

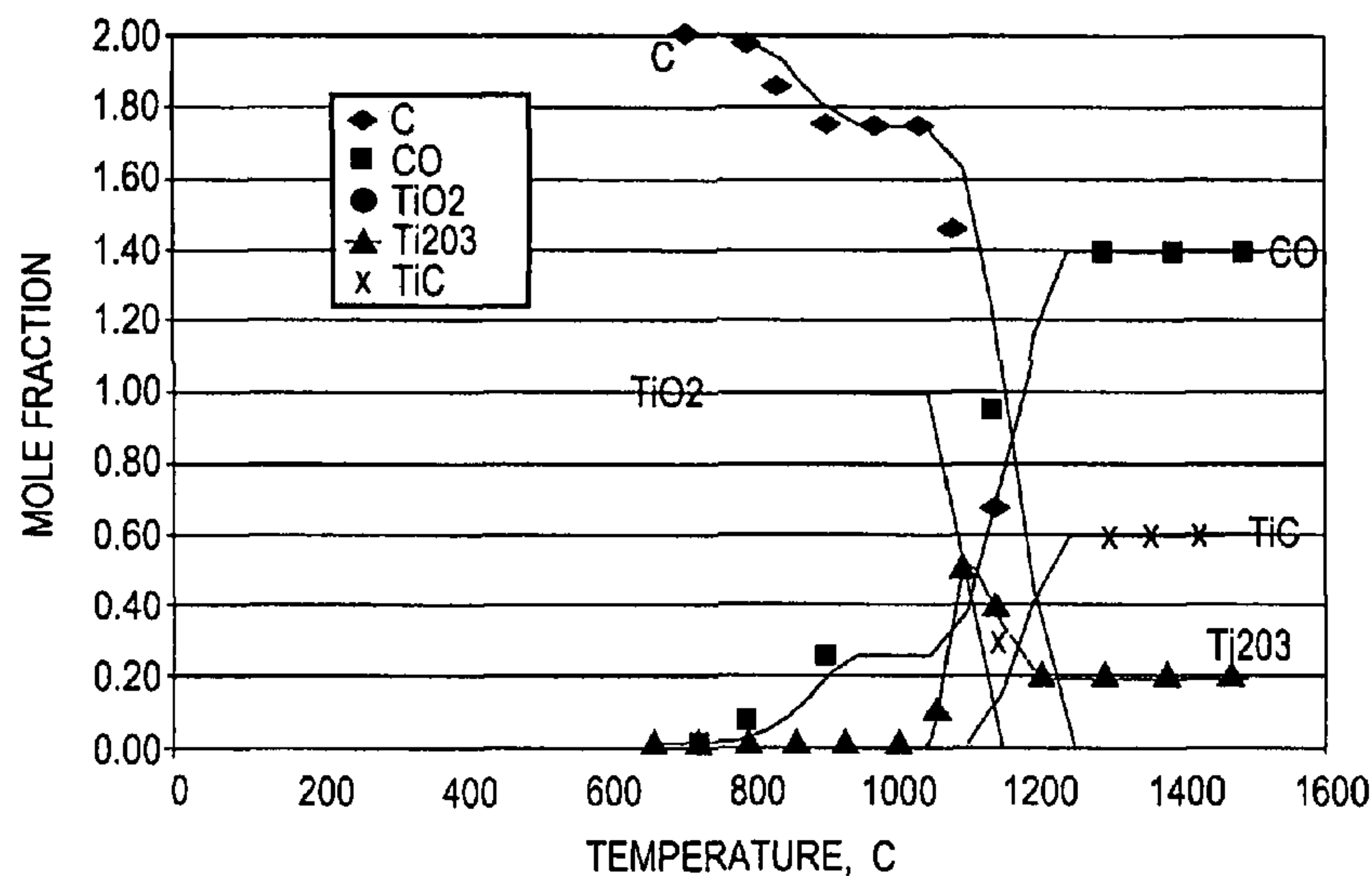


(86) **Date de dépôt PCT/PCT Filing Date:** 2006/12/01  
(87) **Date publication PCT/PCT Publication Date:** 2007/08/30  
(45) **Date de délivrance/Issue Date:** 2016/06/14  
(85) **Entrée phase nationale/National Entry:** 2008/03/05  
(86) **N° demande PCT/PCT Application No.:** US 2006/061461  
(87)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

## (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).

## (72) Inventors; and

(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).

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

(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.

(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).

## Published:

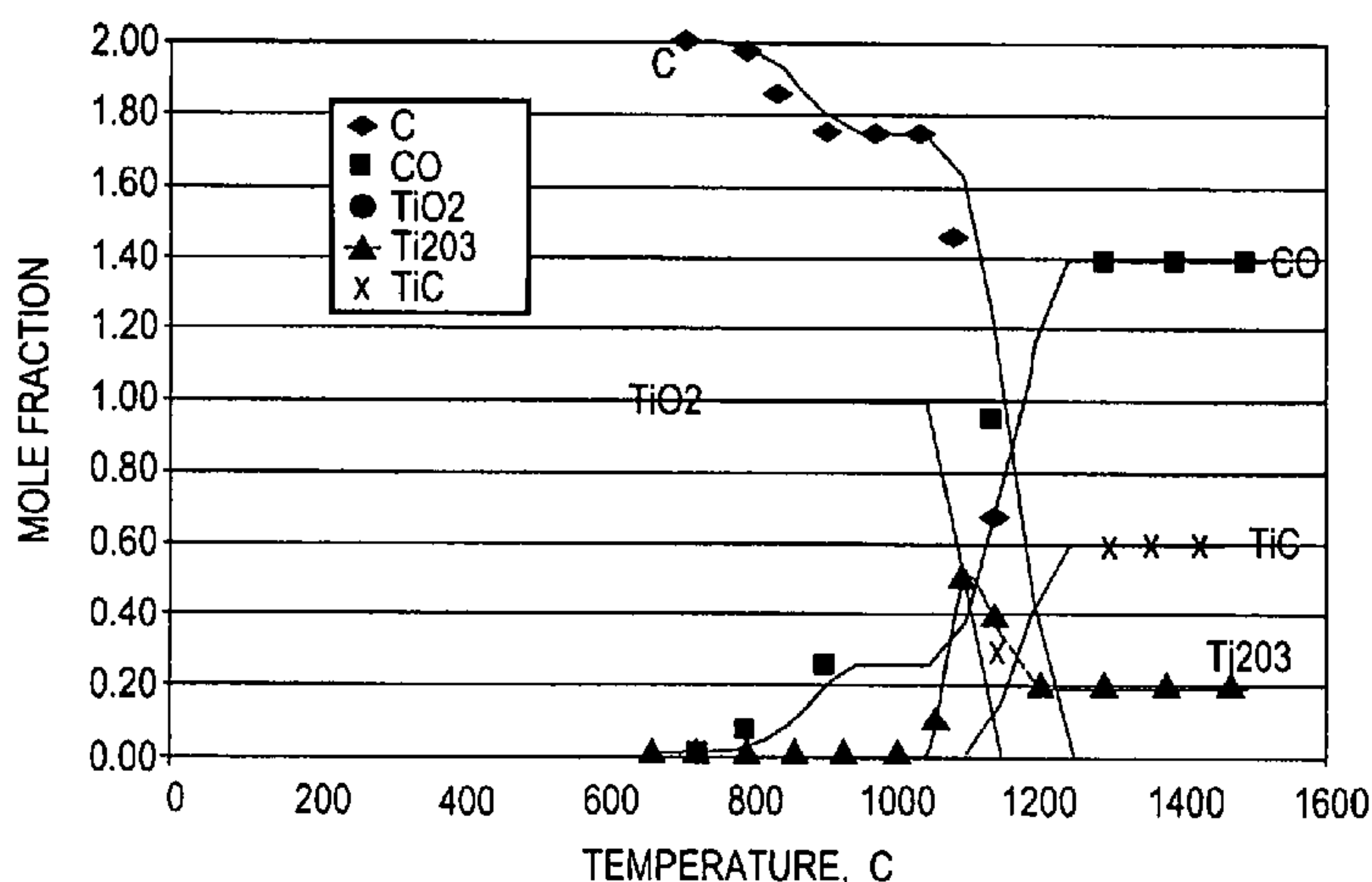
- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

(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

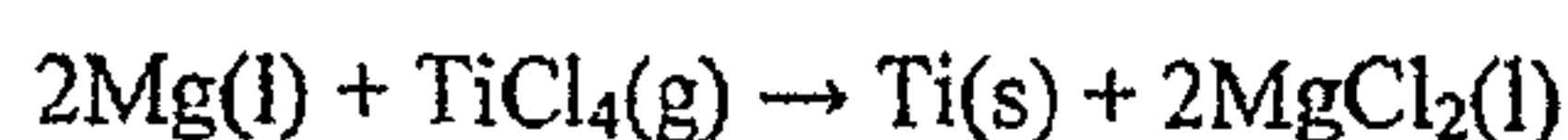
3 The present invention relates to the production of metals. The invention has  
 4 particular utility in connection with the production of titanium and will be described in  
 5 connection with such utility, although other utilities are contemplated, e.g., production of  
 6 other high value multi-valence and high (2 or more) valence 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.

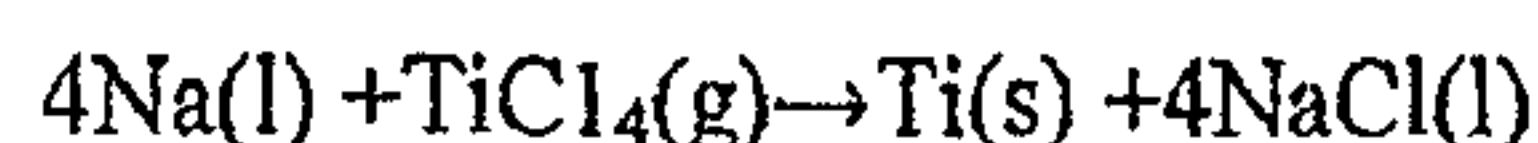
12 Despite the many methods investigated to produce titanium, the only methods currently  
 13 utilized commercially are the Kroll and Hunter processes. These processes utilize  
 14 titanium tetrachloride ( $\text{TiCl}_4$ ) which is produced from the carbo-chlorination of a refined  
 15 titanium dioxide ( $\text{TiO}_2$ ) according to the reaction:



17 In the Kroll process  $\text{TiCl}_4$  is reduced with molten magnesium at  $\approx 800^\circ\text{C}$  in an  
 18 atmosphere of argon. This produces metallic titanium as a spongy mass according to the  
 19 reaction:



21 from which the excess Mg and  $\text{MgCl}_2$  is removed by volatilization, under vacuum at  $\approx$   
 22  $1000^\circ\text{C}$ . The  $\text{MgCl}_2$  is then separated and recycled electrolytically to produce Mg as the  
 23 reductant to further reduce the  $\text{TiCl}_4$ . In the Hunter process sodium is used as a  
 24 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  $\text{TiCl}_4$ , 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 ( $\text{TiO}_2$ ), it can be conceived that an oxide feed to produce titanium could be more  
7 economical than making the chloride ( $\text{TiCl}_4$ ) by carbo-chlorination of the oxide as the  
8 feed ( $\text{TiCl}_4$ ) 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  $\text{TiO}_2$  and plasma reduction of  
15  $\text{TiCl}_4$  without measurable success. Direct reduction of  $\text{TiO}_2$  or  $\text{TiCl}_4$  using  
16 mechanochemical processing of ball milling with appropriate reductants of Mg or  
17 calcium hydride ( $\text{CaH}_2$ ) 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  $\text{TiO}_2$  as a cathode and  
22 carbon or graphite as the anode in a calcium chloride electrolyte operated at  $900^\circ\text{C}$ . By  
23 this process, calcium is deposited on the  $\text{TiO}_2$  cathode, which reduces the  $\text{TiO}_2$  to  
24 titanium and calcium oxide. However, this process is limited by diffusion of calcium  
25 into the  $\text{TiO}_2$  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  $\text{TiO}_2$  cathode is not fully reduced which leaves contamination of  $\text{TiO}_2$  or reduced oxides  
28 such as  $\text{TiO}$ , mixed oxides such as calcium titanate 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 ( $\text{TiO}_2$ ) is utilized as a cathode and electrolyzed with a graphite anode in  
32 molten calcium chloride ( $\text{CaCl}_2$ ) which allegedly removes the oxygen from the  $\text{TiO}_2$  in  
33 pellet form leaving titanium and with the graphite anode produces  $\text{CO}_2$  at the anode. A



1 fundamental teaching is that the oxygen ionized from the  $\text{TiO}_2$  in the cathode must be  
2 dissolved in the electrolyte which is  $\text{CaCl}_2$  for transport to the anode. In addition, it is  
3 stated that calcium titanites ( $\text{Ca}_x\text{Ti}_y\text{O}_z$ ) 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  $\text{TiO}_2$  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 ( $\text{TiO}_2$ ) cathode under applied potential which oxygen removed or  
18 ionized from the  $\text{TiO}_2$  cathode is dissolved in the  $\text{CaCl}_2$  electrolyte and is transported to a  
19 graphite anode to be discharged as  $\text{CO}_2$ . The first aspect of the teachings of WO  
20 02/066711 A1 is that the electrical contact to the  $\text{TiO}_2$  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  $\text{TiO}_2$  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  $\text{CaCl}_2$  electrolyte. It is stated  $\text{Al}_2\text{O}_3$  in the cathode with  
26  $\text{TiO}_2$  can also be reduced but non-uniformly with the only reduction taking place where  
27 the  $\text{Al}_2\text{O}_3$  touches the cathode conductor. The publication WO 02/066711 A1 teaches the  
28  $\text{TiO}_2$  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 ( $\text{TiO}_2$ )  
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  $\text{TiO}_2$  must be calcium chloride containing CaO. This  
4 publication states that the  $\text{CaCl}_2$  electrolyte is operated to produce  $\text{Ca}^{++}$  cations which  
5 provide the driving force that facilitate extraction of  $\text{O}^-$  anions produced by the  
6 electrolytic reduction of titania ( $\text{TiO}_2$ ) 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 ( $\text{TiO}_2$ ). 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  $\text{TiO}_2$ . 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 ( $\text{TiO}_2$ ) 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 titania ( $\text{TiO}_2$ ) is  
17 ionized under electrolysis which dissolves in the  $\text{CaCl}_2$  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/ $\text{TiO}_2$ . It is further stated that chlorine ( $\text{Cl}_2$ )  
20 gas is removed at the anode at potentials well below the theoretical deposition, that  
21  $\text{Ca}_x\text{Ti}_y\text{O}_z$  is present at the  $\text{TiO}_2$  cathode and that CaO is formed in the molten electrolyte  
22 bath which is  $\text{CaCl}_2$  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  $\text{TiO}_2$  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  $\text{TiO}_2$  requiring refreshing the electrolyte and/or changing/increasing the cell  
28 potential. The method teaches carrying out the reduction of  $\text{TiO}_2$  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  $\text{TiO}_2$ .



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  $\text{Ca}^{++}$  ions which reduce the titania ( $\text{TiO}_2$ ) in the cathode with oxygen  
4 ( $\text{O}^-$ ) migrating to the anode. This is very unlikely the mechanism. If Ca in metallic  
5 ( $\text{Ca}^0$ ) or ionic ( $\text{Ca}^{++}$ ) form reduces the  $\text{TiO}_2$  the product of reduction will be CaO i.e.,  
6  $\text{TiO}_2 + 2\text{Ca} = \text{Ti} + 2\text{CaO}$ . The produced calcium from electrolysis must diffuse into the  
7 titania ( $\text{TiO}_2$ ) pellet to achieve chemical reduction as claimed and the formed CaO will  
8 then have to diffuse out of the  $\text{Ti}/\text{TiO}_2$  which has been preformed and sintered into a  
9 pellet. If calcium metal ( $\text{Ca}^0$ ) or ions ( $\text{Ca}^{++}$ ) are produced by electrolysis, the oxygen  
10 ions ( $\text{O}^-$ ) 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  $\text{TiO}_2$ , will form CaO which must become soluble in the electrolyte ( $\text{CaCl}_2$ )  
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 ( $\text{CaTiO}_3$ ) forms as the  $\text{TiO}_2$  is reduced. A possible reaction is  $\text{O}^{2-} + \text{Ca}^{2+} + \text{TiO}_2 =$   
17  $\text{CaTiO}_3$  which remains as a contaminate in the cathodically reduced  $\text{TiO}_2$  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  $\text{UO}_2$ . The example is  $\text{Li}_2\text{O}$  in  
20  $\text{LiCl}$  and the oxygen-ion species is dissolved in the electrolyte for transport to the anode  
21 which is shrouded with a  $\text{MgO}$  tube to prevent back diffusion of oxygen. It is reported  
22 the cathodic reduction of the oxide (examples  $\text{UO}_2$  and  $\text{Nb}_2\text{O}_3$ ) 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 ( $\text{LiCl}$ ) 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  $\text{Al}_2\text{O}_3$  in cryolite/sodium fluoride. While the Redey patent teaches  
31 cathodic reduction of  $\text{UO}_2$  and  $\text{Nb}_2\text{O}_3$  in a  $\text{LiCl}/\text{Li}_2\text{O}$  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  $\text{TiO}_2$  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 titania is used as a  
 6 cathode on a cell bottom with an electrolyte such as CaF<sub>2</sub> 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  $\text{TiO}_2 (\text{liquid}) + \text{C} (\text{solid}) = \text{Ti} (\text{liquid})\downarrow + \text{CO}_2 (\text{gas})\uparrow$ .

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

15 Thus, current TiO<sub>2</sub> 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<sub>2</sub>O<sub>3</sub>) have not produced pure aluminum by carbothermic  
 24 reduction. Similarly TiO<sub>2</sub> 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 TiO<sub>2</sub> 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<sub>2</sub> as the first process step of producing titanium from TiO<sub>2</sub> 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 ( $\text{TiO}_2$ ) and ilmenite ( $\text{FeTiO}_3$ ).  
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  $\text{TiO}_2$   
5 is the most utilized compound which has applications as pigment and for carbo  
6 chlorination to produce  $\text{TiCl}_4$  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  $\text{Ti}^{+4}$ ,  $\text{Ti}^{+3}$ , and  $\text{Ti}^{+2}$  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  $\text{TiO}_2$  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  $\text{TiO}$   
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 ( $\text{Al}_2\text{O}_3$ ) exhibiting solubility in fused cryolite ( $\text{Na}_3\text{AlF}_6$ )



1 which is electrolyzed with a carbon anode that produces  $\text{CO}_2$  with some CO and the  
2 metal aluminum. However, no equivalent process has been developed for solubilizing  
3  $\text{TiO}_2$ . 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  $\text{TiO}_2$ , 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 than 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 ( $\text{SiO}$ ) can be produced by reducing  $\text{SiO}_2$  with silicon ( $\text{Si}$ ). That is  $\text{SiO}_2 + \text{Si} + \text{heat} =$   
16  $2\text{SiO}$ . The  $\text{SiO}_2$  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  $\text{SiO}_2 + \text{C} + \text{heat} = \text{SiO}$  and  $\text{SiC} + \text{CO}$ . Producing a titanium suboxide by reducing  $\text{TiO}_2$   
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  $\text{TiC}$  is approximately  
23 183 KJ/mole which makes its 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  $\text{TiO}_2$  would be ideal to produce  
27 titanium suboxides if the formation of  $\text{TiC}$  can be prevented and only one suboxide  
28 produced such as  $\text{Ti}_2\text{O}_3$  or  $\text{TiO}$ .

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  $\text{TiO}_2$ -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  $\text{TiO}_2\text{-C}$  heat treated to  $1450^\circ\text{C}$   
3 in one step followed by heat treatment at  $2100^\circ\text{C}$  in vacuum;

4 Fig. 6 shows the XRD patterns of 1:1: $\text{TiO}_2\text{-Ti}$  heat treated to  $1760^\circ\text{C}$  in vacuum;

5 Fig. 7 shows the XRD patterns of stoichiometric  $\text{TiO}_2\text{-C}$  heat treated to  $1450^\circ\text{C}$   
6 with a second heat treatment to  $1800^\circ\text{C}$  in high vacuum;

7 Fig. 8 shows the XRD patterns of stoichiometric  $\text{TiO}_2\text{-C}$  from phenolic in a pre-  
8 mix heat to  $1450^\circ\text{C}$  at one atmosphere pressure in argon;

9 Fig. 9 shows the XRD patterns of stoichiometric  $\text{TiO}_2\text{-C}$  from a  $110^\circ\text{C}$  softening  
10 point coal tar pitch mixed at  $190^\circ\text{C}$  and heat treated at  $1650^\circ\text{C}$  at atmospheric pressure in  
11 argon;

12 Fig. 10 shows the XRD patterns of slag-C from a  $110^\circ\text{C}$  softening point coal tar  
13 pitch mixed at  $190^\circ\text{C}$  and heat treated at  $1650^\circ\text{C}$  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  $1650^\circ\text{C}$  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  $1650^\circ\text{C}$  in argon plus  $1800^\circ\text{C}$  in a vacuum  
18 lower than  $10^{-3}$  Torr;

19 Fig. 13 shows the XRD patterns of  $\text{TiO}_2$  treated with an intimate mixture of  
20 carbon with heat treatment to  $2100^\circ\text{C}$  at atmospheric pressure in argon; and

21 Fig. 14 shows the XRD patterns for Anatase  $\text{TiO}_2$  with an intimate mixture of  
22 carbon with heat treatment to  $2100^\circ\text{C}$  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  $\text{TiO}_2$  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  $\text{TiO}_2$  and carbon were then heat treated in a graphite element furnace  
29 purged with argon. The initial heat treatment was performed at  $1300^\circ\text{C}$  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  $\text{TiC}$  with a minor amount of  
32  $\text{Ti}_3\text{O}_5$ . A sample of the  $\text{TiO}_2\text{-C}$  was heat treated to  $1400^\circ\text{C}$  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 <sub>2</sub> O <sub>3</sub> %	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<sub>2</sub>O<sub>3</sub>. The TiC composition  
 12 was reduced with an increase in Ti<sub>2</sub>O<sub>3</sub>. 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<sub>2</sub>.  
 24 Different ratios of TiO<sub>2</sub> 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<sub>3</sub>O<sub>5</sub>  
 26 and Ti<sub>2</sub>O<sub>3</sub> 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<sub>2</sub> powder followed by the heat treatment steps discussed. A different approach to  
7 producing carbon and TiO<sub>2</sub> is to utilize a liquid which when pyrolyzed will provide a  
8 high yield of carbon. The TiO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> was mixed with phenolic resin such as Borden B1008  
15 and heated to form a solid at approximately 110°C. TiO<sub>2</sub> 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<sub>2</sub>O<sub>3</sub> remains; however,  
21 the amount of TiO produced is greater than when only particles of carbon and TiO<sub>2</sub> 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 I 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<sub>2</sub> 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 TiO<sub>2</sub> 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 TiO<sub>2</sub> slag is shown in Fig. 10.

8 Ilmenite which is iron titanite FeTiO<sub>3</sub> with a variety of impurities consists  
 9 typically of the composition shown in Table 3.

10

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

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

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 1650°C.**

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

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.

- 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<sup>-3</sup> 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<sub>2</sub> or impure ore  
 6 are given in the following working examples:

7

Example 1 - Preparation:

- 8 1. A TiO<sub>2</sub> 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<sub>2</sub> 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  $\text{TiO}_2$  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  $1700^\circ\text{C}$  under atmosphere pressure in a non-oxidizing  
5 atmosphere which is typically argon,  $\text{CO}_2$ , CO, etc. Nitrogen atmosphere is avoided to  
6 prevent the formation of titanium nitride. After the  $1700^\circ\text{C}$  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  $110^\circ\text{C}$  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  $\text{CO}_2/\text{CO}$ . The mixture was pressed in a steel die at  $190^\circ\text{C}$  to  
13 provide a solid on cooling. The composite anode was heated in an inert atmosphere  
14 to  $1200^\circ\text{C}$  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  $\text{amp}/\text{cm}^2$  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%  $\text{CaCl}_2$ -20% LiCl  
23 operated at  $850^\circ\text{C}$ . 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  $\text{CO}_2$  with traces of CO.

30 **Trial 3**-The same electrolyte as in Trial 2 was utilized at the same temperature of  
31  $850^\circ\text{C}$ . 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  $1 \text{ amp/cm}^2$  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 ( $\text{CaF}_2$ ) was used as the electrolyte and power applied to the tungsten  
13 resistors that brought the  $\text{CaF}_2$  to a molten state and  $1700^\circ\text{C}$ . In Trial 4A, a TiO  
14 particle as given in Trial 2 was placed in a molybdenum screen and electrolyzed at  
15  $3.0\text{V}$  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  $\text{CaF}_2$   
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  $\text{CaF}_2$  electrolyte at  $1700^\circ\text{C}$  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  $110^\circ\text{C}$   
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  $1700^\circ\text{C}$  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  $1800^\circ\text{C}$  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<sub>2</sub> to the metal it is  
9     necessary to produce a porous perform in order that current can flow to the TiO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> (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<sub>2</sub> 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<sub>2</sub>-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  $\text{TiO}_2$  and carbon are heated above about  $1200^\circ\text{C}$  the  
2 product is a mixture of  $\text{TiO}$  and  $\text{TiC}$ . It is noted here that  $\text{TiO}_2$  when heated at  
3 atmospheric pressure and/or at reduced pressure only  $\text{TiO}$  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  $\text{TiC}$  formation with a remaining oxygen content depending on the heat treatment  
7 temperature of down to about 5% oxygen at  $2100^\circ\text{C}$ . It was also noted there was some  
8 difference in reactivity between the crystal forms of  $\text{TiO}_2$  in rutile and anatase. The  
9 qualitative results showed that anatase was more likely than rutile to produce a slight  
10 amount of  $\text{TiC}$  at  $2100^\circ\text{C}$  than rutile as shown in the XRD pattern in Fig. 14. To produce  
11  $\text{TiO}_x$   $X \leq 1$  at atmospheric pressure and/or vacuum an enabling step is the intimate  
12 mixing of the  $\text{TiO}_2$ /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  $\text{TiO}_2$ -C HEAT TREATED  
IN ARGON AT 1300 °C FOR ONE HOUR

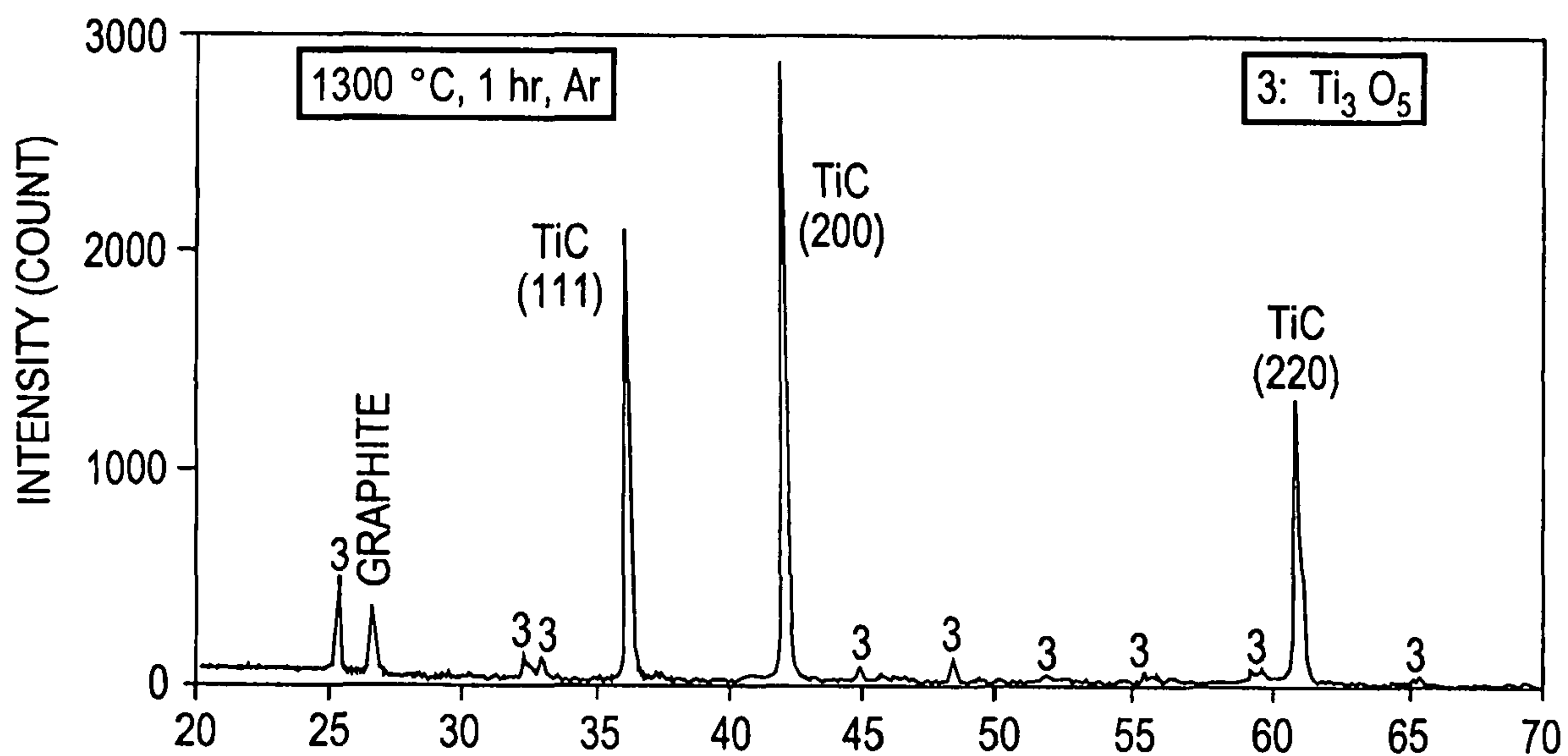


FIG. 2

XRD OF STOICHIOMETRIC  $\text{TiO}_2$ -C HEAT TREATED  
IN ARGON AT 1400 °C FOR ONE HOUR

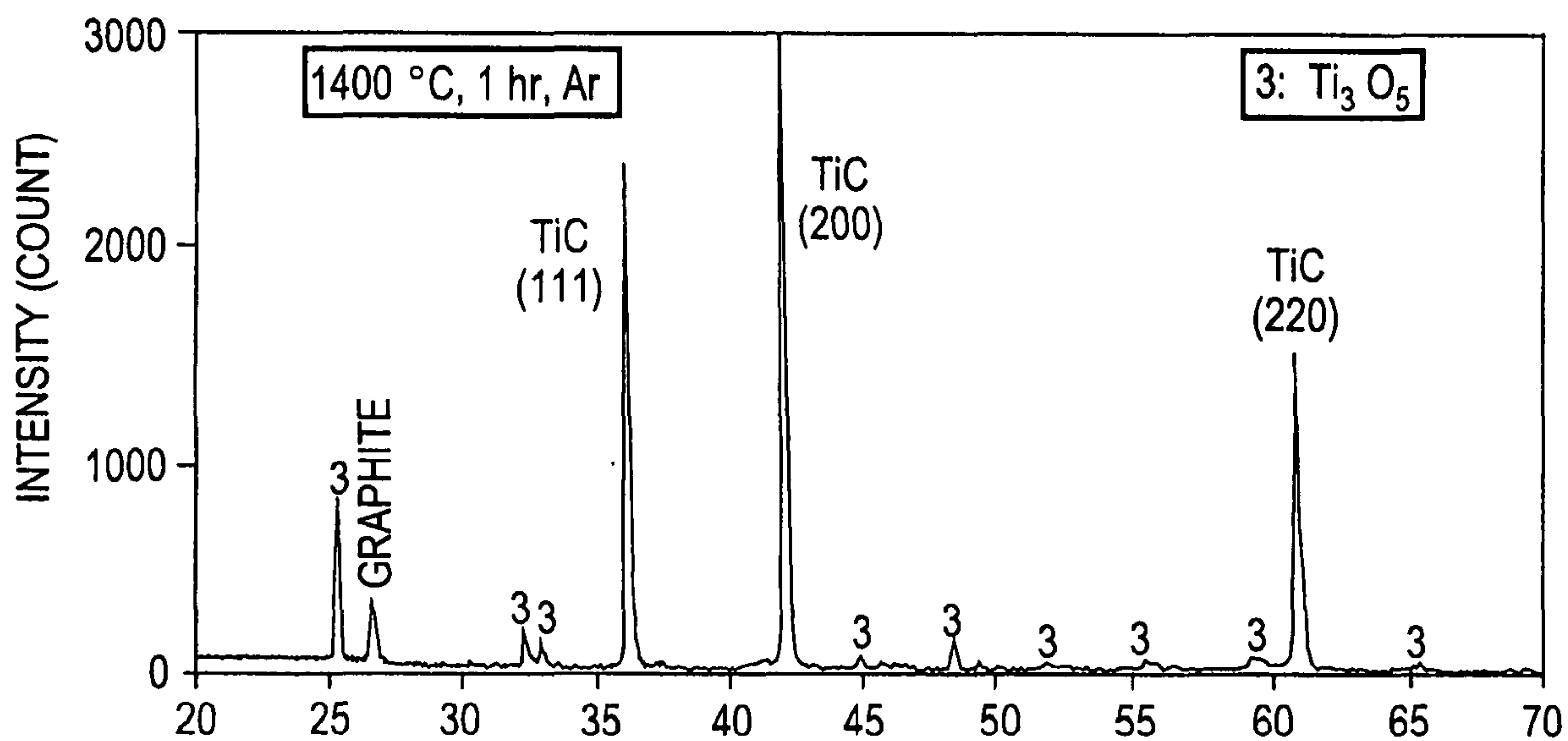




FIG. 3

XRD OF STOICHIOMETRIC  $\text{TiO}_2$ -C HEAT TREATED  
IN ARGON AT 1750°C FOR ONE HOUR

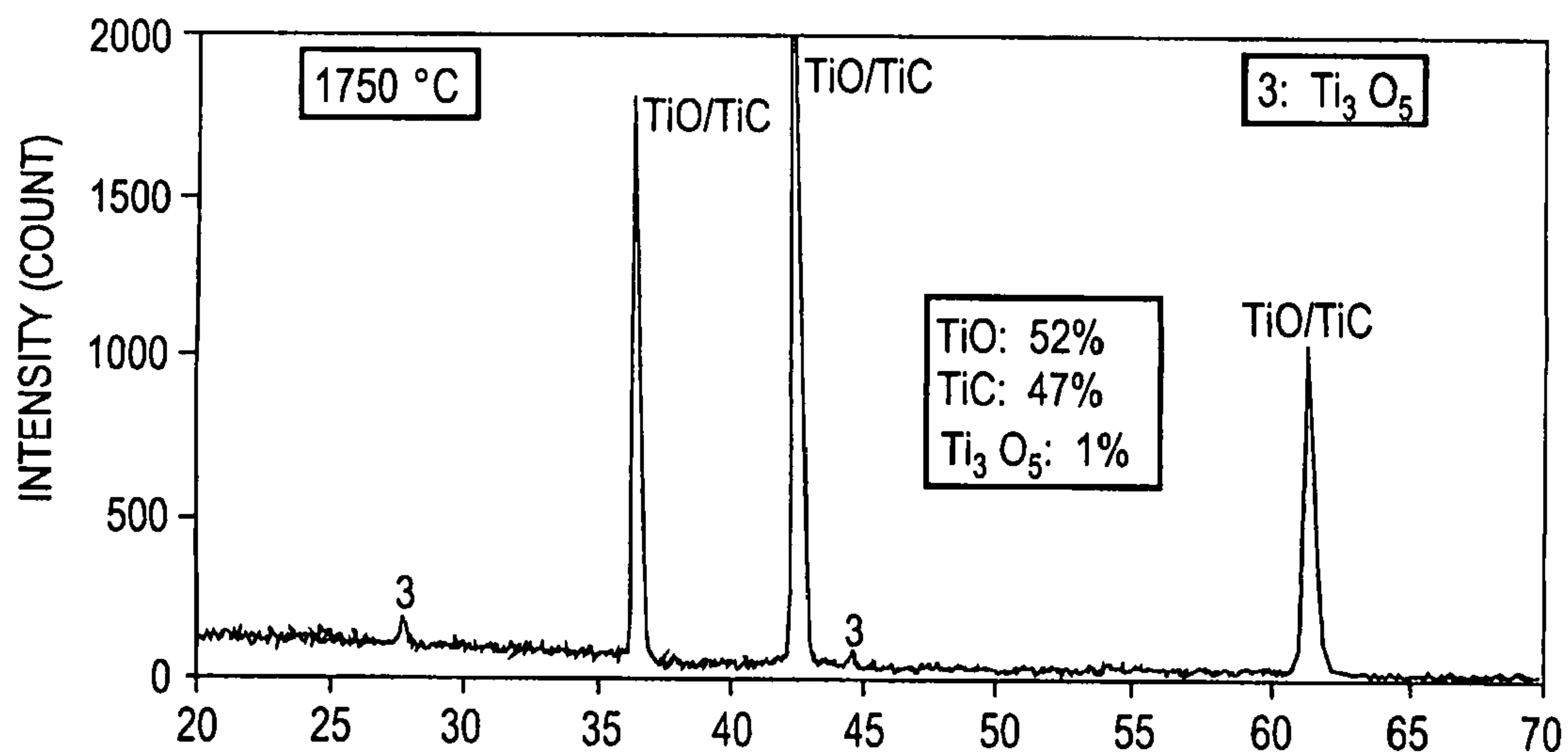
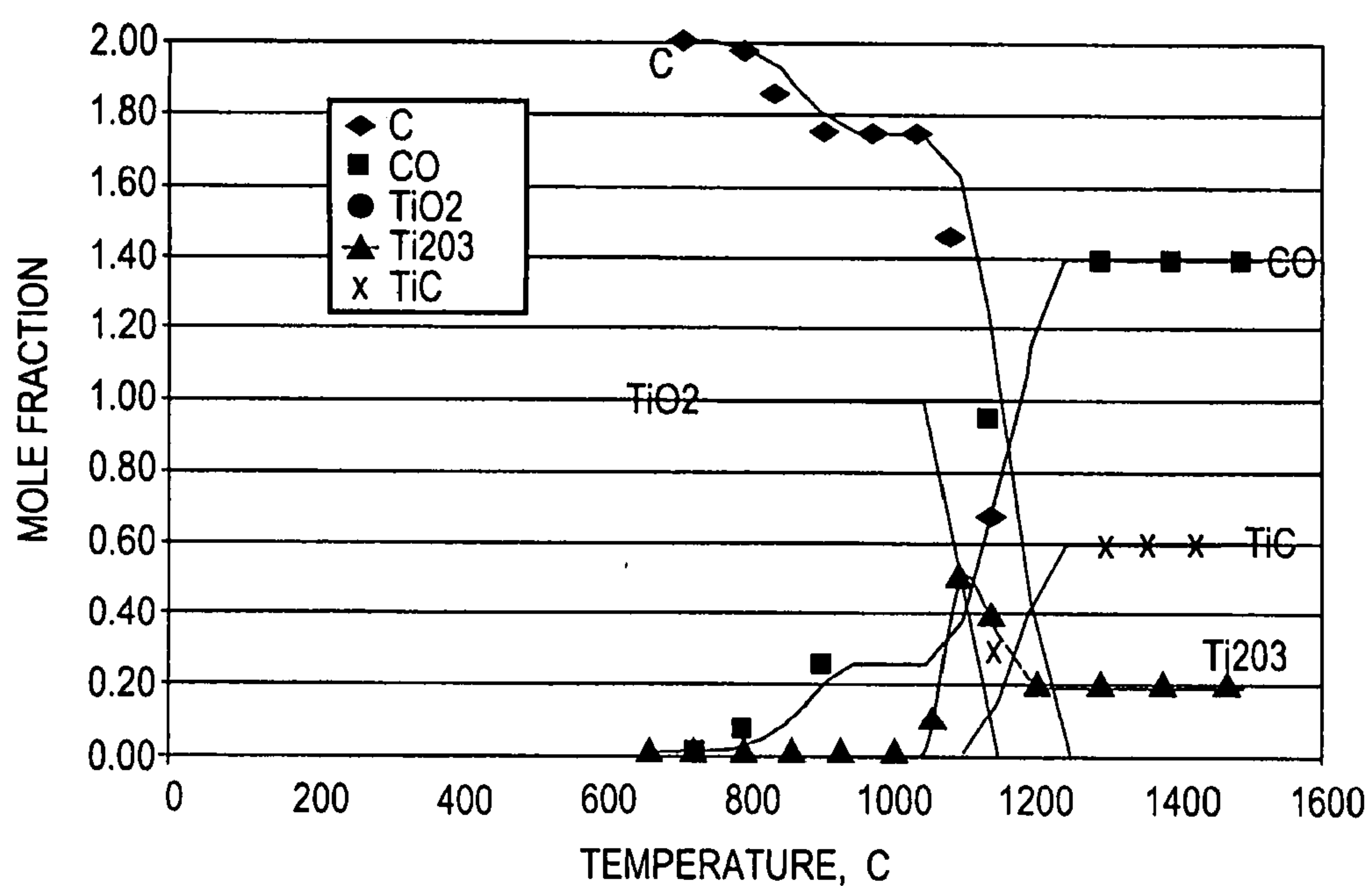


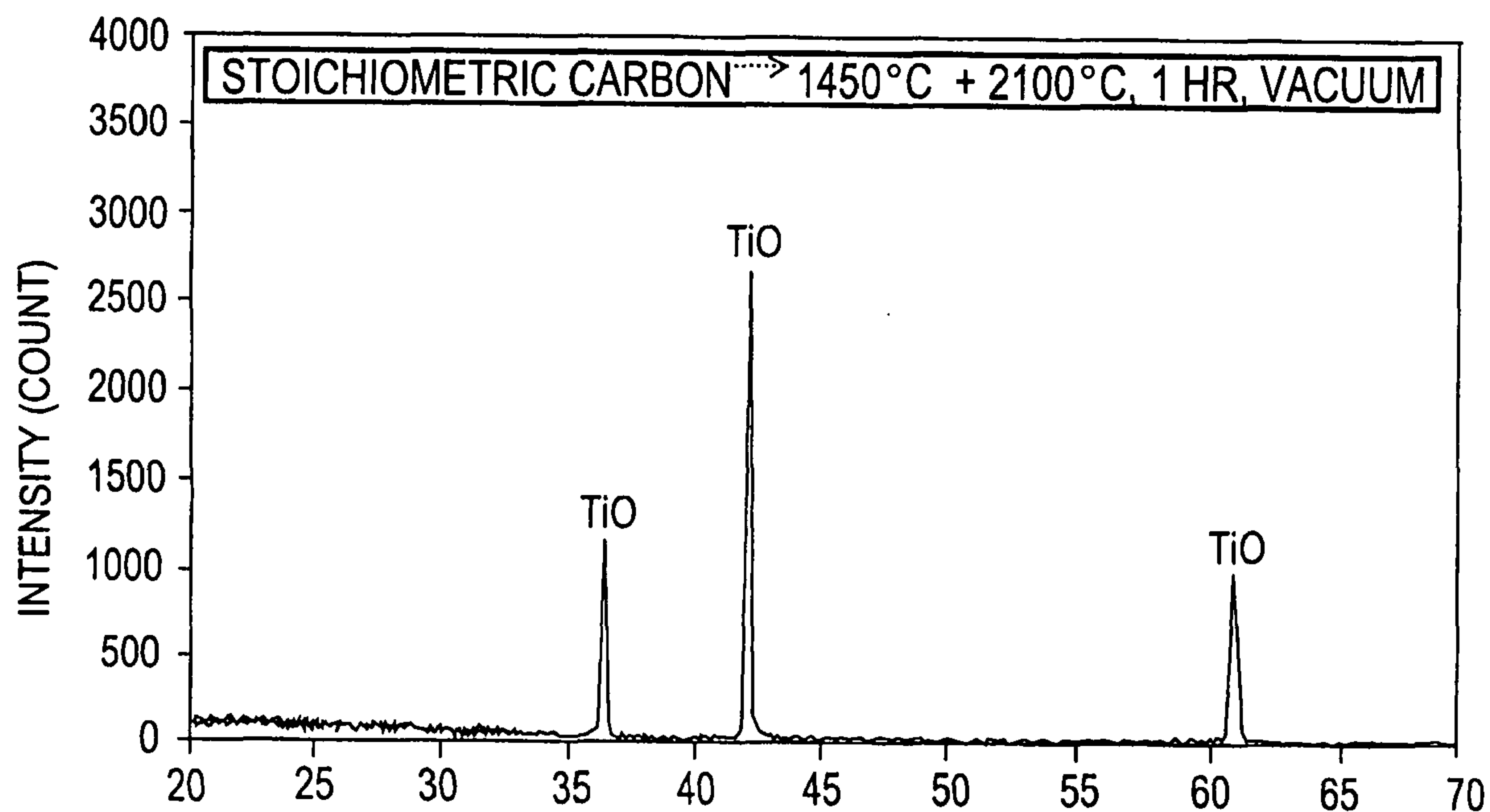
FIG. 4

THERMODYNAMIC EQUILIBRIUM CALCULATION



## FIG. 5

XRD OF STOICHIOMETRIC  $\text{TiO}_2$ -C HEAT TREATED  
TO  $1450^\circ\text{C}$  IN ONE STEP FOLLOWED BY HEAT  
TREATMENT AT  $2100^\circ\text{C}$  IN VACUUM



## FIG. 6

XRD OF 1:1  $\text{TiO}_2$ -Ti HEAT TREATED  
TO  $1760^\circ\text{C}$  IN VACUUM

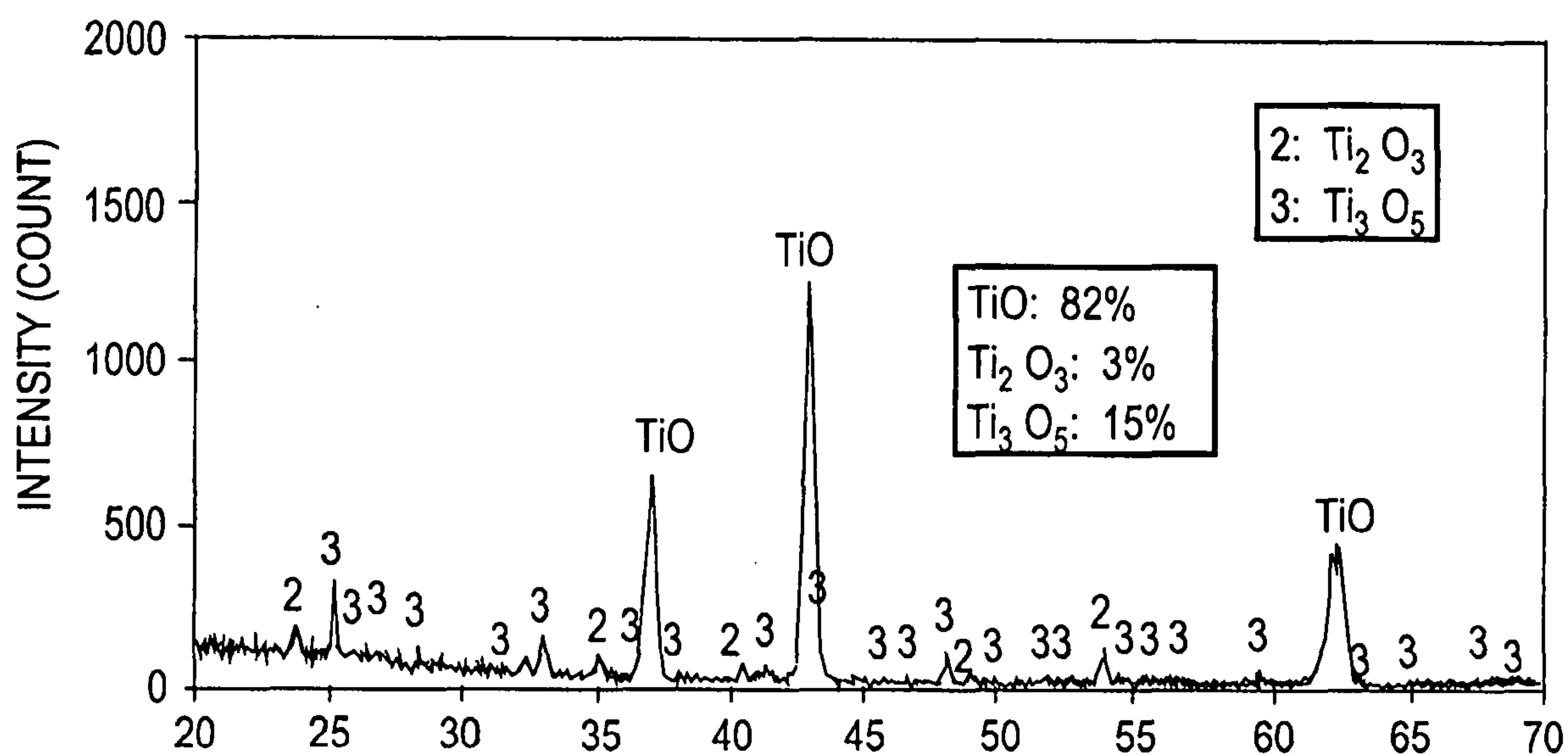




FIG. 7

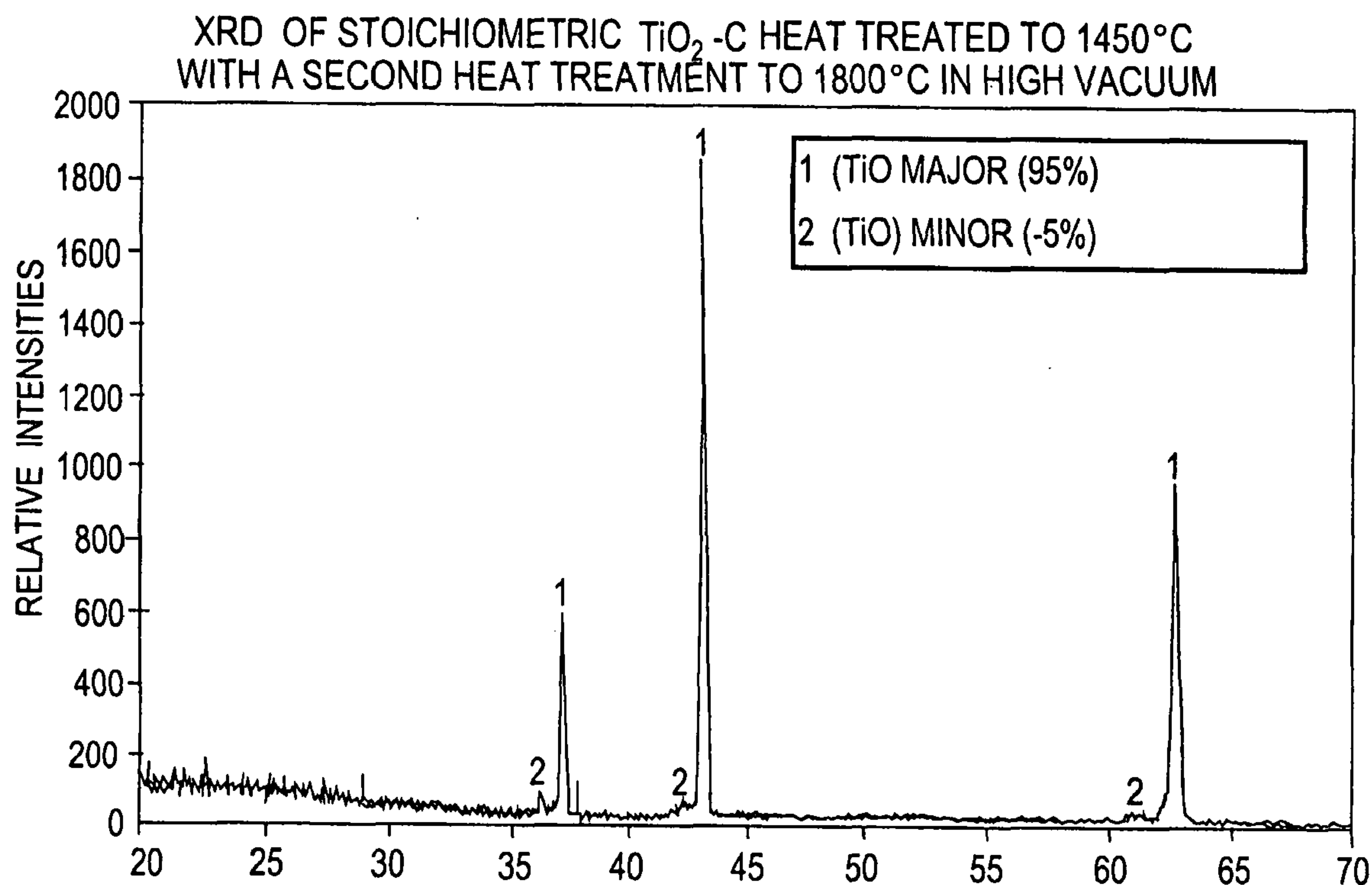
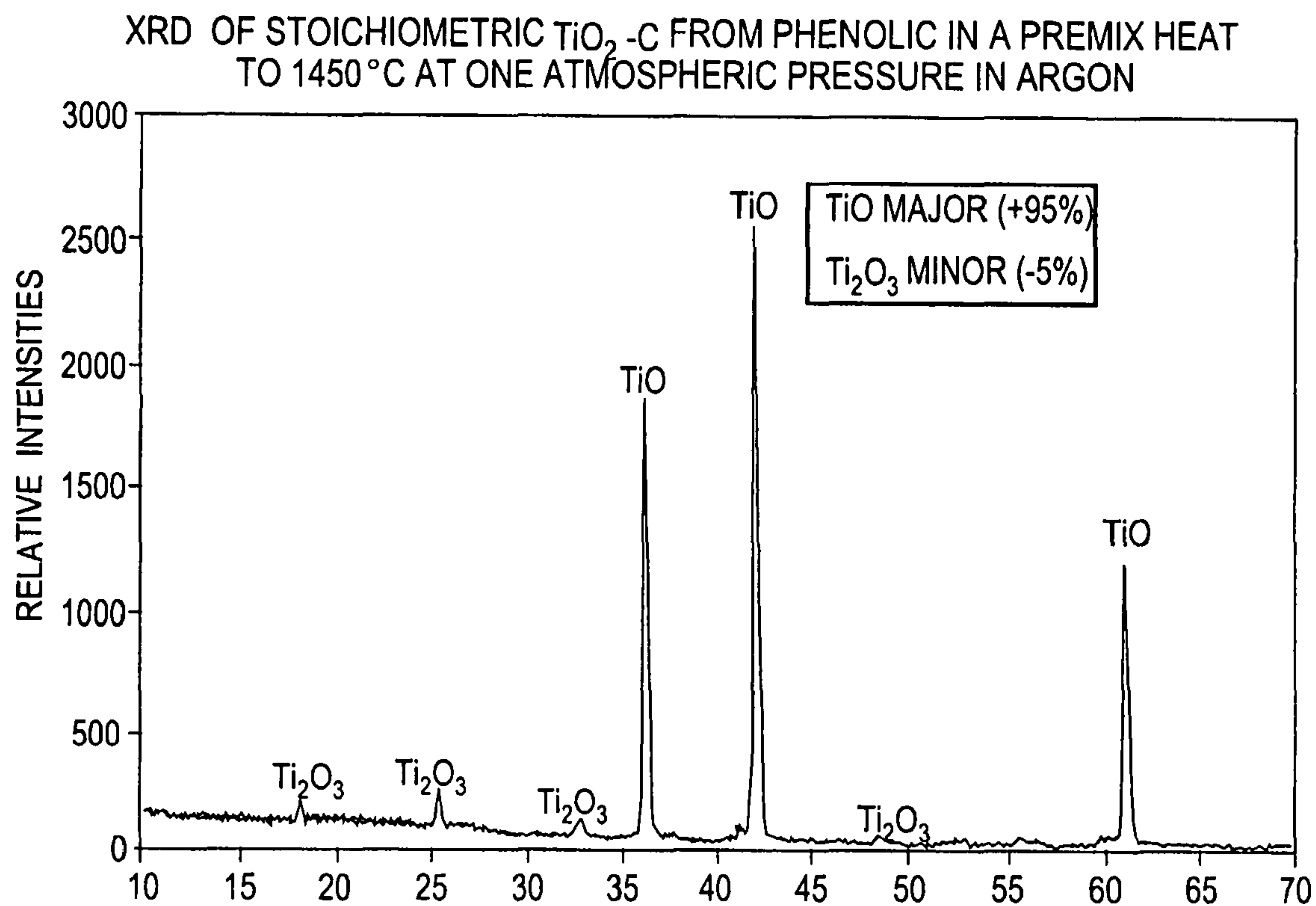
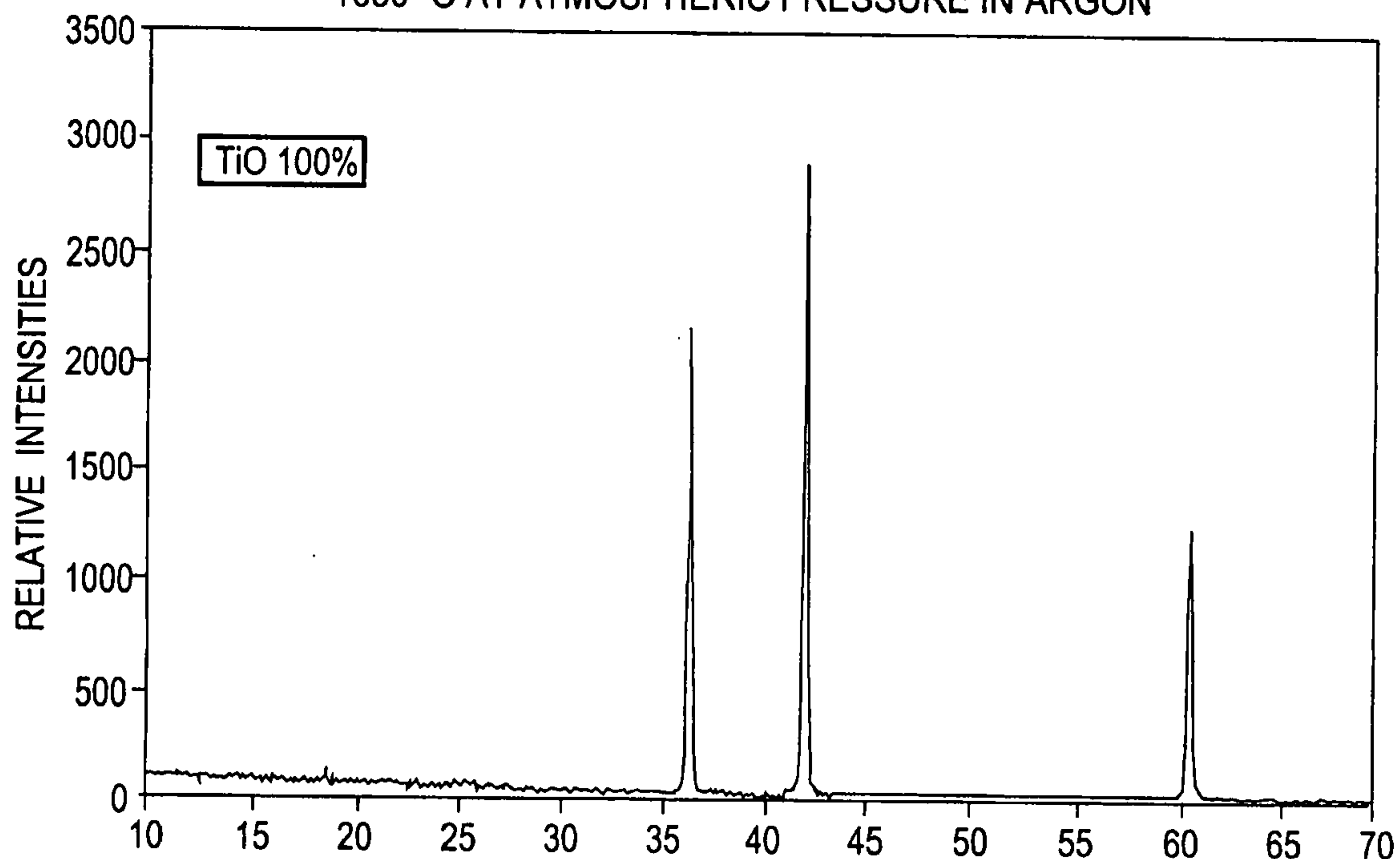


FIG. 8



**FIG. 9**

XRD OF STOICHIOMETRIC  $\text{TiO}_2$ -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

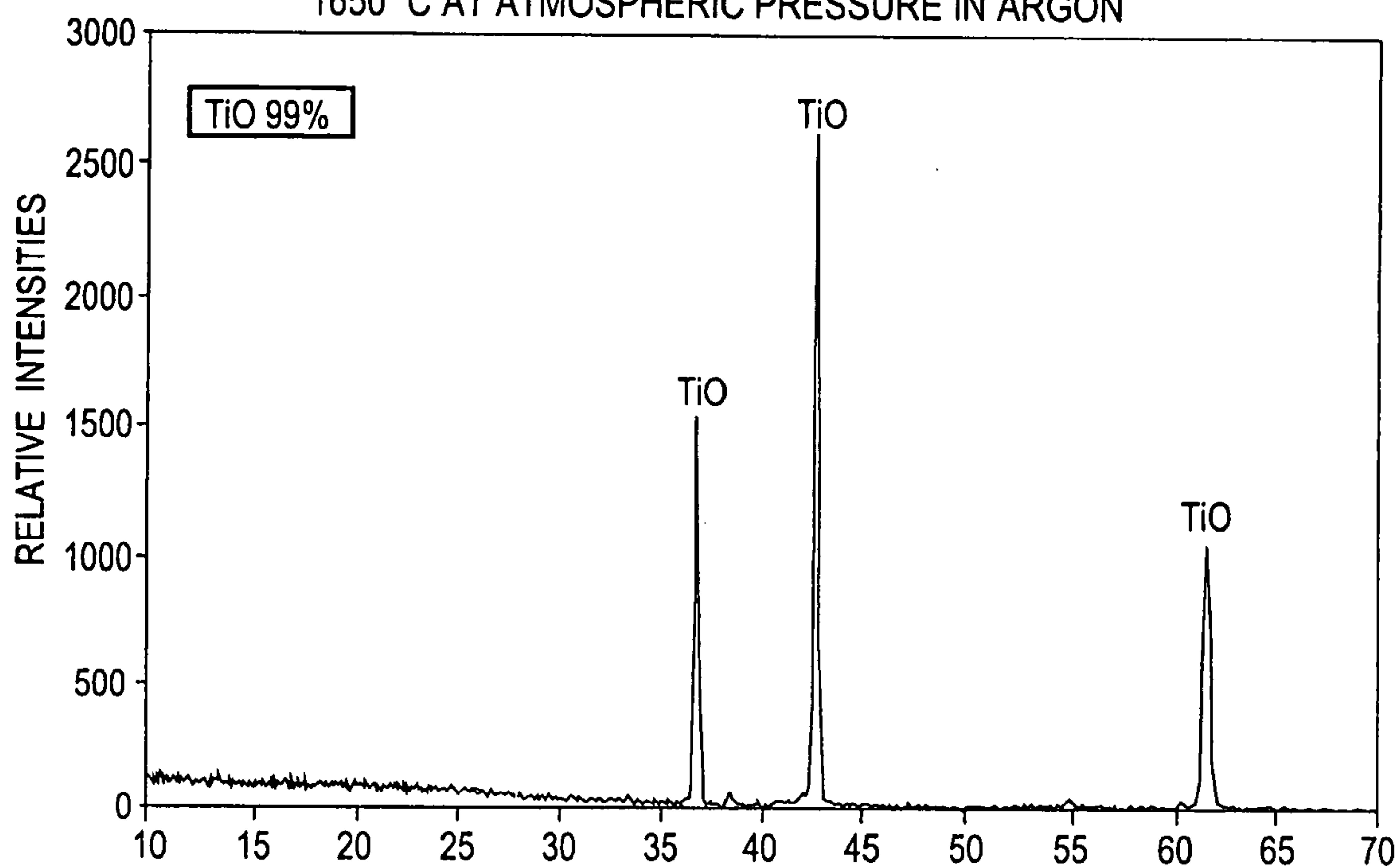




FIG. 11

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

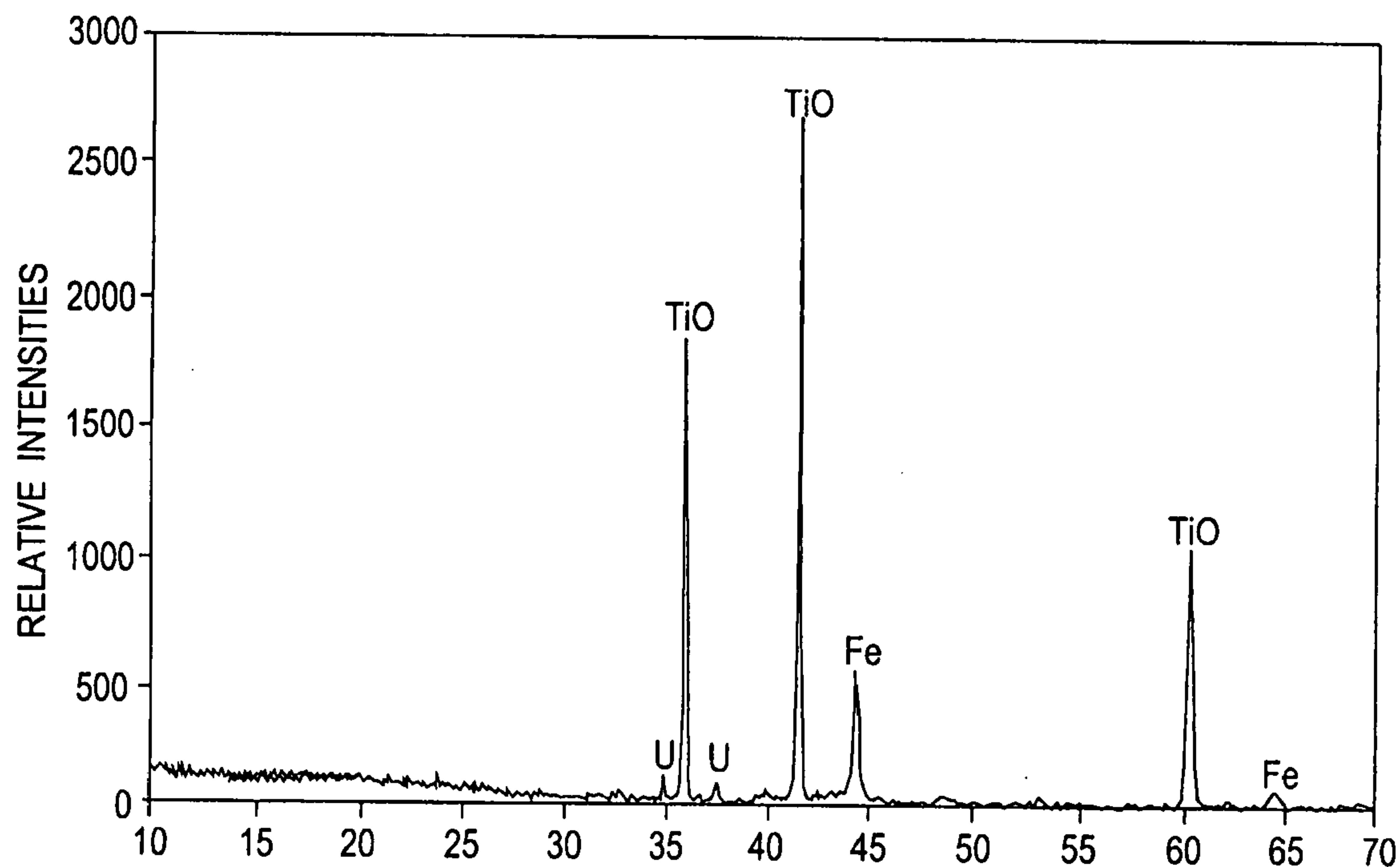


FIG. 12

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

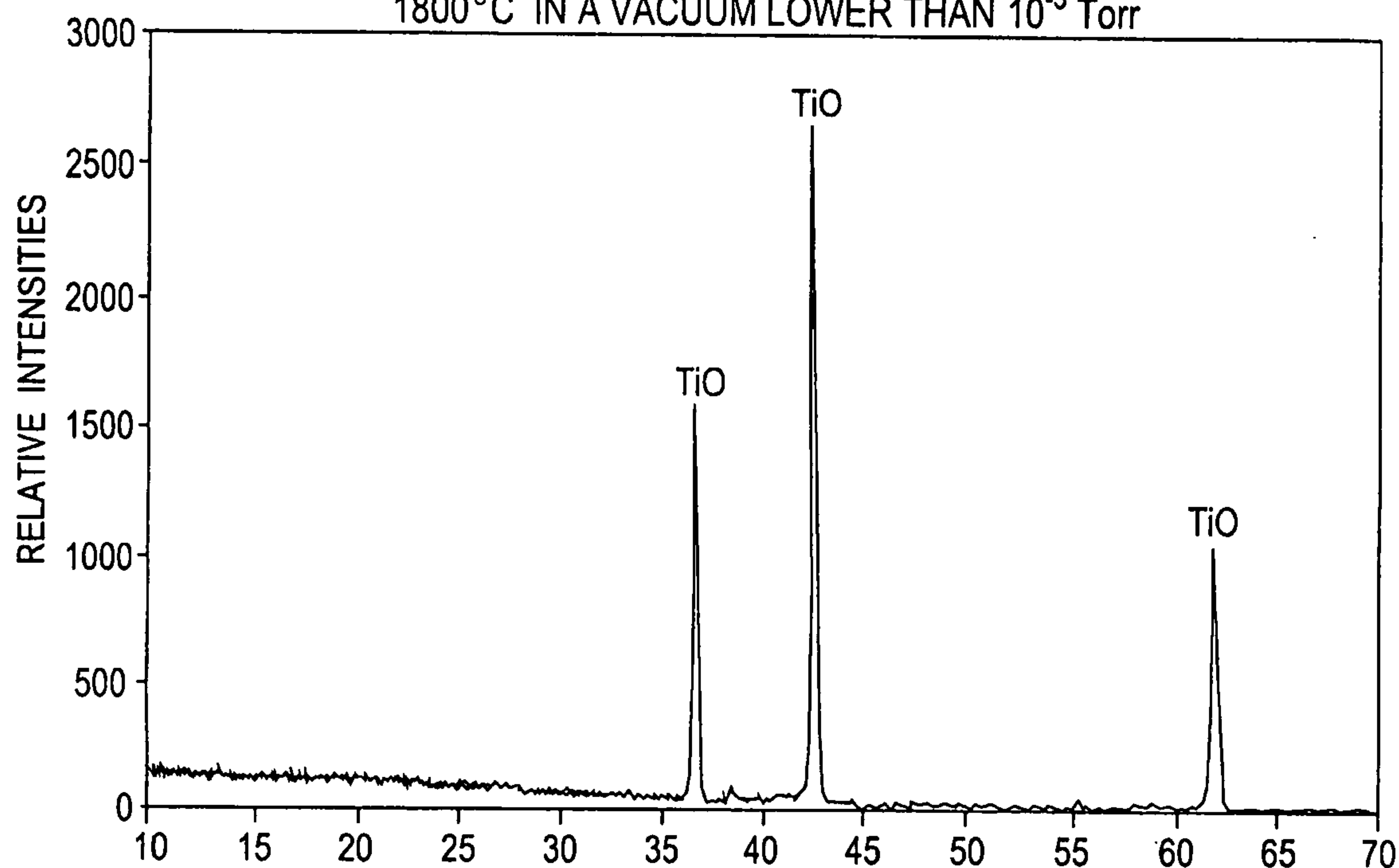


FIG. 13

XRD OF  $\text{TiO}_2$  TREATED WITH AN INTIMATE MIXTURE OF CARBON  
WITH HEAT TREATMENT TO  $2100^\circ\text{C}$  AT ATMOSPHERIC PRESSURE IN ARGON

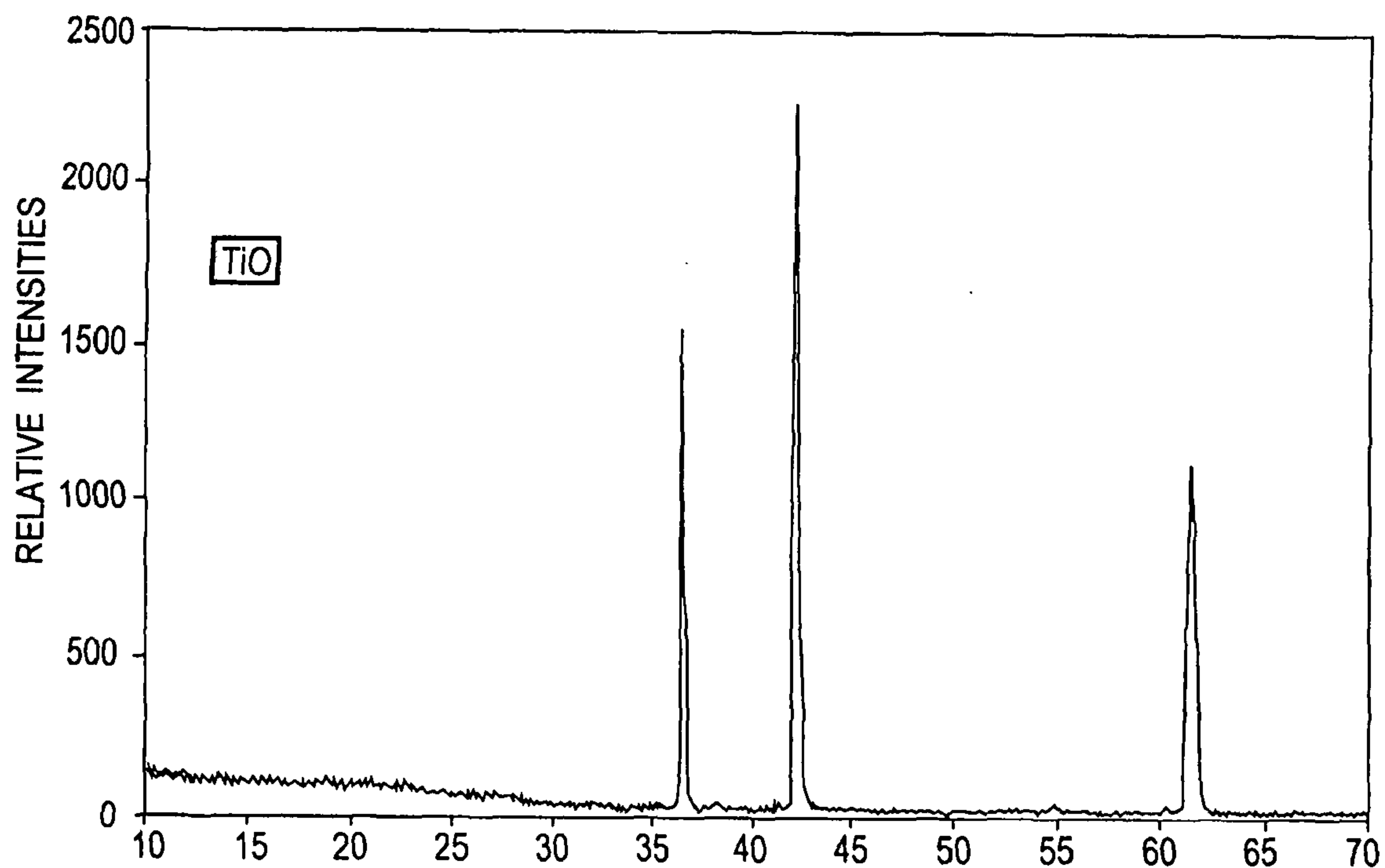
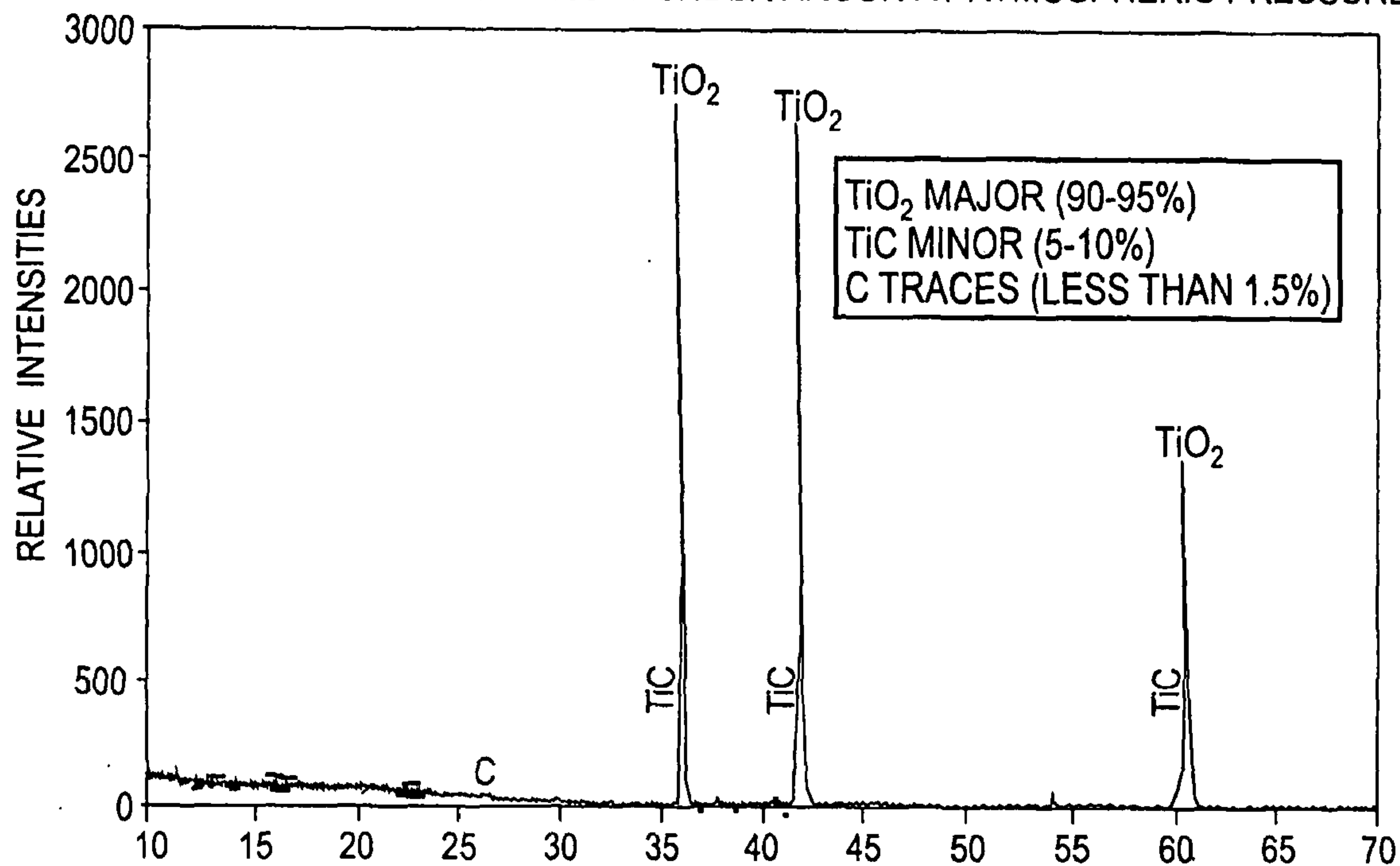


FIG. 14

XRD OF ANATASE  $\text{TiO}_2$  WITH AN INTIMATE MIXTURE OF CARBON  
WITH HEAT TREATMENT TO  $2100^\circ\text{C}$  UNDER ARGON AT ATMOSPHERIC PRESSURE





# THERMODYNAMIC EQUILIBRIUM CALCULATION

