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# Coreduction of $TiCl_4$ , $AlCl_3$ , and $VCl_4$ To Produce Titanium Alloy Sponge

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UNITED STATES DEPARTMENT OF THE INTERIOR



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**UNITED STATES DEPARTMENT OF THE INTERIOR  
Donald Paul Hodel, Secretary**

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

Å	angstrom	lb/(ft <sup>2</sup> ·h)	pound per square foot per hour
°C	degree Celsius		
cfm	cubic foot per minute	min	minute
cm	centimeter	mL	milliliter
ft <sup>3</sup>	cubic foot	mL/min	milliliter per minute
g	gram	mm	millimeter
gal	gallon	µm	micrometer
g/L	gram per liter	pct	percent
h	hour	ppm	part per million
in	inch	psig	pound per square inch, gage
kW	kilowatt	vol pct	volume percent
lb	pound	wt pct	weight percent

# COREDUCATION OF $TiCl_4$ , $AlCl_3$ , AND $VCl_4$ TO PRODUCE TITANIUM ALLOY SPONGE

By Davis E. Traut,<sup>1</sup> G. J. Slavens,<sup>2</sup>  
and Dennis A. Hansen<sup>2</sup>

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## ABSTRACT

$TiCl_4$ ,  $AlCl_3$ , and  $VCl_4$  were coreduced simultaneously via a Kroll-type magnesium reduction to form an alloy sponge as part of a research effort by the Bureau of Mines to produce titanium alloy powder. Reduction temperatures of 750°, 850°, and 950° C, a range of chloride feed rates from 34 to 152 lb/(ft<sup>2</sup>·h), and crucible diameters of 7-3/4 and 10-1/4 in were tested. Microprobe analyses using a 40- $\mu$ m-diam spot showed no effect on alloy microhomogeneity (distribution of Al and V in the Ti, considered critical as a powder property), due to changes in process variables within these ranges. Statistical analysis of these data for alloy sponge indicated greater variation in the chemical composition (Al and V) than that found in commercial Ti-6Al-4V plate or Plasma Rotating Electrode Process (PREP) powder. Therefore, a one-step approach to powder, such as grinding the Ti alloy sponge, would not produce a powder product of acceptable chemical homogeneity. An approach that homogenized the sponge, such as with a melting step, would produce an acceptable powder product with respect to chemical homogeneity.

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## INTRODUCTION

Titanium is a lightweight, high-strength-to-weight-ratio, noncorrosive metal that is used extensively in the aircraft, chemical, and energy industries. However, high manufacturing costs, especially machine costs and waste, prevent greater use of this abundant material. Powder metallurgy approaches such as near-net-shape technology might provide a more economical route to final Ti alloy parts. The Bureau of Mines is investigating several methods to produce Ti alloy powder, one of which involves starting with a Ti alloy sponge. This report discusses the effects of operating conditions on production of Ti alloy sponge along with the evaluation of the sponge product.

Industry has commonly used the Kroll process (magnesium reduction) for the production of Ti sponge since the process was developed in the early 1950's (1-3).<sup>3</sup> An analogous coreduction of the chlorides of Ti and alloying metals was investigated on a pioneering basis by Henry (4) for a Ti-6Al-4V alloy. Others (5-7) have also proved the feasibility of the coreduction approach for alloys of Ti-Mo, Ti-W, etc. Sodium coreduction routes have also been suggested (8-9).

The important possible advantage in the coreduction approach as related to powder production is the elimination of the master alloy addition step and subsequent vacuum arc melts. This allows, as a simple approach to powder production, the possible comminution of the alloy sponge directly to powder, which might be a tremendous cost savings (10-11). The use of coreduction for manufacture of master alloys of Ti for systems with large amounts of refractory metals is also seen as an advantage (12). But the current industrial practice has up to three vacuum arc melting steps that serve both to homogenize the alloying metals with the Ti and to purify the Ti alloy by removing residual chloride (Cl) and magnesium (Mg) left from the reduction step. Therefore

the homogeneity of the coreduced alloy sponge and conditions to improve this homogeneity in order to circumvent the lack of these melting steps are addressed in this paper. The lack of a purification step is left as an important objective for a yet-to-be developed powder production method.

The homogeneity of the final powder product is considered critical to final part integrity (13). Therefore, the homogeneity in the Ti alloy sponge, as intermediate homogenizing steps might prove impractical or uneconomical, would also be critical. Discussions on the quantification of homogeneity have not produced a universal definition (14). For previous work (4) homogeneity was determined on a "macro" scale, i.e., chunks weighing several grams were taken from different areas of the sponge and analyzed in toto for distribution of Ti, Al, and V. However, for powder work each chunk from the sponge may be ground or melted to provide many powder particles, and each of these particles should have the desired (e.g., Ti-6Al-4V) composition to ensure final part integrity. A discussion of homogeneity (14) suggested that the desired composition in a size range of 10 to 100 Å would be considered homogeneous, while in the 1- to 2- $\mu$ m (10,000- to 20,000-Å) range, it would not.

Poor homogeneity or uniformity of composition on a macro scale was found to be a problem in a previous study (4). That study used a TiCl<sub>4</sub>-VCl<sub>4</sub> solution feed while AlCl<sub>3</sub> was separately fed as a solid. Problems with plugging were experienced with the AlCl<sub>3</sub> feed equipment; there were also problems with calibration and coordination of the two-feed apparatus. It was suggested (4) that dissolving the solid AlCl<sub>3</sub> in TiCl<sub>4</sub> and VCl<sub>4</sub> at elevated temperature and pressure could improve this uniformity. The solubility of AlCl<sub>3</sub> in TiCl<sub>4</sub> had been previously reported (15-18). However, no solubility data were found for AlCl<sub>3</sub> in the ternary system of TiCl<sub>4</sub> and VCl<sub>4</sub>. A companion research study with this effort defined such a solubility diagram (19).

<sup>3</sup>Underlined numbers in parentheses refer to items in the list of references at the end of this report.

Therefore the objectives of the research reported here were to produce small (14-lb) batches of Ti alloy sponge under various operating conditions using a homogeneous feed solution and to determine the homogeneity of that sponge

with respect to the even distribution of V and Al in the Ti on a micro scale. The emphasis of the project was producing Ti alloy sponge suitable for further processing to powder for use in powder metallurgy.

#### ACKNOWLEDGMENTS

The authors are grateful to R. R. Esau, physical science technician at the Albany Research Center, who operated the sponge pilot plane and prepared samples for analysis. In addition, they thank P. A. Romans and J. C. Watson, supervisory research physicists at the Bureau of Mines

Albany Research Center, for many helpful discussions and suggestions on the analysis of homogeneity, in particular the use of the microprobe, and M. L. Boucher, geologist, Twin Cities Research Center, for microprobe analyses of the sponge samples.

#### MATERIALS

The titanium tetrachloride ( $TiCl_4$ ) used in this study was obtained from a major Ti sponge producer in 55-gal drums (approximately 800 lb). Vanadium tetrachloride ( $VCl_4$ ) was obtained in 100-lb cylinders. Aluminum chloride ( $AlCl_3$ ) was obtained as technical-grade material in 100-lb, 15-gal drums. The  $AlCl_3$  contained 1.64 wt pct  $Al_2O_3$ , which was considered insoluble and was filtered out during the feed preparation step. Magnesium was obtained as approximately 2-1/4-in cubic blocks weighing about 300 g. Typical spectrographic impurity analyses of the materials used in this study are shown in table 1.

The original objective of the project was to produce a Ti-6Al-4V alloy sponge (90 wt pct Ti, 6 wt pct Al, and 4 wt pct V); this is the most commonly produced and used alloy. However, early in the study it became evident that  $AlCl_3$  solubility in  $TiCl_4$  and  $VCl_4$  was negligible at room temperature, and it was estimated that the solubility necessary to obtain the Ti-6Al-4V alloy as the end product would require a dissolution temperature of about 160° to 170° C. This range was predicted by preliminary solubility studies. A later, more complete study indicated that 145° C should be adequate (19). However, the filtration tank and feed tank were designed and constructed for safe operation with respect to pressure only up to about 140° C. As the use

of a chloride feed solution corresponding to the Ti-6Al-4V alloy would require fabrication of new vessels and would, in addition, present a greater safety hazard at the higher temperature, it was decided to make up and use a feed solution that would produce a Ti-1Al-4V alloy. The  $AlCl_3$  for this alloy could be dissolved in the  $TiCl_4$ - $VCl_4$  solution at about 115° C. It was felt both at that time and now, after project completion, that the lower Al content would not impact the

TABLE 1. - Impurity analyses for test materials, <sup>1</sup> weight percent

Element	$TiCl_4$	$VCl_4$	$AlCl_3$	Mg
Al.....	<0.002	0.002	>10	<0.01
B.....	<.03	ND	ND	ND
Cu.....	<.003	<.001	<.001	<.003
Fe.....	ND	<.01	<.01	ND
Mg.....	<.001	<.001	<.1	>10
Mn.....	ND	ND	ND	<.1
Ni.....	ND	<.1	<.03	ND
O.....	NA	NA	.77	NA
Pb.....	<.03	ND	ND	ND
Si.....	<.003	<.03	<.03	<.01
Sn.....	ND	ND	ND	<.03
Ti.....	>10	ND	ND	<.003
V.....	ND	>10	<.1	ND

NA Not analyzed. ND Not detected.

<sup>1</sup>The following elements were not detected in any of the materials: As, Be, Ca, Cb, Cd, Co, Cr, Hf, Mo, Na, P, Pt, Sb, W, Zn, Zr.

project emphasis, i.e., determination and evaluation of homogeneity.

Helium (He) and argon (Ar) used during the study were typical high-purity grades

obtained in 1A-size cylinders (245 ft<sup>3</sup> at 2,490 psig and 290 ft<sup>3</sup> at 2,490 psig, respectively).

#### EQUIPMENT

The reduction and distillation systems are shown in figures 1-4. An overview of the equipment as installed is shown in figure 5. Stainless steel was used for construction of most equipment--retorts, shields, baffles, salt receiver, feed and filtrate tanks, liquid transfer lines and valves, gas lines to the system, and thermocouple sheaths. The stainless steel crucibles were lined with 0.063-in-thick chemically pure Ti to avoid contamination of the sponge. The crucible grate was also Ti.

The filtration tank and feed tank were both 11-in-ID by 23-in-tall steam-jacketed tanks. They were stirred by variable-speed electric motors and 6-in-diam 5-bladed impellers. Teflon<sup>4</sup> fluorocarbon polymer braided packing was used in stuffing boxes of both tanks. The tanks were also fitted with pressure relief valves and type J thermocouples. A 6-kW steam generator supplied steam to the steam jackets. Teflon filter cloth was used in the filtration tank. Teflon O-rings were used in the filtration tank for the main flange seal; asbestos was used for the feed tank. In early preliminary testing a sight glass was used to indicate the liquid level of the feed tank. As the sight glass was not heated, AlCl<sub>3</sub> would precipitate out, causing erroneous readings and other clogging problems within the system. Therefore, an ultrasonic level indicator was installed inside the feed tank. The level indicator also provided a backup indication of flow rate. The feed solution flow was controlled by a metering valve into the reduction retort. In preliminary tests a rotameter was used to measure flow rate, but it too was not heated and clogged with precipitated AlCl<sub>3</sub>. A thermal-type flowmeter was subsequently installed and,

after temperature calibration, proved adequate for the test program. One-fourth inch stainless steel tubing was used initially between the feed tank and the reduction retort. Even though this tubing was heated with heat tape and insulated, clogging with precipitated AlCl<sub>3</sub> interrupted several preliminary tests. Replacement with 1/2-in tubing alleviated this problem.

The reduction retort was an 11-7/8-in-ID by 26-1/2-in-deep, flanged containment vessel. A rubber O-ring sealed the water-cooled flange. A water-cooled view port, chloride feed line, pressure release-gas inlet pipe, and vacuum port were installed in the top flange plate. A thermocouple vacuum gage and a pressure-vacuum gage were placed in the vacuum line. Two different-sized, Ti-lined crucibles were used in the study: One was 10-1/4 in in ID by 24 in tall, and the other was 7-3/4 in in ID by 24 in tall. A 3-1/2-in-tall grate was fitted inside both crucibles to aid in sponge removal. A 5.6-cfm mechanical vacuum pump was used on the reduction equipment. The reduction furnace was a 23-kW electric resistance furnace controlled by temperature controllers including a safety override. Type K thermocouples were used for temperature sensors.

The distillation retort was a 13-in-ID by 82-in-tall vacuum vessel with a water jacket on the lower half. Vacuum was provided by (1) a 15.2-cfm mechanical roughing pump or (2) a 6-in-diam diffusion pump backed by a 17.7-cfm mechanical forepump. An 8-in-diam water-cooled oil baffle was installed above the diffusion pump. Thermocouple vacuum gages, mechanical vacuum gages, and vacuum-ionization-type sensors were all used for vacuum measurement. Type K thermocouples were used for temperature sensors. A 12-in-diam by 14-in-tall cylindrical can was used to collect magnesium chloride (MgCl<sub>2</sub>) and Mg during the distillation

<sup>4</sup>Reference to specific products does not imply endorsement by the Bureau of Mines.

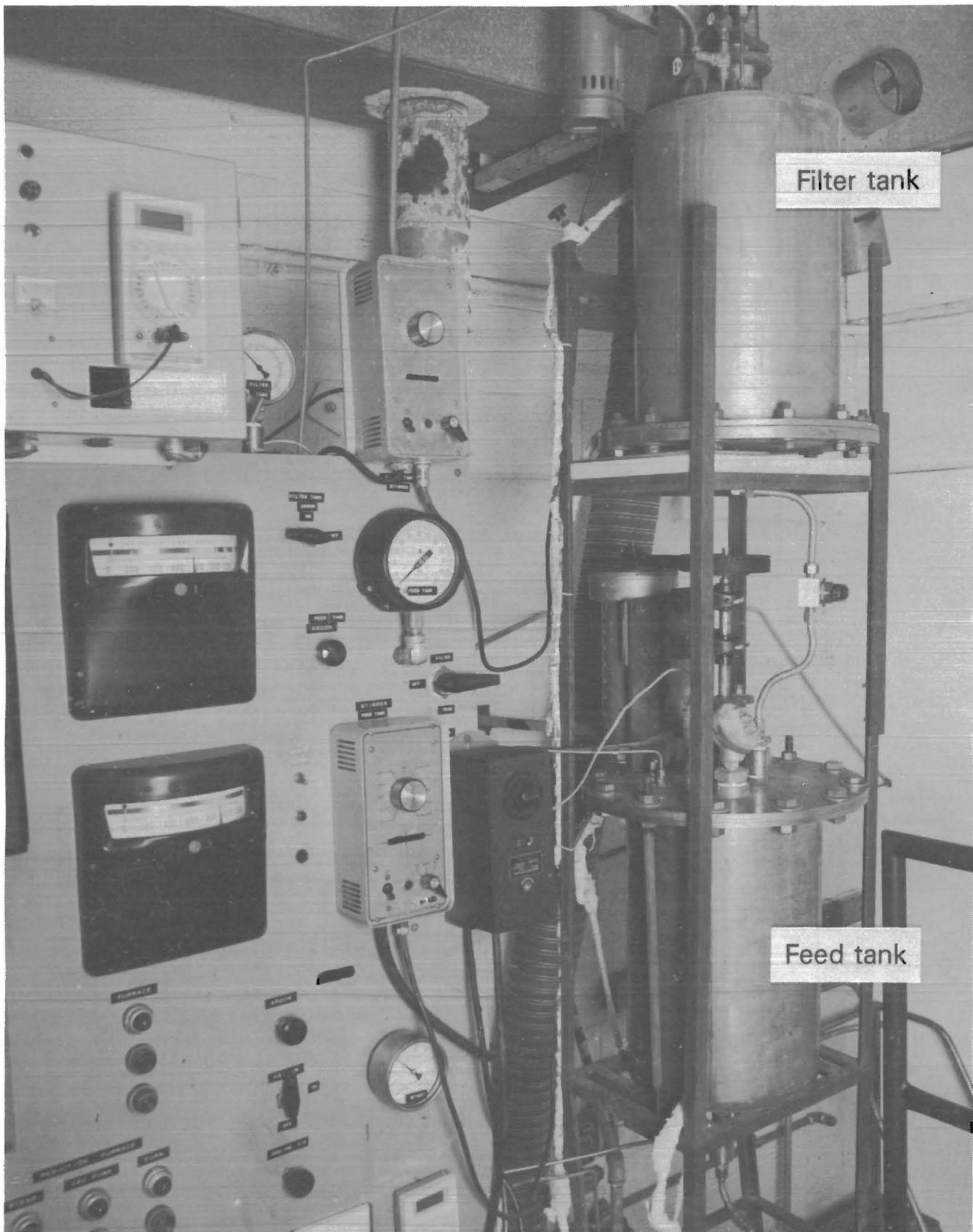


FIGURE 1.—Reduction system controls, filter tank, and feed tank.

operation. Below this can was a 12-3/4-in-diam by 8-in-tall cylindrical can set (two cans, one of which was inverted) used to form a "tortuous path" to collect remaining  $MgCl_2$  and Mg. A set of four 12-in-diam baffle plates with 1-in-diam

holes was used below the set of cans for further retention of condensed  $MgCl_2$  and Mg. The distillation furnace was a 30-kW electric resistance furnace controlled by temperature controllers including a safety override.

#### EXPERIMENTAL PROCEDURES

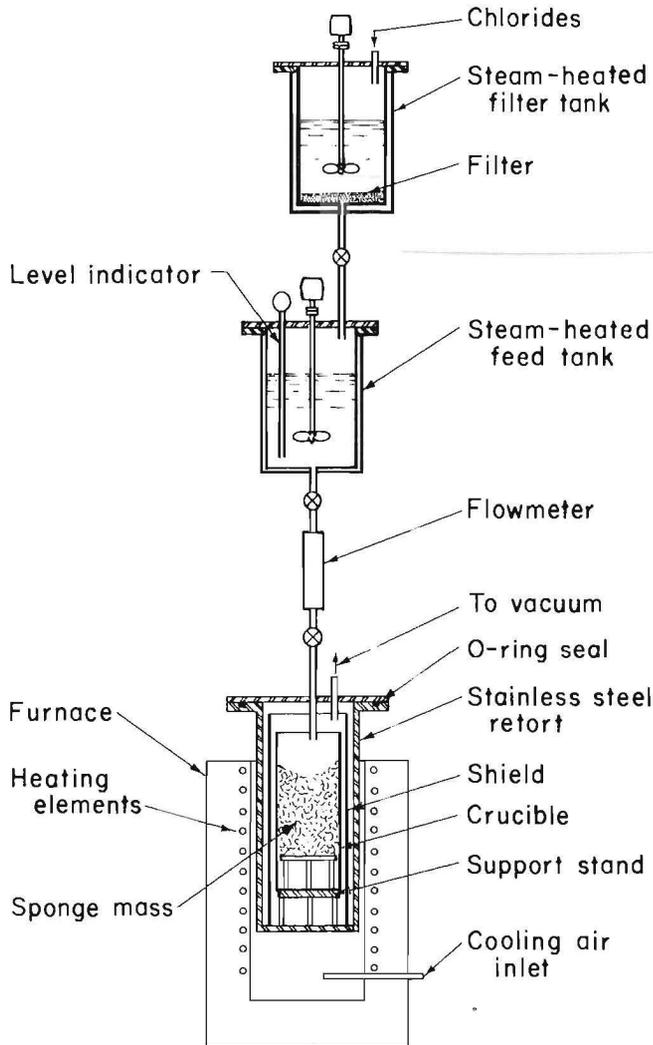
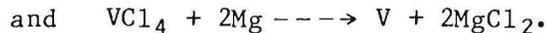


FIGURE 2.—Reduction system equipment.

An operation similar to the standard industrial Kroll reduction was desired. Therefore, Mg was used to form alloy sponge from the chlorides of Ti, Al, and V, and this reduction was followed by a distillation of the sponge to remove Mg and  $MgCl_2$ . A typical test produced about 12 to 14 lb of sponge. The general chemical reactions occurring during this operation are--



The Mg reductant was prepared by pickling it in 5-vol-pct hydrochloric acid (HCl) to remove the oxide layer (dross) from the Mg surface. The Mg blocks were then rinsed in water, dried with a clean rag, further dried in a 100° C oven, weighed, and placed on a grate in the crucible within the reduction retort. Approximately 20 lb Mg was used for each test.

The chloride feed solution (approximately 17 L) was prepared by pumping the desired amount of  $TiCl_4$  into the filtration tank. Argon was used both to blanket the  $TiCl_4$  storage barrel and to purge the filtration tank. Next, the allotted  $AlCl_3$  powder was poured into the stirred tank. The liquid  $VCl_4$  was added last. With the solution stirring, the tank was brought up to the desired temperature

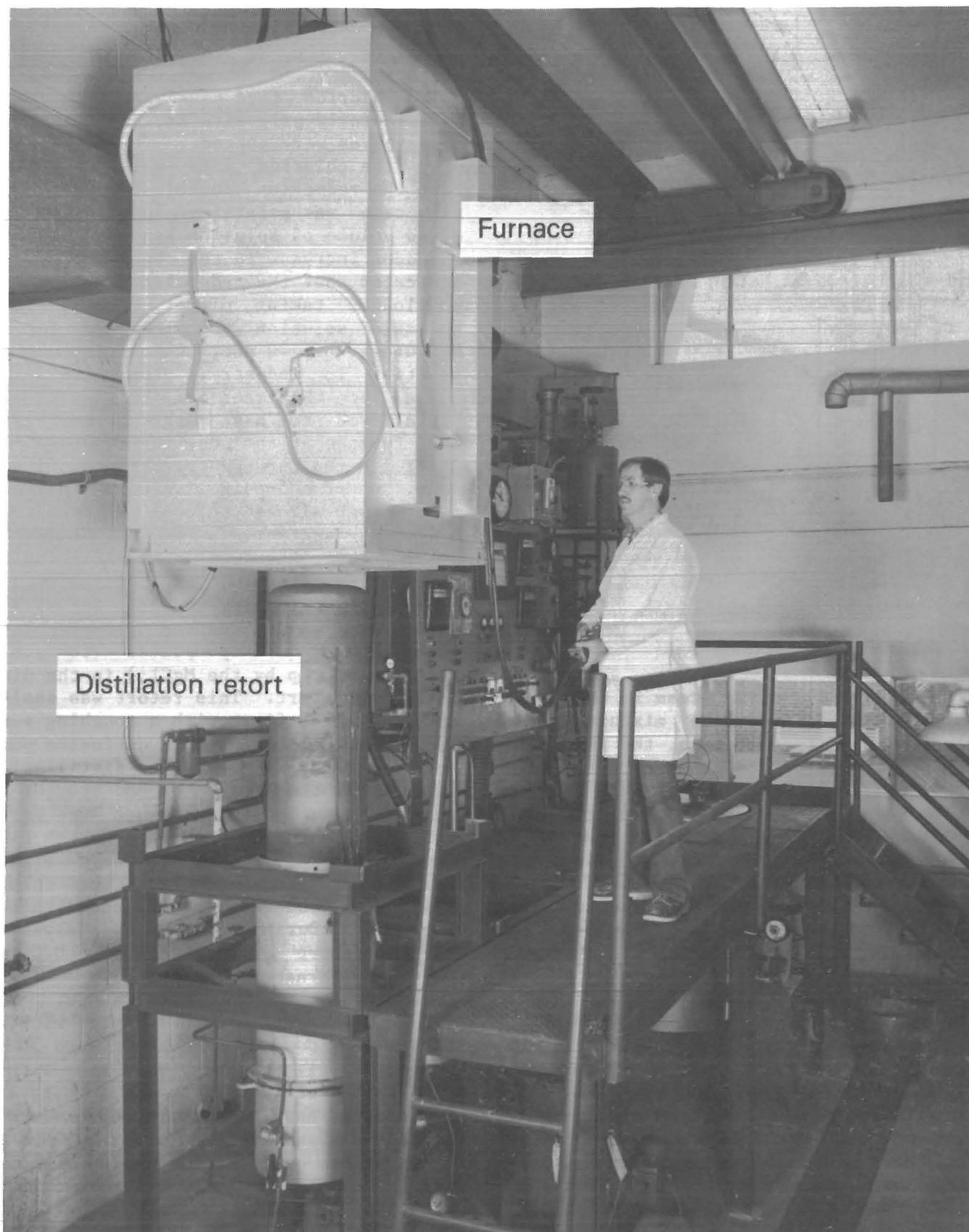


FIGURE 3.—Distillation system equipment. Operator is removing furnace from distillation retort.

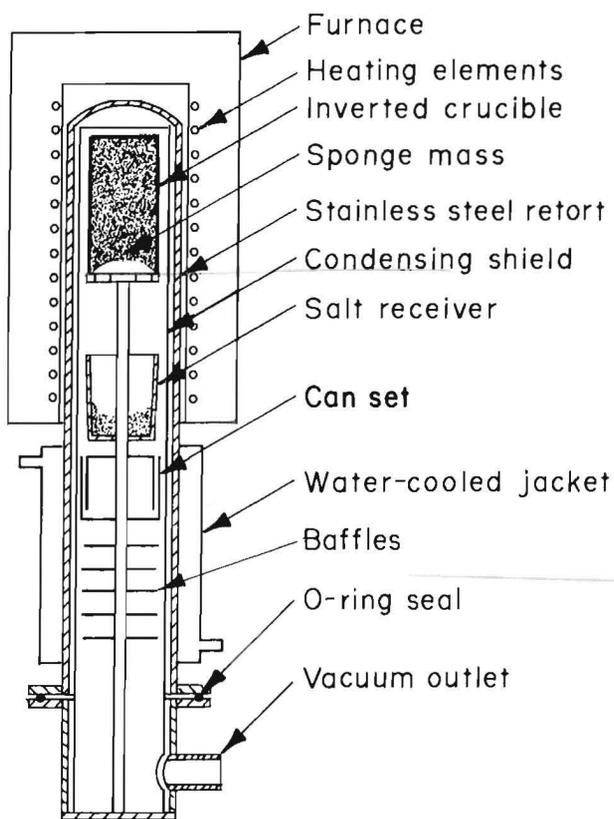


FIGURE 4.—Distillation retort.

(about 115° C), using steam in the jacket of the tank. After the mixture had at least 2 h of contact time, the filtration tank was pressurized with Ar, the valve between the filtration tank and the feed tank was opened, and the solution was filtered into the steam-heated (120° C) feed tank. Argon was used to purge this tank also. This filtration step was designed to provide a one-phase liquid feed to the reduction step. Insolubles, such as  $Al_2O_3$ , would therefore be removed during this filtration.

After preparing the feed material, a test was started by sealing the reduction retort containing the Mg, evacuating the system down to less than 30  $\mu$ m, and backfilling with He to 3 psig pressure. The evacuation-backfilling operation was repeated once again to ensure an air-free system. Helium, although more expensive, was used because the heat transfer coefficient for He is higher than for the alternative Ar. The reduction furnace with retort in place was then brought up

to the desired temperature, and that temperature was maintained for at least 1 h to allow the Mg to become totally molten.

The chloride feed tank was then pressurized to 12 psig with Ar, and the feed line valves were opened. The test began when the chloride feed solution flowed into the reduction crucible. A constant flow rate was maintained until the desired volume of solution had been used or a sudden increase in the reactor pressure indicated that the reduction reaction was no longer taking place. The desired volume of solution was calculated for an Mg usage of 70 pct, which is common practice in industry. The feed line valves were then shut off, and the retort was allowed to "heat soak" (remain) in the furnace at the desired temperature. After 1 h the furnace was turned off and then, under a 5-psig blanket of He, the retort was allowed to cool to room temperature overnight.

After the retort was completely cooled to room temperature, the crucible containing the Ti alloy sponge, excess Mg,  $MgCl_2$ , and any unreacted chlorides was removed and quickly placed (to avoid moisture pickup by the  $MgCl_2$ ) in the distillation retort. This retort was sealed and evacuated, first with a roughing pump to <75  $\mu$ m, and then with a diffusion pump vacuum system to <5  $\mu$ m. The distillation furnace was then turned on and brought up to 900° C. This temperature was maintained for about 30 h, during which time the  $MgCl_2$  and Mg, which were either drained or vaporized from the sponge mass, were condensed and collected in the salt can. During this period the vacuum in the retort dropped to about 0.2  $\mu$ m. Next the furnace was shut down and allowed to cool to room temperature. The retort was backfilled to 12 psig with Ar for 1 h. It was then evacuated to 30 mm Hg and backfilled again, this time with a combination of 12 psig Ar and 3 psig air for another hour. This procedure was designed to "passivate" (oxidize) the Ti alloy sponge surface to avoid a sponge fire. Afterwards the retort was opened, the crucible was removed and weighed, and the sponge was removed from the crucible, sampled, and analyzed.

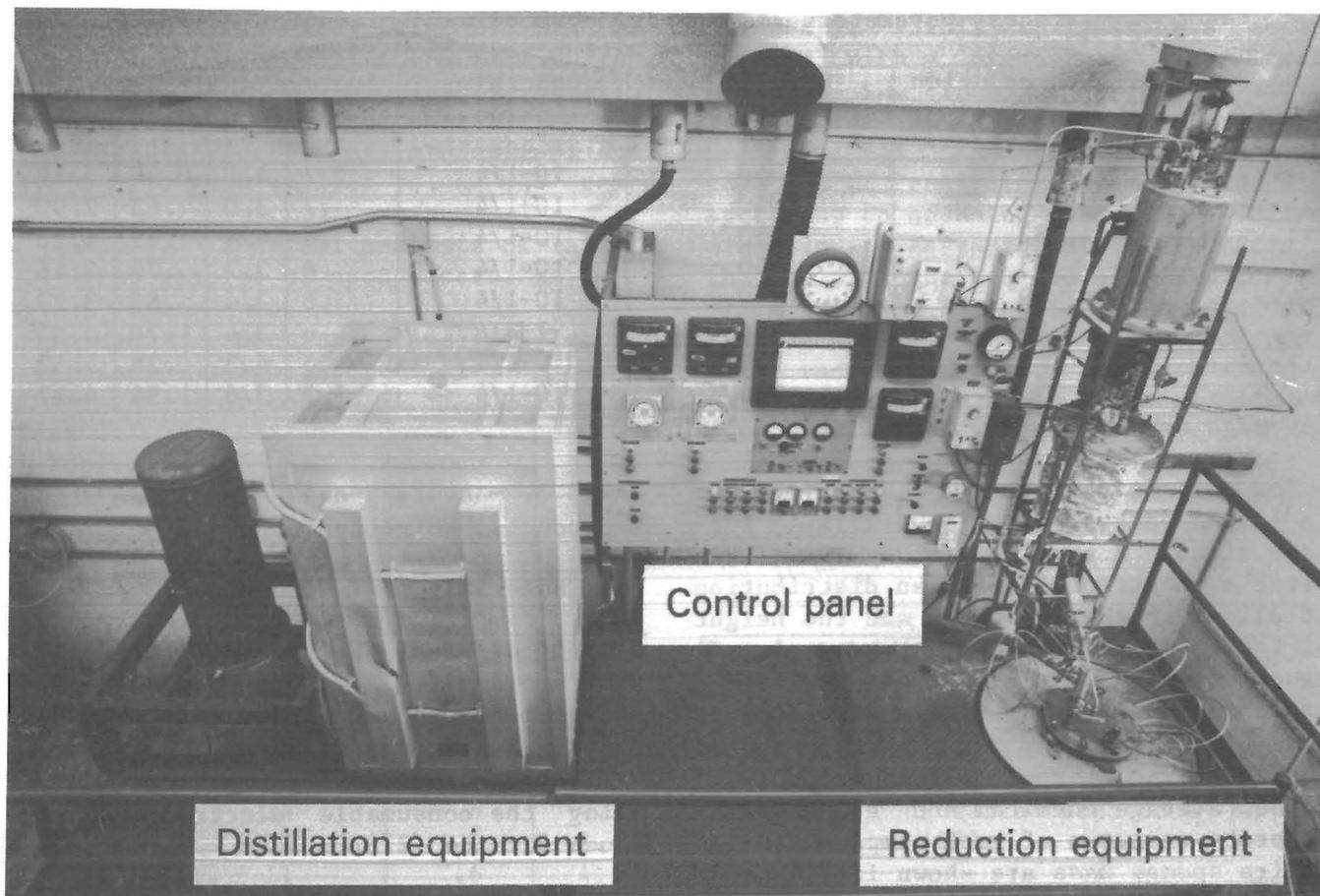


FIGURE 5.—Overview of experimental equipment.

## RESULTS AND DISCUSSION

Three process parameters were evaluated to determine the impact on process operation and sponge homogeneity, as follows: (1) reduction temperature, (2) chloride solution feed rate, and (3) crucible diameter. The parameter levels tested are shown in table 2.

The temperature range was defined by physical property limits. Molten Mg and  $MgCl_2$  are required for operation of the reduction process. The melting temperature of Mg is  $650^\circ\text{C}$ , while  $MgCl_2$  melts at  $714^\circ\text{C}$ . Therefore the lower reduction temperature was chosen as  $750^\circ\text{C}$ . The upper temperature limit for the steel equipment is approximately  $1,050^\circ\text{C}$ . Sintering of Ti also takes place in this range. To provide a safety cushion, an upper reduction temperature for the test series of  $950^\circ\text{C}$  was used. The common reduction temperature used by commercial

Ti sponge producers for the Kroll reduction is  $850^\circ\text{C}$ .

A previous coreduction study (4) used chloride feed flow rates of 66 and 68  $\text{lb}/(\text{ft}^2\cdot\text{h})$  (defined as mass flow rate per unit area of crucible cross section) for an 11-in-diam crucible. This range was therefore chosen as the approximate mid-range for the present study. Target flow rates of 50 pct, 100 pct, and 200 pct of this midrange value were then chosen. A subsequent study (20) of the effect of  $TiCl_4$  flow rate on the quality of pure Ti sponge indicated that the best quality sponge (with respect to purity and topography) was produced at an initial flow rate of 67  $\text{lb}/(\text{ft}^2\cdot\text{h})$ . The flow rate range tested in that study was 48 to 198  $\text{lb}/(\text{ft}^2\cdot\text{h})$ . Commercial Ti sponge producers are thought to operate in this flow rate range.

TABLE 2. - Process parameters and average chemical and microprobe analysis

Test	Chloride solution feed rate, <sup>1</sup> lb/(ft <sup>2</sup> ·h)	Reduction temperature, °C	Crucible inside diameter, in	Average analysis, wt pct			
				Chemical		Microprobe	
				Al	V	Al	V
1.....	34	850	10-1/4	0.7	4.1	0.98	3.89
2.....	74	750	10-1/4	.7	3.0	.63	2.90
3.....	82	750	10-1/4	.6	4.4	.69	4.28
4.....	83	850	10-1/4	.8	3.7	.77	3.46
5.....	79	950	10-1/4	.6	3.4	.85	3.29
6.....	86	850	7-3/4	.6	3.4	.70	3.05
7.....	118	750	10-1/4	.4	4.3	.28	4.56
8.....	152	850	10-1/4	1.1	3.6	.94	4.17

<sup>1</sup>Average sp gr = 1.73.

The maximum crucible diameter (10-1/4-in ID) was dictated by the available furnace size. A previous study (5) indicated a relationship between distribution of alloys in the Ti sponge and the height of the sponge sample in the vessel. A crucible approximately 50 pct smaller in cross-sectional area (7-3/4-in ID) was used to evaluate any advantage of greater sponge height as regards homogeneity.

The average chemical and electron microprobe analyses of grab samples for the entire sponge mass are shown in table 2. For comparison, other Ti alloy materials are shown in table 3. The chemical analysis for Al and V for a particular test is the weighted average value calculated from the individual grab sample for a sponge section and the weight of that section. The microprobe average analysis is calculated the same way. Good agreement was obtained between the two analytical techniques. The initial target sponge concentrations were 1 wt pct for Al and 4 wt pct for V. These values were not achieved consistently even though the same AlCl<sub>3</sub> and VCl<sub>4</sub> weight additions were made and the same procedures followed for each test. However, the range of concentration of the chemical analyses between tests (0.4 to 1.1 wt pct for Al, and 3.0 to 4.4 wt pct for V) for the test series does not preclude analysis of homogeneity, as that analysis is done within the individual sponge mass for each test. Nor does it preclude evaluation of effects of process parameters between tests, as the statistical treatment used is designed to circumvent this lack of consistency.

TABLE 3. - Average analysis of comparison products, weight percent

Material	Chemical		Microprobe	
	Al	V	Al	V
Commerical Ti-6A-4V..	6.2	4.3	6.48	4.34
PREP <sup>1</sup> powder.....	6.1	3.9	6.18	3.99
Sponge melt product <sup>2</sup> .	.6	3.1	.75	3.23

<sup>1</sup>Plasma Rotating Electrode Process.

<sup>2</sup>Sponge from test 2 that was melted using the consumable electrode annular anode furnace (27).

The chemical analyses of grab samples from each sponge section are presented in table 4 along with the percent of the total sponge mass represented by that section; other Ti alloy materials are shown in table 5. The sponge sections were subjectively identified and divided, although noticeable differences in section structure (fig. 6) were consistent throughout the test series. Titanium sponge is seen (6) as forming first at the walls (i.e., sides) as the walls present available reaction sites. Then Ti is formed on existing Ti on the bottom, core, and top of the sponge mass in that order. No trends between tests were noted in the distribution of Al and V in these sections with respect to the chemical analysis. The lower reduction temperature of 750° C in tests 2, 3, and 7 did produce more consistent analysis between sections. Different chloride flow rates of 34, 83, and 152 lb/(ft<sup>2</sup>·h) at 850° C (tests 1, 4, and 8, respectively) did not significantly change the Al and V distribution between sponge sections. In addition no significant difference in

distribution was seen between 7-3/4- and 10-1/4-in-diam crucibles (tests 6 and 4).

To evaluate the homogeneity of alloy sponge with respect to possible use as raw material for powder production, analysis of a much smaller volume was deemed

TABLE 4. - Chemical analysis of large grab samples of sponge sections

Sponge section	Section weight, pct of total	Analysis, wt pct	
		Al	V
Test 1:			
Top.....	6	0.6	3.9
Bottom..	24	.7	2.9
Sides...	57	.8	4.8
Core....	13	.7	3.2
Test 2:			
Top.....	14	.7	3.2
Bottom..	28	.6	2.8
Sides...	35	.7	3.2
Core....	23	.7	3.1
Test 3:			
Top.....	15	.6	4.6
Bottom..	24	.6	4.2
Sides...	50	.6	4.4
Core....	11	.6	4.5
Test 4:			
Top.....	11	.6	2.9
Bottom..	16	.8	3.9
Sides...	64	.8	3.7
Core....	9	.5	4.2
Test 5:			
Top.....	19	.6	3.3
Bottom..	19	.5	3.8
Sides...	48	.7	3.4
Core....	14	.4	3.1
Test 6:			
Top.....	10	.6	2.9
Bottom..	19	.5	4.5
Sides...	60	.7	3.2
Core....	11	.6	3.3
Test 7:			
Top.....	4	.3	4.2
Bottom..	71	.4	4.4
Sides...	21	.3	4.1
Core....	4	.3	4.3
Test 8: <sup>1</sup>			
Bottom..	74	1.1	3.4
Core....	26	1.1	4.0

<sup>1</sup>Test 8 was abbreviated owing to an operation problem. Therefore, only what was considered to be the bottom and core sections were formed and thus reported.

necessary. This analysis was accomplished with a microprobe. The grain size in the Ti alloy sponge produced ranged from 10 to 40 μm and averaged 22 μm (fig. 7). The microprobes used are capable of analyzing from 1- to 2-μm spots up to scanning areas of a desired dimension. As vanadium concentrates on the grain boundaries and aluminum concentrates within the grain during a slow cooling process such as the coreduction, wide variations occur in the analyses with small (1- to 2-μm) microprobe areas (fig. 8). To circumvent this problem,

TABLE 5. - Chemical analysis of large grab samples of comparison products, weight percent

Material	Al	V
Commercial Ti-6Al-4V plate.....	6.2	4.3
PREP <sup>1</sup> powder.....	6.1	3.9
Sponge melt product <sup>2</sup> .....	.6	3.1

<sup>1</sup>Plasma Rotating Electrode Process.

<sup>2</sup>Sponge from test 2 that was melted using the consumable electrode annular anode furnace (27).

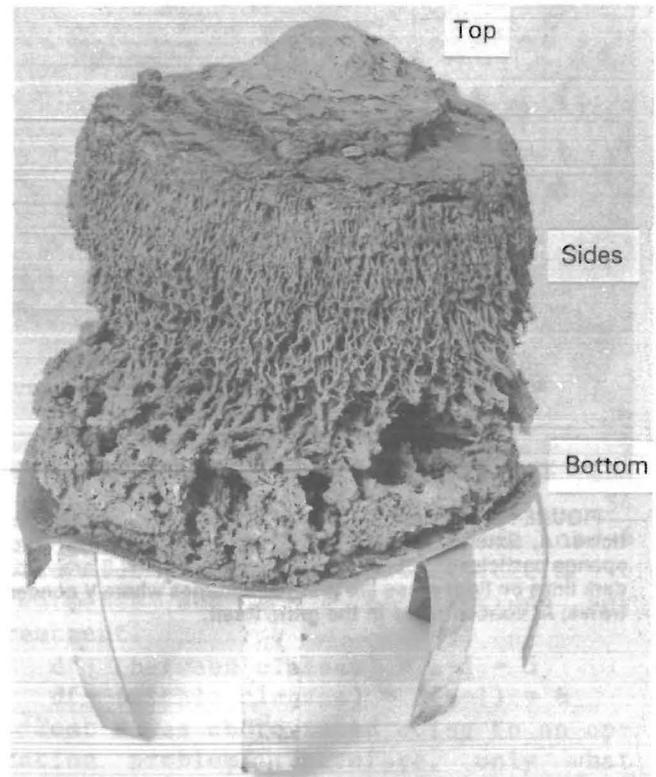
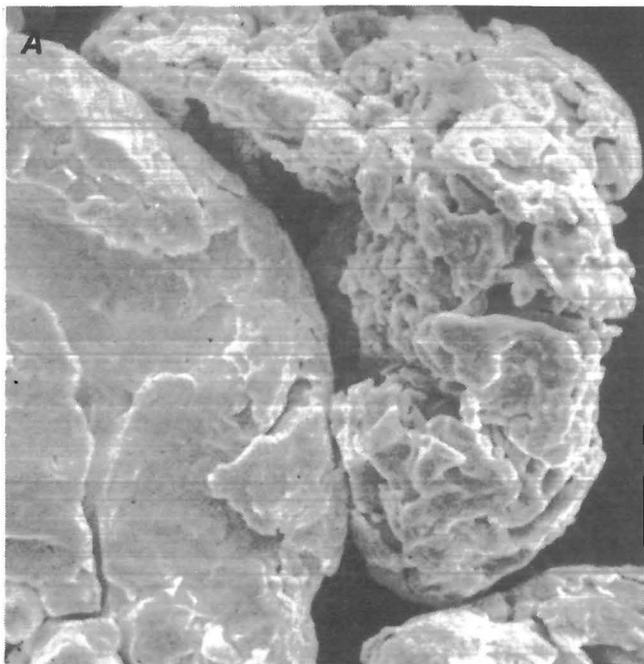
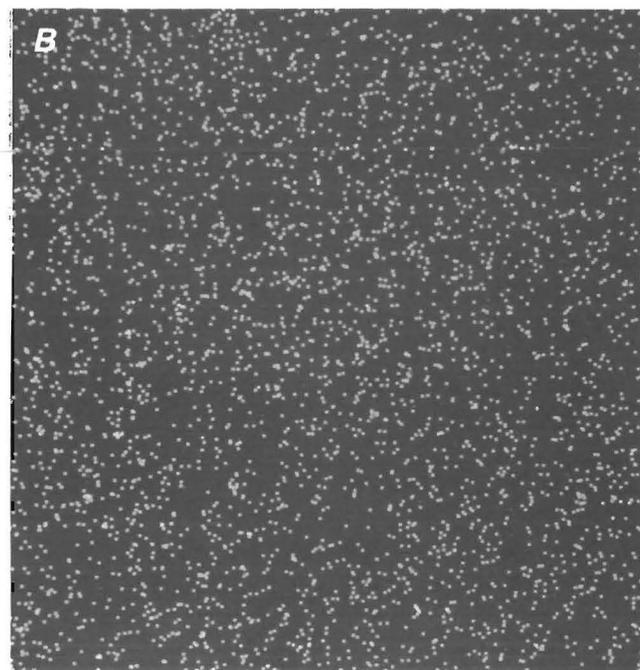
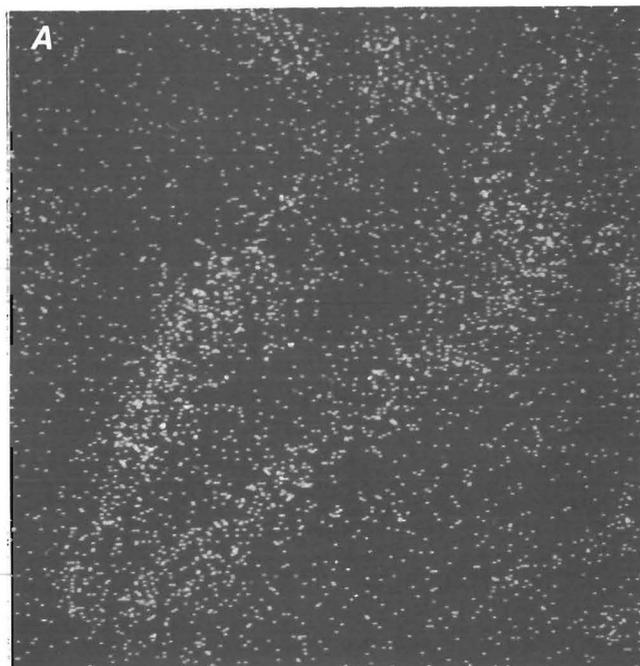


FIGURE 6.—Typical Ti alloy sponge mass as removed from crucible.



**FIGURE 7.**—Photomicrograph of typical Ti alloy sponge particles. *A*, Exterior (X 500); *B*, polished and etched Ti alloy sponge particles (X 250). Large dark areas in panel *B* are voids; dark lines on light areas are grain boundaries where V concentrates; Al concentrates in the grain itself.



**FIGURE 8.**—Microprobe X-ray maps (X 2,000). *A*, Test 3 alloy sponge with the white dots indicating V concentration; note the increased concentration along the grain boundaries. *B*, PREP powder—in contrast to panel *A*, the V concentration is evenly distributed throughout the material in both the grains and the grain boundaries.

different scans (20- by 15- $\mu\text{m}$  rectangle, 20- $\mu\text{m}$ -diam, 20- by 20- $\mu\text{m}$ -sq, 40- by 30- $\mu\text{m}$  rectangle, and 40- $\mu\text{m}$ -diam) of the material were made to encompass both grain boundaries and grains. Scans of areas greater than 40  $\mu\text{m}$  in diam were not advisable because voids present (fig. 7B) in the sponge caused difficulty in analysis spot selection and erroneous readings. No significant differences were noted between the scan dimensions or geometries tested. Therefore a 40- $\mu\text{m}$ -diam scan was chosen for the test series, and duplicate microprobe analyses were made of six separate 40- $\mu\text{m}$ -diam scans of each grab sample for each sponge section.

The microprobe analyses were then statistically analyzed to evaluate the homogeneity of individual sponge particles. A one-way analysis of variance was used to test if the observed difference among the scan means could be attributed to chance or whether the differences were actual. The means of the scans, along with the F ratios (variance ratios) for each sponge section, are presented in table 6; table 7 gives data for comparison materials. The F ratio is defined as--

$$F = \frac{\text{TrMS}}{\text{EMS}},$$

where TrMS = treatments mean square = mean square between classes,

and EMS = error mean square = mean square within classes.

The terms and calculations are defined in greater detail in references 21-23.

Evaluation of the F ratio requires the use of a F probability distribution table (23, pp. 560-567). For the test series, the degrees of freedom were  $df_1 = 5$  (for the numerator) and  $df_2 = 6$  (for the denominator). Using the corresponding F table, the value for a 0.05 significance level is 4.39. Therefore if the null hypothesis is true, i.e., if the material is totally homogeneous, then the F value of 4.39 would be exceeded 5 pct of the time by the values given in table 4. For

TABLE 6. -- Microprobe analyses and statistical treatment of microprobe data

Sponge section	Al		V	
	Mean, wt pct	F ratio <sup>1</sup>	Mean, wt pct	F ratio
Test 1:				
Top.....	0.97	19	4.03	97
Bottom..	.87	135	4.07	246
Sides...	1.09	21	3.91	116
Core....	.65	51	3.28	47
Test 2:				
Top.....	.54	370	2.47	297
Bottom..	.53	121	2.70	30
Sides...	.70	460	3.22	28
Core....	.70	86	2.93	185
Test 3:				
Top.....	.53	390	3.36	1,000
Bottom..	.73	100	4.60	35
Sides...	.75	51	4.43	18
Core....	.54	26	4.23	70
Test 4:				
Top.....	.71	72	2.73	87
Bottom..	.75	34	3.56	107
Sides...	.80	27	3.46	323
Core....	.62	49	4.18	41
Test 5:				
Top.....	.75	105	2.43	146
Bottom..	1.11	102	3.40	297
Sides...	.87	1,000	3.47	523
Core....	.57	31	3.72	53
Test 6:				
Top.....	.69	55	3.22	86
Bottom..	.75	282	3.16	52
Sides...	.72	167	2.88	92
Core....	.55	238	3.64	142
Test 7:				
Top.....	.05	1	2.50	86
Bottom..	.27	706	4.61	425
Sides...	.33	9	4.67	5
Core....	.31	19	5.19	46
Test 8: <sup>2</sup>				
Bottom..	1.00	579	4.27	284
Core....	.75	159	3.88	54

<sup>1</sup>Duplicate analyses were made on 6 spots for each sample. Therefore a = 6 treatments and n = 2 observations per treatment.

$df_1$  (between classes) = a-1 = 5

$df_2$  (within classes) = a(n-1) = 6

<sup>2</sup>Test 8 was abbreviated owing to an operation problem. Therefore, only what was considered to be the bottom and core sections were formed and thus reported.

TABLE 7. - Microprobe analyses of comparison products and statistical treatment of microprobe data

Test	Al		V	
	Mean, wt pct	F ratio	Mean, wt pct	F ratio
Commercial Ti-6Al-4V plate..	6.48	20	4.34	6
PREP <sup>1</sup> powder...	6.18	.5	3.99	5
Sponge melt product <sup>2</sup> .....	.75	1.9	3.23	2.5

<sup>1</sup>Plasma Rotating Electrode Process.

<sup>2</sup>Sponge from test 2 that was melted using the consumable electrode annular anode furnace (27).

a significance level of 0.01, the F value is 8.75; i.e., if the material is totally homogeneous, the F value of 8.75 would be exceeded 1 pct of the time by values given in table 4.

For the test series none of the process parameters produced an alloy sponge that could be considered homogeneous as, at the 0.05 significance level, 59 out of 60 F values were greater than the F table value of 4.39. At the 0.01 significance level, 57 out of the 60 values were greater than the F table value of 8.75. In addition, no trends could be discerned from the data as to any effects of the process parameters tested (within the limited ranges) on the homogeneity of the alloy sponge product. None of the parameters tested produced an alloy sponge that compared with the homogeneity defined by commercial Ti-6Al-4V plate or Plasma Rotating Electrode Process (PREP) powder (24). Commercial Ti-6Al-4V plate was chosen for comparison as it is a standard commercial product acceptable to the industry, although it, too, cannot be considered homogeneous on a micro scale. PREP powder was chosen as it also represents an industry standard (25-26). PREP powder, however, was considered homogeneous. Homogeneity of individual powder particles produced by comminuting the alloy sponge produced in this study without a homogenizing step such as melting would not meet the ideal criteria set forth by Ti researchers and end product users (14).

Therefore, as part of a companion research study, Ti alloy sponge was melted in a consumable-electrode, annular-anode furnace as a preliminary effort to convert the sponge to powder. That furnace and effort were directed toward producing a stream of molten Ti or Ti alloy from a pressed-sponge electrode (27). Although the molten material was collected as an ingot in that effort, it is projected that the molten stream obtained could be dispersed into powder via gas atomization or a spinning cup. Both ingot and powder should have equal homogeneity. Test 2 alloy sponge was melted in this furnace to form an ingot, which was then sampled; the results are shown in tables 3 and 4. The F values found with this material were equivalent to those of the PREP powder and better than those of commercial Ti-6Al-4V plate (Table 7). In addition Mg and Cl were reduced to acceptable levels (20 ppm and <10 ppm, respectively). This indicates that although sponge produced by this coreduction method may not be directly suitable for powder, it may be converted to acceptable powder by a melting step.

The lack of definite trends in the effect of the process parameters on sponge homogeneity may be attributed to the complex reactions and variables present (6, pp. 45-52; 28). The dynamic nonequilibrium (28) of this process is seen to impact the production of pure titanium as temperature and pressure, among other conditions, exist as gradients rather than the desired constants. A significant influence is seen from noncontrollable physical effects such as evaporation, condensation, crystallization, and diffusion. Another such variable is the state of the reactants. Magnesium, TiCl<sub>4</sub>, and VCl<sub>4</sub> may be present as both liquid and vapor during the reduction step. Aluminum chloride may be present as a dissolved solid in TiCl<sub>4</sub> and VCl<sub>4</sub> or as a vapor. Obviously many reaction mechanisms are possible with the numerous combinations of these states. In addition, Ti sponge, once formed, provides initiation sites, causing transient conditions for the reactions taking place. During the run, the supply of Mg is diminishing so it too is a transient

mechanism for the reactions. Another study (29) suggested that a longer vacuum distillation may facilitate recrystallization, which might have affected homogeneity in the present study. These are

but a few of the variables that were beyond the scope of this study to control or evaluate, but that may have significantly impacted or controlled the results of the test series.

### CONCLUSIONS

The coreduction of a  $TiCl_4-AlCl_3-VCl_4$  solution system to produce an approximate Ti-1Al-4V alloy sponge was studied by the Bureau of Mines as part of a research project to make Ti alloy powder. From this effort the following general conclusions may be drawn:

1. No effects were noted within the ranges tested for the process parameters of chloride flow rate, reduction temperature, and crucible diameter on the homogeneity (distribution of Al and V in the Ti) on a micro (40- $\mu$ m-diam) scale.

2. The statistical analysis of microprobe data from the individual sponge particles indicated much greater variation in chemical composition (Al and V) than that found in commercial Ti-6Al-4V plate or PREP powder. Thus a one-step approach to powder, such as grinding the alloy sponge, would not produce a powder product of acceptable chemical homogeneity. However, melting the alloy sponge in a consumable-electrode, annular-anode furnace would produce a material with acceptable homogeneity.

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