PRODUCTION OF TITANIUM BY A PLASMA PROCESS

K A Bunting
The Electricity Council Research Centre, Capenhurst, Chester, CH1 6ES

ABSTRACT

A single stage plasma route to titanium metal is desribed which involves the reduction of $TiCl_4$ by sodium when both are injected into a stream of hydrogen plasma. Results are presented which show that titanium free from both sodium and chlorine was produced. The overall yield of titanium has been determined.

Keywords Hydrogen plasma, metal extraction
Compounds Titanium tetrachloride, titanium

1. INTRODUCTION

Titanium metal is currently produced commercially by the Kroll[1-3], Hunter[3-7] and Van Arkel de Boer processes[3,8]. The vast majority of the titanium produced is manufactured using the Kroll or the Hunter processes; the Van Arkel de Boer process is relatively expensive and its' use is restricted to the production of very high purity titanium. The Kroll process involves the reduction of titanium tetrachloride by liquid magnesium chloride; in the Hunter process sodium replaces magnesium. In both processes the reaction product, which consists of a matte of titanium metal, the chloride of the reducing agent and unreacted reducing agent, is dug out of the reactor, crushed and leached to separate the titanium. The separated titanium granules are compacted into briquettes, which are subsequently welded together to form electrodes. These are fed into a vacuum arc to be refined into billets of titanium. In principle, by raising the reaction temperature so that all products are in the gaseous phase with titanium present as a supersaturated vapour[9,10], the reaction, preparation and refining can be performed in a single operation with consequent economies in plant and cost.

The concept of the high temperature gas phase system, which was also presented at the I.U.P.A.C. Conference in Kejl and patented in 1971, forms the basis of the ECRC plasma route to titanium[10,11]. This route involves the heating of titanium tetrachloride and sodium in a hydrogen plasma to a temperature in excess of 2000K[10,11]. The titanium tetrachloride and sodium react and the titanium metal is collected at a temperature of approximately 2000K[9,12] which is some 60K higher than its melting point[13]. By this means the sub-chlorides of titanium are kept to negligible proportions, Figure 1, and all reaction products, except titanium, are above their dew-points. At 2000K the proportion of titanium present as vapour rather than liquid is negligible. Thus, with a suitably designed reactor and collector system, there is the prospect of obtaining titanium metal, free from contamination with sodium and sodium chloride, in a single stage process. It is noteworthy that Westinghouse announced that they were using the same approach for the production of silicon[14,15].

2. APPARATUS

Briefly, the apparatus[9,12,16,17,20] consisted of a reactor of internal diameter 18 cm in which a mixing chamber of internal diameter 8cm and collector were located concentrically (Figure 2). The hydrogen plasma was generated by an arc heater[18,19], which, together with its magnetic field coil, was mounted on top of the reactor. The plasma gases which emerged from the heater entered the mixing chamber axially. An inverted cone was inserted into the mixing chamber to generate recirculation of the plasma, thus improving the mixing and balancing the flow of heat to the top and bottom of the reactor. Liquid sodium was sprayed directly into the mixing chamber whilst the titanium tetrachloride was sprayed into a flash boiler, the vapour being expelled into the mixing chamber. The collector was mounted underneath the mixing chamber and both were thermally screened by three radiation shields. A stainless steel tank surrounded the reactor and the space between the reactor and the walls was filled with Kao-wool insulation. The collector was exhausted through a condenser to remove condensible solids (principally sodium chloride) by a liquid ring pump which also served as a gas scrubber. The pressure in the reactor was maintained very close to ambient by bleeding nitrogen into the exhaust line. Finally, the undissolved gases were separated and burned before being exhausted to atmosphere.

3. PROCEDURE

The residence time of the reactants in the plasma is short, of the order of 20 ms. Thus, it was important to determine the degree of reaction. Experimental values for the degree of reaction are difficult to determine from yield measurements because not all of the titanium formed within the plasma may be collected (although high collection efficiencies are theoretically possible[9]. Nevertheless, because of lack of practical alternatives, in this work the degree of reaction had to be estimated from the experimental values of the yield. This is a conservative measure since the degree of reaction is at least equal to the yield.

To determine the yield, the run conditions were selected according to criteria detailed elsewhere[12], the reactor brought up to approximately 2000K, and the sodium and titanium tetrachloride feed systems heated to their respective operating temperatures. When the temperature of the reactor, mixing chamber and the collector were above the melting point of titanium and the temperature of the exhaust line was above the dew-point of sodium chloride ($\sim$1250^{o}C) sodium and titanium tetrachloride were injected into the hydrogen plasma for a time determined by the charge of sodium and the selected feed rates. It was convenient to work with a flow rate of 0.5 g/s of sodium for which the run time was nominally 16$\frac{3}{4}$ minutes. The sodium was introduced into the plasma as droplets via a suitable spray atomiser[4]. Two different titanium tetrachloride feed systems were used. One of these had a heated stainless steel coil serving as the vaporiser. The titanium tetrachloride was driven from a reservoir by pressurised argon; the flow rate of the former being determined by measuring the flow rate of argon. This system was difficult to control due to oscillations caused by slug boiling in the vaporizer. These problems were subsequently overcome by spraying the titanium tetrachloride into a flash boiler[17]. The latter was used for run 3 only (Table 1) when, unfortunately, the drive unit in the feed system failed. Thus, in practice the run time and the weight of titanium produced in all cases were determined more by the titanium tetrachloride feed system than by the charge of sodium or any other experimental difficulties. The titanium formed was sampled when the system had cooled down.

4. RESULTS AND DISCUSSION

(i) Theoretical

The equilibrium partial pressures of the reaction products over a range of 1.6 - 6.0 moles Na and 1.0 - 2.00 moles H_2 have been calculated[11,21,22]. The results are illusted for 1.0 moles $TiCl_4$, 4.4 moles Na and 13.8 moles H_2 in Figures 2 and 3. In order to obtain molten titanium a collection temperature close to 2000K is ideal since the yield of titanium is close to the maximum and the temperature is high enough for the titanium to be free running liquid.

The proportion of liquid titanium (referred to as the conversion) is dependent upon the relative proportions of sodium, titanium tetrachloride, and hydrogen, and the temperature. Theoretical values of the conversion, which assume that the reaction goes to completion, showing the effect of varying the proportions of sodium and hydrogen are presented in Figures 3 and 4. As the proportion of sodium increases or the proportion of hydrogen decreases, the conversion increases. For large excesses of titanium tetrachloride the conversion is zero whilst, for more than the stoichiometric amount of sodium the rate of increase in the conversion falls as the number of moles of sodium increases. The flows selected for the experiments reported were 0.86 g/s $TiCl_4$, 0.5 g/s Na and 841/min H_2 (equivalent to 1.0 moles, 4.8 moles and 13.8 moles, respectively) giving a theoretical conversion for equilibrium of 97.3%.

(ii) Experimental

In order to maintain the required conversion, the absolute flow rates of the reactants ($TiCl_4$ and Na) must be maintained constant on a timescale which is short compared with the 20 ms residence time in the reactor. It is inadequate for the relative flow rates to be maintained constant, since a change in flow rate will affect the thermal balance of the system, thereby altering the temperature and hence the conversion - see Figure 3. In principle, adequate control can be achieved with the reactant feed systems used in the experiments[16,17]. In practice, for various reasons, some of which have been briefly mentioned above, the flow rate of titanium tetrachloride was not well controlled. In runs 2 and 3 (Table 1) the effect on thermal balance was such that the collector temperature fell below the melting temperature and became either blocked or partially blocked. The amount of titanium collected was, therefore, reduced to a lower level than would otherwise have been possible. During run 1 an air leak into the stainless steel containing vessel resulted in the destruction of the exhaust and consequently, the collector ceased to function.

The composition of some samples taken from the collector in run 3 is shown in Table 2. The samples were free from both chlorine and sodium but were contaminated with carbon (which is consistent with x-ray diffraction analysis) copper, tungsten and elements from the reactor. Possible sources of these impurities were the reactor, the mixing chamber, the copper anode of the arc heater, the materials from which the reactant feed systems were made and the collector walls. X-ray diffraction techniques employed on other samples from the collector showed that the samples were α - titanium having a small lattice expansion ($\simeq$ 1%) indicative of a solid solution, which was most likely to be a solid solution involving hydrogen or carbon. This was consistent with hot vacuum extraction which indicated a carbon content of 0.25%. A life size photograph of samples taken from the collector (run 2) is shown in Figure 5.

Run	Weight of Ti collected	Weight of Ti for 100% degree of reaction, 100% collection based on Na used	Overall yield
1	34.4 g	116.9g	29%
2	8.9 g	99 g	9%
3	34.0 g	177 g	19%

TABLE 1 OVERALL YIELD OF TITANIUM, RUNS 1-3

Ti	C	Contamination with reactor/ collector material	W	Trace elements
72%	Micro-analysis	5%	7%	non-detected
89%	indicated	1%	1%	
68%	few %	5%	11%	
89%		1%	1%	

TABLE 2 WET ANALYSIS OF SAMPLES FROM COLLECTOR, RUN 3

The yields (Table 1) are deliberately pessimistic estimates and do not include allowances for the substantial amount of sample that could not be removed and in some cases all the titanium collected. Nevertheless, the overall yields determined vary from 9% to 29%. Due to failure of the drive motor during run 3 the flow of $TiCl_4$ vapour into the reactor was zero for 5 minutes, exceeded the stoichiometric value by approximately 76% for 3 minutes and equalled the desired flowrate for 3 min. For the first 8 minutes the conversion of Ti was zero[12]. When this is accounted for, a value of approximately 90% was obtained for the yield. Thus, the degree of reaction that can be obtained in the present system is not less than 29% and could be of the order of 90%.

5. CONCLUSIONS

1. The laboratory tests on the high temperature sodium reduction of titanium tetrachloride appear to support the very favourable thermodynamics .

2. The titanium deposited within the collector is free from sodium and chlorine contamination.

3. The degree of reaction, or yield, is greater than 29% and may be of the order of 90%.

REFERENCES

1. W. Kroll, Trans Electrochem. Soc. V78, 35, 1910
2. W. Kroll, J. Less Common Metals, Vol. 8, 361, 1965
3. Encyclopedia Chemical Technology, 2nd edn., V20
4. M.A. Hunter, J. Am. Chem. Soc. V32, 330, 1910
5. S. Abkowitz, J.J. Bruke & R.H. Hilty, Jr, "Titanium in Industry" D. van Nostrand Co., Inc. New York, 1955
6. J. Barksdale, "Titanium" 2nd edition, (The Ronald Press Co.,New York, 1955)
7. S.C. Williams, "Report on titanium" Brundage, Story & Rose, New York, 1965
8. A.E. Van Arkel & J.H. de Boer, anorg. undallgem Chem. V148, 345, 1925
9. K.A. Bunting, "Collection from plasmas" to be published
10. P.D. Johnston, J. Lawton & I.M. Parker "Proposed plasma route for the production of titanium by the reduction of titanium tetrachloride" ECRC/R401, July 1971
11. K.A. Bunting, "The ECRC plasma route to titanium : The yield and degree of reaction", ECRC R1208, Jan. 1978
12. K.A. Bunting, "The ECRC plasma route to titanium : Apparatus selection of operating parameters and operating procedure" to be published
13. Handbook of Chemistry and Physics, 58th Edn. CRC Press Inc., Cleveland, Ohio, 1977-1978
14. M.G. Fey, et al, Quarterley Progress Report, ERDA/JPL 954-589-76/1, Aug.-Oct. 1976
15. M.G. Fey, T.N. Meyer and W.H. Reed "An electric arc heater process to produce solar grade silicon", 4th Int. Symp. on Plasma Chem. ISPC, Zurich, Aug.-Sept., 1979

16. K.A. Bunting, "The ECRC plasma route to titanium : The sodium feed system" ECRC/M1331 , April 1980

17. K.A. Bunting, "The ECRC plasma route to titanium : The titanium tetrachloride feed system", ECRC/M1345, Aug. 1980

18. K.A. Bunting, "An arc heater with hydrogen as the plasma working fluid" ECRC/M554, November 1972

19. K.A. Bunting, "Magnetically rotated arcs with superimposed gas flow" ECRC/M1229, April, 1979

20. K.A. Bunting, "The ECRC plasma route to titanium : Materials", to be published

21. Janaf Thermochemical Tables, 2nd Edn. June 1971

22. A.D. Cross "A complete program to calculate high temperature chemical equilibrium", ECRC/M1096, October 1977

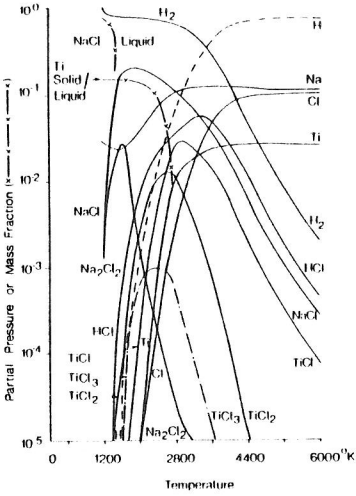

Figure 1 COMPOSITION AS A FUNCTION OF TEMPERATURE FOR 1.0 MOLES $TiCl_4$, 4.4 MOLES Na, 13.8 MOLES H_2

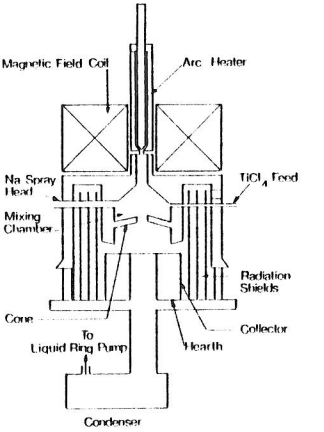

Figure 2 SCHEMATIC DIAGRAM SHOWING REACTOR AND ARC HEATER.

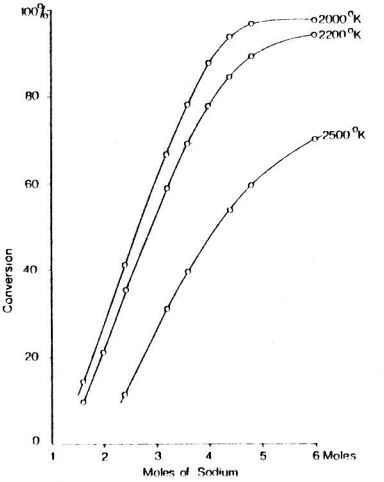

Figure 3 CONVERSION TO LIQUID TITANIUM AS A FUNCTION OF THE NUMBER OF MOLES OF SODIUM AT VARIOUS TEMPERATURES, 1.0 MOLES $TiCl_4$, 13.8 MOLES H_2

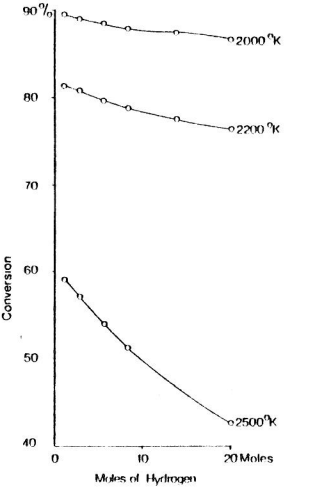

Figure 4 CONVERSION TO LIQUID TITANIUM AS A FUNCTION OF THE NUMBER OF MOLES OF HYDROGEN AT VARIOUS TEMPERATURES, 1.0 MOLES $TiCl_4$, 4.0 MOLES Na

Figure 5 EXAMPLES OF TITANIUM TAKEN FROM THE COLLECTOR, RUN 2