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FORMATION OF TITANIUM POWDER BY POTASSIUM REDUCTION OF TITANIUM SALTS

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The Bureau of Mines has investigated a process to produce titanium powder directly from titanium salts. If successful, such a process could lower the cost and increase the use of titanium. In this study, K_2TiF_6, K_2TiF_5, and TiF_3 were reduced with potassium in the temperature range of 650° to 750° C. Under certain conditions, titanium powder 1.6 to 3.3 microns in size was produced. After leaching the product with a 0.1<u>M</u> HCl solution, powder impurities as low as 0.04 pct potassium and 0.28 pct fluorine were obtained. However, oxygen levels of over 1 pct and the frequent formation of insoluble byproducts demonstrate the need for further research to make the powder suitable for powder metallurgy applications.

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FOREWORD

This report was prepared by the Bureau of Mines, U.S. Department of the Interior. The project was initiated under the Bureau of Mines' Vapor Phase Preparation of Titanium Powder Project. It was administered under the technical supervision of Richard G. Sandberg. This report is a summary of the work completed during period April 1983 to October 1983. This report was submitted by the author in August 1987.

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ILLUSTRATIONS

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

° C	degree Celsius	mL	milliliter
diam	diameter	$\underline{M}$	molar
ft	foot	min	minute
h	hour	pct	percent
in	inch		

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By Donna D. Harbuck[1]

ABSTRACT

The Bureau of Mines has investigated a process to produce titanium powder directly from titanium salts. If successful, such a process could lower the cost and increase the use of titanium. In this study, K_2TiF_6, K_2TiF_5, and TiF_3 were reduced with potassium in the temperature range of 650° to 750° C. Under certain conditions, titanium powder 1.6 to 3.3 microns in size was produced. After leaching the product with a 0.1M HCl solution, powder impurities as low as 0.04 pct potassium and 0.28 pct fluorine were obtained. However, oxygen levels of over 1 pct and the frequent formation of insoluble byproducts demonstrate the need for further research to make the powder suitable for powder metallurgy applications.

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INTRODUCTION

Titanium metal, with its desirable traits of high strength, low weight, and corrosion and temperature resistance, has many potential uses in aerospace and commercial applications. Unfortunately, because of the high cost of conventional titanium production, its use has been limited. These high costs arise from the many, often labor intensive, waste producing steps required in proceeding from titanium extraction from ore to fabrication of finished titanium components. Although new technologies, such as powder metallurgy, have been developed to reduce part of the fabrication costs, significant cost reduction will only come when titanium powder is produced directly from titanium ore or a beneficiated intermediate.

Current Titanium Production

Conventional titanium production in the Kroll Process (1)[2] begins with the chlorination of rutile (TiO_2) to make titanium tetrachloride ($TiCl_4$). Molten magnesium is then reacted with $TiCl_4$ vapor to form sponge titanium, which is purified, compressed into bars of consumable electrodes, and arc welded to form ingots. These ingots are forged and converted to billets, bars, and sheets. The final step, where up to 80 pct of the titanium ingot is lost as scrap (2), is component fabrication by casting, stamping, or machining.

Powder metallurgy can be used to reduce titanium forging and machining costs. With this technology, titanium parts are formed by pressing powders and sintering the compacts rather than by melting and casting. A container with the general oversize shape of the final desired article is filled with powder and compacted by hot isostatic pressing. The compact is sintered in a vacuum furnace at temperatures greater than 1,200° C to bring the compact up to full (95 to 99.5 pct) density. Powder metallurgy produces parts to near-net shape, which minimizes machining costs and scrap loss. Where this technique is applicable, cost savings of up to 70 pct compared to conventional fabrication methods have been reported (3).

Production of titanium powder suitable for powder metallurgy applications has been difficult. Because of the reactivity of molten titanium, conventional gas atomization techniques have not produced clean titanium powder. Peebles and Kelto (4) have summarized several alternative methods for converting titanium metal to powder. However, high production costs and/or unacceptable impurity levels of the powders show there is room for improvement.

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[2] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

Direct Methods for Making Titanium Powder

Research work by several groups has shown a number of potential methods for obtaining titanium powder directly from titanium ore or a beneficiated intermediate. Hurd (5-6) showed the reaction between sodium and $TiCl_4$ can be carried out so titanium powder is produced separate from NaCl. The $TiCl_4$ and sodium are heated in an argon-filled sealed vessel at 98° C. Agitating the vessel initiates the reaction which is completed in 2 sec. When the cooled vessel is opened, titanium powder is found separate from the NaCl. Down (7) has shown that when liquid sodium and $TiCl_4$ vapor are injected into the hot region of a plasma spray torch, titanium crystals condense on a collector wall. Becker and Careatti (8) have produced zirconium powder in a molten salt mixture. In this method, $ZrCl_4$ vapor and magnesium powder are fed to the bottom of a molten NaCl-KCl-$ZrCl_4$ mixture. The subsequent reaction between $ZrCl_4$ and magnesium produces zirconium powder. Similarities between zirconium and titanium suggest a comparable process could be developed for titanium. Although these methods are promising, they are only at the experimental stage.

Titanium Powder From Titanium Salts

This paper presents the results of a Bureau of Mines investigation to make titanium powder by potassium reduction of TiF_3 and its potassium double salts--K_2TiF_6 and K_2TiF_5. Because these salts are nonvolatile and potassium vaporizes at a relatively low temperature, this gas-solid reaction produces an unsintered solid product. Any of the alkali or alkaline earth metals--potassium, magnesium, sodium, or calcium--could be used as the reducing agent. However, potassium has the lowest boiling temperature and the resulting reaction product, KF, dissolves more readily than does MgF, NaF, or CaF_2 in water.

The reduction of titanium compounds with potassium to produce titanium metal is not an entirely new process. Berzelius (9) reduced K_2TiF_6 with molten potassium making brittle titanium as early as 1825. This method was apparently used for many years to make small quantities of the metal. A 1910 book (10) on rare metals stated that titanium was usually prepared by heating K_2TiF_6 with potassium in a covered crucible. Schuller and Wartha (11) showed that the product actually contained a large amount of titanium nitride impurity. Titanium was a novelty at that time with no substantial use; therefore, the process was not further developed. However, because of the potential of producing titanium powder directly from titanium salts, the Bureau of Mines has further studied the process.

EXPERIMENTAL PROCEDURES AND EQUIPMENT

Preparation of Reactants

The titanium salts to be tested were prepared in-house. K_2TiF_6 was formed by dissolving anatase (TiO_2) in a heated 10 wt-pct HF solution and subsequently adding a stoichiometric amount of KF solution. Within seconds, white crystals of K_2TiF_6 precipitated. Filtering the solution and drying the precipitate gave excellent K_2TiF_6 as determined by X-ray diffraction (XRD).

K_2TiF_5 was prepared by hydrogen reduction of K_2TiF_6 for 2 h at 600° C via reaction A. All of the K_2TiF_6 was reduced under these conditions.

$$K_2TiF_6 + .5H_2 = K_2TiF_5 + HF \qquad \text{(A)}$$

TiF_3 was formed by a two-step process. First, $TiCl_4$ and H_2 were passed through a charcoal bed at 850° C to produce $TiCl_3$. Because the reduction of $TiCl_4$ to $TiCl_3$ was only about 10 pct complete, unreacted $TiCl_4$ was recycled through the charcoal bed. The $TiCl_3$ was then treated with anhydrous HF at room temperature to form TiF_3.

Potassium Reduction Equipment

The reactions for potassium reduction of titanium salts were performed in two different experimental setups. One setup, shown in figure 1, consisted of a 3-ft-long, three-zone horizontal laboratory furnace with a 2.5-in diam 316 stainless steel tube. A 6-in-long nickel boat containing the titanium salt was placed in the center zone of the furnace, while a similar boat holding potassium was placed in the first zone. An inert gas flowed from the potassium to the titanium salt. During a run, after the center zone reached reaction temperature, the first zone was heated. As the temperature increased, potassium vaporized and was carried by the inert gas to the titanium salt, where the reaction occurred.

The other setup, shown in figure 2, involved a vertical 5-ft-long tube furnace with a 316 stainless steel 3-in-diam tube. A round 3-in-diam plate with a 1/8-in-diam hole in the center was welded in place half way up the inside of the tube. A 1-in-high, 1-in-diam perforated bubble cap was placed over the hole to allow the passage of gas. Titanium salt was placed on top of the plate and bubble cap. At the bottom of the tube was a 2.5-in-diam, 2-in-high pot attached to a 2-ft-long, 1-in-diam rod. The rod passed through the bottom flange of the reactor tube and allowed the pot containing the potassium to be raised into the hot zone. Inert gas flowed from the bottom to the top of the tube and carried potassium vapor through the bubble cap into the titanium salt.

Powder Purification and Analysis

Reaction products were leached with HCl solutions to remove KF and any impurities on the titanium powder. Leaching was done using a 500-mL glass beaker, a magnetic stirring rod, and a stirrer-hot plate. The powder was mixed with the acid solution and heated for 30 min at various temperatures. When the leach test was completed, the powder was filtered from the solution and dried.

Compounds present before and after leaching were identified by XRD. After leaching, potassium and fluorine impurities in the titanium powder were analyzed by fusing the sample, dissolving the fused material into solution, and analyzing the solution by inductively coupled plasma. Titanium powder particle size was evaluated using a scanning electron microscope (SEM). Samples were sent to the Albany Bureau Research Center for oxygen analyses.

RESULTS AND DISCUSSION

Initial experiments performed in the horizontal furnace showed the difficulty of obtaining adequate gas diffusion in this system. To overcome these problems, a more efficient system using a vertical furnace was designed. However, many useful results were obtained in the horizontal furnace which help to better understand the reactions.

Horizontal Furnace Tests

Selection of Carrier Gas and Titanium Starting Salt

Helium, argon, and hydrogen were investigated for use as the carrier gas used to transport the potassium vapor to the titanium salt for reaction. Hydrogen reacted with the titanium salt forming titanium hydride. Argon was adsorbed onto the potassium, making potassium vaporization difficult. Helium presented no problems and was therefore used as the carrier gas in all experiments.

The three titanium salts--TiF_3, K_2TiF_6, and K_2TiF_5--were tested by reducing each with potassium at temperatures of 600°, 700°, and 800° C for 4 h. Table 1 shows that when K_2TiF_5 and K_2TiF_6 were reduced under these conditions, an unwanted impurity K_3TiF_6 almost always formed. Another compound with a distinct XRD pattern, but no identifiable formula in the XRD file was formed at 600° C when reducing K_2TiF_6. (For convenience, the unknown compound is named $K_xTi_yF_z$.) The reduction of TiF_3 at 600° and 700° C produced titanium powder and KF with no byproducts. Therefore, TiF_3 was used in most further experiments.

TABLE 1. - Reaction products using K_2TiF_5, K_2TiF_6, and TiF_3 as starting materials in the horizontal furnace (4 h reaction time, 50 pct excess potassium)

Reaction temp., °C	Titanium salts		
	K_2TiF_5	K_2TiF_6	TiF_3
600	KF, Ti, K_3TiF_6	KF, Ti, $K_xTi_yF_z$	KF, Ti
700	KF, Ti, K_3TiF_6	KF, Ti	KF, Ti
800	K_3TiF_6, KF	KF, Ti, K_3TiF_6	KF,Ti,K_3TiF_6

Diffusion Problem in Horizontal Furnace

A major drawback in using the horizontal furnace was the difficulty in assuring that the potassium diffused completely through the titanium salt bed. If the salt is not contacted with potassium, reduction cannot occur; and unused potassium flows with the helium out of the reactor tube.

This diffusion problem was better seen when TiF_3 was reduced with a stoichiometric amount of potassium according to reaction B at 600° C.

$$TiF_3 + 3K = 3KF + Ti \qquad (B)$$

After 2-h reaction time, the sample was removed and visually examined. The powder at the bottom of the bed was lighter in color than the powder at the top. The bottom and top layers were separated and examined by XRD. TiF_3 and K_3TiF_6 were present at the bottom of the bed with titanium and KF present on top. The byproduct K_3TiF_6 is an undesired stable compound which cannot be separated from the titanium. It is postulated that if insufficient potassium contacts the TiF_3 then reaction C becomes more favorable than reaction B, thus explaining the presence of K_3TiF_6.

$$3TiF_3 + 6K = K_3TiF_6 + 2Ti + 3KF \qquad (C)$$

It is clear that under these conditions, the potassium vapor did not completely diffuse through the salt bed.

To counter the diffusion problem and to assure that all of the titanium salt was reduced, excess potassium was used. The required amount was determined by reducing K_2TiF_6 with 10, 21.5, 37.8, and 50 pct excess potassium at 700° C for 4 h each. With less then 50 pct excess potassium, XRD showed the presence of K_3TiF_6 along with the titanium and KF. Only with 50 pct excess potassium was there no K_3TiF_6 formation. Although using excess potassium is inefficient, it does help overcome the diffusion problem.

Reaction Time and Temperature

The effect of reaction time and temperature was investigated by reducing TiF_3 with 50 pct excess potassium in the horizontal furnace for times of 2, 4, and 6 h at 600°, 700°, and 800° C. The products of reaction as determined by XRD are given in table 2. At 2-h reaction time for all three temperatures, K_3TiF_6 and $K_xTi_yF_z$ were present. Apparently 2 h was not enough time for complete diffusion of potassium through the salt. Thus, the formation of K_3TiF_6 was favored over titanium and KF.

From table 2, it appears that K_3TiF_6 can form not only with insufficient potassium, but also at high temperatures, i.e., 800° C. One possible explanation is given by reaction D.

$$3KF + TiF_3 = K_3TiF_6 \quad (D)$$

After KF is produced by reaction B, it may react with TiF_3 to produce K_3TiF_6.

Table 2. - Reaction products formed in the horizontal furnace at various reaction temperatures and times when reducing TiF_3 with 50 pct excess potassium

Reaction temp., °C	2 h	4 h	6 h
600	KF, TiF_3, K_3TiF_6 $K_xTi_yF_z$	Ti, KF	Ti, KF
700	KF, Ti, K_3TiF_6 KxTiyFz	Ti, KF	Ti,KF K_3TiF_6
800	KF, Ti, K_3TiF_6 $K_xTi_yF_z$	Ti, KF, K_3TiF_6	Ti,KF,K_3TiF_6 $K_xTi_yF_z$

Figure 3 shows a plot of free energy versus temperature for reactions B and D. (Although no thermodynamic data is given for K_3TiF_6, it is assumed to be comparable to K_3AlF_6 because of the similarity in formula and crystal structure.) As the temperature increases, reaction D, the formation of K_3TiF_6, becomes more favorable than reaction B, the formation of titanium and KF. For this particular system, the best reduction of TiF_3 without forming K_3TiF_6 occurred with a reaction time of 4 h at 600° C.

Vertical Furnace Tests

To rectify the diffusion problem, a vertical furnace system was designed so that potassium vapor would be forced through the titanium salt bed. Because this system allowed for better diffusion, the amount of excess potassium needed was much less than with the horizontal system. This was verified when TiF_3 was reduced with 5 pct excess potassium at 600°, 650°, 700°, and 750° C for various reaction times. The products of reaction given in table 3 show titanium and KF without K_3TiF_6 or $K_xTi_yF_z$ are formed under most conditions. Temperatures of 650° and 700° C with reaction times of 6 and 8 h gave the best results. These are much more favorable results than those obtained using the horizontal system. At 600° C after 8 h, TiF_3 is still present. This temperature appears too low for reaction completion. At 750° C, K_3TiF_6 was present for all reaction times. As previously explained, high temperatures may favor the formation of K_3TiF_6.

Table 3. Reaction products formed in the vertical furnace at various reaction temperatures and times when reducing TiF_3 with 5 pct excess potassium

Reaction temp., °C	4 h	6 h	8 h	21 h
600	NA	NA	Ti, TiF_3, KF	NA
650	NA	Ti, KF	Ti, KF	NA
700	Ti, KF	Ti, KF	Ti, KF	NA
750	Ti, KF, K_3TiF_6	Ti, KF, K_3TiF_6	Ti, KF, K_3TiF_6	Ti, KF, K_3TiF_6

NA Not analyzed.

Product Analysis

Potassium and Fluorine Impurity Levels

Various leaching experiments were performed to determine the optimum conditions for removing KF from the titanium product. Leach temperatures of 25°, 50°, and 90° C and HCl concentrations of 0, 0.05M, 0.1M and 1.0M were studied. Each sample was leached five consecutive times for 1/2 h with fresh solution. Table 4 shows the final impurity concentrations of the solid product after leaching. Increasing the leach temperature decreased the level of potassium and fluorine impurities. For example, with 0.1M HCl, the level of potassium impurity dropped from 0.28 to 0.04 pct in titanium powder formed at 650° C for 6 h when the leach temperature increased from 25° to 90° C. At the same time, the fluorine impurity dropped from 5.15 to 0.28 pct. Because potassium and fluorine are not impurities encountered in the Kroll Process, standards for their tolerable limits have not been set.

TABLE 4. - Potassium and fluorine impurities of leached titanium powder, percent

Reaction temp., °C	HCl concentration							
	0 0M		0.05M		0.1M		1.0M	
	K	F	K	F	K	F	K	F
650°C, 6 h[1]								
25	0.26	2.13	0.24	5.64	0.28	5.15	0.30	1.80
50	.16	.84	.20	.57	.22	1.15	.40	.43
90	.14	.50	.16	.22	.04	.28	.04	1.20
650°C, 8 h[1]								
25	.24	.19	.20	.61	.20	.58	NA	.07
50	1.00	.09	NA	.25	.16	.31	NA	.09
90	1.30	.02	.06	.51	.06	.41	NA	NA
700°C, 6 h[1]								
25	.82	.46	NA	NA	.20	.10	NA	NA
50	.20	.30	.10	.61	.20	.34	NA	.21
90	.22	.53	NA	NA	.14	.52	NA	NA

NA Not analyzed.

[1] Conditions at which titanium powder was formed.

The effect of increasing the acid concentration was not clear due to scatter in the data; however, increasing acid concentration did not noticeably decrease the level of potassium and fluorine concentrations.

Particle Size Analysis

After the KF was leached away, the titanium powder particle size was determined using SEM. Table 5 gives the particle size of the product formed at 650°, 700°, and 750° C after 6-h reaction time. As the reaction temperature increased, the particle size increased (1.6 to 8.6 micron). XRD analyses of the product at 650° and 700°C showed only titanium, while at 750° C, K_3TiF_6 was also present.

TABLE 5. - Effect of reaction temperature on particle size (6-h reaction time)

Reaction temp., °C	Particle size, micron
650	1.6
700	2.1-3.3
750	5.3-8.6

The current techniques for making titanium powder (4) produce particles in the size range of 60 to 500 microns, significantly larger than obtained in this study. However, it is well documented in the powder metallurgy literature (12) that increases in density lead to increases in strength and toughness. The finer the particle size, the greater the density of pressed parts. Therefore, the powders produced by potassium reduction of titanium salts have great potential.

Oxygen Analysis

Titanium powder has a high affinity for oxygen, which decreases the properties of the metal and should be kept to a minimum. When the titanium powder product was examined by XRD, the pattern revealed only titanium. However, when the powder was analyzed for oxygen at the Bureau of Mines Albany Research Center, the values were significant (>1 pct). Some of the powder product was heated in an inert helium atmosphere at 900° C for 1 h to crystallize any amorphous formations and allowed to cool. X-ray diffraction analysis of the powder revealed the presence of TiO_2. Therefore, oxygen was present either on the surface of the titanium powder or it was dissolved in the powder.

The level of oxygen impurity in these powders is not acceptable to the titanium industry where values of 0.13 to 0.20 pct oxygen are standard (4). Although no further work was done on this topic, there are at least two prominent solutions for reducing the oxygen content. First, these powders were exposed to air after they were removed from the furnace. A procedure should be adopted so the samples can be removed and processed in an inert atmosphere. Second, the powders were leached in aqueous solutions, another source of oxygen exposure. A vacuum distillation system or an inert gas sweep, similar to those used in the Kroll Process for removing $MgCl_2$ impurities, could replace the leaching process.

CONCLUSIONS AND RECOMMENDATIONS

Research has shown that it is possible to reduce the titanium salts K_2TiF_5, K_2TiF_6, and TiF_3 with potassium to produce fine size titanium powder. Best results were obtained reducing TiF_3 at temperatures of 600° to 700° C for 4 to 6 h. Reduction of K_2TiF_5 and K_2TiF_6 often produced K_3TiF_6, in addition to KF and titanium. Unlike KF, K_3TiF_6 could not be leached from the titanium. Even when reducing TiF_3, K_3TiF_6 formed if insufficient potassium was used or if the reaction temperature was over 700° C. When KF was leached from the titanium at 90° C in 0.1M HCl solutions, titanium powders with impurities as low as 0.04 pct K and 0.28 pct F were obtained.

The high level of oxygen impurity in the powder product and the formation of K_3TiF_6 and $K_xT_yF_z$ byproducts are areas that require additional research. As seen in this work, byproduct formation can be reduced by maintaining proper control of the reaction conditions. Titanium oxygen content could be significantly reduced by eliminating powder exposure to air and water. Possibilities include the following:

- Remove and process powders in an inert atmosphere.
- Use vacuum distillation or an inert gas sweep to remove KF from the titanium.
- Perform the reduction step in a zinc carrier medium.

The zinc medium method has been used by Megy (13) to obtain titanium powder from Na_2TiF_6. He claims the method not only decreases oxygen content, but also reduces the amount of byproduct formation. It is recommended that these suggestions be tested.

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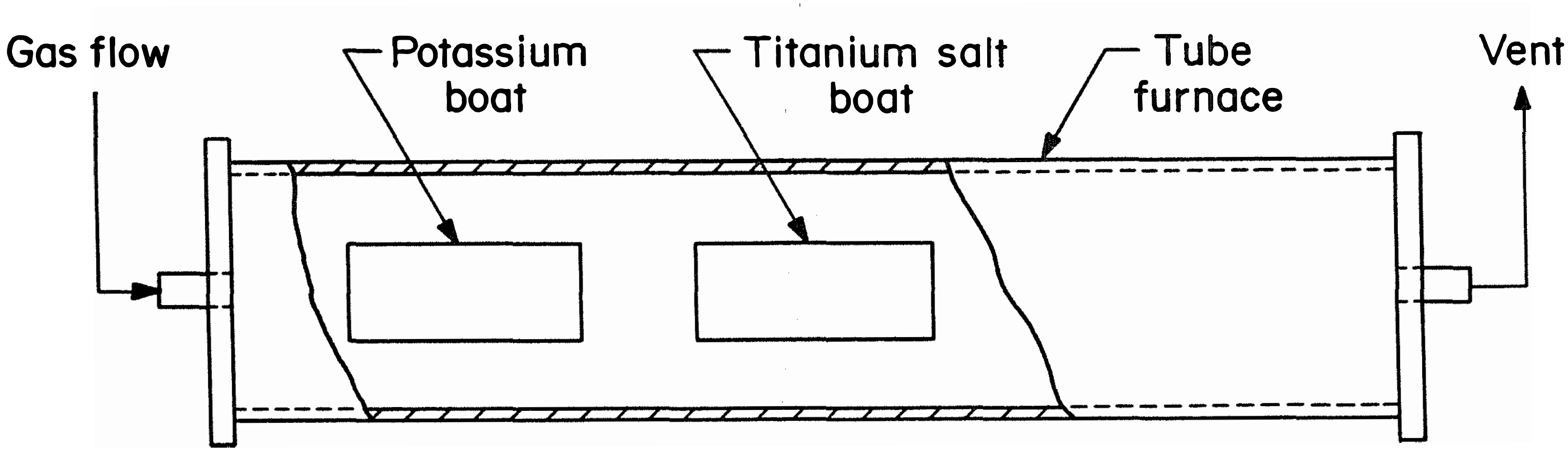

FIGURE 1. - Horizontal reactor used to produce titanium powder.

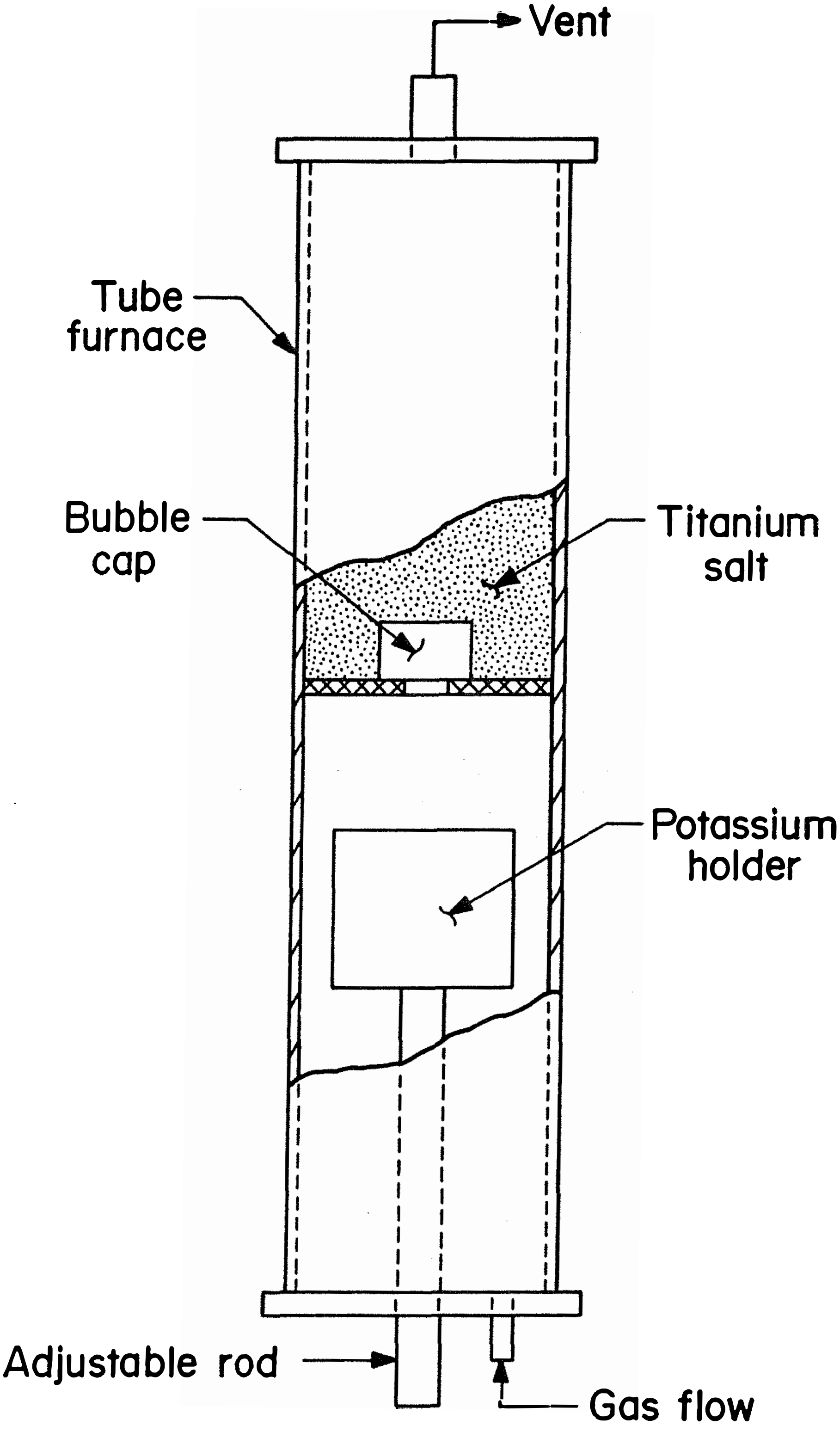

FIGURE 2. - Vertical reactor used to produce titanium powder.

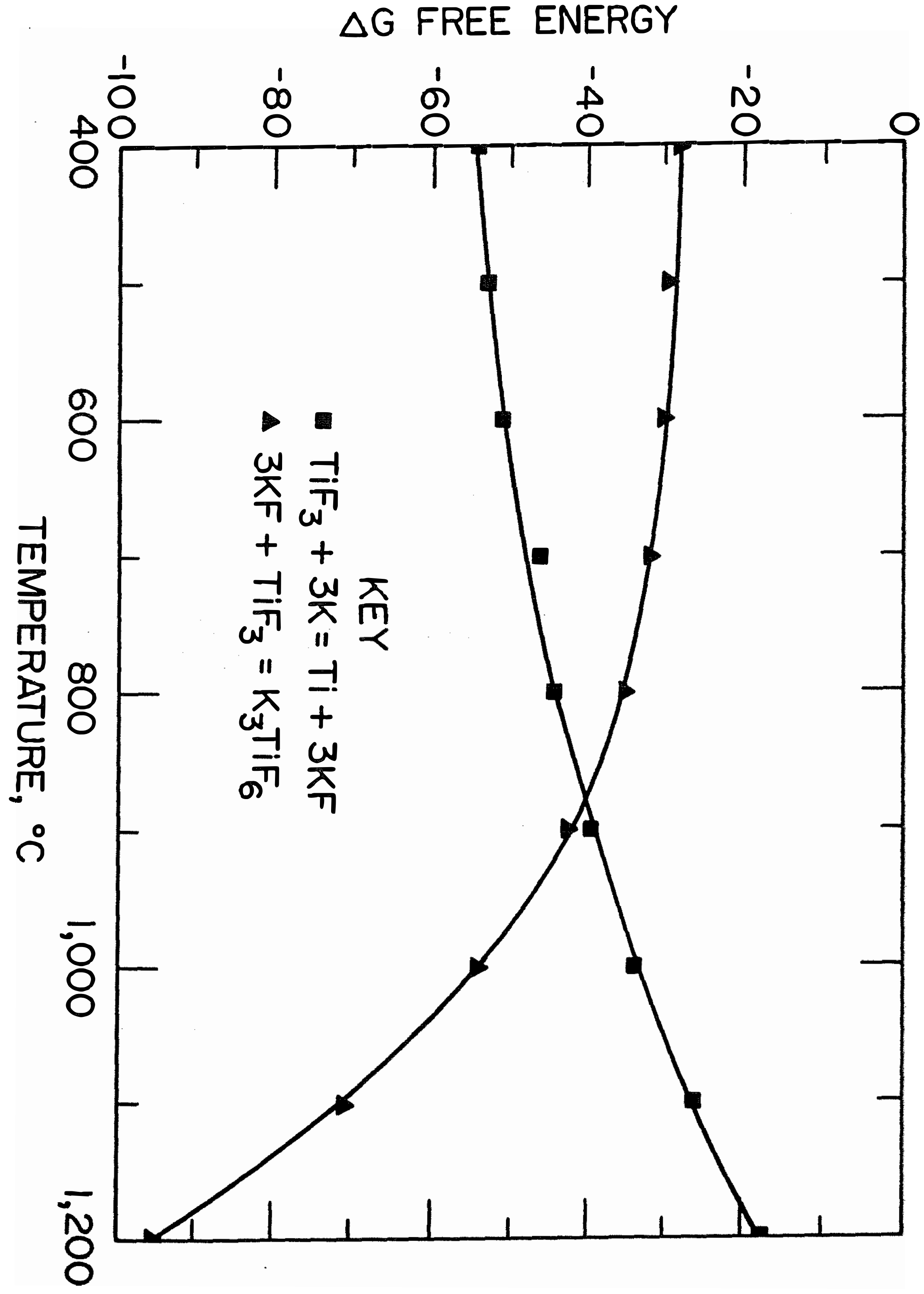

FIGURE 3. - Free energy versus temperature for the formation of Ti and K_3TiF_6.