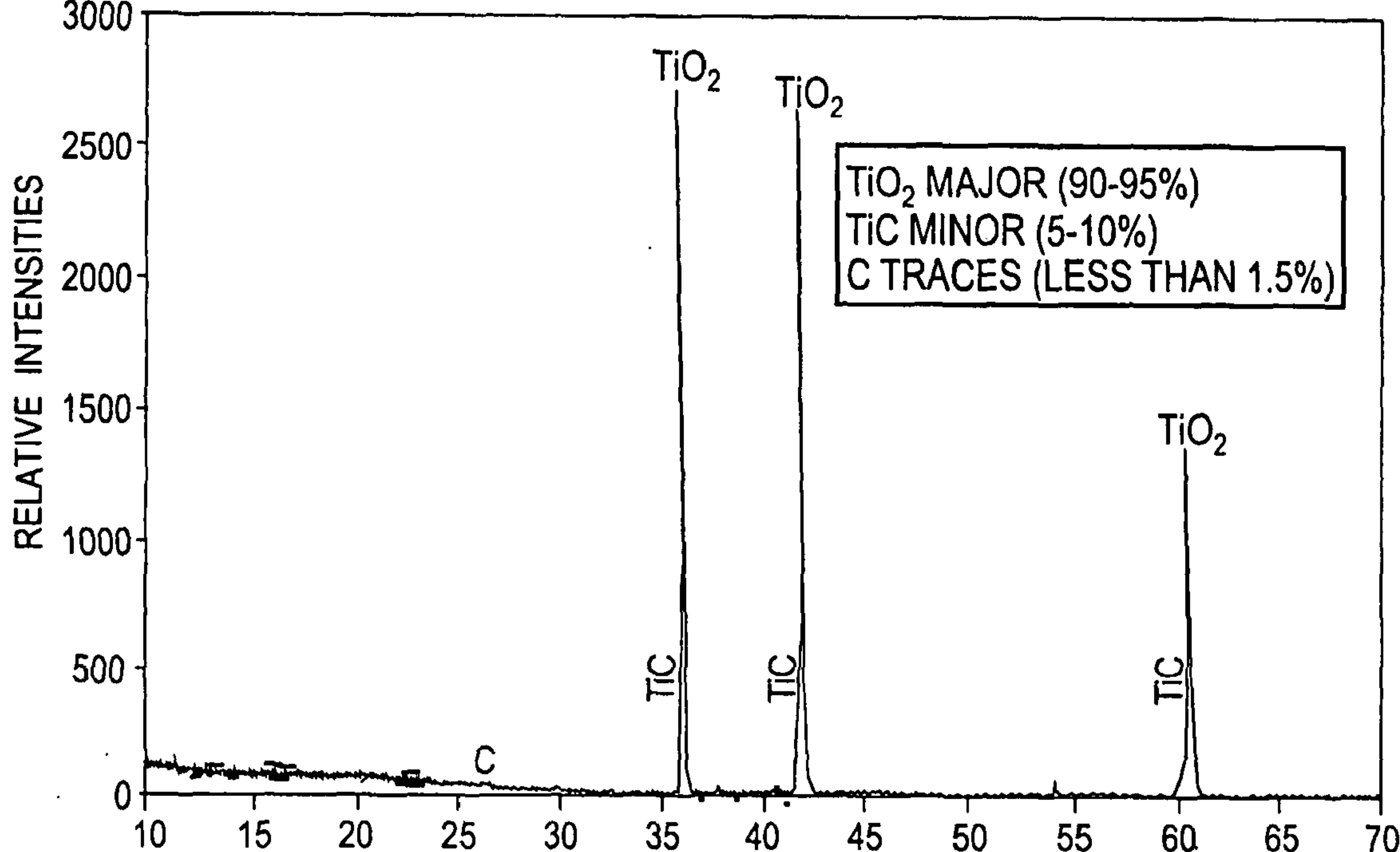


FIG. 14

XRD OF ANATASE TiO_2 WITH AN INTIMATE MIXTURE OF CARBON
WITH HEAT TREATMENT TO 2100°C UNDER ARGON AT ATMOSPHERIC PRESSURE



THERMODYNAMIC EQUILIBRIUM CALCULATION

