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KINETICS OF THE TITANIUM-NITROGEN REACTION WITH APPLICATION TO THE DESIGN OF GETTERING SYSTEMS

by

M. L. Kyle, L. F. Coleman,
R. D. Pierce, and J. D. Arntzen

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Chemical Engineering Division

April 1967

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SUMMARY

The rate of reaction between titanium-metal sponge and nitrogen in argon-nitrogen mixtures was studied at 900°C. The reaction rate depends upon the partial pressure of nitrogen in the gas phase. At least three titanium-nitrogen solid phases are formed as the reaction proceeds, and the rate-controlling mechanism is believed to be the diffusion rate of atomic nitrogen through the $\text{TiN}_x(\delta)$ phase. Early reaction kinetics can be described by the conventional parabolic relationship, but this relationship is not valid for extended periods of time. A single relation has been developed which satisfactorily describes the reaction kinetics at nitrogen partial pressures from 100 to 50,000 ppm (by volume) and times to 1000 hr.

Additional mathematical relationships have been developed to permit the design of titanium gettering systems for the removal of nitrogen from argon. These relationships apply to the following operating conditions: (1) nitrogen concentrations in argon from 50 to 50,000 ppm, (2) a reacting temperature of 900°C, (3) total pressure near 1 atm, (4) titanium-metal sponge of a surface area near 800 cm²/g, and (5) low (~1 ppm) oxygen and water content of the gas. Under these conditions, the relations presented should permit the design of a gettering system with an uncertainty of about $\pm 10\%$ in the required bed size and useful life.

I. INTRODUCTION

The production and maintenance of high-purity inert atmospheres present a continuing problem to the atomic-energy industry. Inert-gas atmospheres are required when working with pyrophoric materials, when welding refractory metals, when conducting pyrochemical processes with reactive liquid-metal solvents, and for other similar applications. In these cases, oxidation or nitridation resulting from contact with air would contaminate the desired product and render it unusable. For example, in the purification and handling of sodium, virtual elimination of oxygen, nitrogen, and water vapor from the surrounding atmosphere is required. The major contaminants in most inert-gas enclosures are oxygen, nitrogen,

water vapor, and carbon dioxide resulting from inleakage of air. For this reason, the enclosure is normally operated at a pressure slightly above ambient so that most leakage is from the enclosure to its surroundings. However, in some applications, such as the handling of radioactive materials, it may be necessary to operate the enclosure at a pressure slightly less than ambient to prevent the escape of hazardous materials.

Either helium or argon is commonly used in these enclosures. Argon possesses the relative advantages of availability, containment (because of its higher molecular weight), and ease of pumping. The advantage of helium is that its lower boiling point simplifies cryogenic purification processes.

Many methods are commonly used to maintain pure atmospheres in inert-gas enclosures. White and Smith,¹ Walton,² and Kohl and Riesenfeld³ have discussed several of these methods. The methods can be classified into the following categories:

1. Continuous purging of the enclosure with a high-purity inert gas.
2. Sorption of impurities on activated materials such as charcoal or Molecular Sieves* at either cryogenic or ambient temperature.
3. Removal of the impurities by reaction with a gettering material such as calcium.
4. Combinations of processes such as the chemical reaction of oxygen with hydrogen to form water vapor and subsequent sorption of the water vapor on Molecular Sieves.

Many of the chemical gas-purification processes involve a gas-solid reaction for removal of impurities. Metals are commonly used for removing oxygen and nitrogen, oxides of metals for removing hydrogen, and, occasionally, suboxides for removing oxygen. These processes are generally carried out dynamically by passing the impure gas continuously through a reactor containing a bed of the reactant in the form of small solid pieces. The principal controllable variables affecting such a reaction are temperature, pressure, gas flow rate, particle size, surface area of the material used, and the dimensions of the bed. The operating temperature should be sufficient to provide adequate reaction rates but not so high as to cause problems in reactor design and operation.

The increasing development and utilization of large inert-gas enclosures have led to interest in purification systems capable of removing impurities from large volumes of inert gas. The leak rate of the enclosure

*Product of the Linde Division, Union Carbide Corporation.

and the required purity of the atmosphere are the major factors that determine the economics of the various purification techniques. For large-volume systems in which a high-purity atmosphere is required, chemical gettering methods are usually economically competitive. In systems of this type, water vapor is removed by activated sorbents such as Molecular Sieves. Oxygen is removed by reaction with copper (at 600°C) or by other relatively low-temperature gettering methods. The removal of the nitrogen impurity presents a greater problem because it is chemically less reactive.

Several gettering materials are available for use in the removal of nitrogen from inert gases. The most common of these are calcium, uranium, and titanium-zirconium alloys. Recently, interest has been expressed in the use of titanium as a nitrogen-gettering material. This interest has stemmed from the fact that titanium possesses several advantages over those gettering materials now commonly used. Titanium-metal sponge, a high-surface-area form suitable for gettering operations, is readily available at a relatively low cost, and it requires no pretreatment before use as a gettering material. Both the oxide and nitride reaction products of titanium are nonpyrophoric and can be handled easily in air. The handling of titanium is also greatly facilitated because neither titanium nor its reaction products are toxic. As a consequence, titanium-metal sponge has a relatively low cost per mole of nitrogen-removal capacity.

The results of several investigations of the kinetics of the titanium-nitrogen reaction are available (see following section). However, none of these investigations was sufficiently complete to allow engineering estimates of the parameters involved in gettering-bed design. None of the previous investigations used metal sponge as the form of the reacting titanium. Therefore, to investigate the possible usefulness of titanium as a gettering material for nitrogen impurities in argon, two sets of experimental equipment were operated: (1) equipment for a study of the kinetics of nitrogen removal from argon on hot titanium sponge, and (2) a pilot plant for obtaining overall process-performance data and information on component reliability.

This report presents the study of the kinetics of the titanium-metal sponge-nitrogen reaction with nitrogen present as a diluent in pure argon. The temperature for this study was 900°C. This temperature was chosen as a compromise between good reaction kinetics and ease of containment of the titanium sponge. Previous work⁴ showed that the titanium-nitrogen reaction rate increases with temperature from 750 to 1400°C. However, titanium sponge cannot readily be contained in stainless steels or other nickel alloys at temperatures above about 955°C because of the existence of a titanium-nickel liquid phase above that temperature.⁵ Therefore, 900°C was chosen as the operating temperature because it provides favorable reaction rates and permits containment of the titanium sponge in stainless steel equipment.

A report on the design and operation of a pilot-plant gettering system employing titanium-metal sponge for the removal of nitrogen from argon was published previously.⁶

II. PREVIOUS WORK

The reaction of nitrogen with titanium is generally represented by the following equation:

Analysis of the published phase diagram⁷ in Fig. 1, however, shows that in a reaction occurring at 900°C at least three phases designated α , ϵ , and δ would probably be present in the reacted material. The phase diagram also shows TiN to be a nonstoichiometric compound, the actual composition

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Fig. 1. Partial Titanium-Nitrogen Phase Diagram⁷

and no previous work dealing directly with the kinetics of the sponge is known. The effect of nitrogen partial pressure on the reaction kinetics was not systematically investigated in any known previous study. The use of titanium sponge as a gettering agent for the removal of nitrogen from inert gases has been reported.^{11,12} However, in these studies, the kinetics of the reaction were not investigated.

The kinetics of the titanium-nitrogen reaction have been described by various investigators as being linear¹³ at 1000°C, parabolic⁹ from 550 to 850°C with an activation energy 36.3 kcal/mole, parabolic¹⁴ from

ranging from about $\text{TiN}_{0.4}$ to about $\text{TiN}_{1.2}$. The standard free energy of formation of TiN at 900°C (according to the above reaction) is about -54.7 kcal/mole.⁸ Since the standard free energy of formation of TiO at 900°C is about -97.9 kcal/mole,⁸ nitrogen free of oxygen and moisture contamination must be used in any study of the kinetics of the titanium-nitrogen system. Gulbransen and Andrew⁹ and Gibbs *et al.*¹⁰ have indicated that oxygen contamination can greatly inhibit the titanium-nitrogen reaction.

Several investigators have studied the kinetics of the titanium-nitrogen reaction. These studies were performed using titanium metal in the form of rod, sheet, or chips,

800 to 1050°C with an activation energy of 45.4 kcal/mole, parabolic¹⁵ from 800 to 900°C (no reported activation energy), and parabolic⁴ (except for initial deviations) from 800 to 1400°C with an activation energy of 41.3 kcal/mole for times less than 60 min, and 53.8 kcal/mole for times greater than 60 min. Other investigations^{16,17} of this reaction have produced similar quantitative results. A report¹⁸ summarizing much of the work on the nitridation of titanium has been published.

The probable reaction mechanism has been postulated by several of these authors, but Wasilewski¹⁹ probably made the most thorough study. Wasilewski (working with titanium-metal cylinders) observed the formation of a number of surface layers in all the specimens reacted. Two surface layers, identified as the nitride (TiN_x) and alpha phase, were found in all specimens that had reacted at temperatures above 950°C (see Fig. 1). These surface layers surrounded an untransformed beta core. A third layer (probably the epsilon phase) was also observed in specimens that were re-acted at 950°C. He concluded that the longer-term reaction rates were controlled by nitrogen diffusion through the titanium nitride film. His data indicate that the diffusion coefficient of nitrogen in the nitride phase (3×10^{-12} cm²/sec at 900°C) is about two orders of magnitude lower than the diffusion coefficient of nitrogen in the alpha phase at the same temperature.

III. EQUIPMENT

Figures 2 and 3 are a schematic diagram and a photograph of the equipment built for the study of the kinetics of nitridation of titanium sponge by argon-nitrogen mixtures. In this apparatus, an argon-nitrogen mixture of carefully controlled composition was continuously circulated through a small bed of titanium sponge. This bed was composed of eight removable sections (hereafter called sample beds). The entire nitrogen content of the gas (as well as any oxygen and water vapor inleakage) was removed after each pass through the series of titanium beds by passing the gas through a large titanium bed in the closed loop. The desired nitrogen content of the circulating gas stream was then re-established immediately before the reaction chamber by mixing the now purified argon stream with a slow bleed of nitrogen. This technique provided a constant nitrogen concentration in the reacting gas stream despite the decrease in reaction rate that occurred as the reaction proceeded. The extent of reaction of the titanium test material was determined at selected intervals during the run by successively and permanently removing the uppermost titanium sample bed, and determining its nitrogen content by semimicro-Kjeldahl analysis.* This procedure was repeated until all sample beds had been removed from the test chamber.

* The analytical procedure used for the nitrogen determination is outlined in Ref. 6, pp. 36-39.

Fig. 2. Schematic Diagram of Titanium-Nitrogen Reaction Loop

108-9367

Fig. 3. Titanium-Nitrogen Reaction Vessel

The circulation rate in the loop (100 to 1250 liters/hr) was such that only a small fraction of the nitrogen present in the gas stream reacted with the titanium in a single pass through the series of beds. The purpose in maintaining the circulation rate so that only a small fraction (less than 5 v/o) of the nitrogen present in the gas stream reacted during any given pass was to approximate a differential titanium bed and thereby facilitate interpretation of the data. Before rate data were taken, it was established that the series of small titanium beds did, in fact, perform as an overall differential bed. It was then assumed that each sample bed in the series reacted with gas having the same nitrogen concentration, and, as a result, no correction was made, in the analysis of the data, for decrease in nitrogen partial pressure of the gas between the beds.

The system (see Fig. 2) operated as follows: Argon gas was circulated in a closed loop by a reciprocating diaphragm pump. A pressure regulator (No. 1 in Fig. 2) controlled the amount of gas passing through the reaction loop. A constant pressure was maintained on the high-pressure side of this regulator by a pump bypass loop, which returned much of the gas to the pump inlet without its passing through the reaction loop. A flow control valve in the bypass loop was manually adjusted to obtain the desired pressure relationships. This system allowed the circulation rate through the loop to remain constant despite variation of the pump-outlet pressure. The flow rate of the argon gas was metered and recorded by both a pressure

transducer and a bellows-type differential pressure recorder, which were connected across a calibrated orifice plate. Another pressure regulator (No. 2) provided additional high-purity, cylinder-grade argon for the loop when required.

The argon gas next passed through a 40-lb bed of titanium sponge, maintained at 950°C, in which all the nitrogen, oxygen, and water-vapor contaminants were removed from the argon. The exhaust gas from this cleanup bed was monitored routinely, and in all cases the levels of nitrogen and oxygen contamination were below the limit of gas chromatographic analysis (about 20 ppm for nitrogen and 10 ppm for oxygen). The desired nitrogen concentration in the argon was then re-established by mixing the purified argon gas with a constant flow of nitrogen entering the loop.

The nitrogen that was mixed with the argon flow was passed through a Molecular Sieve bed (operated at room temperature) and a copper bed (maintained at 600°C) to remove water and oxygen contaminants. The flow rate of the nitrogen was controlled by the pressure drop across a "standard leak" (normally used for calibration of vacuum-system leak detectors), which consisted of a flattened length of tubing in which there was a small opening. The pressure on the inlet side of the standard leak was controlled by a pressure regulator (No. 4).

The circulating argon-nitrogen mixture then passed into a gas pre-heater (filled with 1-in.-OD chrome steel balls), where it was heated to about 500°C before passing into the test chamber, in which the temperature was increased to 900°C. The gas then passed through the stack of eight sample beds (Figs. 4 and 5). Each sample bed consisted of 1 to 10 g of

Fig. 4

Titanium-sponge Sample Bed

108-9374

108-9375

Fig. 5. Stack of Eight Sample Beds

-8 +10 mesh titanium sponge (see Table I) contained in a 2-in.-OD by 0.5-in.-high circular tray, the bottom of which was constructed of two layers of 70-mesh stainless steel (Type 310) screen. Lava* spacers were used between the individual sample beds to facilitate their removal after being heated to 900°C. After passing through the test chamber, the gas was cooled and recirculated through the flow control equipment.

TABLE I. Approximate Composition of Titanium-metal Sponge

Constituent ^a	Weight Percent	Constituent ^a	Weight Percent
Ti ^b	99.3 min	Cl ^b	0.12
Fe ^c	0.05	H ₂ ^b	0.005
N ₂ ^d	0.004	Mn ^b	0.05
O ₂ ^e	0.09	Si ^b	0.04
Mg ^c	0.08	H ₂ O ^b	0.08
C ^b	0.02		

^aAll other metallic impurities below mass spectrographic level of determination.

^bManufacturer's specification.

^cBy mass-spectrographic analysis.

^dBy semimicro-Kjeldahl analysis.

^eBy vacuum-fusion analysis.

A sample bed was removed by opening the slide valve on the test chamber, inserting the lifting tool, which grasped the uppermost bed from above, lifting it into the cooling chamber (argon atmosphere), reclosing the slide valve, and allowing the bed to cool to room temperature before removal from the chamber. The gas flow was not interrupted during sampling. Figure 6 shows an individual sample bed and the head of the lifting tool used to remove the bed from the test chamber.

Fig. 6
Sample Bed, Lava Spacer,
and Lifting Tool.

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*Aluminum silicate product of Maryland Lava Company, Inc.

IV. PROCEDURE

Various components of the nitridation test loop were calibrated before any experimental runs were made. The five square-edged orifice plates were calibrated with a liquid-sealed gas meter and agreed within 1/2% of theoretically calculated values. The four standard leaks were calibrated by water displacement at the gas pressures of interest. The differential-pressure recorder was checked against a standard manometer. The entire system was leak-tested with a mass-spectrometer helium leak detector.

All titanium used to load the titanium cleanup bed was vacuum-retorted and degassed at 900°C to remove trace amounts of contaminants, including residual magnesium in the titanium sponge. This magnesium remains after a magnesium-reduction step in the manufacture of the sponge and was troublesome in the experimental apparatus because it volatilized and deposited in cool places in the loop, causing flow restrictions in the tubing. Vacuum retorting of the sponge eliminated this problem. The sponge used in the sample beds was not pretreated, and the small amount of residual magnesium present caused no problems.

Before each run, the sample-bed containers were weighed empty, loaded with an appropriate amount of titanium sponge, and reweighed. The amount of titanium sponge used in the beds depended upon the conditions of the run, and was adjusted to obtain a differential reactor. The beds with their lava spacers were then individually lowered and stacked in the reaction chamber. Each bed was contacted by a thermocouple, which was inserted through the wall of the vessel. Fresh titanium sponge was placed in the titanium cleanup bed if necessary, and the appropriate standard leak and orifice plate were installed in the system. A radiation-shielded thermocouple* was installed above the sample beds, and the sample vessel was closed.

The entire system was then sealed and evacuated at room temperature until the attainment of a vacuum of less than 45 μ Hg indicated that the system was virtually leak-tight. At this time, the cleanup bed was heated to 300-400°C, and the sample bed vessel was heated to about 200°C. After these temperatures were reached and degassing was complete (indicated by a vacuum of 25 μ Hg or less), the system was pressurized with argon gas and the gas circulating pump was turned on. The cleanup bed was then heated to its operating temperature of 950°C. When the cleanup-bed temperature had risen to 700°C, the temperature of the sample beds was raised to 900°C. The temperature of the sample beds was always maintained at least 50°C below that of the cleanup bed. This temperature difference promoted removal of the contaminants in the cleanup bed rather than in the sample beds.

*This thermocouple had three concentric-tube radiation shields to reduce the error in gas temperature measurement because of the absorption of radiation from the furnace walls.

When all operating temperatures had reached steady state, the first titanium sample bed was removed as a blank sample for oxygen and nitrogen analysis. This, and all other sample beds were removed by the following procedure: The radiation-shielded thermocouple was raised through the vacuum slide valve, and the valve was closed. After a cooling period of approximately 5 min, the thermocouple assembly was removed and the bed-removal device was inserted into the cooling chamber. After the cooling chamber had been evacuated and purged with argon several times, the slide valve was again opened. All system flow rates and temperatures were recorded, and the thermocouple contacting the sample bed to be removed was withdrawn approximately 1 in. At the appropriate time, the bed-removal device was lowered and attached to the bed, and the bed was lifted from the stack into the cooling chamber. The time of removal was recorded, the slide valve closed, and the bed allowed to cool under an argon atmosphere to a temperature at which it would not react with air ($<75^{\circ}\text{C}$) before it was removed from the cooling chamber.

After removal of the first bed for blank oxygen and nitrogen analyses, the shielded thermocouple assembly was reinserted above the test beds. When all temperatures and the argon flow rate had attained steady-state operation, nitrogen flow was started. The time at which the nitrogen flow was first introduced was taken as the start of the run. The other sample beds were removed at desired time intervals during the run.

Gas samples were taken periodically at locations before and after the nitrogen addition point. These samples provided a check on the purity of the gas leaving the cleanup bed and on the concentration of the mixture entering the test beds. These samples were taken in Pyrex sampling tubes and analyzed by gas chromatographic techniques.

When the last bed had been removed, the run was terminated. The system was cooled to room temperature at a static argon pressure of approximately 1 psig.

The sample beds, which had been withdrawn during the run, were weighed before and after the titanium was removed. A small sample (~ 0.1 g taken as three or four small particles) was removed from the bed material for oxygen analysis, and the remainder of the bed was analyzed for nitrogen.

The nitrogen concentration of each sample from the titanium bed was determined by a semimicro-Kjeldahl analysis. (The general method is outlined by Thompson.²⁰) However, the highly nitrided titanium (above approximately 2 w/o nitrogen) did not dissolve completely when the recommended procedure was used. Complete dissolution was achieved by the analytical procedures outlined in Ref. 6. This procedure is believed to have an accuracy of about $\pm 1\%$ (relative). The accuracy of this analysis is

overshadowed by the differences in the reaction rates of individual sponge particles, so that the reproducibility of the experimental data is believed to be only $\pm 10\%$.

V. PERFORMANCE OF EQUIPMENT

Before experimental data were taken, it was necessary to demonstrate several aspects of the performance of the experimental apparatus. These included:

1. The differential nature of the stack of sample beds.
2. The ability to maintain all reacting sample beds at 900°C .
3. The ability to maintain a constant and known nitrogen concentration in the circulating gas.
4. Low oxygen and water contamination of the circulating gas.
5. The effect of titanium-sponge particle size on the reaction rate.

The differential nature of the stack of sample beds was verified by removing the eight sample beds simultaneously and determining the nitrogen content of each one by the semimicro-Kjeldahl technique. Table II presents the experimental results of one of these runs. A run of this type was conducted at each chosen nitrogen concentration before data at that concentration were taken.

TABLE II. Experimental Results Verifying Differential Reactor Operation

Argon Flow Rate: 800 liters/hr
 Gas Composition: 291 ppm nitrogen in argon
 Sample Bed Size: ~ 1 g
 Run Length: 24.15 hr
 Temperature: 900°C
 Total Pressure: 835 mm Hg
 Flow Direction: Downward through bed

Sample Bed	Weight Percent Nitrogen
1 (top)	8.15
2	7.88
3	6.78
4	8.62
5	8.72
6	8.84
7	8.91
8 (bottom)	8.44
Ave. 8.29 ± 0.66	

The temperature variation between the eight sample beds was maintained within $\pm 10^\circ\text{C}$ (usually $\pm 3^\circ\text{C}$) of 900°C by means of a three-zone furnace and a gas preheater. The individual bed temperatures were continuously monitored by calibrated contact thermocouples (Chromel-Alumel).

Three independent methods were used to determine the nitrogen concentration in the circulating gas. These were: (1) calibration of the nitrogen input rate and argon circulation rate with a liquid-sealed gas meter, (2) rate of pressure change of a known gas volume in the nitrogen addition system, and (3) gas chromatographic analysis of gas samples. The

results from these three methods were normally within $\pm 1\%$ (relative) agreement on the nitrogen concentration in the circulating gas.

The levels of oxygen and water contamination in the circulating gas were too low for convenient analytical measurement. Vacuum-fusion oxygen analyses were made on the reacted sponge particles to determine if these contaminants were present at a significant level. The analyses showed an increase to 0.42 ± 0.22 w/o from an initial value of 0.10 ± 0.04 w/o. No effect of nitrogen concentration or length of run on the final oxygen value was observed. If it is assumed that all water and oxygen present in the argon-nitrogen mixture entering the reaction chamber reacted to form TiO , an oxygen contamination of 0.42 w/o in the reacted sponge would correspond to a gas-phase contamination of less than 1 ppm.

Two different-size fractions of the sponge were reacted with nitrogen in a differential bed run to determine if particle size exhibited a pronounced effect on the reaction rate. In this run, samples consisting of screened particles having average diameters of 0.159 ± 0.065 in. ($-1/4$ in. +8 mesh) and 0.072 ± 0.007 in. (-10 +12 mesh) were used in alternate sample beds. The beds were maintained at 900°C for 95 hr while argon containing 1030 ppm nitrogen was passed through the bed at a flow rate of 840 liters/hr. Analysis of the eight sample beds upon removal indicated essentially the same conversion (conversion = nitrogen atoms/titanium atoms) for both size fractions. The conversions were 0.51 ± 0.02 and 0.52 ± 0.05 for the larger and smaller sizes, respectively.

The surface area of commercially available titanium sponge was measured by the krypton-gas adsorption technique. The results are presented in Table III. Table III also presents the results of a screen analysis of 150 lb of commercial titanium sponge. This material was purchased as " $-1/2$ in. +20 mesh, grade A-1" titanium sponge. Sponge from two different commercial suppliers was screened, and the results were similar, so only the average analysis is reported.

TABLE III. Surface-area Measurements of Titanium-sponge Sieve Fractions

Sieve Size ^a	Surface Area, ^b cm^2/g	Weight Percent of Sponge ^c
$-1/2$ in. +1/4 in.	623	55.4
$-1/4$ in. +8 mesh	1289	30.1
-8 +10 mesh	792	5.3
-10 +12 mesh	672	3.5
-12 mesh	746	5.7

^a $-1/2$ in. +1/4 in. fraction sieved with $1/4$ -in. square opening screen, all other fractions by U.S. Sieve Series screens.

^bAverage of two measurements.

^cTotal weight of sponge: 150 lb.

The reason for the high value of the surface area for the $-1/4$ in. +8 mesh fraction of this material is not known. Visually, this material appears similar to the other size fractions tested. No further attempts were made to determine if this difference is real or, more probably, the result of a nonrepresentative sample, since this particular sieve fraction (-8 +10 mesh was used) was not used in obtaining experimental data. However, since titanium sponge of a specific size fraction can be purchased at little additional cost, purchase of a fraction that has a larger surface area may be beneficial.

VI. RESULTS

Data were obtained on the rate of reaction of titanium-metal sponge with pure nitrogen and with argon-nitrogen mixtures at nitrogen concentrations of 100, 300, 1000, 5000, and 50,000 ppm at total pressures of 767 to 844 mm Hg. The experimental data are presented in Figs. 7-12. Scatter

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Fig. 7. Rate of Reaction of Titanium-metal Sponge with 100 ppm Nitrogen in Argon

Fig. 8. Rate of Reaction of Titanium-metal Sponge with 300 ppm Nitrogen in Argon

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Fig. 9. Rate of Reaction of Titanium-metal Sponge with 1000 ppm Nitrogen in Argon

Fig. 10. Rate of Reaction of Titanium-metal Sponge with 5000 ppm Nitrogen in Argon

308-796

Fig. 11. Rate of Reaction of Titanium-metal Sponge with 50,000 ppm Nitrogen in Argon

308-797

Fig. 12. Rate of Reaction of Titanium-metal Sponge with Pure Nitrogen

in the data is attributed to the variation in surface area between individual sponge particles. The use of larger beds to minimize these variations should result in less scatter of the data. In Figs. 7-12, no corrections were made for the slight variation in nitrogen concentration between runs at the same nominal concentration. In the analysis of the data, however, these slight corrections were made.

These data could be correlated by the equation

$$C = \frac{3.08\sqrt{p}}{1 + 4.42\sqrt{p}} (1 - e^{-0.2\sqrt{t}}), \quad (1)$$

where

C = conversion nitrogen atoms/titanium atoms;

p = partial pressure of nitrogen, mm Hg;

and

t = time, hr.

The curves shown in Figs. 7-12 were obtained from Eq. 1. The following sections discuss the reason for selecting this form of the equation and its applicability to similar situations.

The reacted sponge particles were examined by metallographic, X-ray-diffraction, and electron-microprobe techniques. These techniques were in agreement in that at least three solid phases were present in each reacted sponge particle. However, the nitrogen content of each phase

could not be measured accurately. In most cases, at least one of the phases was extremely thin (<0.005 mm), and because of the geometry of the sponge particles and subsequent intermingling of the phase boundaries, none of the phases could be isolated for chemical analysis. X-ray-diffraction analysis indicated that the three phases were probably TiN_x (δ phase), ϵ -TiN, and a solid solution of titanium and nitrogen (α phase). The lattice parameter in the TiN_x phase was 4.227 Å. This corresponds to $\text{TiN}_{0.6}$ according to the data of Ehrlich,²¹ and to $\text{TiN}_{1.1}$ according to the data of Brager.²² The effect of oxygen on the lattice parameter should also be taken into account, and because its effects are unknown, the above values must be viewed with some skepticism since oxygen was known to be present.

Four additional runs were made to estimate a maximum amount of nitrogen that could be reacted with titanium sponge under practical conditions. In these runs approximately 2 g of sponge were reacted with nitrogen-argon mixtures for 1000 hr at 900°C. Quartz reaction vessels were used. Table IV presents the results of these runs and their comparison with the conversion estimated from Eq. 1.

TABLE IV. Results of 1000-hr Reaction Runs

Gas Composition	Conversion Obtained, N Atoms/Ti Atoms	Conversion Predicted (Eq. 1)
50,000 ppm N_2 in Ar	0.63	0.67
5,000 ppm N_2 in Ar	0.65	0.62
380 ppm N_2 in Ar	0.41	0.49
130 ppm N_2 in Ar	0.32	0.40

VII. DISCUSSION

The objective of this investigation was to provide data on the titanium-nitrogen reaction that would permit the design of titanium-metal sponge gettering systems for removing nitrogen from argon. Although the program was not designed to determine the mechanism of the titanium-nitrogen reaction, the resulting data support the contention that the rate-controlling reaction mechanism is diffusion of nitrogen in the solid phase. The reaction rates were too slow to be the result of nitrogen diffusion through the gas film. Moreover, an increase in the gas velocity from 0.3 to 1.0 ft/sec had no effect on the reaction rate. This conclusion is also supported by earlier work²³ in which the reaction rate of partially nitrified titanium was temporarily increased by annealing the titanium for several hours in a nitrogen-free atmosphere. In this case, the solid-state diffusion of nitrogen would continue during the annealing period, and the nitrogen content at the surface would decrease, thereby allowing a temporary increase in reaction rate when the reacting gas was reintroduced.

The dependence of the reaction rate on the partial pressure of nitrogen in the reacting gas requires that the correlating equation include a pressure-dependent term. The data also indicate that the reaction rate approaches a limiting value. The conventional linear and parabolic rate expressions cannot accurately describe the reaction rate at long reaction times since neither of these expressions has a limiting value. The pressure-dependent term selected was the Langmuir adsorption isotherm for dissociated atoms of diatomic gases. (This and other adsorption isotherms are discussed by Dushman and Lafferty.²⁴) For a model of this type, the following relationship for adsorption is obtained:

$$\theta = \frac{a \sqrt{p}}{1 + a \sqrt{p}}, \quad (2)$$

where

θ = fraction of the active sites covered by adsorbed-gas atoms,

a = constant,

and

p = pressure of adsorbed gas in the gas phase.

If the adsorbed-gas atoms react with the matrix solid (TiN_x), the equilibrium relationship should be

$$c = k\theta, \quad (3)$$

where

c = concentration of adsorbed-gas atoms in the solid matrix,

and

k = equilibrium constant.

Combining the two equations produces

$$C = \frac{ka \sqrt{p}}{1 + a \sqrt{p}} \quad (4)$$

This relationship should describe the effect of pressure on the reaction kinetics.

This isotherm agreed well with the experimental data. The agreement between the Langmuir isotherm and the experimental data suggest that the ultimate solid-phase composition of the nonstoichiometric compound, TiN_x , may depend upon the partial pressure of nitrogen in the gas phase. This effect has been observed elsewhere, such as in the uranium-carbon system.²⁵

The experimental evidence obtained is not sufficient to establish the dependence of the TiN_x composition on the nitrogen partial pressure unequivocally. The possibility that a pseudoequilibrium was being obtained because of extremely slow solid-state diffusion cannot be completely eliminated. This pseudoequilibrium may also be dependent on the gas-phase pressure because of some effect such as its influence on the surface density of the TiN_x phase. The X-ray diffraction data tend to support the "pseudoequilibrium" theory. There was no difference in the lattice parameter of the TiN_x phase when the titanium sponge was reacted with different concentrations of nitrogen. The correlating equation predicts different concentrations of nitrogen in this phase. The X-ray diffraction data, however, are not considered conclusive because of the unknown effect of oxygen contamination on the lattice. In addition, the combined Langmuir isotherm and surface-matrix relationship predict only an average solid-phase composition and do not interpret how this average is obtained. For example, the phase that forms may not be of uniform composition throughout. This would confuse interpretation of the X-ray diffraction data.

The pressure dependency of the reaction would suggest that the nitrogen content of the TiN_x formed at a constant nitrogen partial pressure could be reduced if the nitrogen partial pressure were reduced for an extended period of time. Pollard and Woodward²⁶ reported the evolution of nitrogen from titanium nitride, despite the widely held view that nitrogen cannot be removed from TiN_x by heating in a high vacuum.²⁷ These two observations may not be entirely inconsistent since, at high temperatures below 1000°C, the kinetics reported by Pollard and Woodward are very slow.

The present study attempted to determine if nitrogen could readily be removed from titanium sponge after nitriding. Titanium sponge, nitrided with pure nitrogen at 900°C to a conversion of 0.39 ± 0.04 , was held in a vacuum ($\sim 2 \mu \text{ Hg}$) for 140 hr at 900°C. Analysis of the sponge after treatment showed a conversion of 0.41 ± 0.04 , indicating that no appreciable nitrogen evolution took place in that time.

An exponential form was chosen to represent the time dependence of the reaction rate. The form chosen, $1 - e^{-0.2\sqrt{t}}$, has the desired characteristics of parabolic behavior for short reaction times and asymptotic behavior for long reaction times. It is reasonable to expect asymptotic behavior at long reaction times because the reaction rate must approach a limiting value as the amount of material available for reaction decreases.

The asymptotes that are approached (determined by the pressure function) were selected entirely on the basis of the experimental data. The data indicate that the asymptotes are pressure-sensitive and are determined by the partial pressure of nitrogen in the reacting gas. An unsuccessful attempt was made to correlate the data on the assumption that the end product of the reaction was $\text{TiN}_{1.0}$ at all nitrogen partial pressures.

The constants in the correlating equation were developed by a variable metric minimization of the function

$$f(X_1, X_2, X_3) = 1/4 \sum_{i=1}^{i=NP} \left[\left(1 - e^{-X_3^2 \sqrt{t_i}} \right) (X_2^2) (X_1^2 + p_i^{-1/2})^{-1} - C_i \right]^2, \quad (5)$$

where

X_1, X_2, X_3 = constants to be determined from NP sets of values of observed C_i, t_i , and p_i ;

C = conversion, N atoms/Ti atoms;

t = time, hr;

and

p = pressure, mm Hg.

Reference 28 describes the mathematical procedure used in determining these constants.

The experimental data used to determine these constants were taken at nitrogen concentrations in argon of 100, 300, 1000, 5000, and 50,000 ppm. Neither the pure nitrogen nor the 1000-hr reaction data were used in the determination of the constants because these data were not of immediate interest in the design of gettering systems. However, the resulting equation was in excellent agreement with these data.

Fig. 13. Oxygen Contamination of Reacted Titanium Sponge

Vacuum-fusion oxygen analyses of the reacted titanium-sponge particles were made. Figure 13 presents these data. The results indicate that oxygen contamination of the titanium increased from an initial average value of $0.10 \pm 0.04 \text{ w/o}$ to a final average of $0.42 \pm 0.22 \text{ w/o}$. There was no correlation of the final oxygen content of the titanium with either the reacting nitrogen concentration or the length of the run. The quantitative effect of this contamination on the titanium-nitrogen reaction

rate is unknown, but it is believed to be small because no measurable difference in nitrogen content was seen between titanium samples with high and low oxygen-contamination levels. Related work of the authors has shown that oxygen-contamination levels in the range of 2 to 3 w/o will inhibit the titanium-nitrogen reaction, but quantitative data were not obtained.

VIII. APPLICATION OF CORRELATING EQUATION TO THE DESIGN OF TITANIUM GETTERING SYSTEMS

The equation used to correlate the experimental data,

$$C = \frac{3.08 \sqrt{p}}{1 + 4.42 \sqrt{p}} (1 - e^{-0.2 \sqrt{t}}), \quad (1)$$

where

C = conversion, N atoms/Ti atoms;

t = time, hr;

and

p = partial pressure of nitrogen, mm Hg;

cannot be used directly in the design of titanium-metal sponge gettering systems for the removal of nitrogen from argon. This equation was developed for a differential bed in which all the titanium present in the bed reacts with nitrogen of approximately the same partial pressure. The nitrogen partial pressure would decrease steadily from the inlet to the outlet of a practical bed designed for removing nitrogen from argon. The major relationships of interest would be those between bed size, nitrogen concentration of inlet gas, and the useful lifetime of the bed before it is no longer effective for removing the nitrogen impurity from the argon.

An analytical solution of Eq. 1 could not be obtained without the expenditure of more effort than was warranted by the scope of this project. An iterative computer solution was obtained by a relaxation technique. For this solution, the composition of the inlet gas to the bed was specified and kept constant throughout a calculation, and the titanium was considered to be initially free of nitrogen. The titanium bed was considered as a number of equally sized segments. Each segment, in reacting with nitrogen, increased from an initial concentration, C , to a final concentration, $C + \Delta C$, during a time interval, Δt . The reaction rate in a bed segment was assumed to be constant during the short time interval. The amount of nitrogen required to increase the concentration of a bed segment by ΔC was equated to the amount of nitrogen removed from the inlet gas, and the nitrogen partial pressure was reduced by this amount before the following segment was

calculated. The assumption of a constant reaction rate in a small bed segment is considered reasonable because the actual change in the nitrogen partial pressure in each bed segment is small.

The solution also required the assumption that the average nitrogen content of the titanium sponge and the instantaneous partial pressure of nitrogen are sufficient information to fully define the reaction rate. This assumption is not strictly valid because of differences in the nitrogen-concentration profiles that have been established in reacted sponge particles. These profiles are determined by the past history of the particles' exposure to nitrogen and do affect the reaction rate. For the present calculations, where the bed concentrations, and consequently the nitrogen profiles, change slowly and uniformly, neglecting the effect of the nitrogen profile on the reaction rate is reasonable.

The nitrogen profile in the bed was calculated as follows: For each iteration, the composition, $C_{j,k}$, of the segment, k , at the start of the j th time interval and the nitrogen content of the gas phase entering that segment were used to calculate $(\partial C / \partial t)_p$. The necessary relationship among these variables was determined from a partial derivative of Eq. 1:

$$\left(\frac{\partial C}{\partial t}\right)_p = \frac{3.08 \sqrt{p}}{1 + 4.42 \sqrt{p}} \cdot \frac{0.2}{\sqrt{t}} e^{-0.2 \sqrt{t}} \quad (6)$$

Solving Eq. 1 for $\sqrt{t}$ resulted in

$$\sqrt{t} = -\frac{1}{0.2} \ln \left[1 - \frac{C(1 + 4.42 \sqrt{p})}{3.08 \sqrt{p}} \right] \quad (7)$$

The value of t that could be determined from Eq. 7 is the time that the bed would have required to reach the present concentration, if the total exposure had been at the present gas composition, and thus has no physical significance in the real case. Substituting Eq. 7 into Eq. 6 results in

$$\left(\frac{\partial C}{\partial t}\right)_p = -\frac{3.08 \sqrt{p}(0.2)^2 \left[1 - \frac{C(1 + 4.42 \sqrt{p})}{3.08 \sqrt{p}} \right]}{(1 + 4.42 \sqrt{p}) \ln \left[1 - \frac{C(1 + 4.42 \sqrt{p})}{3.08 \sqrt{p}} \right]} \quad (8)$$

The concentration change, $\Delta C_{j,k}$, for the given segment was then evaluated as $(\partial C / \partial t)_p \Delta t$ and $C_{j+1,k} = C_{j,k} + \Delta C_{j,k}$. The corresponding reduction in the nitrogen pressure in the gas was calculated by material balance. This calculated pressure was employed in the calculation for the next bed segment:

It was also assumed that the reacting gas passed through the bed in "plug" flow. Flow patterns throughout a bed and variables such as the length-to-diameter ratio of the bed were not taken into account. This assumption is not precise for a real bed, but an estimate of the flow characteristics requires a specific bed design. The assumption of plug flow offers maximum utilization of the titanium sponge, and if channeling or dead-spaces exist, the size of the bed required would be larger than that calculated from these data.

The effects of both the number of bed segments chosen and the number of time-interval iterations required on the calculated breakthrough time were studied. Reference values of 100 bed segments and time intervals, corresponding to between 200 and 700 time-interval iterations, were selected. An increase of an order of magnitude in either of these values resulted in a change of only about $\pm 2\%$ in the calculated breakthrough time and average conversion of the bed at breakthrough. Since the calculated breakthrough time itself is believed accurate to only $\pm 10\%$, a further refinement of the calculations was considered unwarranted.

Solutions of the relationships between gas flow rate, nitrogen contamination level, titanium-sponge bed size, and expected bed lifetime were obtained at nitrogen contamination levels in argon of 50, 100, 300, 1000, 5,000, 20,000 and 50,000 ppm and bed lifetimes from 20 to 20,000 hr. These data are presented in Fig. 14. Each curve is the result of approximately seven computations made across the range of interest. For ease of interpretation, these data were graphed as $\log [(\text{moles } N_2/\text{hr at inlet})/(\text{moles Ti present in bed})]$ versus $\log (\text{time to breakthrough, hr})$. The parameters shown on the graph are the concentration of nitrogen in the inlet gas expressed in parts per million by volume. Breakthrough has been defined as that time when the nitrogen concentration in the outlet gas reaches 1% of the inlet concentration.

This graph was developed on the basis of the experimental data obtained at 900°C , a total pressure of approximately 1 atm, titanium sponge of a surface area of approximately $800 \text{ cm}^2/\text{g}$, and low (~ 1 ppm) oxygen and water contamination of the inlet gas. This relationship would probably be valid for reasonable variations of total pressure, but it could be appreciably in error for significant changes in the other variables.

Figure 15 shows the relationship between breakthrough time and average bed conversion, nitrogen atoms/titanium atoms, at breakthrough. In this figure, time to breakthrough is shown versus titanium sponge utilization. Titanium sponge utilization is defined as the ratio of the average bed conversion when breakthrough occurs, C , to the maximum bed conversion that could be obtained at the inlet-gas partial pressure of nitrogen, C_s .

The saturation value, C_s , was determined from Eq. 1 by setting $e^{-0.2\sqrt{t}}$ equal to zero. Figure 16 shows the saturation value, C_s , for concentrations from 10 to 100,000 ppm nitrogen in argon at a total pressure of 1 atm. The titanium utilization data obtained at nitrogen partial pressures from 50 to 50,000 ppm were so similar that only one curve was drawn through the data in Fig. 15. The function $1 - e^{-0.2\sqrt{t}}$ of Eq. 1 is also shown on this graph since it presents a limiting value of sponge utilization.

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Fig. 14. Estimated Lifetime of Titanium-sponge Gettering Bed

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Fig. 15. Effect of Breakthrough Time on Titanium Utilization

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Fig. 16. Effect of Nitrogen Concentration on Titanium Conversion

Many factors, such as capital equipment costs, power costs, and maintenance costs and scheduling, will influence the optimum size of an

installed titanium-sponge gettering bed. However, design lifetimes in the range of 200 to 1000 hr appear to offer a good balance between efficient sponge utilization and small bed size (see Fig. 15). For design lifetimes below 200 hr, the sponge utilization is below 80%, and above 1000 hr, the sponge utilization increases very slowly.

IX. CONCLUSIONS

Titanium-metal sponge is useful for removing nitrogen from argon. The reaction rate depends upon the partial pressure of nitrogen in the gas phase, and the controlling mechanism is believed to be the diffusion rate of atomic nitrogen through the TiN_x (δ) phase. At 900°C, the amount of nitrogen that can be reacted with titanium sponge in a reasonable time varies from a conversion, nitrogen atoms/titanium atoms, of 0.32 with a reacting-gas concentration of 50 ppm nitrogen to a conversion of 0.68 for 50,000 ppm nitrogen in argon.

The design equations presented permit estimation of the size and useful lifetime of titanium-sponge gettering systems for removing nitrogen from argon. Systems of this type should contain additional components for the removal of oxidizing impurities such as oxygen and water vapor before the nitrogen-removal step. The advantages of titanium sponge are that (1) it is a commercially available high-surface-area product, (2) its cost is relatively low, and (3) it requires no pretreatment before use. Both the oxide and nitride reaction products of titanium are nonpyrophoric and can be handled in air. The handling of titanium is also facilitated because neither titanium nor its reaction products are toxic.

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