

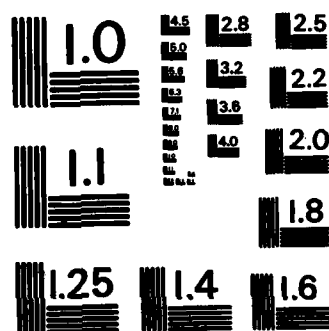
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TITANIUM PRODUCTION BY A PLASMA PROCESS

M. G. Down

**Westinghouse Electric Corporation
Research and Development Center
1310 Beulah Road
Pittsburgh, PA 15235**

May 1982

Final Technical Report for Period 15 May 1980 to 15 September 1981

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PREFACE

This effort was conducted under the AFWAL Materials Laboratory Director's Fund Program, Wright-Patterson Air Force Base, Ohio, under the direction of Mr. A. M. Adair. This work was performed under Contract No. F33615-80-C-5091, Work Unit ILIR0131, by the Westinghouse Electric Corporation's Research and Development Center, Pittsburgh, Pennsylvania. Dr. M. G. Down was the Principal Investigator for this effort which covered the time period 15 May 1980 to 15 September 1981.

The following Westinghouse personnel took part in various stages of the program and their valuable contributions are gratefully acknowledged:

J. V. R. Heberlein - plasma consultancy and equipment design,
R. W. Liebermann - thermochemical calculations, W. H. Reed - economic analysis, P. A. Ciarelli - experimental, F. V. Wooldridge - experimental,
T. J. Mullen - SEM/EDXA, T. N. Meyer - product collection analysis,
F. G. Arcella - discussion, M. G. Fey - discussion. This report was released by the author in June 1982.

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TABLE OF CONTENTS

Section	Page
I. INTRODUCTION	1
II. CONCLUSIONS	4
III. RECOMMENDATIONS	5
IV. TECHNICAL BACKGROUND	6
V. THERMOCHEMICAL ANALYSIS	9
VI. ECONOMIC ANALYSIS	14
VII. EXPERIMENTAL VERIFICATION	22
1. EQUIPMENT	22
2. RESULTS	26
3. PRODUCT EVALUATION	30
a. Experiment #1	30
b. Experiment #2	31
c. Experiment #5	32
d. Experiment #6	33
VIII. DISCUSSION	34
1. PROCESS FEASIBILITY	34
2. REACTOR DESIGN	34
REFERENCES	37

LIST OF ILLUSTRATIONS

FIGURE		PAGE
1	Thermochemical equilibrium for the hydrogen reduction of TiCl_4	38
2	Thermochemical equilibrium for the sodium/hydrogen reduction of TiCl_4	39
3	Thermochemical equilibrium for the sodium/hydrogen reduction of TiCl_4 (excess sodium)	40
4	Assembly drawing of test apparatus	41
5	Reactant injection nozzle	42
6	Photograph of test section	43
7	Photograph of experimental apparatus	44
8	Schematic of the TiCl_4 supply system	45
9	Photograph of the sodium storage tank	46
10	Plasma/reactants injection flange after experiment #1	47
11	Optical photograph of titanium product from experiment #1	48
12	Plasma/reactants injection flange after experiment #2	49
13	Silicon carbide reaction tube (hot end) after experiment #2	50
14	Metallic Titanium Product from experiment #2 (X100)	51
15	SEM/EDXA analysis of product from experiment #1	52
16	SEM/EDXA analysis of bulk product from experiment #2	53
17	SEM/EDXA analysis of crystalline product from experiment #2	54

LIST OF ILLUSTRATIONS
(continued)

FIGURE		PAGE
18	SEM/EDXA analysis of product from experiment #5 (from first inch of graphite tube)	55
19	SEM/EDXA analysis of product from experiment #5 (from first 6" of reaction tube)	56
20	SEM/EDXA analysis of the ultrafine reaction product after leaching away NaCl and sodium -- experiment #5	57
21	SEM/EDXA analysis of product from experiment #6. Titanium-rich area	58
22	SEM/EDXA analysis of product from experiment #6. Shows vanadium-rich substrate with titanium-rich crystals	59
23	Plasma reactor for titanium production	60

LIST OF TABLES

TABLE		PAGE
1	Purchased equipment cost -- 5000 MT/YR (purchased reactants)	16
2	Estimation of fixed capital 5000 MT/YR TI (purchased reactants)	17
3	Estimate of product cost 5000 MT/YR (purchased reactants)	18
4	Purchased equipment cost -- 1000 MT/YR (purchased reactants)	19
5	Estimation of fixed capital 1000 MT/YR TI (purchased reactants)	20
6	Estimate of product cost 1000 MT/YR TI (purchased reactants)	21
7	Titanium tetrachloride analysis report	25
8	Summary of plasma titanium experiments	27

Section I

INTRODUCTION

The properties of high corrosion resistance and strength, combined with relatively low density, result in titanium alloys being ideally suited to many applications in aerospace systems. Applications in chemical and power plants are also attractive. Unfortunately, the widespread use of titanium has been severely limited by its high cost which is a direct consequence of the high energy consumption and batch nature of the conventional Kroll and Hunter processes for metal production.

These large scale production processes have been relatively unchanged for many years and involve the following essential steps: (1) Chlorination of impure oxide ore, (2) purification of $TiCl_4$, (3) reduction by sodium or magnesium to produce titanium sponge, (4) removal of sponge, and (5) leaching, distillation and vacuum remelting to remove Cl, Na, and Mg impurities. The combined effects of the inherent cost of this process, the difficulty associated with forging and machining titanium and, in recent years, a shortfall in sponge availability have contributed to the overall titanium utilization picture.

One of the most promising techniques currently undergoing development to circumvent the high cost of titanium alloy parts is powder metallurgy (PM) for near net shape fabrication. For instance, it has been estimated that for every kilogram of titanium presently utilized in an aircraft, 8 kilograms of scrap are created. PM can substantially improve this ratio. Although this technology essentially involves the simple steps of powder production followed by compaction into a solid article, considerable development is currently underway to optimize the process such that the final product possesses at least equal properties and lower cost than wrought or cast material. One potential PM route to

titanium alloy parts involves the direct blending of elemental metal powders before compaction. Presently, titanium sponge fines from the Kroll process are used, but a major drawback is the high residual impurity content, principally chlorides, which results in porosity in the final material. The other PM alternative involves the direct use of titanium alloy powder which is subjected to hot isostatic pressing (HIP). Currently several programs are involved in the optimization of alloy powders and results are highly promising, but all involve Kroll titanium as a starting material followed by a number of expensive purification and alloying steps.

The present program seeks to determine the feasibility of a new plasma process for the direct and continuous production of high purity titanium powder and/or ingot. Steps (1) and (2) of the Kroll or Hunter processes (see above) are retained, but steps (3), (4), and (5) are replaced by a single, high temperature process which directly produces high purity titanium, with the elimination of subsequent purification steps. Depending upon collection conditions the product could be either a powder suitable for the elemental blend approach to powder metallurgy or in the form of ingot or sponge-substitute. The possibility also exists for direct plasma production of titanium alloy powders in a single step process.

The new plasma process is based on the Westinghouse technique previously developed for production of photovoltaic grade silicon via the vapor phase reaction between sodium and silicon tetrachloride. Energy input for the process is provided by AC arc heaters. The process is continuous since the sodium chloride co-product is removed as a vapor thereby separating it from the lower vapor pressure titanium metal.

The program described in this report constituted an initial feasibility study for this plasma process and was split into several related tasks. Firstly, a techno-economic study utilizing thermochemical and price projection analyses was performed to determine the desirability of investigating the process further. Secondly, the basic

plasma reaction was studied experimentally on a small scale laboratory unit rated at 40 kW. The results of this study were then integrated into a design for a plasma reactor which would be capable of producing larger quantities of product and could be scaled up to a production unit.

Section II

CONCLUSIONS

1. Calculations indicated that a plasma process operating in the range 1700-2200 K should produce a titanium yield close to 100% of theoretical with little or no production of subchlorides.
2. Experimental verification of such a process successfully demonstrated that an effective separation of the co-product sodium chloride could be achieved at these temperatures.
3. It was demonstrated that collection of the titanium product from such a process could be achieved either as a liquid for continuous casting or directly as a powder suitable for powder metallurgical applications.
4. Economic projections, made on a conservative basis, indicate that a continuous plasma process could operate competitively with existing Kroll or Hunter batch processes.

Section III
RECOMMENDATIONS

1. It is recommended that a further series of tests at the 40 kW, laboratory scale be performed in order to optimize the injection of reactants and collection of product. These tests should be performed on a vertically oriented reactor and close attention should be paid to the materials of construction for the titanium collection zone.
2. These tests should be followed by a series of experiments utilizing a relatively small Westinghouse arc heater (200- 500 kW). This intermediate-scale reactor would be able to provide the final design information and operating experience necessary to enable the construction of a full scale pilot plant. It would also permit refinement of process economic projections.

Section IV

TECHNICAL BACKGROUND

The formation of titanium under plasma conditions has received intermittent attention in the literature over the last 30 years. Reports have generally been concerned with the hydrogen reduction of titanium tetrachloride or dioxide with some isolated references to sodium or magnesium reduction.

The use of hydrogen for reducing titanium tetrachloride has been studied in an arc furnace⁽¹⁾ but only partial reduction took place at 2100 K. The same reaction system has been more extensively studied in a plasma flame and patented for the production of titanium subchloride^(2,3) and titanium metal.^(4,5,6) Although early thermodynamic calculations indicated that the reduction of titanium tetrachloride to metallic titanium by hydrogen could start at 2500 K, the system is not a simple one. As our calculations show later, the formation of titanium subchloride would be thermodynamically more favorable in that temperature region. A patent⁽⁶⁾ claims that the reduction to liquid titanium can be successfully carried out by heating the reactants (TiCl_4 and H_2) at least to, and preferably in excess of, the boiling point of titanium (3535 K). At such a high temperature, it was claimed that titanium tetrachloride vapor is effectively reduced by atomic hydrogen, the tendency of H_2 to dissolve in or react with Ti is insignificant, the HCl formed is only about 10% dissociated, and the formation of titanium subchlorides could be much less favorable. The titanium vapor product is then either condensed to liquid in a water-cooled steel condenser at ~3000 K, from which it overflows into a mold, or flash-cooled by hydrogen to powder, which is collected in a bin. Since the liquid titanium is condensed from gas with only gaseous by-products or impurities, its purity, except for hydrogen, was expected to be high. Another patent⁽⁵⁾ describes reaction conditions as follows: a mixture of TiCl_4 gas and H_2

(50% in excess) is led through a 5 mm i.d. nozzle of a tungsten electrode at a rate of $4 \times 10^{-3} \text{ m}^3/\text{min}$ and an electric discharge (3720 V and 533 mA) made to another electrode at a distance of 15 mm. The resulting powdery crystals are heated in vacuo to produce 99.4% pure titanium. In neither patent is the energy consumption clearly mentioned.

Attempts to develop the hydrogen reduction process on an industrial scale were made by the Rem-Cru Titanium Company using a skull-melting furnace,⁽⁸⁾ but the effort was discontinued.

More recently, a claim was made by Thorpe⁽⁹⁾ that a small quantity of titanium had been produced in a hydrogen plasma, but this was later retracted⁽¹⁰⁾ when the product was truly identified as titanium carbide.

In summary, the history of attempts to treat TiCl_4 in hydrogen plasmas appears to indicate that only partial reduction, i.e., to a mixture of titanium and its subchlorides, is possible unless very high temperatures ($>4000 \text{ K}$) are reached. This experimental finding was rationalized in 1974 by Yean and Ritter⁽¹⁰⁾ who performed equilibrium calculations on the system, similar to those described in section 5.0 of this report. They concluded that extremely rapid, preferential condensation of vapor phase titanium would be required in order to overcome the unfavorable thermodynamics of the system.

An alternative plasma route to titanium which could overcome the thermodynamic obstacles present in the hydrogen system, is to perform the traditional Kroll-type, sodium or magnesium reduction at plasma temperatures. References to this method are fewer than for the hydrogen reduction, presumably due to the additional experimental expertise required for the injection of reactive metals into a plasma furnace. Some work has been performed by the Electricity Council in England, based on a patent⁽¹¹⁾ issued in 1974. The conceptual patent describes a plasma reaction between titanium tetrachloride and sodium or magnesium, at temperatures such that the titanium is formed as a liquid and the co-product salt and other impurities are removed as gases. Results of an

experimental program to verify the process have very recently been reported,⁽¹²⁾ and the favorable conclusions are similar in most respects to those contained in this report. Metallic titanium was prepared in a 30 kW plasma furnace and shown to be substantially free of chloride co-product.

Although not specific to titanium, another relevant effort was the recent development of a plasma process for the sodium reduction of silicon tetrachloride to produce photovoltaic-grade silicon metal.⁽¹³⁾ This process has reached the stage of successful initial operation of a 1.5 MW pilot plant, and has provided much valuable experience and background for the implementation of the present work on titanium.

Section V
THERMOCHEMICAL ANALYSIS

As a first step in the study of the plasma process for reduction of titanium tetrachloride, a thermochemical analysis using the Westinghouse computer library program CHEMEQ was carried out with the following objectives.

1. Definition of the equilibrium chemistry in the following reaction systems

Ti-Cl-H-Ar-Na
Ti-Cl-H-Ar-Mg
Ti-Cl-H-Ar-Zn
Ti-Cl-H-Ar
Ti-Cl-H-Ar-Na-V-Al

2. Calculation of the specific energy required for plasma production of titanium.

The achievement of these two objectives has been based on the solving of the complex equilibria associated with such multi-component, heterogeneous systems. In the Ti-Cl-H-Ar-Na system, for example, the species to be considered, in the temperature range of interest, included Ar (g), H₂ (g), NaH (g), HCl (g), H (g), TiCl₄ (g), TiCl₃ (g), TiCl₂ (g), TiCl (g), Na₂Cl₂ (g), Na₂ (g), NaCl (g), Na (g), Ti (l), Ti (c), Ti (g), Cl₂ (g), Cl (g), TiH₂ (c), NaH (c), and TiCl₄ (l), where g = gaseous, l = liquid and c = condensed phase.

Equilibria were solved by free energy minimization techniques for the following reactant ratios (molar):

Computer Run #	Reactant Ratio (Molar)								
	Ti	Cl	H ₂	Ar	Na	Mg	Zn	Al	V
1	1	4	67	33	4				
2	1	4	670	330	4				
3	1	4	6.7	33	4				
4	1	4	67	33	1				
5	1	4	67	33	2				
6	1	4	67	33	3				
7	1	4	67	33	6				
8	1	4	67	33	8				
9	1	4	2	1					
10	1	4	10	1					
11	1	4	6.7	3.3		2			
12	1	4	67	33		2			
13	1	4	6.7	3.3			2		
14	1	4	67	33			2		
15	1	4.5	28	13.8	4.5			0.12	0.04
16	1	4	670	167	4				
17	1	4	6.7	1.7	4				
18	1	4	13.4	3.35	4				
19	1	4	13.4	3.35	8				
20	1	4	13.4	3.35	12				

The compositions of the gaseous and condensed phases for these twenty cases were calculated at 100 degree intervals in the temperature range 1500-3500 K. As shown in the above table, the Ti:Cl ratio was usually 1:4, corresponding to the injection of TiCl_4 , and the arc heater gas ratio was taken as $\text{H}_2:\text{Ar} = 2:1$ or $4:1$. The pressure of the system was 1 atmosphere. The main variables investigated were the reductant to titanium ratios, principally for sodium but also for hydrogen alone and for magnesium and zinc.

The composition of the gas mixture as a function of temperature for each of the twenty cases was calculated and depicted graphically in the first quarterly report.⁽¹⁴⁾ Here, only three typical examples are shown, for hydrogen (#10) and sodium (#18, 19) reduction, Figures 1, 2 and 3. Although many minority species are predicted to be present, these diagrams have been simplified so that they show only the titanium-bearing species. In this way the yield of titanium, either in the condensed phase (c) or as a gas (g), is clearly depicted.

The reaction systems which contain no metal other than titanium, and therefore rely on hydrogen alone as reducing agent, were studied in computer runs 9 and 10. Case 9 was for the stoichiometric amount of hydrogen required, assuming complete conversion to HCl, and case 10 (see Figure 1) considered a fivefold excess of hydrogen. The formation of metallic titanium was shown not to be the preferred reaction, and in fact at all temperatures of interest the predominant gaseous species are the titanium subchlorides. Even with excess hydrogen, no pure titanium is predicted to be present in the gas phase until a temperature in excess of 2600 K is achieved and even at 3500 K the yield is less than 40%. Since condensed titanium is not stable, even at the lower temperatures, it is hard to conceive of pure titanium being produced when such a gas mixture is cooled. These results are in good agreement with the calculation of Yean and Ritter⁽¹⁰⁾ and the experimental findings discussed in Section 4.0.

From these results it is clear that another reducing agent, in addition to hydrogen, is desirable in order to form pure titanium in a gas phase reaction. Computer runs 4, 5, 6, 1, 7 and 8 studied the effect of introducing increasing quantities of sodium into the equilibrium. This sequence of cases corresponds to sodium to titanium ratios of 1:1, 2:1, 3:1, 4:1, 6:1 and 8:1, respectively. A ratio of 4:1 is the stoichiometric amount used to form pure titanium and sodium chloride under typical low temperature Hunter process conditions. The inclusion of even a low level of sodium (Case 4) dramatically altered the degree of reduction achievable with hydrogen alone. At low temperatures (<2300 K) condensed titanium is predicted to be present and at higher temperatures the gaseous titanium yield increases to over 80% at 3500 K. Increasing the sodium level to the 4:1 ratio (Case 1) demonstrated, as expected, that at temperatures below 2100 K the reaction $\text{TiCl}_4 + 4\text{Na} \rightarrow \text{Ti} + 4\text{NaCl}$ proceeds at 100% yield. This is, of course, the normal Hunter process. At higher plasma temperatures, however, titanium chlorides do become stable, although at 3500 K the gaseous titanium yield is still ~80%.

Taking the 4:1 sodium to titanium ratio as a reference case, runs 1-3 showed the effect of varying hydrogen levels on the overall equilibrium. Case 2 showed that, in the presence of sodium, an increased hydrogen concentration can result in virtually 100% titanium yields both at low (<1800 K) and high (>3000 K) temperatures. The exact hydrogen to sodium ratio to be used in a commercial plasma process, however, is more likely to be determined by economics and arc heater efficiency considerations. Cases 18-20 are thought to be more realistic than the high hydrogen levels of case 2, as far as a commercial plant is concerned, and for this reason Figure 3 shows that a slight excess of sodium above the stoichiometric amount is desirable in order to fully suppress the formation of titanium subchlorides.

Alternative metallic reducing agents were considered in Runs 11 and 12 (magnesium) and 13 and 14 (zinc). In these cases a reducing agent to titanium ratio of 2:1 is equivalent to the stoichiometric conversion to pure titanium plus MgCl_2 or ZnCl_2 . Magnesium appears to perform almost as well as sodium under the conditions calculated, but zinc was appreciably worse as regards both condensed and gaseous titanium yield. In light of these results and the fact that sodium lends itself more easily to a continuous purification and feeding into a reactor,⁽¹³⁾ the choice of this reductant appeared justified for the experimental verification task of this program.

Case 15 provided an interesting study of a system containing the chlorides of titanium, vanadium and aluminum in the ratios usually found in Ti/V/Al alloy. Sufficient sodium is present to react with the chlorine should the reaction go to completion. At 3500 K the yield of each metal present is ~67% Ti, ~50% Al and ~10% V. The implications of this are that even if the reactants were injected in the correct ratio, the resulting pure metal powder mixture would not represent the desired alloy mix for Ti/V/Al alloy. However, this type of alloy system is more complicated since consideration of the relative vapor pressures of the components must also be made before predicting condensed phase compositions. This will be discussed in more detail in Section 7.0 and 8.0.

The Westinghouse developed CHEMEQ computer program also provides enthalpy data and this was used to calculate the specific energy requirement for the sodium reduction plasma process. Clearly, from Figure 3, the optimum titanium yield would be achieved if the reaction zone temperature was in the range 1700-2200 K. Lower temperatures are excluded because NaCl would condense with the product, and at higher temperatures subchlorides begin to form. Obviously, for higher reaction zone temperatures more energy input is required. Between 1700 and 2200 K the energy requirement increases from 4 to 6.5 kWh per kg of titanium produced, assuming the predicted thermodynamic yield of ~100% in this region.

If we divide these numbers by the gas heating efficiency of the arc heater (60 to 80%, depending on design), we obtain a theoretical minimum energy requirement for the process. However, in an actual operating system other considerations will have an effect. The most important of these considerations is the product collection scheme. If the reaction zone was in the above temperature range, ultrafine Ti particles would form because condensation would take place immediately after the reactants are mixed. We found in the experiments that the product titanium can be collected in the form of larger particles (~50 μ m diameter) when the reaction zone temperature was above 3000 K. Although we do not, at present, fully understand the product formation mechanism, the possible simplification of the process by product collection on the reactor walls could warrant a slightly higher power input per kilogram of product.

Section VI

ECONOMIC ANALYSIS

Economic analyses were conducted for two titanium production levels; i.e., 1000 metric tons/year and 5000 metric tons/year. Both of these production levels were evaluated based on a mode of operation in which the starting materials (TiCl_4 and Na) are purchased and not produced within the process (recycle mode). Certain base case assumptions were required for these analyses and are listed as follows:

Process Duty Cycle - 7500 hours/year

Arc Heater Efficiency - 75%

Yield Efficiency - 80%

Plasma Gas - Ar-H_2

The standardized economic projection techniques, developed by Lamar University for the JPL/DOE solar silicon projects were utilized for these analyses. For each production level evaluated (i.e., 1000 MT/yr and 5000 MT/yr) a listing of purchased equipment costs was compiled. Table 1 presents the estimated equipment cost for the 5000 MT/yr case which would require \$2.38 million of equipment. For the 1000 MT/yr case, an estimated \$907,000 of purchased equipment would be required (see Table 4). In all the economics presented, March 1981 dollar values have been utilized.

Once the purchased equipment costs have been assembled, an estimate of plant capital (fixed capital) is required. As shown in Table 2, the fixed capital is calculated based upon percentages of purchased equipment costs (PE). For the 5000 MT/yr case, an estimated fixed capital of \$9.75 million was calculated. As listed in Table 5, a fixed capital of \$3.62 million was computed for the 1000 MT/yr case.

The final economic factor that was computed is the estimated product cost (without profit). This factor consists of the following categories: direct costs, indirect costs, plant overhead, and general expenses. Table 3 presents the estimated product cost for the 5000 MT/yr case which yields an estimated titanium cost of \$4.31 per pound. A similar computation was developed for the estimated product cost of titanium assuming a 1000 MT/yr production level. At the lower production rate, an estimated titanium cost of \$4.84 per pound was projected (see Table 6).

Based on the two production levels (5000 and 1000 MT/yr) evaluated to date, the estimated product costs of titanium (\$4.31 and 4.84 per pound, respectively) are quite favorable for the plasma process since the recent selling price of conventional titanium sponge is of the order of \$7-8/pound. The plasma produced titanium should be free of impurities (Cl, Na, Mg) and could be in an alloy (Ti-V-Al) form, whereas additional processing is required to remove impurities from the presently produced Kroll or Hunter sponge.

TABLE 1

PURCHASED EQUIPMENT COST -- 5000 MT/YR (PURCHASED REACTANTS)

<u>ITEM</u>	<u>COST, K \$</u>
Arc Heaters/Reactor System	787
Reactant Injection Systems	319
Gas/Salt Separator and Piping	54
Gas Recycle, Make-up, and Burnoff	189
Titanium Collection	462
Electrical Systems	439
Cooling Water System	128
Total *	\$2,378

* Chemical Engr. Plant Cost Index
Jan. 81 - 280.5 (March 1981 issue)

TABLE 2

ESTIMATION OF FIXED CAPITAL 5000 MT/YR TI
(PURCHASED REACTANTS)

<u>ITEM</u>	<u>% OF P.E.</u>	<u>INVEST., K\$</u>
1. Purchased Equip. (PE)	100%	2,378
2. Install. Purch. Equip.	43% (PE)	1,023
3. Instru. and Control	13.5% (PE)	321
4. Bldgs. with Services	23.5% (PE)	559
5. Yard Improvements	11.5% (PE)	273
6. Service Facilities, Installed	55% (PE)	1,308
7. Land	6% (PE)	143
8. Engr. and Supervision	32.5% (PE)	773
9. Construction Expense	37.5% (PE)	892
10. Contractor's Fee	19% (PE)	452
	Subtotal	\$8,122
	Contingency (20%)	1,624
	Total Fixed Capital	\$9,746

TABLE 3

ESTIMATE OF PRODUCT COST 5000 MT/YR (PURCHASED REACTANTS)

<u>ITEM</u>	<u>TI COST, \$/KG</u>
1. DIRECT MANUF. COST	
a. Raw Materials	6.60
b. Direct Operat. Labor	.12
c. Utilities (electricity)	.23
d. Supervision & Clerical (15% of 1b)	.02
e. Maint. & Repair (10% of fixed capital)	.19
f. Operating Supplies (20% of 1e)	.04
g. Lab Charges (15% of 1b)	.02
h. Patents & Royalties (3% of product cost)	.28
	7.50
2. INDIRECT MANUF. COSTS	
a. Depreciation (10% of fixed capital)	.19
b. Local Taxes (2% of fixed capital)	.04
c. Insurance (1% of fixed capital)	.02
d. Interest (15% of fixed capital)	.29
	.54
3. PLANT OVERHEAD (60% of 1b + 1d + 1e)	.20
4. TOTAL MANUF. COST (1. + 2. + 3.)	8.24
5. GENERAL EXPENSES	1.24
a. Administration (6% manuf. cost)	
b. Distribution & Sales (6% manuf. cost)	
c. Research & Devel. (3% manuf. cost)	
6. TOTAL PRODUCT COST (4 + 5) WITHOUT PROFIT	\$9.48/kg (\$4.31/lb.)

TABLE 4

PURCHASED EQUIPMENT COST -- 1000 MT/YR. (PURCHASED REACTANTS)

<u>ITEM</u>	<u>COST K \$</u>
Arc Heaters/Reactor System	300
Reactant Injection Systems	122
Gas/Salt Separator and Piping	21
Gas Recycle, Make-up and Burnoff	72
Titanium Collection	176
Electrical Systems	167
Cooling water System	<u>49</u>
Total	\$907

TABLE 5

ESTIMATION OF FIXED CAPITAL 1000 MT/YR TI
(PURCHASED REACTANTS)

<u>ITEM</u>	<u>% OF P.E.</u>	<u>BATCH INVEST., K\$</u>
1. Purchased Equip. (PE)	100%	907
2. Install. Purch. Equip.	43% (PE)	309
3. Instru. and Control	13.5% (PE)	122
4. Bldgs. with Services	23.5% (PE)	213
5. Yard Improvements	11.5% (PE)	104
6. Service Facilities, Installed	55% (PE)	499
7. Land	6% (PE)	54
8. Engr. and Supervision	32.5% (PE)	295
9. Construction Expense	37.5% (PE)	340
10 Contractor's Fee	19% (PE)	172
	Subtotal	<u>\$3,015</u>
	Contingency (20%)	<u>603</u>
	Total Fixed Capital	<u>\$3,618</u>

TABLE 6

ESTIMATE OF PRODUCT COST 1000 MT/YR TI
(PURCHASED REACTANTS)

1. DIRECT MANUF. COST		
a. Raw Materials	6.60	
b. Direct Operat. Labor	.30	
c. Utilities (electricity)	.07	
d. Supervision & Clerical (15% of 1b)	.05	
e. Maint. & Repair (10% of fixed capital)	.36	
f. Operating Supplies (20% of 1e)	.07	
g. Lab Charges (15% of 1b)	.05	
h. Patents & Royalties (3% of product cost)	.32	
		7.82
2. INDIRECT MANUF. COSTS		
a. Depreciation (10% of fixed capital)	.36	
b. Local Taxes (2% of fixed capital)	.07	
c. Insurance (1% of fixed capital)	.04	
d. Interest (15% of fixed capital)	.54	
		1.01
3. PLANT OVERHEAD (60% of 1b + 1d + 1e)		
4. TOTAL MANUF. COST (1. + 2. + 3.)	9.26	
5. GENERAL EXPENSES	1.39	
a. Administration (6% manuf. cost)		
b. Distribution & Sales (6% manuf. cost)		
c. Research & Devel. (3% manuf. cost)		
6. TOTAL PRODUCT COST (4 + 5) WITHOUT PROFIT	\$10.65/kg	
	(4.84/lb.)	

Section VII

EXPERIMENTAL VERIFICATION

A laboratory scale experimental program was performed in order to verify the results of the thermochemical analysis and to learn more about the mechanism of titanium nucleation and growth and the effectiveness of product separation in a plasma system. The experiments were not intended to test a miniature version of a production-type reactor but to obtain basic information that could be incorporated into the design of such a reactor for the next phase of development.

1. EQUIPMENT

The equipment was originally designed for silicon reduction and has been described previously.⁽¹⁵⁾ An overview sketch of the test apparatus is shown in Figure 4. The plasma torch (40 kW, Plasmadyne, Inc.) is located at the left end of the system. Immediately adjacent to the torch are the reactant injection nozzles. The test section consisted of a refractory reaction tube (silicon carbide or graphite) inside a water-cooled, cylindrical stainless steel chamber consisting of four separate sections. The reaction tube was divided into several straight axial tube sections for investigating the product separation process, and provision was made for surrounding it with concentric zirconia radiation shields.

A sketch of the injection assembly is shown in Figure 5. There are three cylindrical stainless steel plenum chambers for liquid Na, TiCl_4 vapor and high pressure cooling water, respectively. Several small channels extend from the Na and TiCl_4 chambers to the nozzle itself, which is constructed from graphite.

Inlets for introducing a tangential flow of argon gas are located in the side wall of the main cylinder of the test section. This

gas provided both additional temperature control for the internal ceramic tube, and acted as an inert cover gas for the test section. At each of two axial locations, there is an arrangement of three viewing ports around the chamber periphery, for gas diagnostic temperature measurements. The quartz windows are protected from condensation of reaction products by shutters. When a shutter is open, its U-shaped flapper provides maximum viewing access. A small amount of gas flow entering close to the window counteracts the diffusion flow of reaction products from the main stream.

Figure 6 shows a photograph of the test chamber. The plasma torch is seen at the left. Above it is a valve which controls the flow rate of cold argon into the outer part of the test chamber. The four front windows of the first two test sections have regular window flanges, the last test section has plexiglass flanges. The vertical connection tube to the scrubber has a provision for injecting water for further cooling of the gas stream before it enters the scrubber. A photograph of the assembled system is shown in Figure 7. The three flowmeters in the center serve to measure cooling water flowrates to different sections. The scrubber and its control panel, which also controls the burn-off igniter above it, is shown on the right. The control cabinet for the plasma torch including the safety circuitry is visible in the left background. The torch power supply is located behind the control cabinet.

A schematic of the TiCl_4 supply system is shown in Figure 8. Liquid TiCl_4 is loaded into the reservoir which is then attached to the system at the Swagelok union. The reservoir is then pressurized with argon to about $3 \times 10^5 \text{ Pa}$ ($\sim 45 \text{ psia}$). The argon pressure is used to deliver TiCl_4 through the system to the injection nozzle. The reservoir capacity is approximately $5.7 \times 10^{-3} \text{ m}^3$ (1.5 gal.), which permits at least 30 min. of operation. The reservoir has an in-line pressure relief valve, which is vented to the exhaust hood. A flat bottom facilitates placement of the reservoir in a dry box for reloading. A removable top cover plate, sealed with a Teflon O-ring, is provided for cleaning and/or

inspection of the interior of the reservoir. All parts are fabricated from type 304 stainless steel.

In the boiling vessel, TiCl_4 is heated to its boiling point (409 K) and vaporized. This vessel consists of two cylindrical, coaxial, stainless steel tubes welded to stainless steel end plates. A 1.0 kW immersion heater is sealed inside the smaller tube, with a suitable heat transfer fluid (silicone oil) at atmospheric pressure, used to transfer heat to the TiCl_4 . A 500 W heating tape is wound around the outside of the vessel. Both heating units are controlled from Variacs. Liquid TiCl_4 enters the bottom of the boiling vessel and TiCl_4 vapor flows out at the top. The tube from the boiling vessel to the injection nozzle is also heated to prevent condensation of TiCl_4 vapor.

An electrically-operated 3-way valve is provided for safety purposes. Under normal operating conditions this valve allows TiCl_4 vapor to pass from the boiling vessel to the injection nozzle, but in the event of a power failure or an automatic or manual emergency shut-down this valve would shut off the flow of TiCl_4 and open the injection nozzle to an argon purge line.

An analysis of the TiCl_4 used in these experiments is given in Table 7.

The sodium supply system consists of a 3 gallon cylindrical stainless steel reservoir with hemispherical end caps, Figure 9. The tank is equipped with two level probes and clamshell type heaters, and is linked to the injection nozzle via a heated stainless steel line. Flow is achieved by pressurizing the supply tank with argon and is measured by a calibrated electromagnetic liquid metal flowmeter. The flow is regulated by adjusting a precision, all welded, stainless steel bellows metering valve, and can be continuously recorded on a digital data logger. The sodium used in these experiments was purified by filtration just above the melting point.

The exact reactor configuration and experimental procedure for the experiments was as follows.

TABLE 7

TITANIUM TETRACHLORIDE ANALYSIS REPORT

TiCl₄ 99.9% minimum

	<u>Specification (ppm)</u>	<u>Analysis (ppm)</u>	
Aluminum	5 max	Within Specification	
Antimony	5 max	"	"
Arsenic	10 max	"	"
Chromium	2 max	"	"
Copper	2 max	"	"
Iron	15 max	"	"
Lead	1 max	"	"
Nickel	2 max	"	"
Silicon	10 max	"	"
Tin	10 max	"	"
Vanadium	5 max	"	"
APHA Color			

Analyses Determined Spectrographically

Three concentric ceramic tubes were assembled within the water-cooled stainless steel reactor. The graphite nozzle through which the argon-hydrogen plasma reactants are injected was butted against one end of a 0.025m (1") I.D. silicon carbide or graphite reaction tube. This primary reaction tube was then surrounded by two radiation shields comprised of a 0.05m (2") silicon carbide tube and a 0.13m (5") zirconium dioxide pipe. The total length of the reaction assembly was approximately 0.91m (36").

The entire reaction chamber was initially purged with argon for approximately 30 minutes before the plasma torch was ignited. Gradual warm-up of the ceramic tubes was achieved by initiating the arc with argon gas only. After a few minutes operation at this lower power level, hydrogen was introduced and the torch brought to final operating conditions of approximately 260 amps and 100 volts, that is ~26 kW. The atomic ratio of hydrogen to argon was 8:1.

Under these conditions, titanium tetrachloride was typically injected in the vapor phase at a rate of $\sim 4 \times 10^{-7} \text{ m}^3/\text{s}$ and liquid sodium at $\sim 3 \times 10^{-7} \text{ m}^3/\text{s}$.

2. RESULTS

Six experimental runs were made in order to study various aspects of the plasma reaction and to investigate product separation/collection schemes. The salient experimental details are summarized in Table 8, and discussed in more detail below.

Experiment #1 was performed without sodium injection in order to gain experience with the system and to evaluate the reduction of TiCl_4 using hydrogen alone. Visual post-test examination of the reaction chamber indicated several features of interest. The most obvious conclusion was that at least some of the injected titanium tetrachloride was still present in the reaction chamber in its original form. The characteristic white fumes caused by reaction of TiCl_4 with moist air were evident when the chamber was opened, although this may have been

TABLE 8
SUMMARY OF PLASMA TITANIUM EXPERIMENTS

Experiment Number	Collection Tube Material	Reactants Injected (moles)				Torch Power	Remarks
		TiCl ₄	Na	H ₂	Ar		
1	Silicon Carbide	2.2	-	29.2	7.3	26	Incomplete reduction - TiCl ₄ , TiCl ₃ , etc. present in reactor. Lustrous crystalline product contaminated by silicon and chlorine.
2	Silicon Carbide	4.8	2.9	64.3	16.1	22.5	Complete reduction - no detectable Cl or Na in metallic product. Severe silicon impurity from reaction tube.
4	Silicon Carbide with Titanium foil liner	3.5	12.3	47.2	11.8	23	Titanium liner melted and mixed with product.
5	Graphite	3.5	9.3	47.2	11.8	27.5	Complete reduction - no apparent Na or Cl in product. Silicon impurity eliminated. Some titanium carbide and nitride in product.
6	Graphite	2.5	6.3	33.5	8.4	23.8	Coinjection of TiCl ₄ and VCl ₄ . Ti/V alloy formed of varying composition but free of Na and Cl impurity. Some TiN in product.

due, in part, to the reduction co-product, HCl. Further evidence of the incomplete reduction of TiCl_4 came from the fact that several silicone rubber 'O' rings used in the cooler parts of the chamber had been seriously attacked. These were subsequently replaced by Buna-N which appears to be compatible with TiCl_4 .

The solid product located within the reaction chamber took several forms. Around the injection flange, Figure 10, fine crystalline material, soluble in water, and varying in color between white and light purple had been deposited. This material was clearly not metallic in nature. Further deposits of whitish powder were located at the cool end of the reaction chamber. The main bulk of solid product, however, was found adhering to the inner wall of the 0.025m (1") I.D. silicon carbide reaction tube. Most of this material was located along the first 0.15m (6") of the tube immediately downstream from the plasma/reactant injection. Optical photographs of this product, Figure 11, show the lustrous metallic appearance of the bulk of this material. The surface which was exposed to the inside of the reaction tube, however, was blackish/purple in color. Detailed analysis of all products produced in this and subsequent tests are described in Section 7.3.

After complete disassembly, cleaning and reassembly of the test system, a second experimental run was performed in order to study the effect of sodium on the reduction. From Table 8 it is clear that an Na:Cl ratio somewhat lower than the stoichiometric amount required for complete conversion to NaCl was injected. Nevertheless, the thermochemical equilibrium calculations described in Section 5.0 indicated that a reactant ratio of this order should produce condensed titanium product, albeit in relatively low yield.

When the reaction chamber was opened after this run there was no evidence of excess TiCl_4 remaining in the system. The injection flange, Figure 12, did not contain any of the water-soluble crystalline material present after the first experiment. Instead the area around the graphite nozzle was covered with metallic-looking granular material. The nozzle

itself had suffered some erosion in the region where the reactants mixed.

The inner wall of the 0.025m (1") silicon carbide reaction tube, immediately adjacent to the injection nozzle, is shown in Figure 13. There was a significant growth of deposited material, shiny and metallic in appearance, on the inner wall of the tube. This type of deposit was evident along the first 9-12" of tube and was composed of a mixture of granular and crystalline materials. The deposits were only loosely adhering to the tube wall and could be easily scraped out. Figure 14 is typical of the bulk of the product which did not appear to have been solidified from a melt, although Figure 13 shows that in some locations, where the layer was thickest, the metal had been in the molten state.

Further downstream, in the 0.3-0.6m (12-24") location, the walls of the reaction tube were coated with a fine black powder, insoluble in water, with shiny, larger particles intermixed. These larger, shiny particles were identical in appearance to those formed at the hot end of the tube and had presumably been swept downstream by the plasma gas flow.

Further downstream still, at the 0.6-0.9m (24-36") location, the lowest segment of the reaction tube contained a solidified melt, believed to be sodium chloride. When this was dissolved in water, it was clear that a considerable amount of black, insoluble powder had been trapped within this sodium chloride matrix, as well as a small amount of free sodium.

Experiment #4 was designed to eliminate contamination from the silicon carbide tube (described in Section 7.3) via the use of a titanium foil liner on the inner diameter of the reaction tube.

This experiment was successful in producing titanium but was not ideal in two respects. Firstly, the sodium flow was set at a level which introduced almost double the stoichiometric amount. Although this should produce greater yields of titanium, it also resulted in considerable excess free sodium being deposited throughout the reaction chamber, including the hot end of the product collection tube. Secondly, although

the torch was operated at reduced power (23 kW) the titanium liner had been melted in certain locations. This made it difficult to differentiate between reaction product and melted liner. This is felt to be due to the lack of efficient heat transfer between the liner and the silicon carbide tube wall. The heat transfer is predominantly by radiation, and the emissivity of the shiny titanium surface was low, thereby causing it to heat rapidly to the melting point. This problem could be overcome in future work by using fully adhered metallic coatings on a ceramic tube, such as those achieved by plasma spraying.

Experiment #5 was similar in most respects to #2 except for the substitution of a graphite collection tube instead of silicon carbide. Experiment #6 incorporated the variation of coinjecting VCl_4 (~10% by volume) with the TiCl_4 , in order to test the in situ formation of refractory metal alloys. In both of these experimental runs the deposition of product along the length of the reaction tube was similar in character to that observed in experiment #2. The chemical nature of the products is discussed in Section 3.

3. PRODUCT EVALUATION

a. Experiment #1

The metallic-looking product from this experiment, shown in Figure 11, was subjected to Scanning Electron and Energy Dispersive X-ray Microscopy (SEM and EDXA), Figure 15. The EDXA result was essentially the same for all locations on the specimen surface, and showed the material to be mainly titanium with low levels (~1%) of silicon and chlorine impurity. This was true for both the black and the lustrous areas, but it should be remembered that the EDXA technique will not detect elements with a lower atomic number than fluorine. The black surface contamination may, therefore, be due to the presence of a non-metal species such as carbon, oxygen or nitrogen.

The presence of chlorine impurity clearly demonstrates either the reduction of TiCl_4 to titanium was not complete or that the co-products were not effectively separated. The former possibility is consistent with the thermochemical equilibrium calculations of Section 5.0. The silicon impurity was derived from the silicon carbide reaction tube wall. Information from the supplier (Carborundum) indicates that metallic silicon is used as a binding agent in the fabrication of silicon carbide tubes. It was apparent from an inspection of the outer wall that this free silicon had flowed out of the tube in regions where the temperature exceeded the melting point of silicon, and had thereby contaminated the titanium product. Powder x-ray diffraction analysis showed that parts of the product even included titanium/silicon intermetallic compounds, TiSi and TiSi_2 , in areas of high silicon concentration.

The crystalline, water-soluble, compounds found on the injection flange and in the downstream portions of the reaction chamber were found by x-ray diffraction to contain titanium subchlorides and ammonium chloride, NH_4Cl . The presence of nitrogen is believed to have been caused by air in-leakage around the injection flange due to the destruction of the silicon 'O' ring by unreacted TiCl_4 .

b. Experiment #2

SEM/EDXA analyses of the metallic product from the sodium reduction run are shown in Figures 16 and 17. The crystalline growth in Figure 17 is not a separate type of material but appears to be growing from a larger mass similar to that shown in Figure 16. The EDXA results show that the only detectable impurity with atomic number greater than 9 was silicon from the reaction tube. The silicon was present in higher concentration than for the first experiment, presumably due to the longer duration of the run. Surface silicon concentrations in Figures 16 and 17 vary from 14 wt% (crystalline areas) to 18 wt% (Figure 17, area scan), but it should be remembered that the EDXA technique cannot determine bulk concentrations. The silicon contamination may be greatest on the surface.

The most significant finding of these analytical results is the absence of both sodium and chlorine from the metallic product. Clearly the additional reducing action of sodium, compared to experiment #1, was instrumental in totally converting the $TiCl_4$ into a chlorine-free product. Also the absence of sodium indicates that the ability to separate the co-products, titanium and sodium chloride, was effectively demonstrated.

c. Experiment #5

The use of a graphite reaction tube for this experiment was successful in eliminating the silicon impurity found in experiments 1 and 2. Figures 18 and 19 show typical SEM/EDXA results of the product from this run. Clearly there is no detectable silicon, sodium or chlorine impurity although X-ray diffraction indicated the presence of titanium nitride, presumably caused by air in-leakage during the experiment. Figure 18 shows material which grew on the graphite wall within a distance of 0.025m (1") from the injection nozzle, whereas Figure 19 depicts powder which was loosely adhering to the first 0.15m (6") of the reaction tube. This powder is of an irregular shape with a mean particle diameter of the order of 50-80 μm . The product was lustrous and clean in appearance and the SEM photographs show very little ultrafine or foreign material adhering to the surface.

As in all the experiments, a certain amount of ultrafine, black-colored powder was entrained in the solidified sodium chloride which collected in the cooler, downstream parts of the apparatus. After the sodium chloride was removed by washing, this powder was analyzed by SEM/EDXA, Figure 20, and shown to contain trace levels of chlorine and calcium impurity. Its ultrafine nature, however, will make this material highly susceptible to non-metallic contamination, particularly after undergoing a leaching process. In addition, X-ray diffraction showed the powder to be amorphous in character.

d. Experiment #6

The deposition of metallic-looking product in this Ti/V coinjection experiment was similar in character to the previous runs when viewed on a macroscopic level. Detailed SEM/EDXA analysis, however, revealed some interesting microscopic features which broadly indicated that while metallic titanium and vanadium were successfully produced in the plasma, the collection conditions on the reactor wall were such that different titanium to vanadium ratios were found, depending on location. Unfortunately, a detailed examination and analysis of the entire reaction tube was beyond the scope of the present contract, but the details described here at least point to the importance of collection temperature on product form and composition. For instance, Figure 21 depicts an area in which the product was largely titanium with only a trace of vanadium (the x-ray peak marked "Ti, V" is caused by a combination of the weaker of the two titanium peaks and the stronger of the two vanadium peaks). On the other hand Figure 22 shows an area of largely vanadium-rich substrate with isolated titanium-rich crystals deposited on the surface. Determination of whether these crystals are metallic titanium or titanium nitride would require further analysis which was not strictly justified for a preliminary 'first-attempt' experiment.

It appears from these observations that it may be necessary to collect the product as a liquid in order to successfully form a homogeneous alloy whereas deposition and growth in the solid state is feasible for the one component, titanium system.

Section VIII

DISCUSSION

1. PROCESS FEASIBILITY

The principal conclusion to be drawn from this theoretical, economic and experimental program is that the sodium reduction of titanium tetrachloride is well suited to a plasma treatment which could result in the process becoming continuous. The main results from these studies which prompt such a conclusion are as follows. The thermochemical calculations indicated that in the temperature range 1700-2200 K the yield of pure titanium should be close to 100% with little or no formation of subchlorides particularly if a slight excess of sodium is employed. Experimental verification tests supported this, and provided definitive evidence that in situ removal of sodium chloride coproduct could be achieved in this temperature range. Further, we believe that the process can be directed towards the collection of solid titanium powder or the direct production of liquid titanium. The latter mode will probably be necessary for the direct synthesis of titanium alloys. Finally, a detailed economic analysis, based on the most conservative of assumptions, concluded that production costs would be at least competitive with existing conventional Kroll or Hunter processes.

2. REACTOR DESIGN

The results from the experimental runs, although preliminary in nature, have already been used to influence design philosophy for a large-scale plasma reactor. The design for the Westinghouse silicon production pilot plant (forerunner of the titanium project) was based on an almost horizontally oriented tubular reactor, with the metallic product being formed and collected as a liquid.⁽¹³⁾ Contamination of the silicon via contact with the reactor wall was to be avoided by means

of a solid silicon skull, formed in-situ, along which molten silicon would flow.

The results obtained so far with titanium suggest that a full-scale plasma reactor might operate with the titanium product always in the solid state. A conceptual design for a vertically oriented reactor is shown in Figure 23. The reactants, typically $TiCl_4$ and Na, are injected near the top of a vertical, cylindrical chamber, downwards into the arc-heated plasma stream (typically an argon/hydrogen mixture of molar ratio $Ar:H_2 = 1:4$). The wall of this chamber will be comprised of a water-cooled outer wall with a solid titanium metal liner and possibly some refractory in between for thermal insulation. During reactor operation, the temperature of this wall is always maintained higher than the vapor point of NaCl ($1385^\circ C$) but lower than the melting point of titanium ($1675^\circ C$), that is, within a $190^\circ C$ temperature window.

We have demonstrated that, under these conditions, the titanium product deposits on the wall in the form of loosely adhering dendrites. While these solid dendrites could be removed mechanically, in a prolonged run it is expected that they will grow until their tips are at a temperature above the melting point of titanium. This will occur because they penetrate the wall boundary layer and are thereby exposed to the hot plasma stream. In addition, the narrower channel will also result in a thinner boundary layer.

These molten dendrite tips will be blown off by the hot plasma stream, and subsequently quenched in the lower, cooler ($1385-1675^\circ C$) parts of the chamber, or will simply fall gravitationally. In this way, the solid product collected in the base of the crucible will be comprised of solidified globules, crystals, granules and larger diameter powders. This type of product is suitable for sieving into the various mesh sizes required for different applications.

The same basic configuration of reactor could be used if the process was to be aimed at the collection of liquid titanium. A different refractory wall material would be required in order that higher

collector temperatures could be achieved, and a protective skull of solid titanium would maintain purity in the final product.

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Curve 724401-A

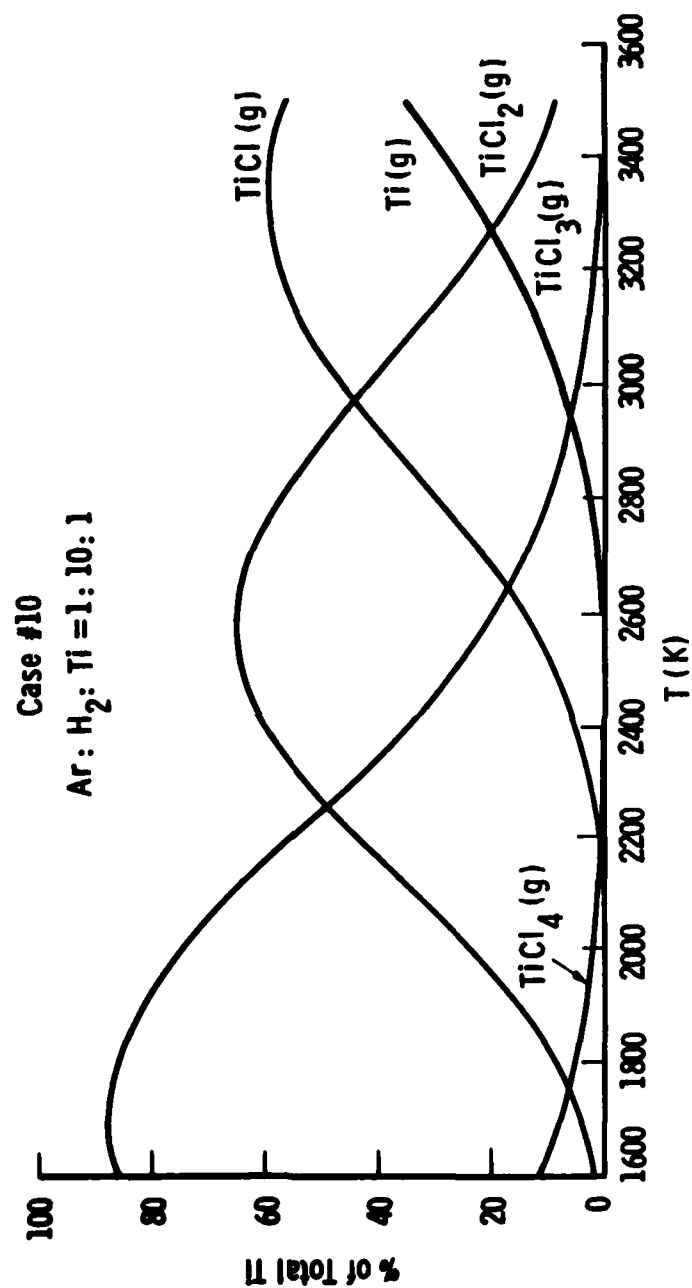


Fig. 1—Thermochemical equilibrium for the hydrogen reduction of TiCl₄

Curve 724393-A

Case #18

$H_2: Ar: Na: Ti: Cl = 13:4: 3: 35: 4: 1: 4$

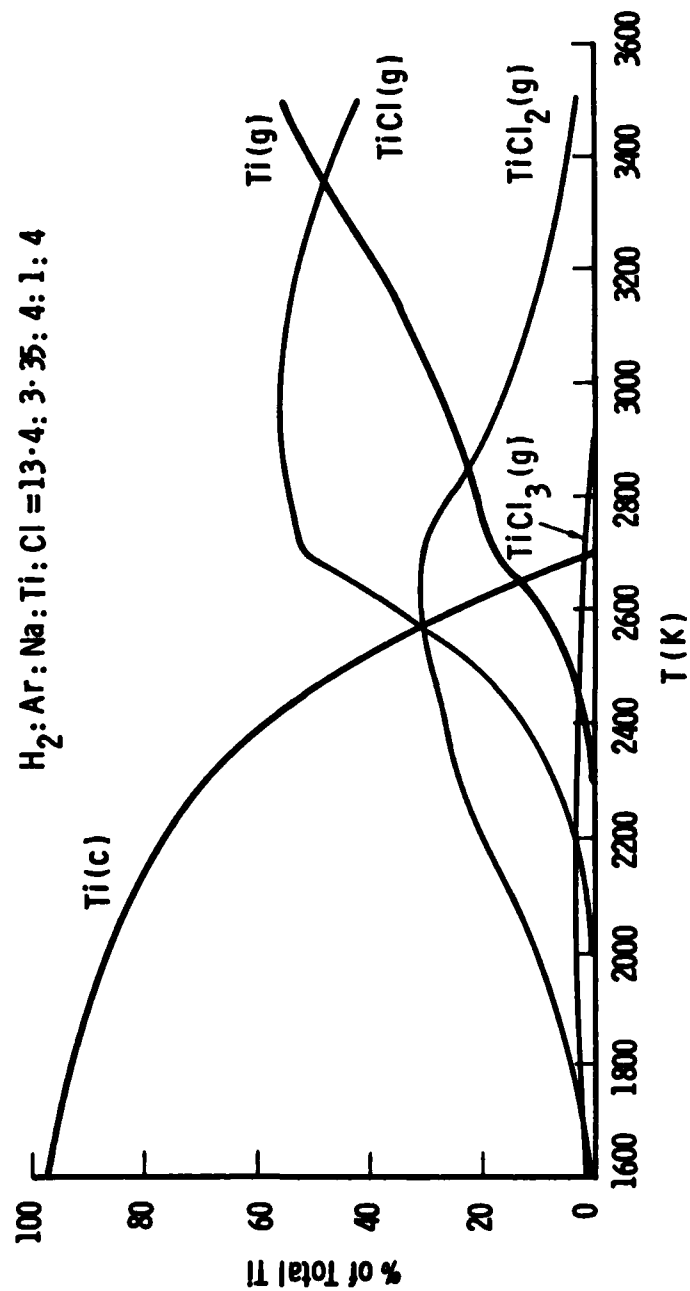


Fig. 2--Thermochemical equilibrium for the sodium/hydrogen reduction of $TiCl_4$

Curve 724395-A

Case #19

$H_2 : Ar : Na : Ti : Cl = 13.4 : 3 : 35 : 8 : 1 : 4$

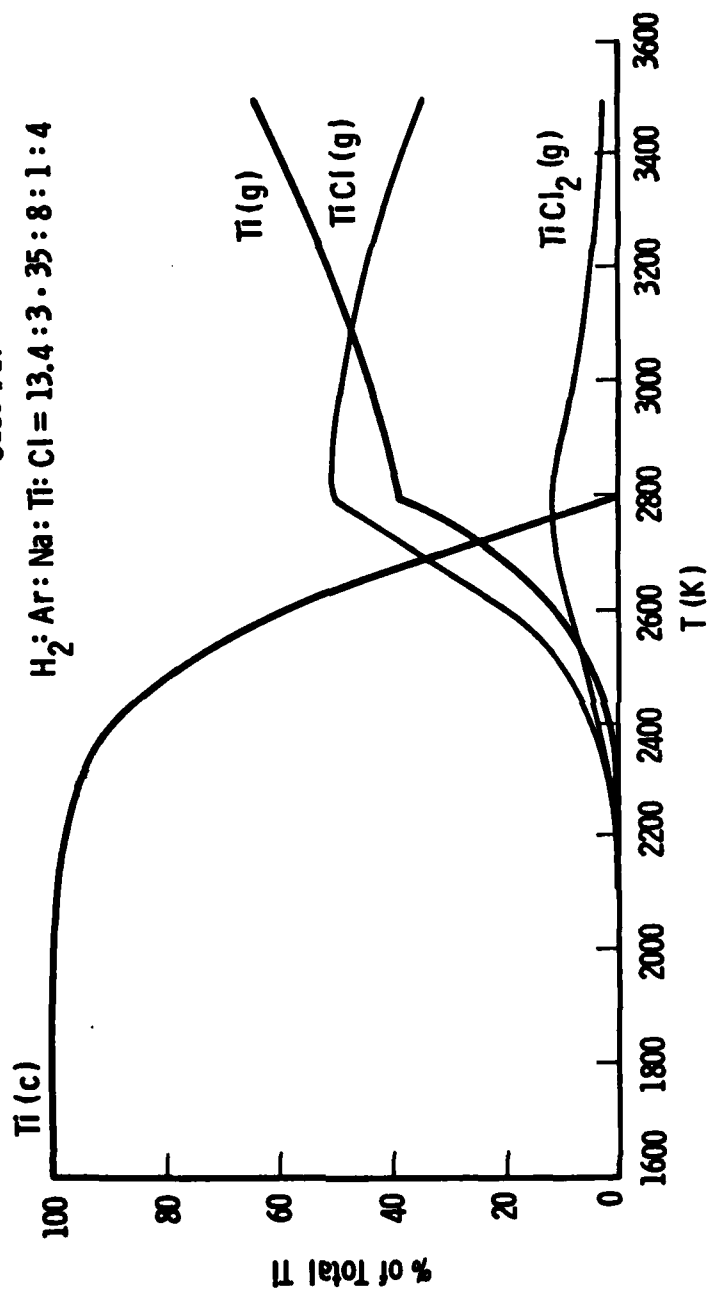


Fig. 3—Thermochemical equilibrium for the sodium/hydrogen reduction of $TiCl_4$ (excess sodium)

Dwg. 7733A85

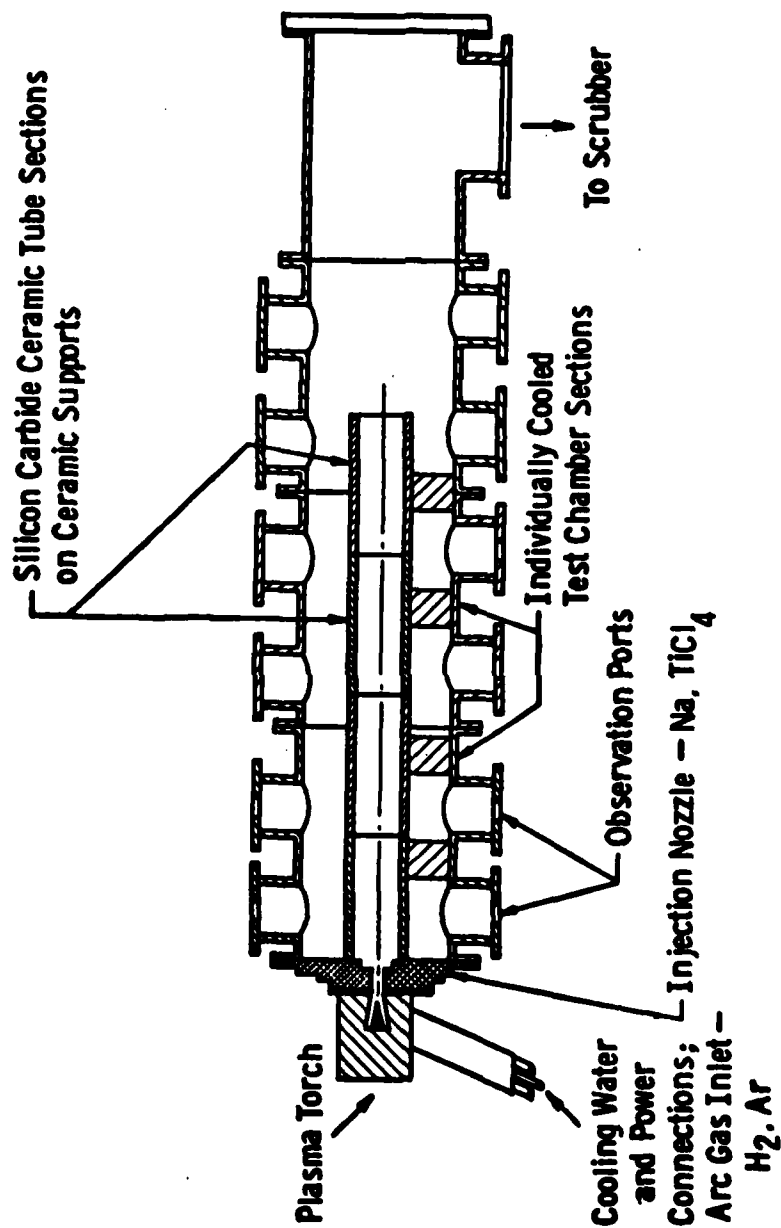


Fig. 4 -- Assembly drawing of test apparatus

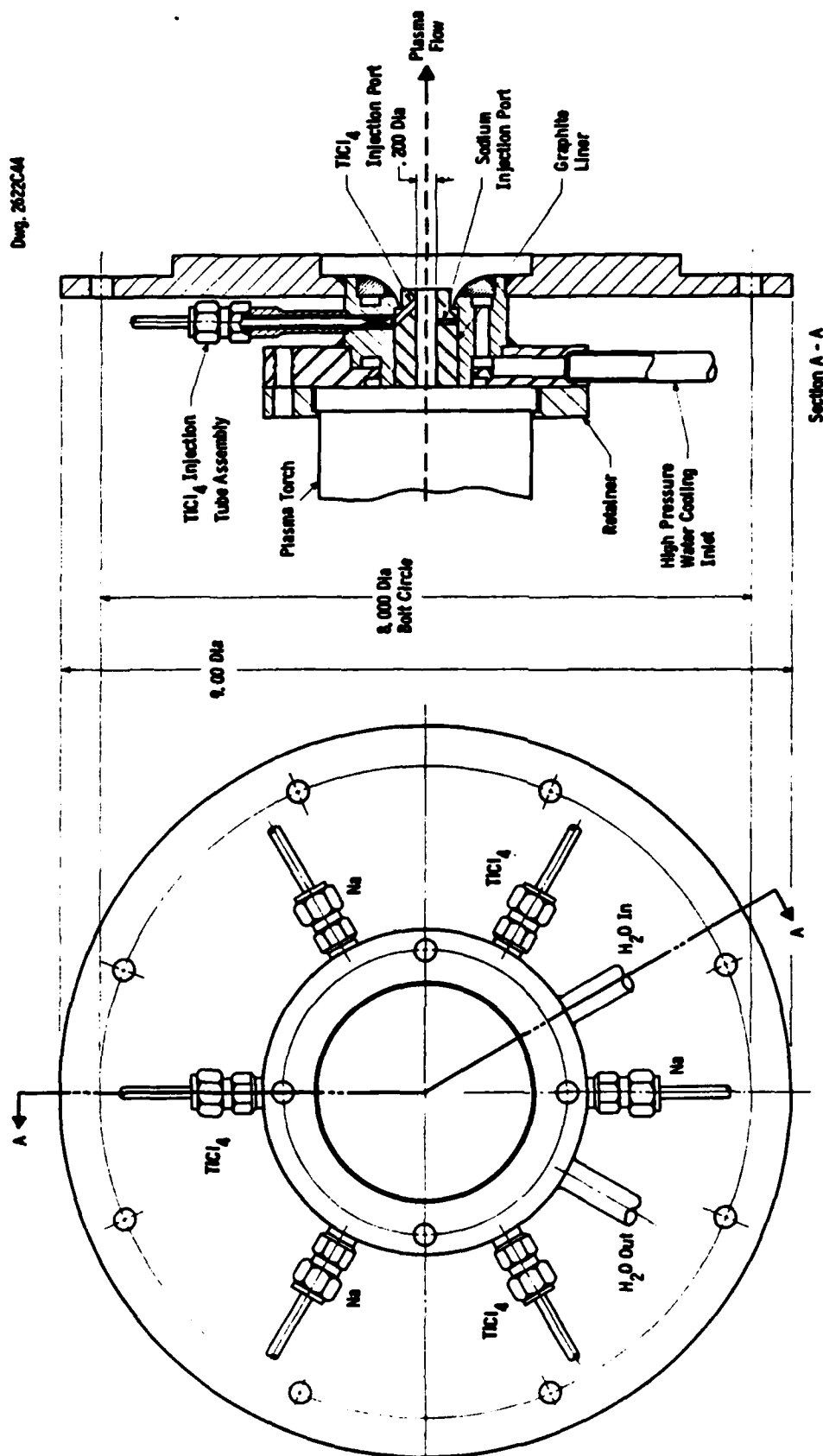


Fig. 5—Reactant Injection nozzle



Figure 6 -- Laboratory-scale 40 kW plasma reactor used to produce high quality titanium.

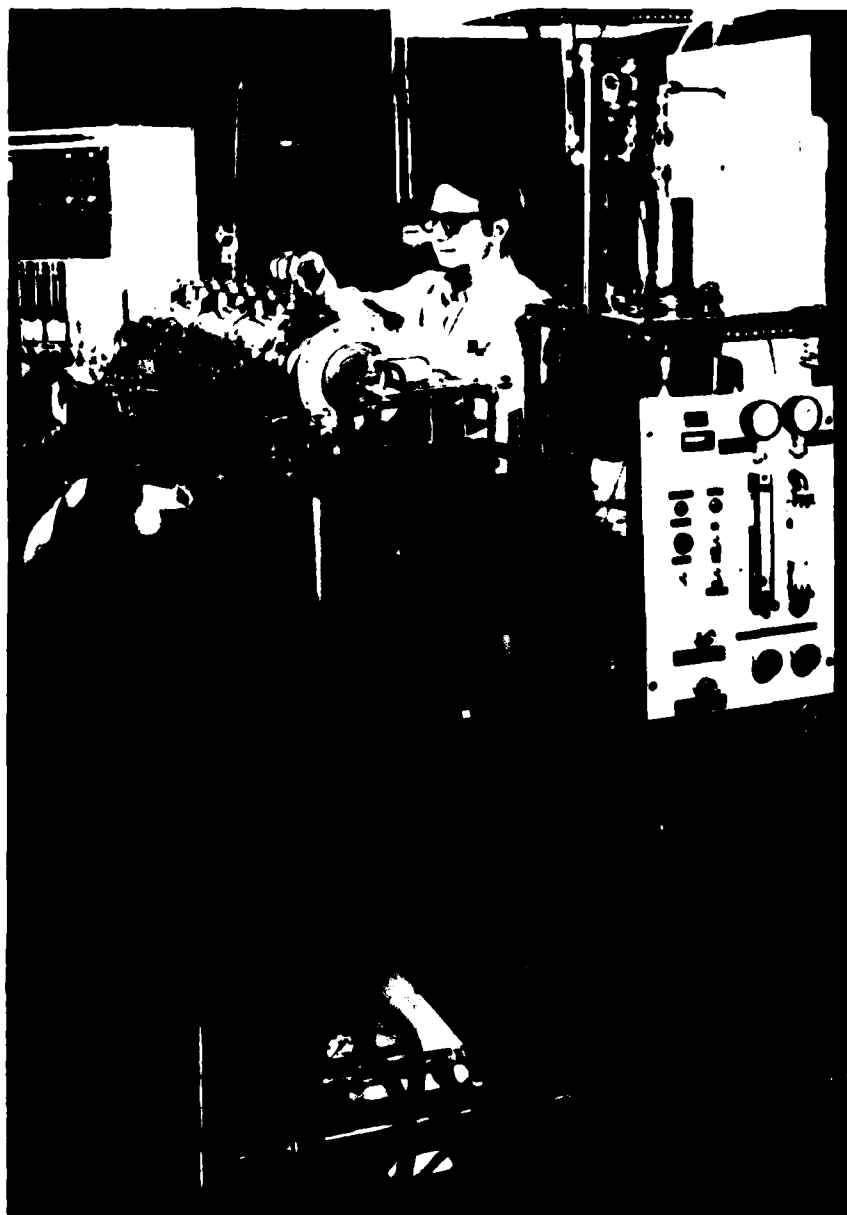


Figure 7. Photograph of Experimental Apparatus

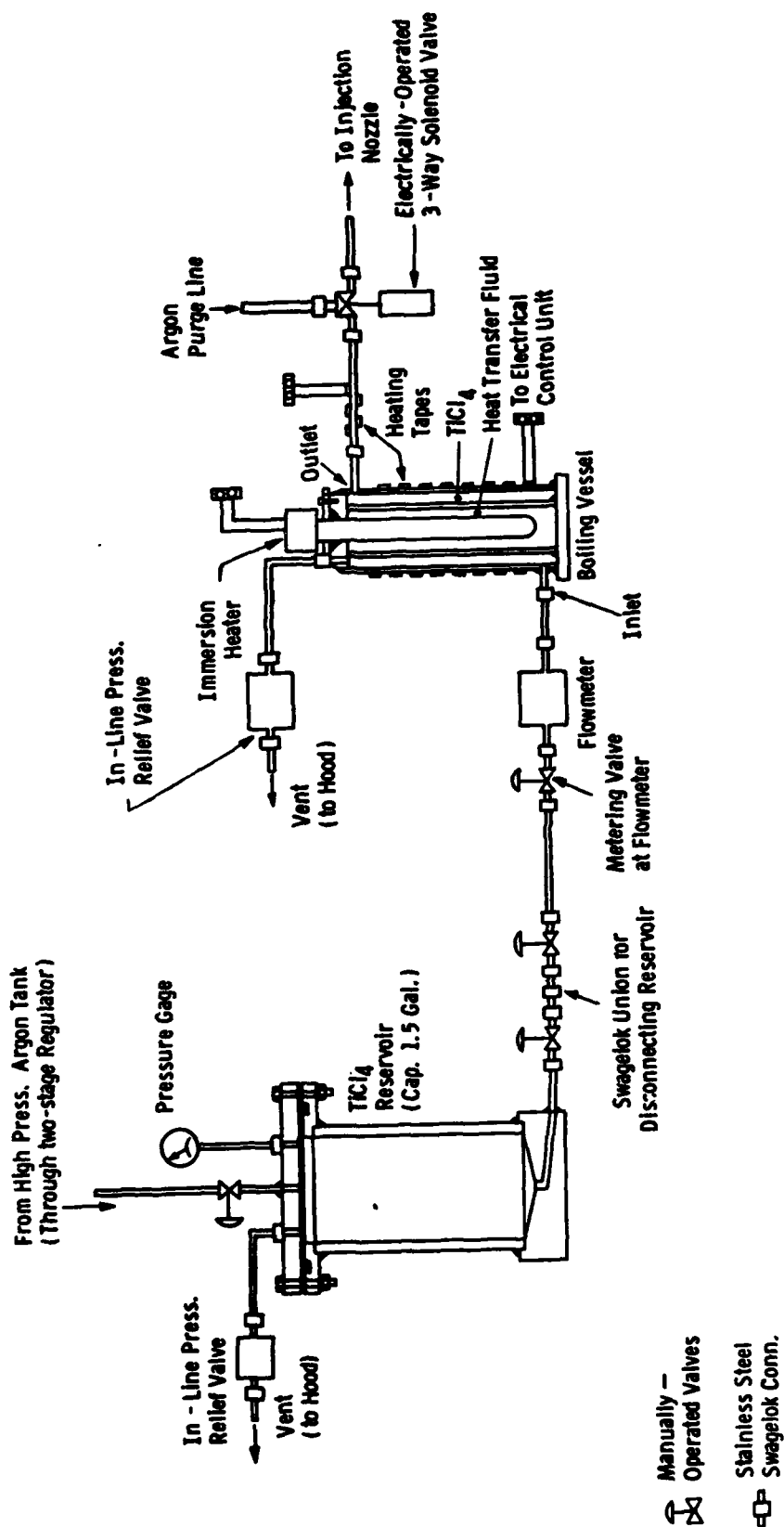


Fig. 8-Schematic of the TiCl₄ supply system



Figure 9. Photograph of the Sodium Storage Tank



Figure 10. Plasma/Reactants Injection Flange After Experiment #1

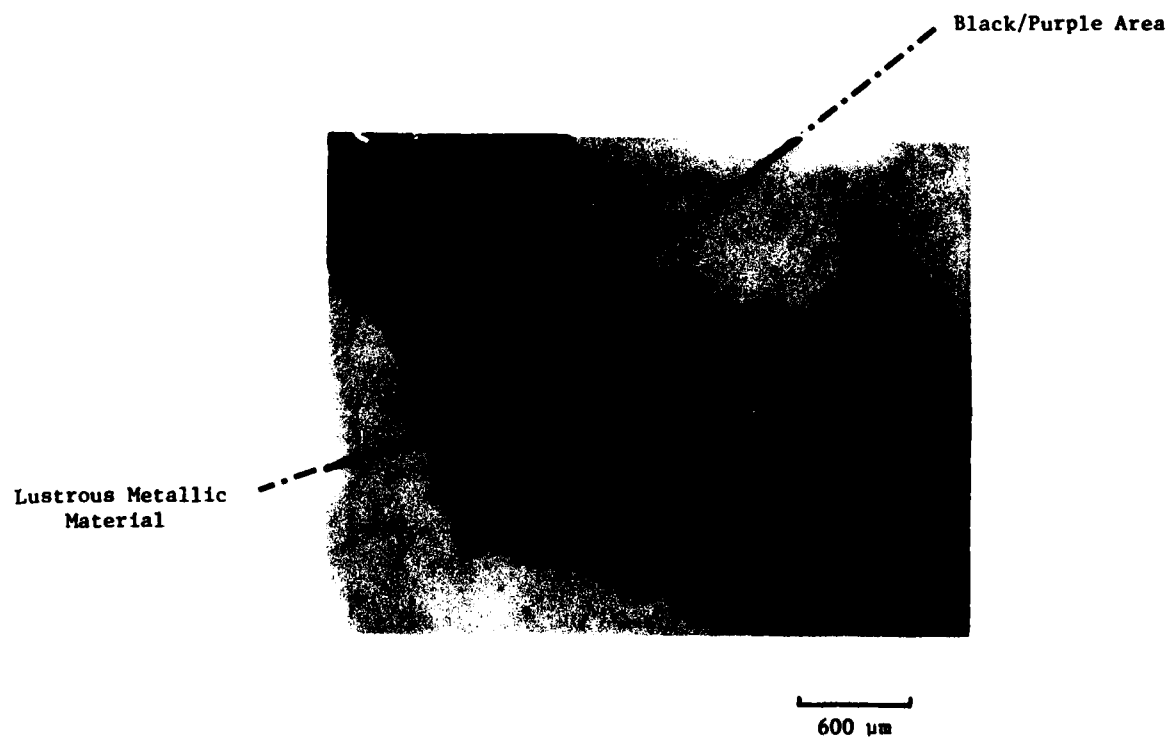
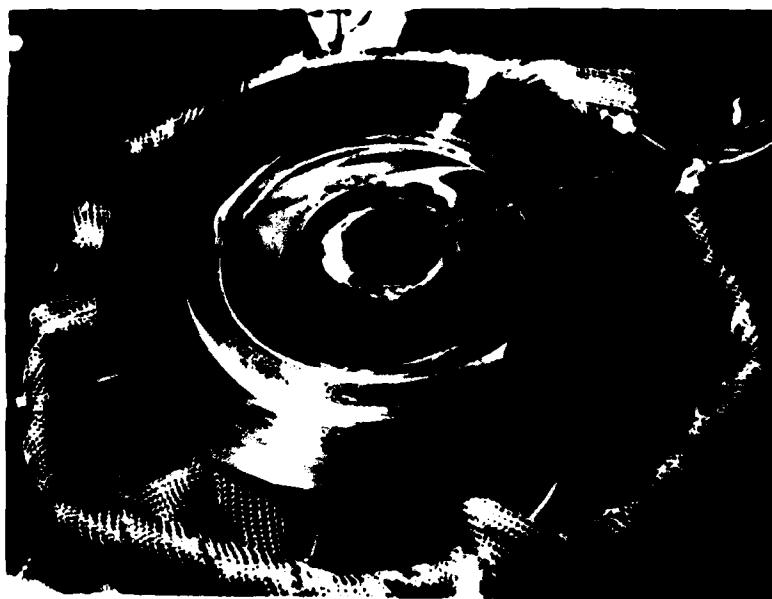


Figure 11. Optical Photograph of Titanium Product from Experiment #1



Titanium Powder

Figure 12. Plasma/Reactants Injection Flange after Experiment #2

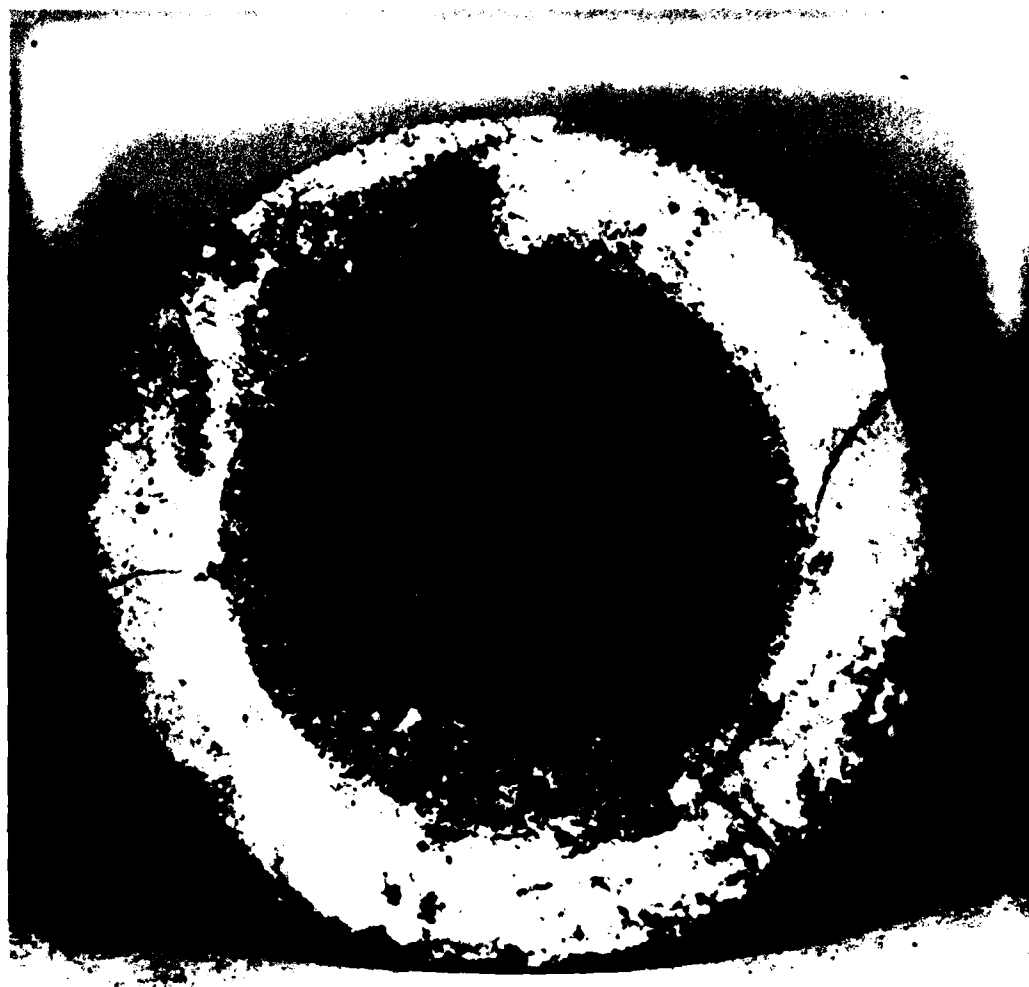


Figure 13. Silicon Carbide Reaction Tube (Hot End) after Experiment #2



Figure 14. Metallic Titanium Product from Experiment #2 (X100)



100 μm

PR= 4055 31SEP 0 INT
 U=4096 H=10KEV 1-10 80=10KEV 10

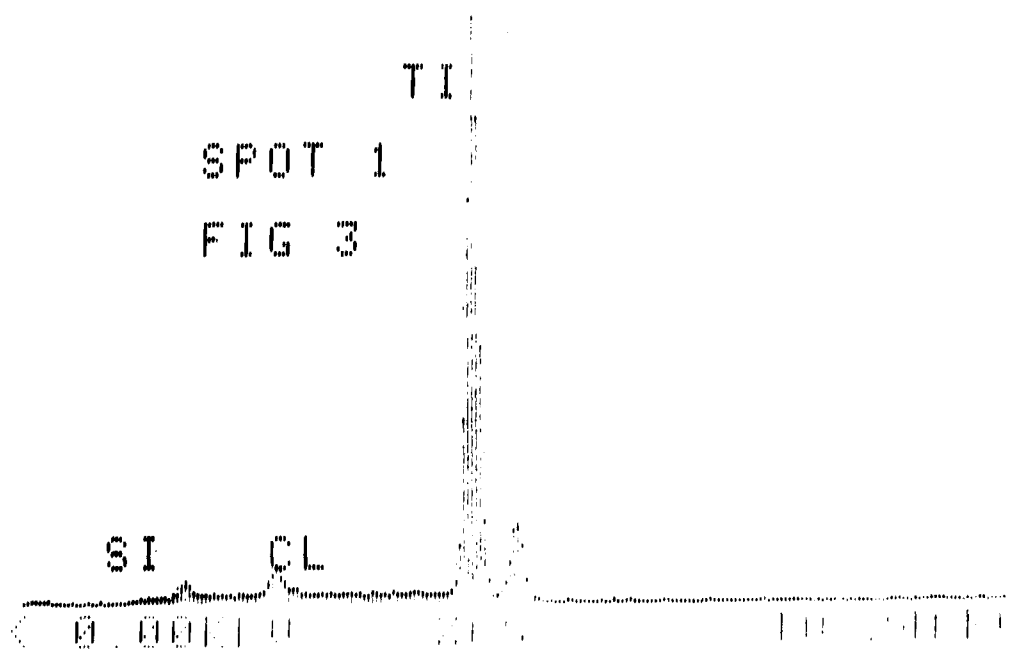
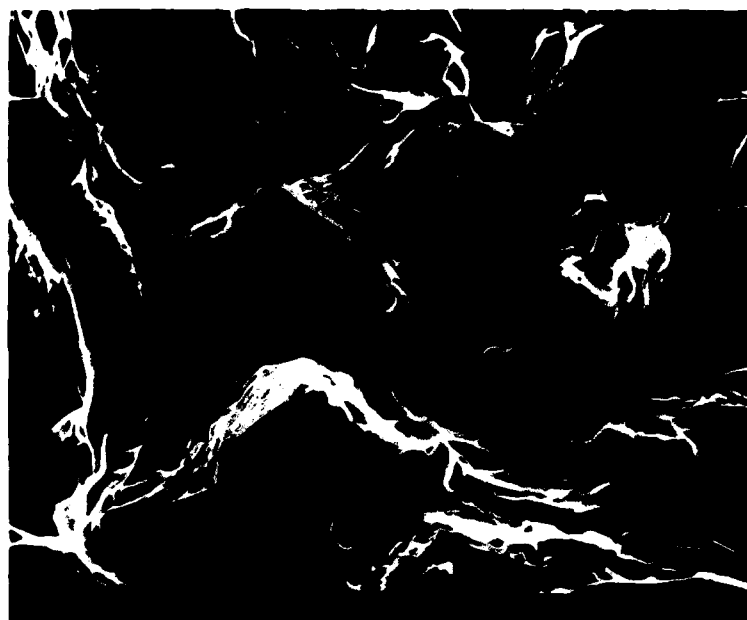


Figure 15. SEM/EDXA Analysis of Product from Experiment #1



PR= S 30SEC 0 INT
 U=2048 H=10KEV 1:30 AQ=10KEV 10

FIG. 4,
 AREA SCAN

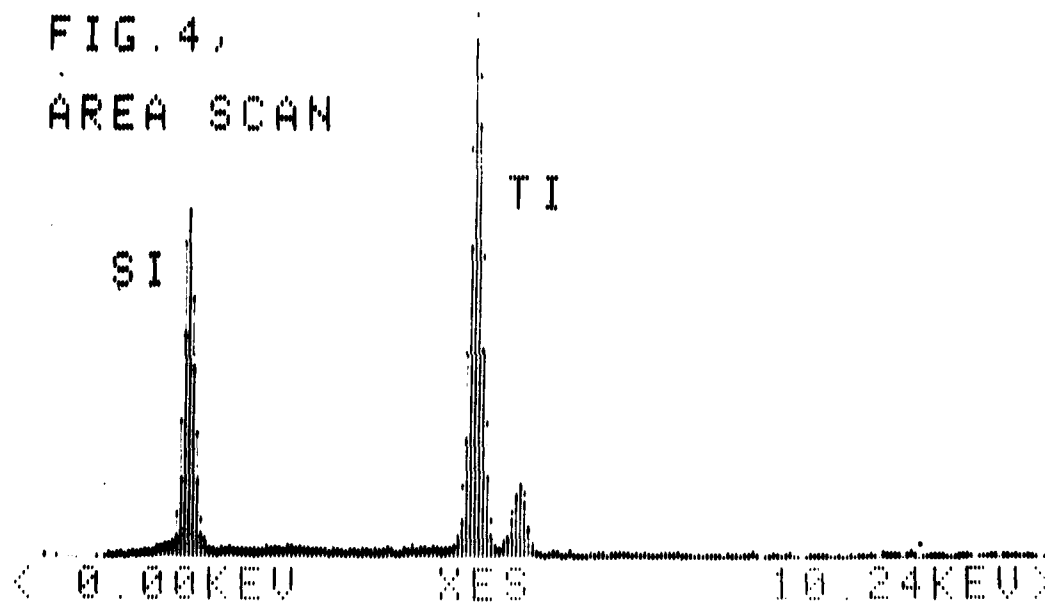


Figure 16. SEM/EDXA Analysis of Bulk Product from Experiment 2



PR= S 17SEC 0 INT
U=4096 H=10KEV 1:10 AD=10KEV 10

FIG. 2, SPOT 1

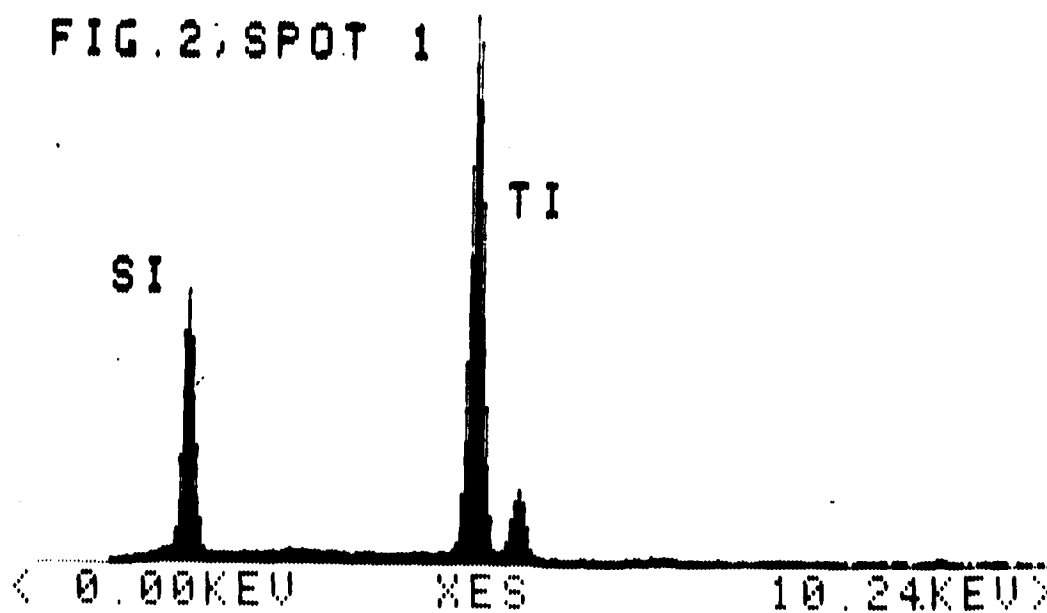
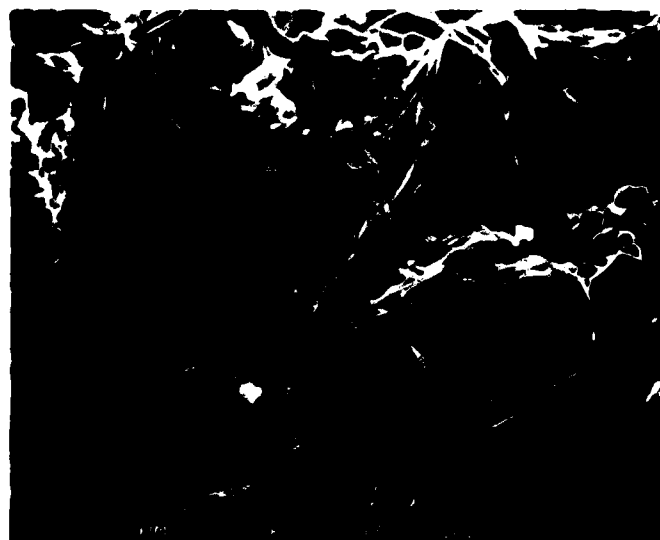


Figure 17. SEM/EDXA Analysis of Crystalline Product from Experiment #2



PR= S 29SEC 0 INT
U=2048 H=10KEV 1:30 AQ=10KEV 10

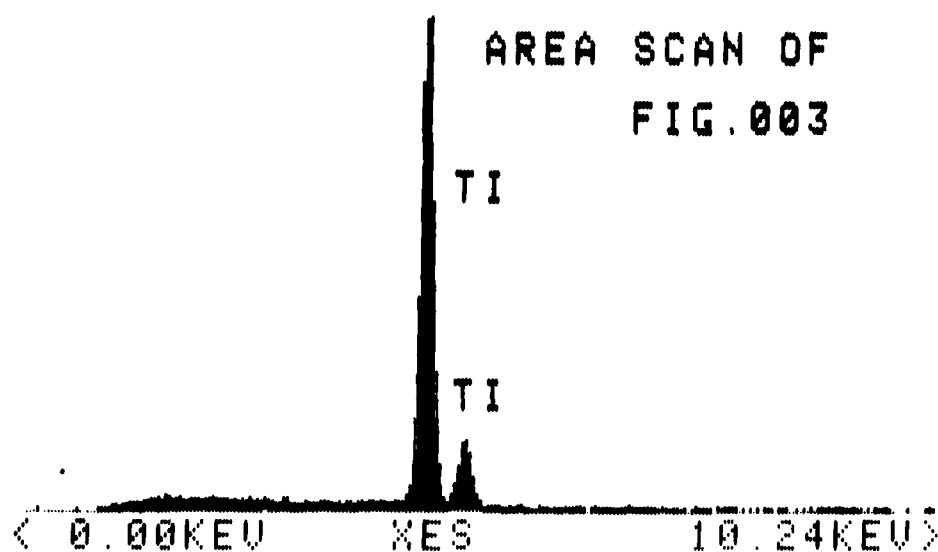


Figure 18. SEM/EDXA analysis of product from Experiment #5. (From first inch of graphite tube)

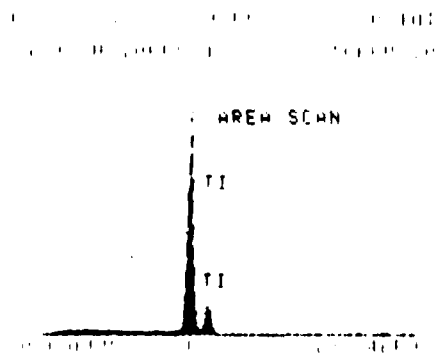
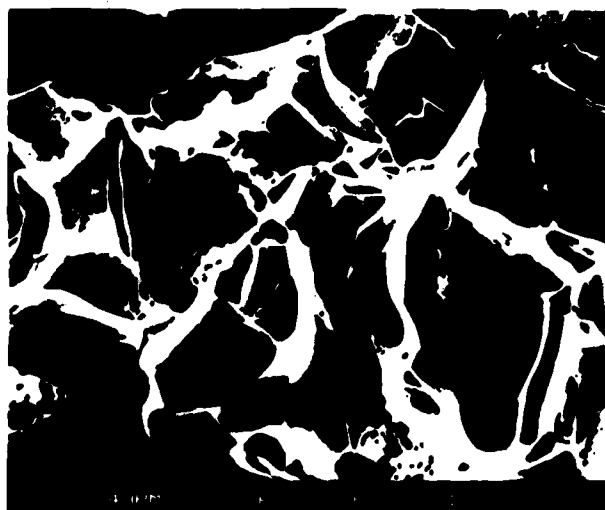
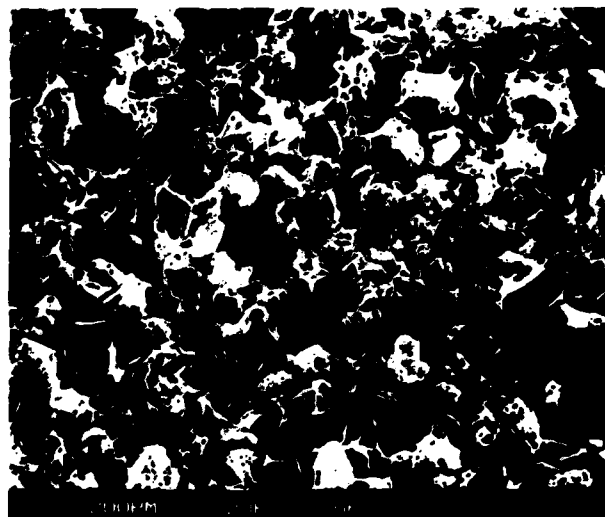
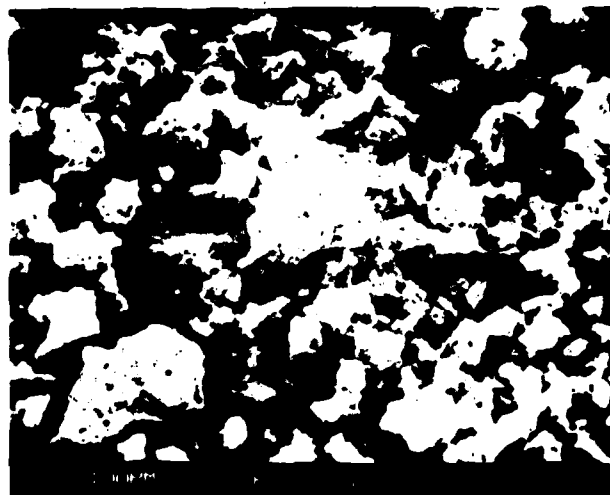


Figure 19. SEM/EDXA analysis of product from Experiment #5. (From first 6" of reaction tube)



PP= S 24SEC 0 INT
 U=4096 H=10KEV 1:30 AQ=10KEV 10

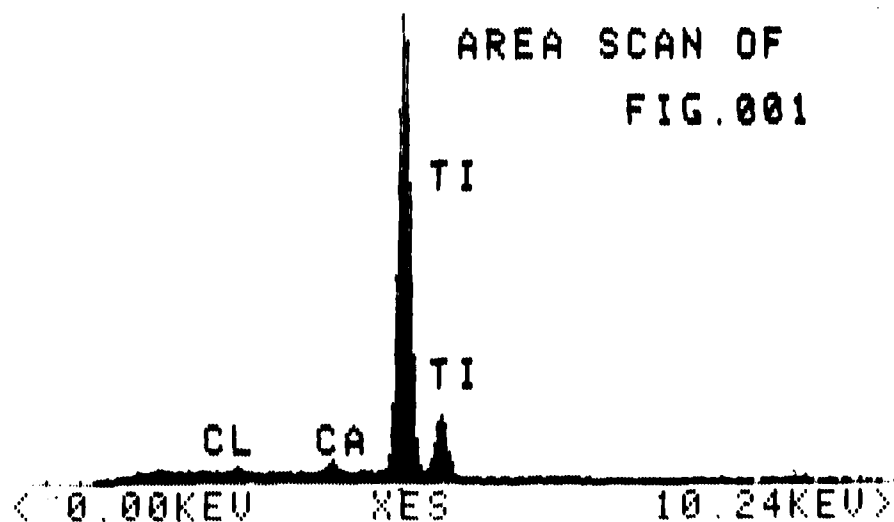


Figure 20. SEM/EDXA analysis of the ultrafine reaction product after leaching away NaCl and sodium - Experiment #5.



#1 Z=00
 PR= S 23SEC 0 INT
 U=2048 H=10KEV 4:40 AQ=10KEV 40

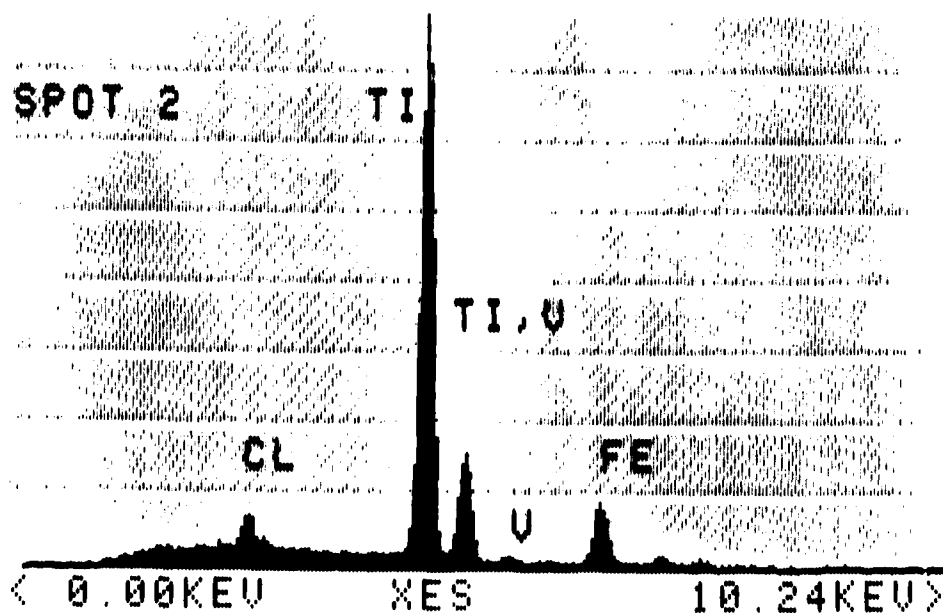


Figure 21. SEM/EDXA analysis of product from Experiment #6.
 Titanium-rich area.



Figure 22. SEM/EDXA analysis of product from Experiment #6. Shows vanadium-rich substrate with titanium-rich crystals.

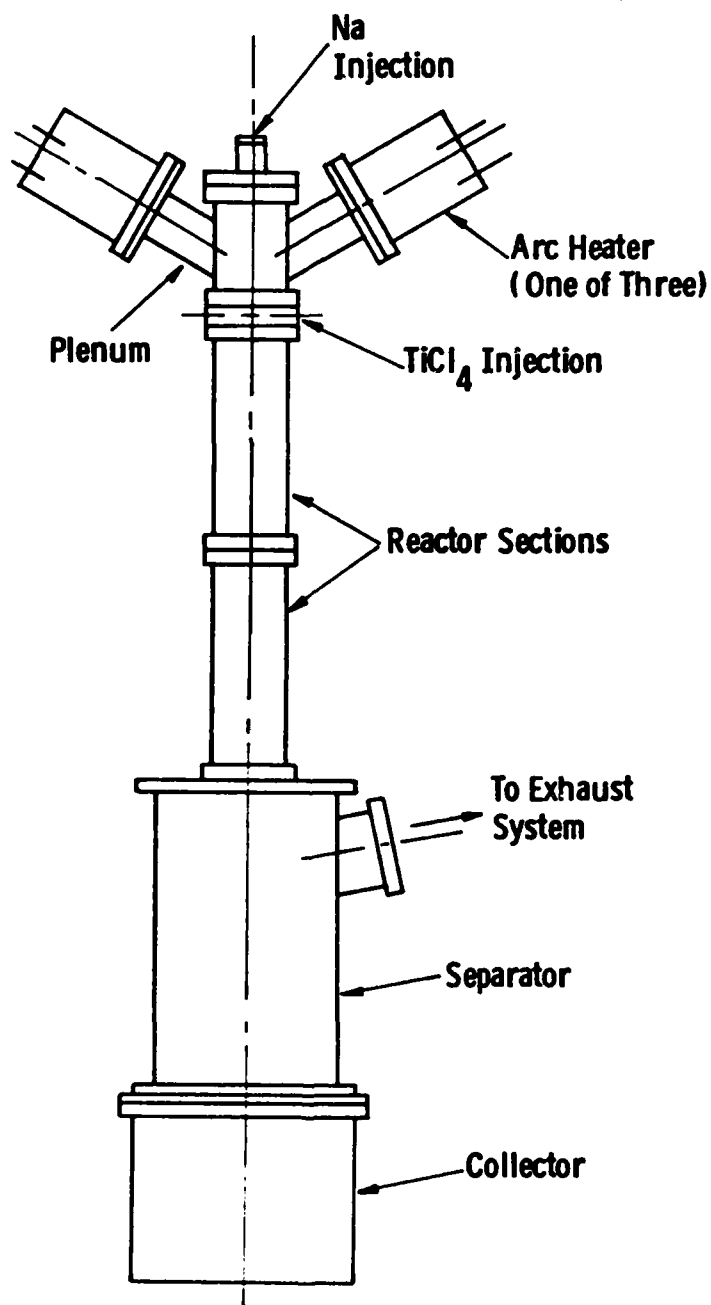


Fig. 23—Plasma reactor for titanium production