325
3/6/64

MASTER

SORPTION OF GASES BY VAPOR-DEPOSITED

TITANIUM FILMS

Ti

R. E. Clausing

OAK RIDGE NATIONAL LABORATORY

operated by

UNION CARBIDE CORPORATION

for the

U.S. ATOMIC ENERGY COMMISSION

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Contract No. W-7405-eng-26

METALS AND CERAMICS DIVISION

SORPTION OF GASES BY VAPOR-DEPOSITED TITANIUM FILMS

R. E. Clausing

MARCH 1964

THIS PAGE

WAS INTENTIONALLY

LEFT BLANK

CONTENTS

SORPTION OF GASES BY VAPOR-DEPOSITED TITANIUM FILMS

R. E. Clausing

ABSTRACT

This report summarizes an investigation of the sorption rates of gases on vapor-deposited titanium films. The usefulness of such films for ultrahigh speed vacuum pumping is appraised. Much of the data contained in this report has been previously reported only in progress reports.[1-6] Part of the work has been published in a topical report[7] and in a thesis.[8] This report presents a comprehensive review of the entire investigation.

The sorption of hydrogen, deuterium, oxygen, nitrogen, carbon monoxide, carbon dioxide, water vapor, helium, argon, and methane onto titanium films was measured for a variety of circumstances using techniques and apparatus developed for this specific purpose. The information obtained and techniques evolved in this study have shown that large-scale getter pumping is feasible and can be a very effective means of pumping many gases.

Sticking fractions larger than 0.8 were obtained for hydrogen, deuterium, oxygen, nitrogen, carbon monoxide, and carbon dioxide.

The experiments have shown that the sticking fraction for gases on vapor-deposited films is a function of the deposition conditions. There is strong evidence to support the supposition that conditions which favor

---

[1]Thermonuclear Project Semiann. Progr. Rept. Jan. 31, 1960, ORNL-2926, pp 100-101.

[2]Thermonuclear Project Semiann. Progr. Rept. July 31, 1960, ORNL-3011, pp 117-125.

[3]Thermonuclear Div. Semiann. Progr. Rept. Jan. 31, 1961, ORNL-3104, pp 123-125.

[4]Thermonuclear Div. Semiann. Progr. Rept. Oct. 31, 1961, ORNL-3239, pp 85-91.

[5]Thermonuclear Div. Semiann. Progr. Rept. April 30, 1962, ORNL-3315, pp 79-81.

[6]Thermonuclear Div. Semiann. Progr. Rept. Oct. 31, 1962, ORNL-3392, pp 86-87.

[7]R. E. Clausing, "A Large Scale Getter Pumping Experiment Using Vapor Deposited Titanium Films," pp 345-356 in 1961 Transactions of the Eighth Vacuum Symposium and Second International Congress, Pergamon Press, 1962.

[8]R. E. Clausing, M.S. thesis, Department of Chemical and Metallurgical Engineering, University of Tennessee.

the formation of a porous, fine-grained film structure with a large surface-to-volume ratio produce films with the highest sorption rates.

The technique for measuring sticking fractions is new and in many respects unique. It utilizes a very large sorption surface, thus minimizing the perturbing effect of the instrumentation and evaporation apparatus and reducing the hazard of film contamination due to small leaks in the system or outgassing of system components. The method gives especially good accuracy for measurements of sticking fractions approaching unity. The quantity of gas adsorbed, the gas flux onto the getter surface, and the gas flux leaving the getter surface are measured directly. Any two of these three independent measurements can be used to determine the sticking fraction, thereby providing a means of checking the data. The evaporation techniques, substrate surface, and substrate area were chosen to very nearly duplicate the conditions likely to be encountered in the practical application of large-scale getter pumping.

INTRODUCTION

Research on controlled thermonuclear fusion often requires the ability to remove hydrogen and other gases from the vicinity of the plasma very efficiently at pressures below 1×10^{-8} torr.[9,10] Conventional diffusion-pumping methods remove gases from vacuum systems at rates which are limited by the rate of diffusion into the entrance of a pumping system. Only by exceptionally good design can one remove as much as 0.3 of the gas diffusing into the pumping system.[11] Moreover, it is very difficult and awkward to arrange an experiment in such a way as to have it completely surrounded by entrances to conventional vacuum-pumping systems. If such arrangements are possible, they are very costly and place severe restrictions on the design of plasma experiments. Pumping of gases by sorption (adsorption and/or absorption) and pumping by the use of ionizing plasmas are attractive methods of achieving high gas removal rates and avoiding some of the problems mentioned above.

---

[9]P. R. Bell et al., Thermonuclear Project Semiann. Progr. Rept. July 31, 1960, ORNL-3011, pp 13–29.

[10]C. F. Barnett et al., DCX-1 Without Arc, ORNL CF-60-7-74 (July 1960).

[11]N. Milleron and L. L. Levenson, Discussion on Optimization of Large Oil-Pumped Ultra-High Vacuum Systems, UCRL-5597 (Sept. 1960).

Condensation of gases on very cold surfaces, "cryopumping," does not seem to be promising for this application because of the high vapor pressure of hydrogen over solid hydrogen, even at the boiling point of helium. For some other applications, however, relatively small quantities of hydrogen may be adsorbed on suitable cryogenic surfaces to produce very low pressures.

This investigation is concerned with the use of vapor-deposited titanium films for sorption pumping. Pumps using active metal surfaces to sorb gases are commonly referred to as getter pumps. These pumps are always used in combination with other pumping methods rather than as the sole means of producing and maintaining vacua. Since the getter surface must be prepared at low pressures, a suitable means of bringing the system to this pressure and maintaining it during getter preparation must be supplied. The getter will not have any appreciable capacity for sorption of inert or chemically inactive gases; thus, an auxiliary method of removing these gases is required. These and other considerations suggest that the combination of getter-pumping and diffusion-pumping or ion-pumping techniques should be quite useful. The getter pump could provide high pumping speeds for the active gases which comprise the bulk of the gas load in most systems and a diffusion pump with an efficient cold trap or an ion-pump system could provide the initial pumpdown and remove the chemically inactive gases. It must be emphasized that the diffusion or ion pump forms an essential part of the system in that it provides the only means of handling the inert gases which are inevitably present. These gases would accumulate in the system and prevent the attainment of low pressures if suitable pump capacity were not supplied to remove them. The system which is considered here is one whose characteristics are determined primarily by the sorption characteristics of a thin film of titanium but which at the same time includes some small diffusion-pump capacity.

The titanium film may be deposited in such a way as to cover substantially the entire inner surface of the vacuum vessel. If the film can capture a large fraction of the incident gas molecules, a very effective pump will result. The ratio of the number of molecules sticking on the film to the number striking the film is known

as the sticking probability or the sticking fraction. This ratio is a convenient figure of merit for comparing the performance of films and for the engineering design of pumping systems.

Hydrogen has been the primary subject of the current work since it is the gas of most importance to the thermonuclear fusion research program. The gas is usually introduced into vacuum systems as ions and in rather large quantities. When the ions are neutralized or escape from the plasma, they must be removed rapidly in order to maintain the required low background pressure.

The primary purpose of this investigation was a determination of the sorption rate of hydrogen (and also the other gases likely to be present in ultrahigh vacuum systems) onto titanium films in order to predict the usefulness of the pumping concept described above.

A new method of determining the sorption rates for gases on getter films was developed during this investigation. The method and equipment used to implement it are to be described. The sorption data obtained will be discussed with particular emphasis on the importance of the film structure. An attempt is made to correlate the film structure with the sorption characteristics.

PREVIOUS WORK

Getters have been used for many years for the removal of gases from electron tubes and experimental devices.[12,13] In recent years, several techniques have been developed for the use of getter-ion pumping for routine application to systems operating at pressures from 10^{-4} torr to

[12]S. Dushman, Scientific Foundations of Vacuum Technique, p 17, Wiley, New York, 1949.

[13]P. Della Porta, Vacuum 4, 284-302 (1954).

well below 10^{-8} torr.[14-17] Barium has wide usage as a getter in electron
tubes and has been used in a few getter-pump designs. Molybdenum has
been used with success in some applications.[17] For other purposes, how-
ever, titanium is the getter material used most frequently. The reasons
for the choice of titanium as the material for getter-pump design seem
to be based upon its excellent gettering characteristics for a wide vari-
ety of gases and the relative ease with which it may be evaporated.[18-23]

While some data for sorption rates on evaporated titanium films
have appeared in the literature prior to this investigation,[16,17,24]
they are insufficient to permit the design of large systems because
either (1) the data have been obtained without adequate attention to the
many variables which may influence the results, (2) the data are incom-
plete, (3) the data are of questionable value because of inadequate
measuring techniques, or (4) the data were obtained under conditions
sufficiently different from those expected in the present application
so as to prevent extrapolation of the data. During the course of this
investigation, some additional data have been published.[25,26] These

[14]R. H. Davis and A. S. Divatia, Rev. Sci. Instr. 25, 1193-1207 (1954).

[15]C. R. Meissner (ed.), 1959 Vacuum Symposium Transactions, pp 307-310,
Pergamon Press, New York, 1959.

[16]Ibid, pp 297-301.

[17]N. Milleron and E. C. Popp, Gettering Hydrogen at Ultra-Low Pressures
by Evaporated Metal Coatings, UCRL-5258 (Nov. 1958).

[18]B. M. W. Trapnell, Proc. Roy Soc. (London), Ser. A, 218, 566-577
(1953).

[19]S. Wagner, J. Phys. Chem. 60, 567 (1956); 61, 267 (1957).

[20]L. F. Ehrke and C. M. Slack, J. Appl. Phys. 11, 129 (1940).

[21]W. Espe, Powder Met. Bull 3, 100 (1956).

[22]W. Espe, M. Knoll, and M. Wilder, Electronics 23, 80 (1950).

[23]A. L. Reimann, Phil. Mag. 18, 1117 (1934).

[24]V. L. Stout and M. D. Gibbons, J. Appl. Phys. 26, 1488 (1955).

[25]V. A. Simonov et al., Nucl. Fusion, Suppl. Part I, 325-339 (1962).

[26]D. R. Sweetman, Nucl. Instr. Methods 13(3), 317-320 (1961).

newer data show large sorption rates and are therefore interesting and encouraging, but do not provide useful design information.

It has been shown that the sorption properties of barium films can be varied considerably by controlling the deposition process.[27] Other investigators have reported changes in the structure of vapor-deposited films of various metals as a result of altering substrate temperatures, evaporation rates, and gas pressure during film formation.[28-31] In general, for a given metal, lower substrate temperatures, higher evaporation rates, and higher gas pressure during film deposition all tend to produce films with finer structures and larger surface area. No data are available, however, on the effect of titanium film structure on sorption rates of gases. The work of previous investigators suggests that a study of the factors influencing the structure of the deposit should be included in any study of the sorption of gases on thin films, that these factors should be controlled as well as possible, and that provision should be made to vary these parameters over considerable ranges.

None of the methods used by previous investigators are entirely satisfactory for the present investigation.[32] Although it is possible that a modified version of Becker's apparatus,[33] used to study sorption of gases on refractory-metal ribbons, might have been adopted for use with vapor-deposited titanium films, there are rather serious problems associated with this technique. In Becker's technique, a sorption surface of known area is placed in an evacuated glass bulb, gas is admitted

[27]K. M. Kazawa, *Vacuum* 10, 210 (1960).

[28]L. Holland, *Vacuum Deposition of Thin Films*, Chap. 7, Chapman and Hall, London, 1956.

[29]DaC. E. N. Andrade and J. G. Martindale, *Phil. Trans. Roy. Soc. (London), Ser. A* 234, 69–101 (1935).

[30]R. G. Picard and O. S. Duffendack, *J. Appl. Phys.* 14, 291 (1943).

[31]H. Levinstein, *J. Appl. Phys.* 20, 306 (1949).

[32]G. R. Love, *Methods for the Study of Gas Metal Reactions in Ultra-High Vacuum*, ORNL CF-58-9-93 (June 1959).

[33]W. G. Frankenburg, V. I. Komarewsky, and E. K. Rideal (eds.), *Advances in Catalysis*, VII, Academic Press, Inc., New York, 1955.

at a small known rate, and the pressure in the bulb is recorded as a function of time. The calculation of sticking fractions from these data is discussed in the section titled "Experimental Methods and Techniques." Becker's technique would require a titanium deposit of controlled area. The area must be small with respect to the size of the measuring bulb to avoid pressure gradients in the system when very large sorption rates are obtained. This requirement is in opposition to a second one, namely the film area must be large enough to minimize the effects of gas sorption onto the walls of the measuring system and the sorption and ionizing effects due to the presence of a hot ion gage filament. The effects of gas sorption onto the walls of the measuring system and the effects of the hot ion gage filament are particularly troublesome when hydrogen sorption is being measured. A method was developed for the present study which uses a very large sorption area and avoids the problem of pressure gradients.

OBJECTIVES

As stated in the Introduction, the primary objective of this work was to obtain data for the sorption of hydrogen and other gases on vapor-deposited titanium films. The data are applied to the design of large pumping systems for research in plasma physics associated with research on controlled thermonuclear fusion; therefore, the sorption data should be obtained in such a manner as to permit easy extrapolation to large, metal, ultrahigh vacuum systems. This implies that the evaporator, the substrate materials, the substrate temperatures, the angle of incidence of the vapor on the substrate, the system pressures, the sorption rates, and, if possible, even the system dimensions should approximate the conditions of the application or that these factors be studied in such a way as to permit extrapolation.

A second objective was the development of techniques required for the operation of large getter-pumped systems and determination of the usefulness of combined getter pumping and diffusion pumping.

A third objective was exploration of the effects of film structure and other variables on the sticking fraction for hydrogen and other gases on titanium films.

All of these objectives were attained. An experimental apparatus was designed which satisfies the requirement of producing data which easily can be extrapolated to large, metal pumping arrangements. The techniques for and reliability of large-scale getter pumping have been established and the effect of film structure and several other variables on the sticking fraction has been explored.

EXPERIMENTAL METHODS AND EQUIPMENT

First Method and Original Equipment

The sticking fraction for a gas on a surface is defined as the ratio of the number of gas molecules "sticking" to the surface to those striking the surface. The number of molecules n_T striking a surface is given by

$$n_T = 1/4 \ n \ v \tag{1}$$

where

    n = number of particles per square centimeter, and

    v = arithmetical average velocity.

Using the relationships from the kinetic theory of gases, the following expression is obtained:

$$n_T = 3.513 \times 10^{22} \ P_{torr} \ M^{-1/2} \ T^{-1/2} \ \text{particles/cm}^2/\text{sec} \tag{2}$$

where

    P = gas pressure in torr,

    M = molecular weight of the gas, and

    T = temperature in °K.

The number of particles sorbed by a film may be determined by admitting a measured amount of gas to a closed container and monitoring its pressure. A simple experiment for determining the sticking fraction can then be made as follows: A large, closed, chemically inert container is evacuated; a titanium film (having a known area) is placed inside the container; gas is admitted at a known rate; and the pressure in the container is monitored. The pressure, temperature, and molecular weight of the gas provide the information required to calculate the rate of gas impingement on the surface. A knowledge of the container volume, the gas pressure, and the

gas temperature allows the calculation of the quantity of unreacted gas
in the container. This can be subtracted from the amount of gas admitted
to the system to give the quantity of gas sorbed on the film. If the
gas-admission rate is small enough to allow adequate measuring time and
the data are obtained continuously, it is possible to calculate sticking
fractions for various conditions.

Figure 1 shows the original experimental equipment which was built
to use the technique described above. The vacuum tank is 36 in. in
diameter and 36 in. high. It is made of aluminum and has a loose-fitting
removable, water-cooled copper liner. The liner is in three sections;
its original purpose was to permit easy removal of the getter deposits.
It was not, however, necessary to clean the liner during approximately
150 days of operation. The 6-in. MCF 700 diffusion pump is separated
from the tank by a Freon-cooled baffle (−40°C) and an isolation valve.
A vacuum lock is provided to permit changing the getter evaporator assem-
bly. The vacuum seals on both the tank and the lock are neoprene gaskets
and O-rings with silicone vacuum grease lubrication.

In this apparatus, measurement of the sorption capacity of the
getter films was made by metering the gas into the space between the
tank and liner so that it enters the liner in a more or less diffused
way rather than as a directed beam. Two Veeco RG-75 ion gages were used
to monitor the pressure in the system. One gage measured the pressure
in the liner while the other measured the pressure in the area between
the tank and the liner. Due to the many holes in the top of the liner,
both gages normally read very nearly the same pressure.

The getter was evaporated from a source near the center of the tank
and deposited on the water-cooled liner. Once the deposit was established,
gas was admitted at a known rate and the pressure increase noted. Stick-
ing fraction data were calculated from these data by dividing the calcu-
lated rate of gas sorption per unit area by the rate at which gas impinges
on the surface, as discussed above. Figure 2 is a photograph of the
original equipment showing its size and physical arrangement.

A large getter area of approximately 35,000 cm^2 was used so that
effects due to gas interaction with the hot ion gage filament or sorption
on surfaces other than the getter were very small.

VACUUM LOCK

ROUGHING VALVE FOR
VACUUM LOCK

TO HYDROGEN LEAK SYSTEM
SHUT-OFF VALVE

ALUMINUM VACUUM TANK

FILAMENT VAPORIZATION
SOURCE

$33\frac{1}{2}"$

WATER COOLED COPPER LINER

VALVE

FREON COOLED COLD TRAP

DIFFUSION PUMP
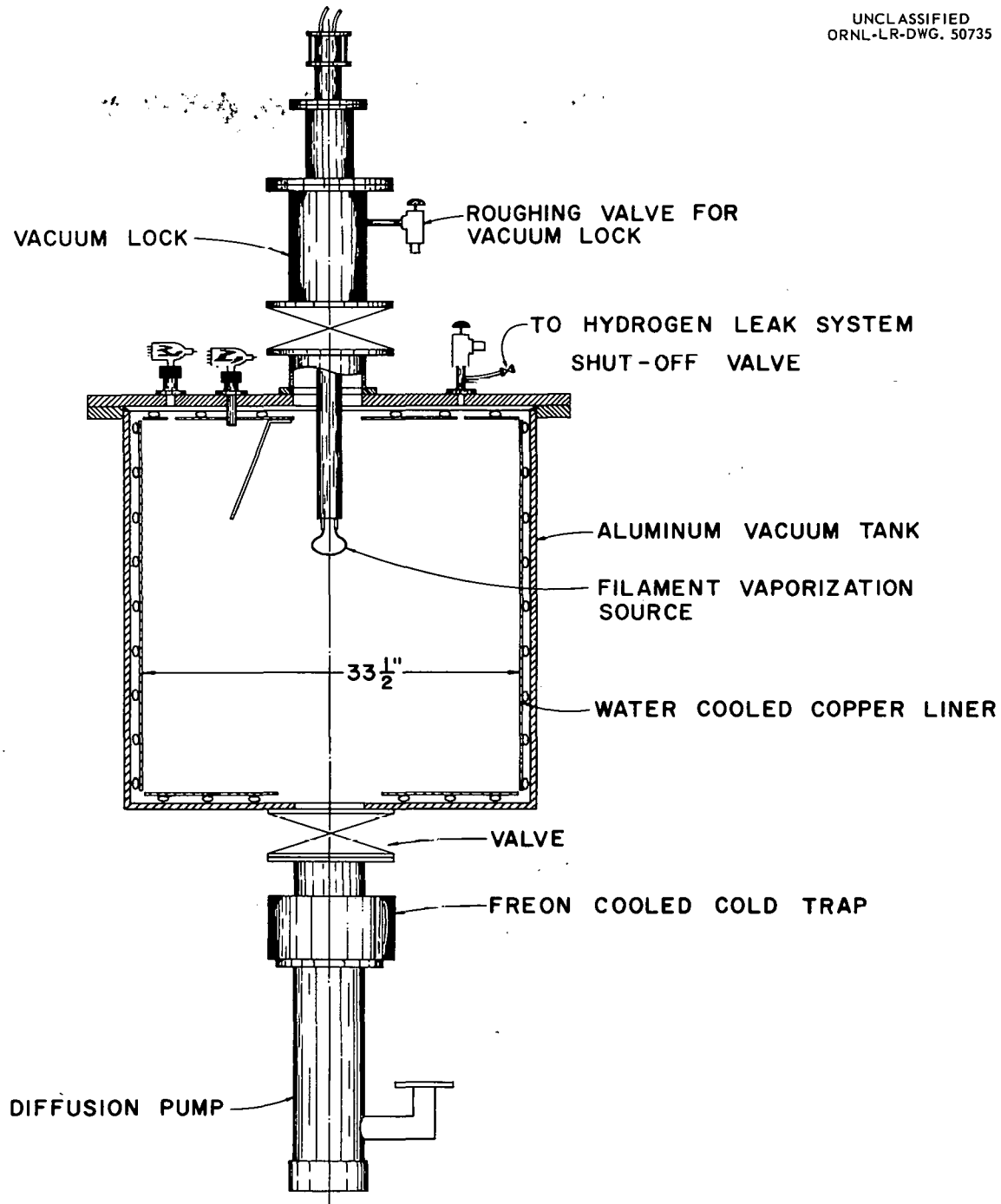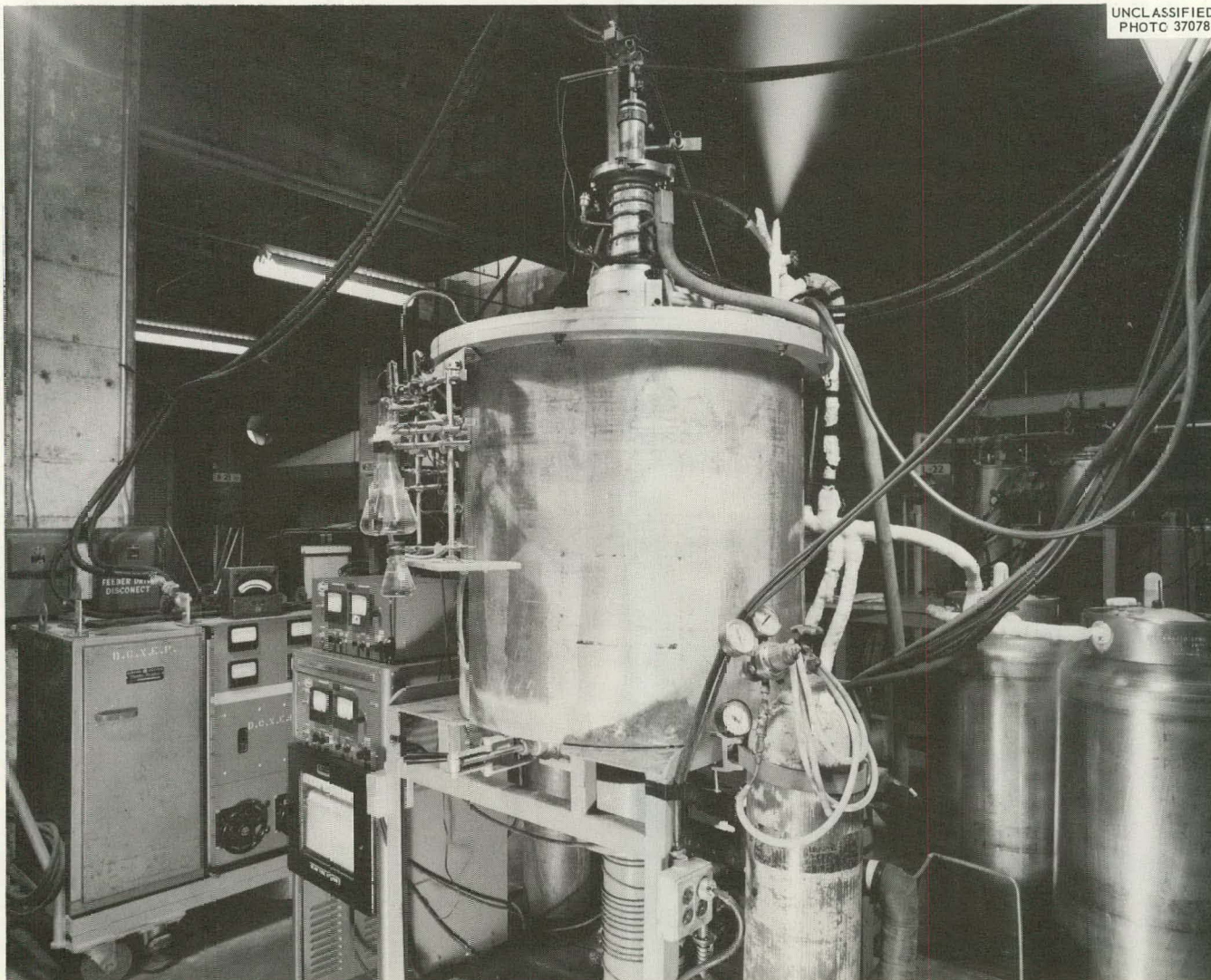
Fig. 1. Large-Scale Getter Pump Test.

Fig. 2. Photograph of the Large-Scale Getter Pump Test During an Evaporation.

An evaporation source typical of those used in nearly all of the experiments is shown in Fig. 3. It was electrically heated by direct resistance. A current of about 450–500 amp was passed through the filament at a low voltage. Approximately 1000–1500 w are required to produce the desired evaporation rate. The source consists of a 10-in. tantalum rod, 0.170 in. in diameter, the center 7 in. of which is wrapped with one layer of close-wound 0.030-in.-diam niobium wire and then two layers of 0.035-in.-diam titanium wire. The wound assembly was bent into the shape shown for convenience in passing it through the vacuum lock. The purpose of the niobium wire was to provide a sump for melted titanium and, by reacting with it, to provide an alloy with a higher melting point. This prevents the molten titanium from dropping from the filament and at
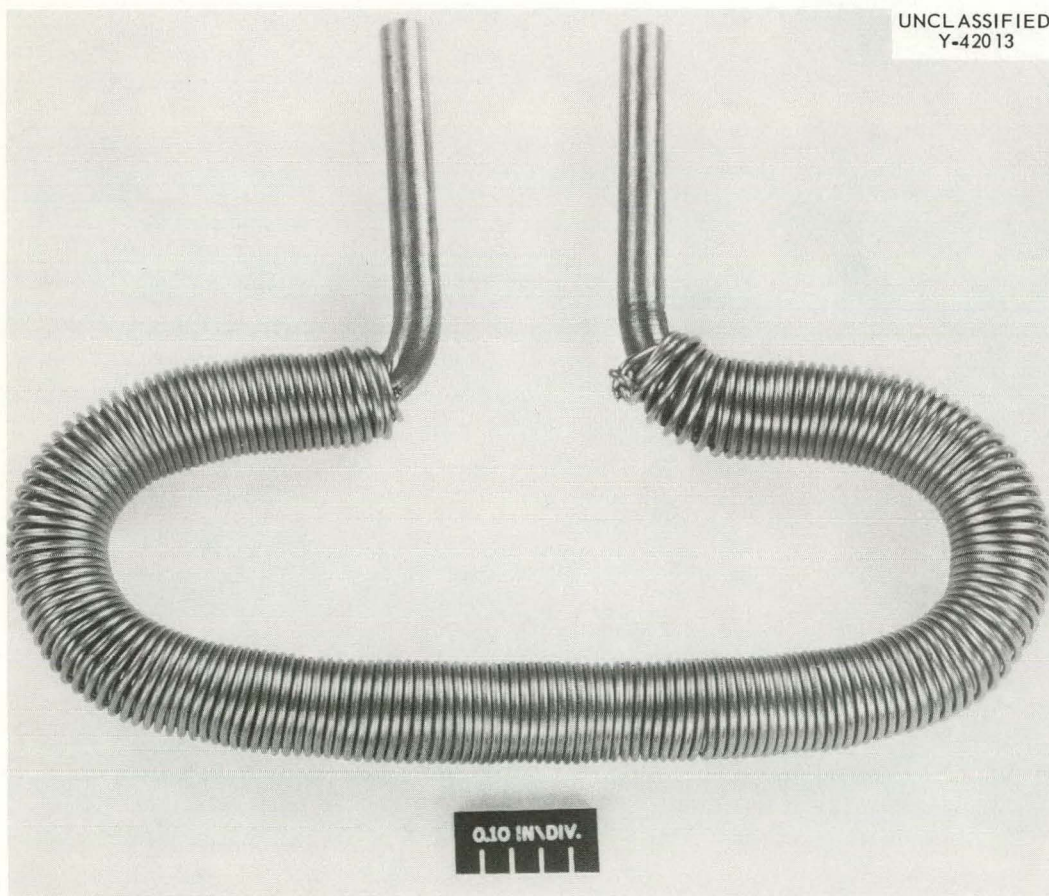
UNCLASSIFIED
Y-42013

Fig. 3. A Source for Evaporation of Titanium Which is Heated by Electrical Resistance.

the same time permits the filament source to operate at temperatures above the melting point of titanium. The vapor pressure of titanium above a 50 at. % Ti—50 at. % Nb alloy at 1950°C is estimated to be 4×10^{-1} torr while the vapor pressure of pure titanium at its melting point of 1720°C is about 8×10^{-2} torr. This technique permits faster, more easily controlled evaporations than can be obtained from filaments wrapped with titanium alone.

The standard operating procedure used a new, carefully weighed filament for each experiment. The filament was heated to the evaporation temperature in several steps. The evaporator is degassed by a short holding time at 300 amp. As the current is again raised, the titanium melts and is drawn by capillary action into the voids between the niobium wires. As the titanium flows into the niobium windings and alloys with them, the current gradually is raised to a predetermined level, depending upon the desired evaporation rate. Auxiliary experiments determined the evaporation rate as a function of filament current. The current was normally set to 500 amp where the evaporation rate was 2 to 3 g/hr. Evaporation is negligible below 350 amp. The changing electrical resistance during the melting of the titanium provides the operator with a confirmation of proper filament operation. Weight-change data showed that the evaporation rates from these filaments are essentially constant for several hours at a given constant current.[34] The deposition rates reported herein were determined from filament weights before and after a run, assuming uniform evaporation rates during the time the filament was at its operating current.

A larger filament with an active length of approximately 35 in., wound into a spiral shape, required approximately 7500 w at 500 amp and evaporated at a rate of 16 g/hr.

Figure 4 shows a homogeneous filament made of an alloy of tantalum and titanium. Evaporation rates from this filament per unit surface area are comparable with those obtained from the previously described sources.

---

[34]For these tests, filaments were removed and weighed every 15 min during evaporation. Identical currents were used for each of the 15-min evaporation periods.
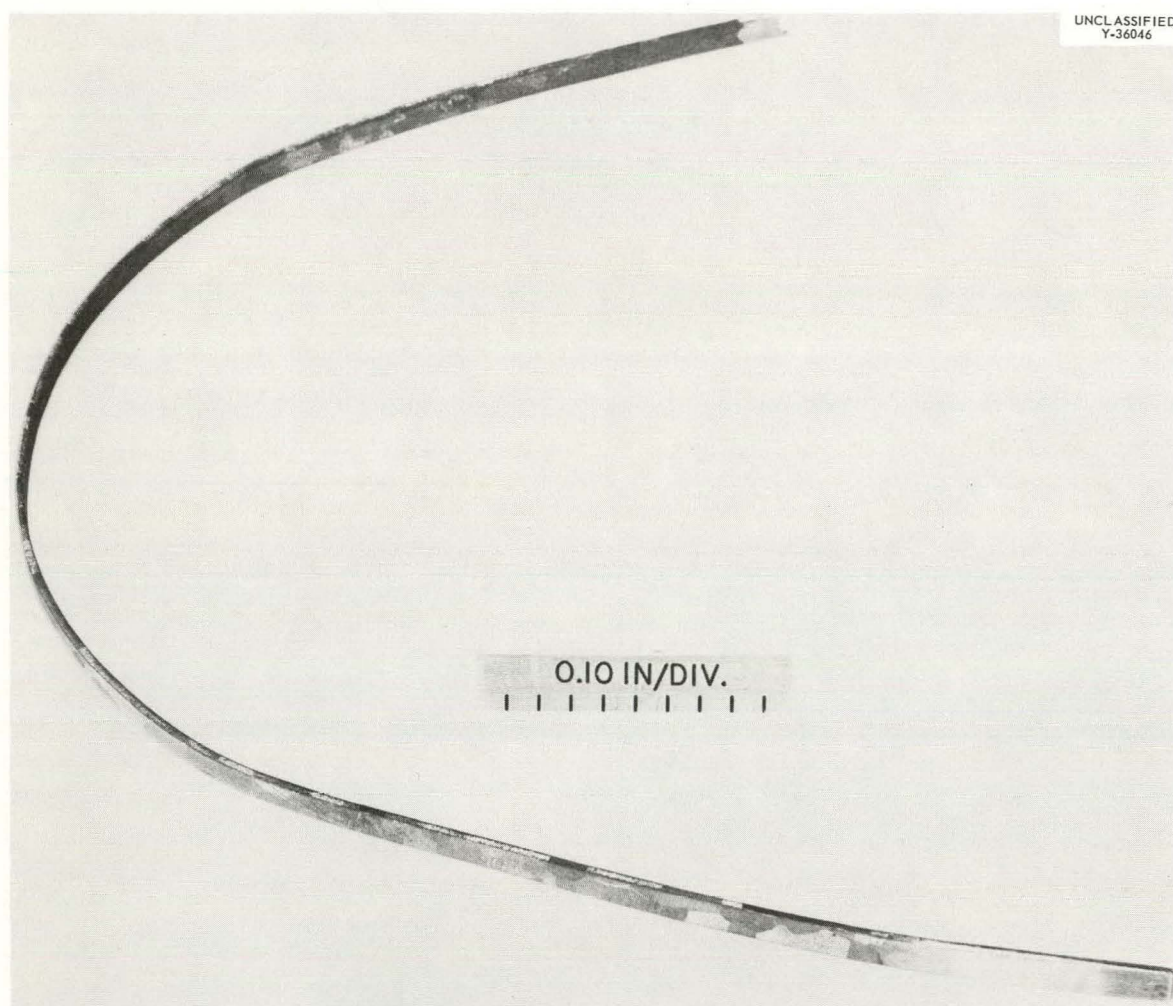
Fig. 4.   A Homogeneous Filament Source for the Evaporation of Titanium Made of an Alloy of Tantalum and Titanium.

These alloy sources are potentially capable of higher evaporation rates
than pure titanium wire because they can be operated at higher tempera-
tures. The alloys can be formed into wire, and heating power may be
supplied directly from a Variac-type autotransformer. A somewhat more
detailed discussion of both of the sources described above has been
published.[35]

The feasibility of large-scale getter pumping, many of the operating
characteristics, and considerable improvement of techniques were estab-
lished with the equipment described. There were, however, two major
difficulties with this apparatus: (1) the interpretation of very high
sorption rates was difficult because of the pressure gradients formed
in the system, and (2) base pressures in the original system were limited
to about 3×10^{-8} torr due to outgassing of system components. The base
pressure limitation was not serious for many experiments and was later
lowered considerably by the use of a bakable liner inside the water-cooled
liner. The difficulty in obtaining accurate data for high sorption rates
was overcome by modifications in the measurement method suggested by the
following analysis.

Principles of the Modified Experiment

Let us consider the hollow spherical geometry, as shown in Fig. 5,
with gas being continuously emitted uniformly in all directions from a
source at the center of the sphere. The inside surface of the spherical
shell is coated with a material which absorbs a fraction s of the gas
molecules incident upon it. The total number of particles impacting on
the wall per second per unit area (n_T) is given by the expression,

$$n_T = n_e + (1-s)n_e + (1-s)^2 n_e + (1-s)^3 n_e \ldots\ldots \quad , \qquad (3)$$

where

n_e = the number of particles emitted from the source per second
divided by the inside area of the sphere, and

$(1-s)$ = the ratio of the particles leaving the absorbing surface to
those striking it.

[35]Thermonulcear Project Semiann. Progr. Rept. July 31, 1960, ORNL-3011.

SURFACE A

I_g

GAS
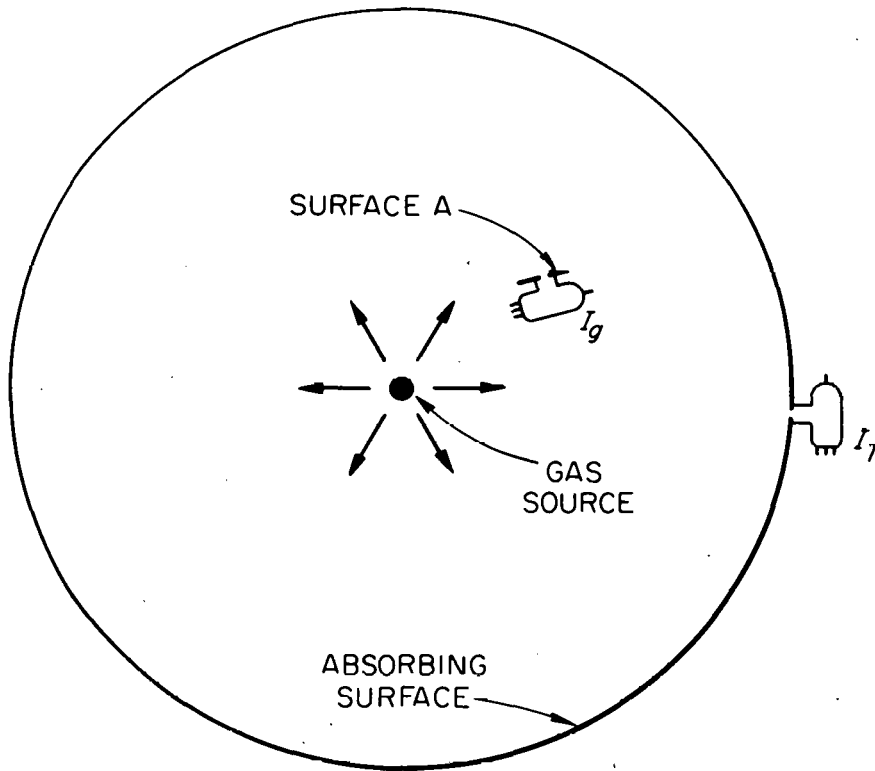SOURCE

I_T

ABSORBING
SURFACE

Fig. 5. Ideal Spherical Geometry.

The term $(1-s)n_e$ then equals the number of molecules that survive the
first collision to strike the wall again and $(1-s)^2 n_e$ equals the number
of molecules that survive the second collision to strike the wall a third
time. This series converges to a finite limit for all values of s
between zero and unity, $0 < s < 1$, so that the total flux against the
wall per second per unit area is given by

$$n_T = \frac{n_e}{1 - (1-s)} \quad , \tag{4}$$

or

$$n_T = \frac{n_e}{s} \tag{5}$$

and

$$s = \frac{n_e}{n_T} \quad . \tag{6}$$

Equation 6 is reasonable since it states that the sticking fraction s is equal to n_e (which in the steady state is the number of molecules introduced into the system per unit time per unit area) divided by the total number of collisions with the wall.

Now consider the flux of particles onto the small surface (A in Fig. 5) positioned so that particles in free molecular flow from the source cannot strike this surface except after first striking the sorbent wall of the sphere. Due to the geometric arrangement, this surface will intercept particles which have made one or more collisions with the wall but none of the particles directly from the source. The flux of particles onto this surface per unit area is the same as that onto the sorbent wall if the flux of particles coming directly from the source is subtracted.[36] The flux of particles onto this surface per unit surface area is then the summation of all the terms on the right side of Eq. (3) except n_e. If this flux of particles is called n_g, then

$$n_g = (1-s)n_e + (1-s)^2 n_e + (1-s)^3 n_e \quad . \tag{7}$$

Substituting Eq. (7) into Eq. (3) gives

$$n_T = n_e + n_g \tag{8}$$

and substituting Eq. (8) into Eq. (6) gives

$$s = \frac{n_e}{n_e + n_g} \tag{9}$$

or

$$s = \frac{1}{1 + n_g/n_e} \quad . \tag{10}$$

Equation 6 may also be written in terms of n_T and n_g by solving Eq. (8) for n_e and substituting the result into Eq. (6)

$$s = \frac{n_T - n_g}{n_T} \quad . \tag{11}$$

---

[36]This statement is true only if there is a suitable angular distribution of particles leaving the getter surface. Partial validation of this assumption has been obtained experimentally. Values of s calculated from Eq. (6) (which does not use this assumption) agree with values calculated from Eqs. (10) and (12) within the estimated experimental error over the range of s values from 0.1 to 0.9. The estimated limit of combined errors is, however, 20–30% of the value of s.

or

$$s = 1 - \frac{n_g}{n_T} \quad .$$ (12)

Now, n_e can be determined if a metered gas leak is used and n_g can be determined from an ion gage connected to an orifice in the plane of the small surface (A). The flux of particles into the gage orifice is assumed equal to the flux out of the gage orifice. One can, therefore, determine the flux of particles n_g from classical kinetic theory based on the pressure and temperature in the gage.

In like manner an ion gage I_T connected to an orifice in the wall of the vessel can be used to determine the flux n_T directly. The three quantities, n_e, n_T, and n_g, can be determined separately and independently. Any combination of two of these quantities is sufficient to determine s.

A thorough analysis of the assumptions involved and the accuracy of the different methods was not attempted because of the difficulty in assigning reasonable values to the errors associated with ion gage measurements. Consideration of the errors inherent in these methods leads, however, to the conclusion that Eq. (10) is the most accurate of the three expressions over the entire range of values of s from 0.01 to unity.

The above conclusion resulted from the assumption that a ±20% error in the ion gage readings was the predominating error. The errors in the value of s calculated from Eqs. (6), (10), and (12) are given in Table 1. For small values of s, the errors for Eqs. (6) and (10) are approximately ±20% of the calculated value. The values for Eq. (12) are not at all accurate below about s = 0.2. As s approaches unity, the error approaches zero for both Eqs. (10) and (12). The values of s from Eq. (6) are approximately ±20% over the entire range of s.

By these comparisons, it is seen that Eq. (10) is the most accurate of the equations over the entire range of s values. Equation 6, however, is useful at low values of s and Eq. (12) at high values; indeed they can provide good checks on the values obtained by the use of Eq. (10).

The method using Eq. (12) provides a simple and convenient measurement of the sticking fraction for substances like water or other condensable vapors which pose problems in the direct measurement of n_e.

Table 1. Effect of a 20% Error in Ion Gage Readings
on the Calculated Sticking Fraction Values

Eq.	Formula	Real Value of s			
		0.01	0.1	0.5	0.9
6	$s = \dfrac{n_e}{n_T}$	0.00865–0.012 −17 to +25%	0.0865–0.0125 −17 to +25%	0.4165–0.625 −17 to +25%	0.865–1.25 −17 to +25%
10	$s = \dfrac{1}{1 + n_g/n_e}$	0.0086–0.0125 −17 to +25%	0.085–0.122 −15 to +22%	0.454–0.556 −9 to +11%	0.885–0.917 −1 to +2%
12	$s = 1 - \dfrac{n_g}{n_T}$	−0.51–0.34 −5100 to +3400%	−0.35–0.40 −350 to +400%	0.25–0.66 −50 to +32%	0.85–0.934 −5 to +4%

Equipment Revisions

The experimental facility was modified as shown in Fig. 6 to approximate the conditions required in the model discussed above. The gas is introduced at the center of the chamber through many small holes drilled in the end of a 1/8-in. stainless steel tube. There is an arrangement to protect the source from titanium evaporation whenever required.

The gas-metering station, shown schematically in Fig. 7, is connected to the stainless steel J tube through a vacuum shut-off valve and a 3-ft length of copper tubing.

The operation of the leak station is as follows: The manifold to valve B is evacuated when the test chamber is evacuated. This part of the manifold is always under vacuum. A cylinder of the gas, whose sorption rate is to be measured, is attached to line E and admitted at a slight positive pressure through valve D so that a small flow of gas passes the opening to valve B, flows through the measuring burette, and bubbles out through the oil reservoir. A portion of the gas flow is drawn through valve B into the test chamber at a rate which is determined by the adjustment of valve B. Whenever it is desired to measure the gas-admission rate, the pinch clamp C is closed and the oil rises in the burette as gas flows through valve B into the system. The length of time for a predetermined quantity of gas to be used is measured with a stop watch or electric timer. Two gases may be admitted simultaneously if a second leak station is used (shown as B′, C′, D′, and E′).

ROUGHING VALVE FOR
VACUUM LOCK

VACUUM LOCK

ION GAGE O

TO HYDROGEN
LEAK SYSTEM

ALUMINUM
VACUUM TANK

ION GAGE g

FILAMENT VAPOR-
IZATION SOURCE

ION GAGE T

GAS SOURCE
DIFFUSER

WATER-COOLED
COPPER LINER

BAKABLE LINER

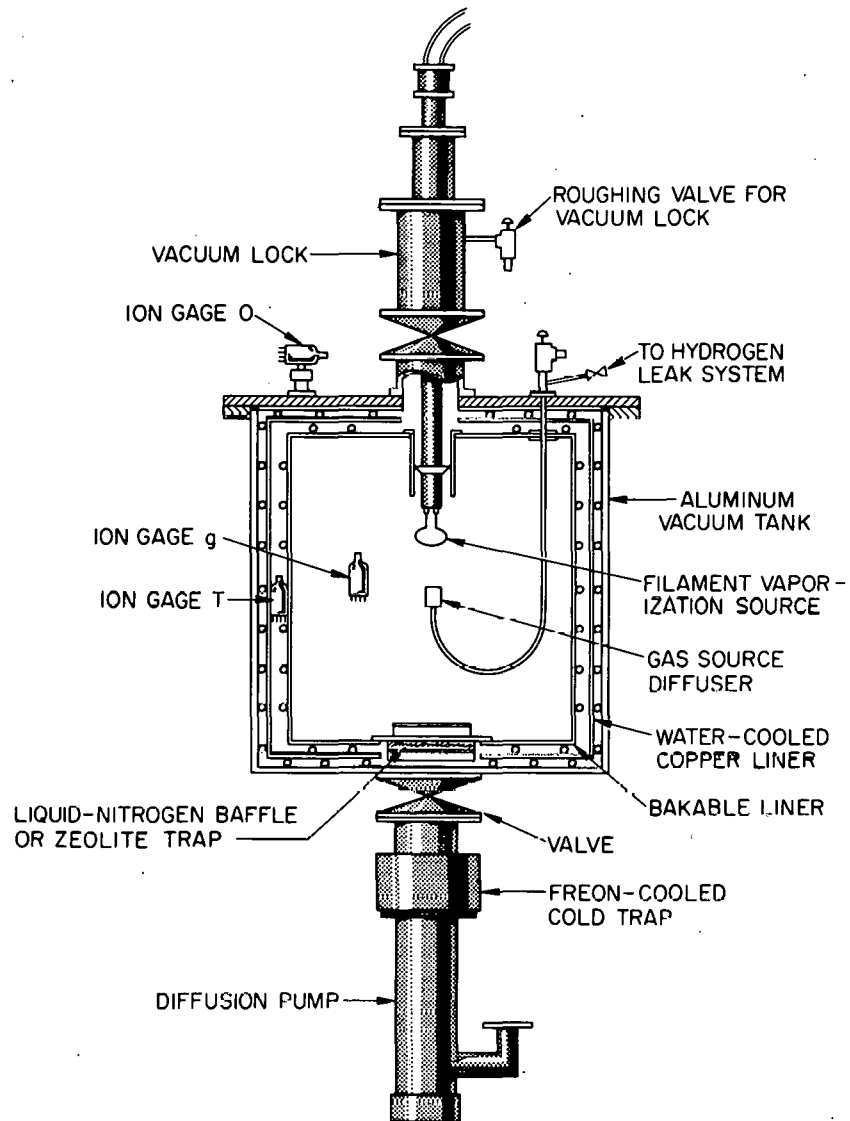LIQUID-NITROGEN BAFFLE
OR ZEOLITE TRAP

VALVE

FREON-COOLED
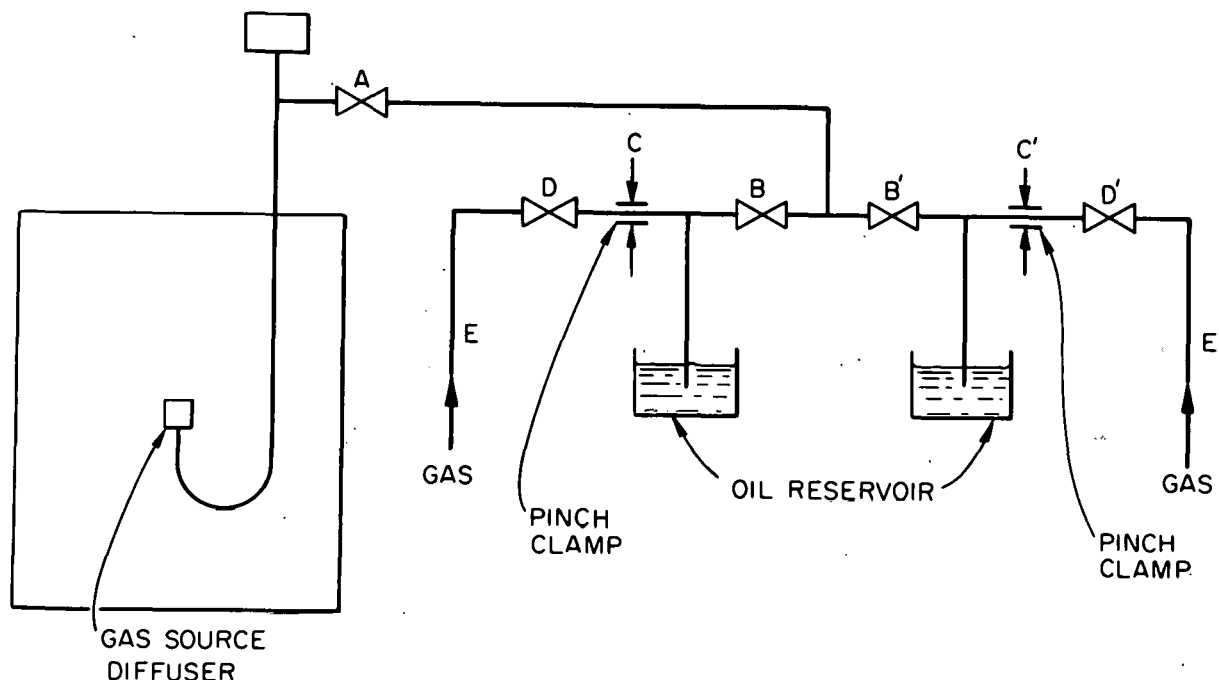COLD TRAP

DIFFUSION PUMP

Fig. 6.   Large-Scale Getter Pump Test with Bakable Liner.

Fig. 7. Gas-Metering Station for Permanent Gases.

The system for admission of water vapor is shown in Fig. 8. The
rate of water vapor admission is difficult to measure; hence the method
associated with Eq. (12) is used. The apparatus shown provides a method
for admitting water vapor at a constant and reproducible rate. Since
the manifold is at a temperature higher than the ice water reservoirs,
no condensation in the manifold is encountered. Because ice is in the
reservoir, the temperature of the bath remains constant, providing a
known constant vapor pressure of water vapor to valve B. The water used
in the reservoir is prepared by boiling, first at atmospheric pressure
and then under vacuum, to remove soluble gases as completely as possible
before each experiment. The innermost ion gage, I_g, a Veeco RG-75,
modified by removing the tabulation, opens into the system in such a
way as to be directly exposed to a large protion of the interior surface
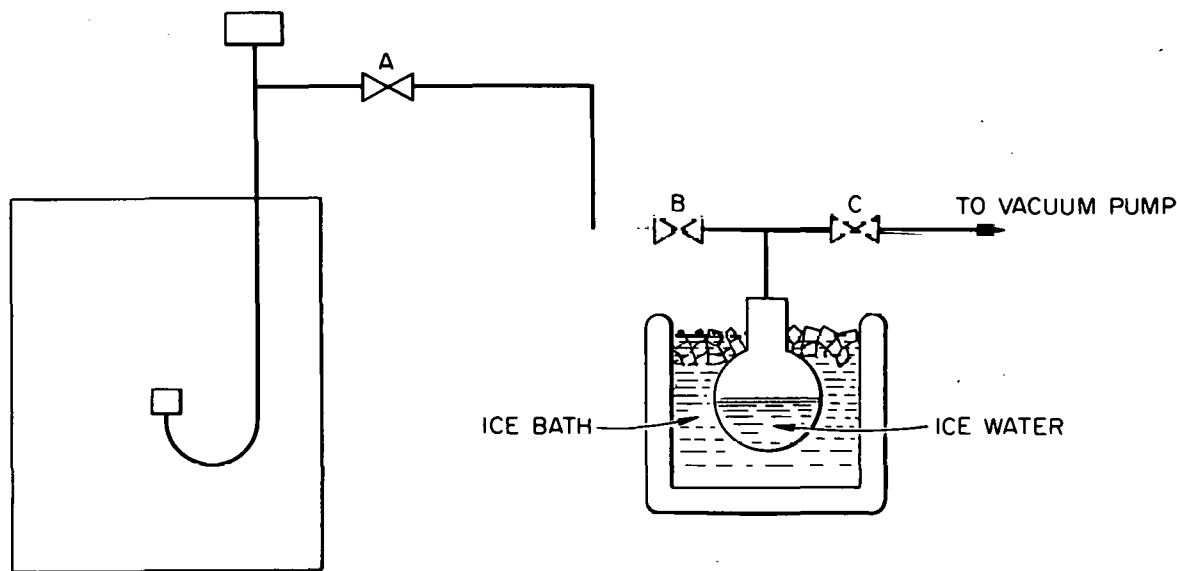but not to the primary gas inlet. This gage is used to determine n_g.

A

B   C   TO VACUUM PUMP

ICE BATH   ICE WATER

Fig. 8. Method for Introducing a Controlled Amount of Water Vapor.

The ion gage opening is protected against titanium deposits by its position. The second ion gage, also a modified Vceco RG-75, located snugly against an opening in the vessel wall, receives gas directly from the source as well as gas from the interior walls of the vessel. It is used to determine n_T. This gage is protected from titanium deposits by a mechanical shutter.

The inner vessel is of copper with all openings effectively sealed except for the pumping area through the isolation trap. This trap is filled with adsorbent material or cooled with liquid nitrogen. It prevents the contamination of the inner vacuum with condensable vapors from the pump or the gaskets and at the same time permits the chemically inert gases to diffuse from the interior of the vessel to the diffusion pump.

The inner vessel is provided with cooling coils for water or liquid nitrogen and with a means of heating it to about 400°C for degassing it in preparation for operation. Pressures as low as 5×10^{-10} torr are obtained during experiments after baking.

Electron Microscopy and Electron Diffraction

The structure and appearance of films produced in this series of experiments were studied by electron-microscopy and electron-diffraction techniques. The films were prepared in the same apparatus used for sorption measurements. A specimen holder was located about 16 in. from the evaporator with the titanium vapor incident normal to the substrate surface. All films used in this examination were evaporated onto cleavage surfaces of sodium chloride.

Replicas of the films for electron microscopy were prepared in the following manner. Immediately following the evaporation of the titanium films and without breaking the vacuum, a layer of platinum, approximately 25-A thick, was evaporated from a point source at an angle of approximately 45° to the surface. The films then were removed from the vacuum in which they had been formed and placed in another vacuum system where a thin layer of carbon was deposited on them at normal incidence. The composite carbon-platinum-titanium films were separated from the sodium chloride substrates by floating them on water. When the sodium chloride had dissolved, the carbon-platinum-titanium films were transferred to baths of concentrated hydrochloric or nitric acids where the titanium was dissolved. After a thorough washing in distilled water, the remaining carbon-platinum film was picked up on standard 200-mesh grids and examined in the electron microscope. In a replica prepared this way, contrast arises from the platinum; the carbon merely serves as a carrier for the fragile platinum film. Regions in the replica containing larger amounts of platinum scatter electrons more strongly and thus appear darker in the electron-microscope image. Conversely, regions which lie in the shadows cast by projections above the surface contain little or no platinum and appear light. This technique was developed to permit the use of high-resolution conditions to study surface features as they existed in the evaporation environment.

Films suitable for electron-diffraction examination were also
evaporated onto sodium chloride substrates. However, to protect the
film from exposure to the atmosphere during transfer from the evaporation
system to the diffraction camera, layers of aluminum, approximately 100-A
thick, were evaporated onto the substrate before and after the titanium
evaporation. Aluminum is used because it forms a continuous protective
film in thin layers, does not scatter electrons strongly so as to
obscure the titanium diffraction pattern, but does give a strong enough
diffraction pattern of its own to serve as a standard.

Substrates at liquid-nitrogen temperature and room-temperature and
evaporation environments of high vacuum and helium at a pressure of
2.5×10^{-3} torr were used in these studies. Films were prepared for
all possible combinations of these variables. For the microscopy studies,
1-hr evaporations were used with the liquid-nitrogen substrates and
10-min evaporations were used with the room-temperature substrates.
Longer evaporations were attempted at room temperature, but the films
which were formed were not continuous and could not be picked up for
electron-microscope examination. Evaporation times of 2—5 min were used
for electron-diffraction studies.

DISCUSSION OF PROCEDURES AND RESULTS

In order to avoid confusion, the procedure for the preparation of
titanium films and measurement of sorption on these films will be dis-
cussed separately for each of the six sets of measurements. The data
obtained are summarized in Table 2.

For simplicity, all of the data are presented in terms of the stick-
ing fraction s. Specific sorption rates in liters per second per square
centimeter may be obtained by multiplying this number by the constants,
F_{25} and F_{-195}, for gas temperatures of 25 and −195°C, respectively. These
constants represent the volume of gases striking 1 cm^2/sec of surface
and are based on Eq. (2). These values are listed for various gases in
Table 3. The total surface pumping speed for the system may be obtained
by multiplying the specific speeds by the area of the liner surface which
is 34,500 cm^2 for the first liner and 25,500 cm^2 for the bakable liner.
Data obtained in the baked system are indicated by the suffix B.

Table 2.   Constants for Conversion of the
Sticking Fraction s to Specific Speeds

Gas Species	F_{25} °C (liters/sec^{-1}-cm^{-2})	F_{-195} °C (liters/sec^{-1}-cm^{-2})
Hydrogen	44.2	22.6
Deuterium	31.2	15.9
Nitrogen	11.9	6.1
Carbon monoxide	11.9	6.1
Oxygen	11.1	5.7
Carbon dioxide	9.5	4.9
Water vapor	14.7	7.5

NOTE: The values of F are calculated from the equation
$F = 3.638 \ T^{1/2} \ M^{-1/2}$ (liters/sec^{-1}-cm^{-2}), where T = tempera-
ture in °K and M = the molecular weight of the gas.   This
equation is derived from Eq. (2).

The pressures in the baked system were generally between 2×10^{-10}
and 2×10^{-9} torr during evaporation with liquid-nitrogen cooling and
5×10^{-9} to 8×10^{-8} torr during evaporations onto substrates at room
temperature.   The corresponding pressures in the unbaked system were
2×10^{-8} to 7×10^{-8} torr for evaporation with liquid-nitrogen cooling
and between 1×10^{-7} and 3×10^{-7} torr for evaporation onto room tempera-
ture substrates.   The pressures usually dropped very slightly after
evaporation was completed.   All other data were obtained using unbaked
substrates.

At this point, it must be pointed out that the techniques for film
preparation which use relatively high gas pressures (that is 1—5 μ) may
depend somewhat on the system size and the mean free path of the vaporized
titanium.   Therefore, caution should be used in applying these data
directly to other systems.

Sorption During Continuous Evaporation

Getter pumping may be employed as a continuous process or as a
pulsed process.   The first mode of operation involves continuous deposi-
tion of titanium on the water-cooled liner during the admission of a gas

Table 3. Initial Sticking Fractions for Various Gases on Titanium
Films Deposited under Several Conditions

| Gas Species | High Vacuum, 10°C | | 2.5-μ Helium 10°C | High Vacuum, −195°C | | 2.5-μ Helium −195°C |
	Continuous Evaporation	Batch Evaporation	Batch Evaporation	Continuous Evaporation	Batch Evaporation	Batch Evaporation
Hydrogen	0.07	0.05 < 0.11B	0.19	0.14	0.24 0.82B[c]	0.85
Deuterium		0.27B	0.14		0.75B	0.78
Nitrogen	> 0.20[a]	0.08 0.10B[c] 0.15B[c]	0.17	> 0.5	0.85 0.90B[c] 0.88B	0.93
Carbon monoxide	0.86	0.33 0.33B	0.66		0.95 0.98B	
Oxygen		0.15[b] 0.068B[b]			0.98B	
Carbon dioxide	> 0.5[a]	> 0.4[a] 0.6B	0.92		0.98	
Water vapor		0.20 0.25B[c]				
Helium	< 0.0005[a]					
Argon	< 0.0005[a]					
Methane	< 0.0005[a]					

[a] These data are estimated from measurements obtained from the original geometry.

[b] The oxygen used in this measurement contained appreciable quantities of argon, thus producing a much lower value of s than is expected from pure oxygen.

[c] These data were obtained in the version of the experiment which uses the baked liner.

while measurements are made to determine its rate of sorption. Data were obtained by starting with large gas-admission rates and making measurements with decreasing gas-admission rates. After each change in admission rate, time was allowed for the system to approach the new equilibrium conditions. This usually required 10 to 15 min. Considerable time is required to approach equilibrium by increasing the admission rate after each measurement, as unreacted titanium may be available from the preceding measurements.

A curve for the sorption of hydrogen during this mode of operation is shown in Fig. 9. The sticking fraction s is plotted as a function of the sorption ratio R which is the ratio of gas molecules (hydrogen in this case) sorbed to titanium atoms deposited. The ordinate on the right indicates the total volumetric sorption rate for the 34,500 cm^2 of active surface in the system.
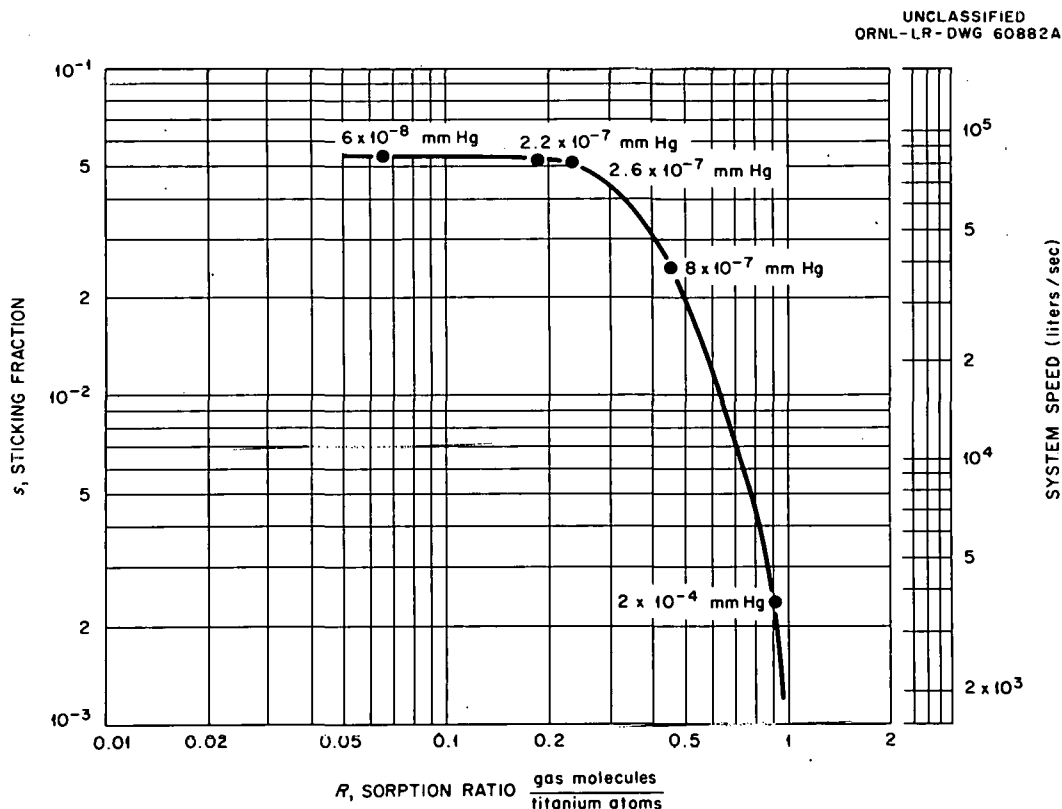
Fig. 9. Sorption of Hydrogen onto the Films Formed During Continuous Evaporation of Titanium onto a Surface at 10°C (s the Sticking Fraction as a Function of R the Sorption Ratio). Titanium evaporation rate: 0.87 × 10^{14} atoms/cm^2/sec.

The curve falls sharply at high leak rates due to saturation of the film as it is deposited. Under these conditions, approximately one molecule of hydrogen is sorbed for every titanium atom evaporated, indicating that a solid solution of hydrogen in titanium is formed which approaches the TiH_2 composition. The portion of the curve for lower leak rates indicates that the sticking fraction increases as the ratio of hydrogen molecules sorbed to titanium atoms evaporated becomes smaller. A definite sticking fraction is established for each titanium-to-hydrogen ratio. This sticking fraction seems to approach some limit as the hydrogen-to-titanium ratio approaches 0.02. Due to uncertainties in the base pressure correction for these early data, this conclusion is not adequately supported. Figure 10 shows the throughput as a function of pressure for the same data shown in Fig. 9. The throughput is limited
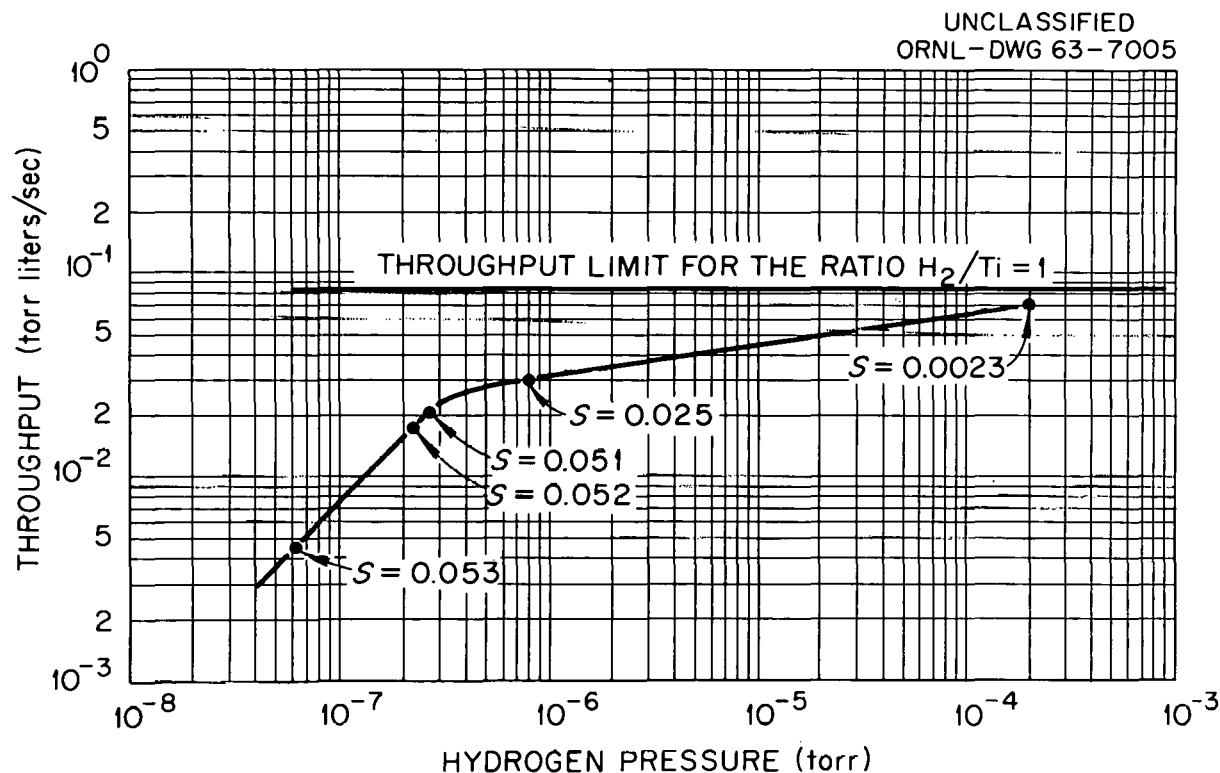

Fig. 10. Sorption of Hydrogen onto the Films Formed During Continuous Evaporation of Titanium onto a Surface at 10°C (Throughput as a Function of Hydrogen Pressure). Titanium evaporation rate: 0.87×10^{14} atoms/cm^2/sec.

by the titanium evaporation rate at high pressures because only one molecule of hydrogen is sorbed for each titanium atom evaporated and by the sticking fraction at low pressures because the throughput is proportional to pressure at low pressure. The available titanium evaporation rates therefore seriously limit the usefulness of getter pumping at relatively high pressures. The evaporation of a gram of titanium per hour in this system will efficiently dispose of about 0.05 torr-liters of hydrogen per second or not quite 200 torr-liters per hour.

Figure 11 is a plot of s vs the sorption ratio for nitrogen, carbon monoxide, and carbon dioxide. (Note the change in scale of the ordinate compared with Fig. 9.) Methane and several inert gases are not measurably sorbed under these conditions and are pumped only by the diffusion pump.

Sorption onto films produced with higher evaporation rates have higher sorption rates. These data for hydrogen are also shown in Fig. 11.

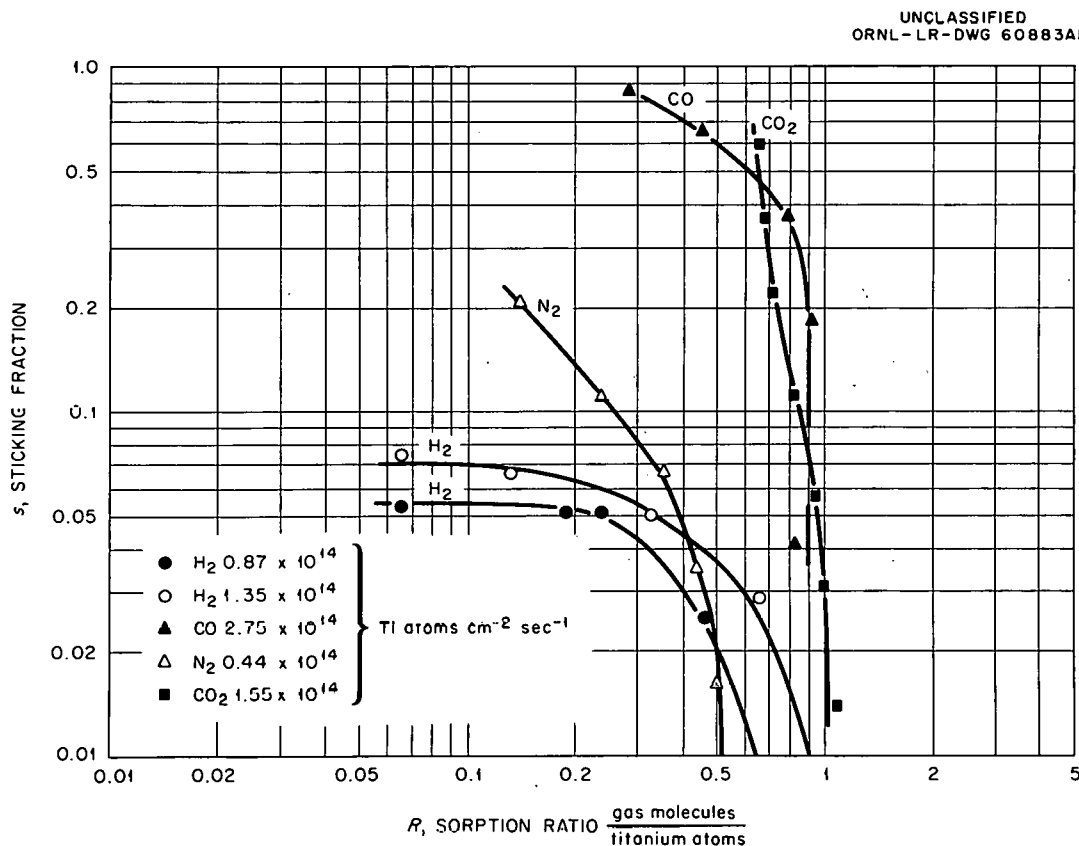UNCLASSIFIED
ORNL-LR-DWG 60883AR

Fig. 11. Sorption of Gases onto Films Formed During Continuous Evaporation of Titanium onto a Surface at 10°C.

The titanium films formed by deposition in high vacuum on the water-cooled substrate are metallic in appearance and have a well-developed crystal structure. The film structure is discussed in more detail later in this section.

Sorption onto Films Previously Deposited in High Vacuum

A second useful pumping technique requires the deposition of the film to be completed before the gas sorption is begun. The data from this technique are plotted as s vs the quantity of gas sorbed on the film. Figure 12 presents data for several gases. Note that for hydrogen three curves are given. The small slope of all of the hydrogen curves, even after 10^{16} atoms/cm^2 were adsorbed, indicates that diffusion of
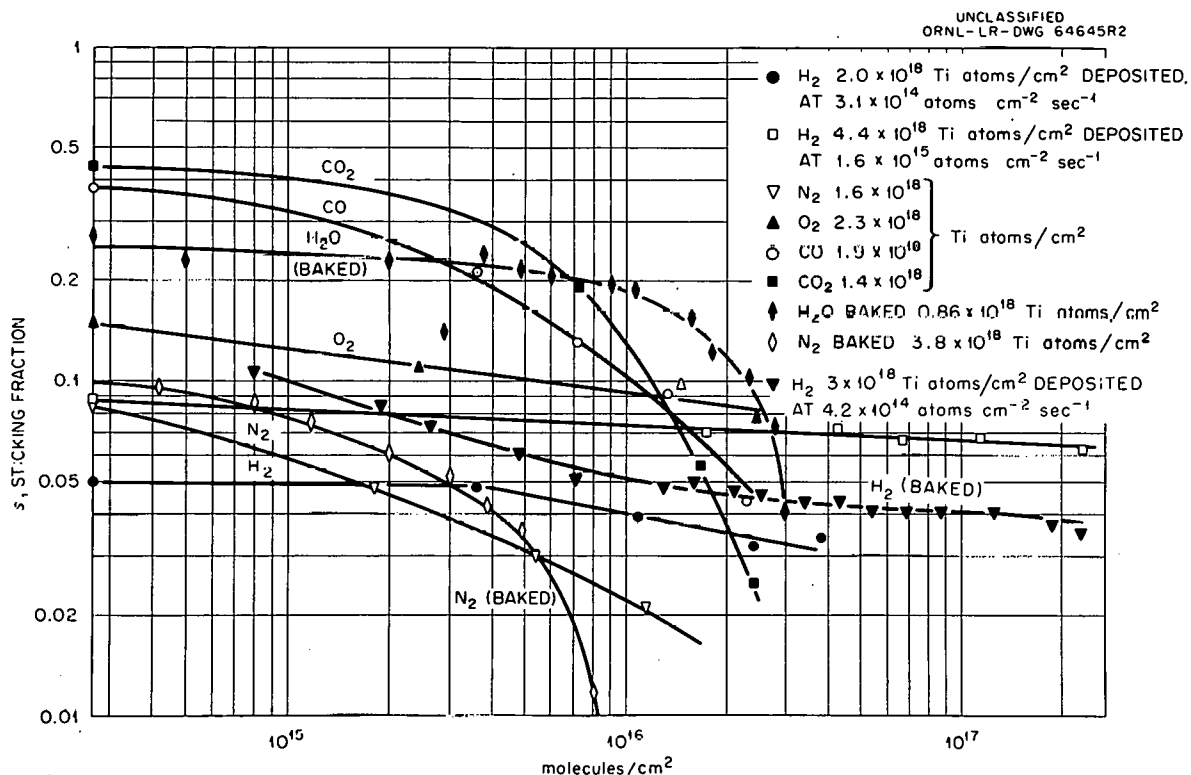

Fig. 12. Sorption of Gases onto Films Formed by Titanium Evaporation in High Vacuum onto a Surface at 10°C.

hydrogen into the film occurs readily and thus that hydrogen has easy access to a very large portion of the deposit. The curve with the largest sorption rate over most of the pressure range was obtained on a film formed with a very high titanium deposition rate (16 g/hr).

The higher sticking fractions obtained during the sorption measurements in the baked system, relative to the values obtained for films deposited at similar rates in unbaked systems, are probably due to a reduction of film contamination in the baked system. In several instances, hydrogen sorption on films deliberately contaminated with oxygen and nitrogen was measured to be considerably slower than for uncontaminated films.

The lower rate of gas admission during the sorption measurements in baked systems might cause an increase in the observed sticking fraction (for a given quantity of sorbed gas) if diffusion of gas into the interior of the film is rapid enough to significantly lower the surface concentration of the gas. A review of the data from many experiments using hydrogen sorption rates from 10^{16} atoms/cm^{-2}/sec^{-1} to 5×10^{12} atoms/cm^{-2}/sec^{-1} shows no apparent correlation of higher sticking fractions with lower sorption rates. However, no series of experiments was sufficiently similar to permit a simple comparison and no experiments were run to deliberately explore this effect over a large enough range of sorption rates. Nearly all of the data obtained in the unbaked system were obtained at rates between 4×10^{14} and 3×10^{13} atoms/cm^{-2}/sec^{-1} while data were usually obtained in the baked system at sorption rates between 4×10^{13} and 2×10^{13} atoms/cm^{-2}/sec^{-1}. In any case, this diffusion effect should not be important for data obtained at liquid-nitrogen temperatures or for any gases except hydrogen.

Diffusion of hydrogen into the film also results in an effect of film thickness on the sorption rate when large amounts of gas have been sorbed (i.c., thicker films maintain slightly higher sticking fractions for a large quantity of sorbed hydrogen). The curves for the gases other than hydrogen are not expected to be very dependent upon the thickness of the deposited film since these gases are likely to diffuse much more slowly into the film.

Sorption onto Films Deposited in the Presence of Inert Gas

Evaporation of titanium films in a pressure of approximately 1 μ of helium or argon pressure produces deposits in the system described which sorbs gases much more rapidly than films deposited under similar circumstances in high vacuum. Data obtained from these evaporations are shown in Fig. 13. This improved sorption rate is associated with a very pronounced change in the appearance and structure of the films. The films obtained in these evaporations have a velvety black appearance and give diffuse electron-diffraction patterns. The increased surface area of these films and their increased surface activity undoubtedly favorably affect the sorption processes. It should be noted again that the conditions required to obtain this type of deposit may be appreciably different for other system sizes or other geometric arrangements.
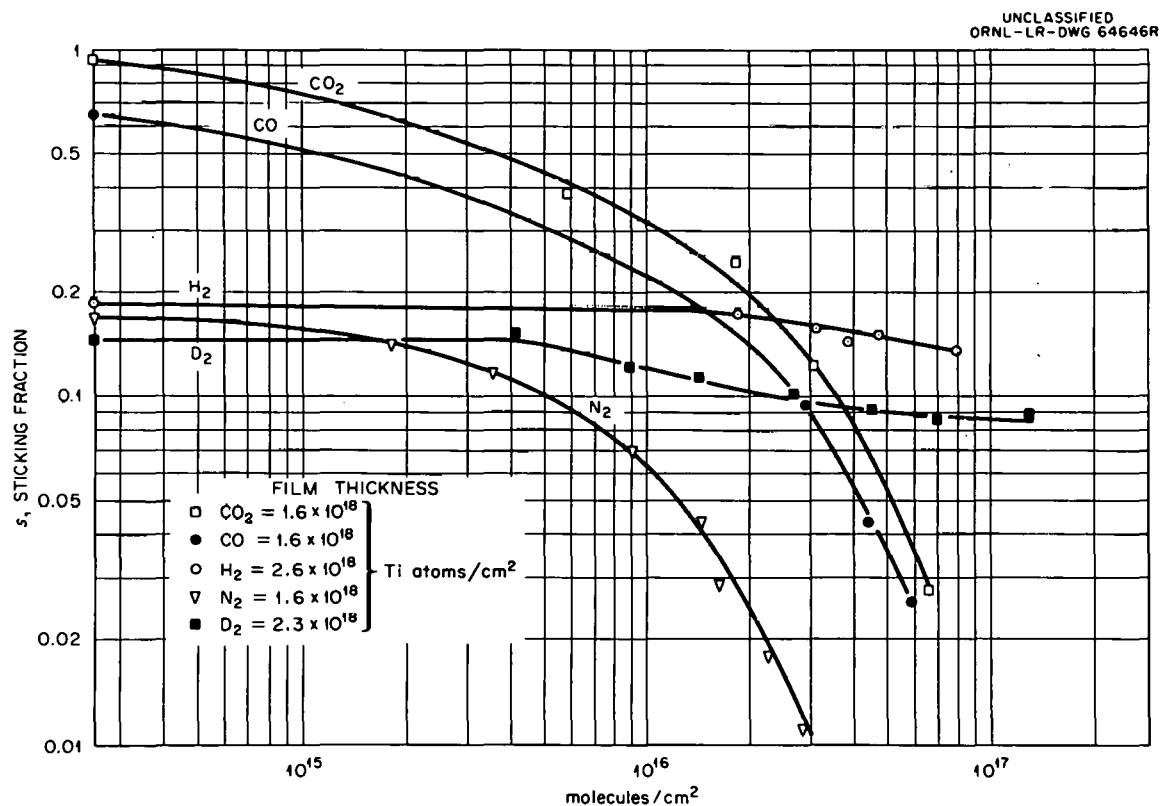

Fig. 13. Sorption of Gases onto Films Formed by Titanium Evaporation in the Presence of 2.5×10^{-3} torr Pressure of Helium onto a Surface at 10°C.

Sorption onto Films Deposited on Substrates
at Liquid-Nitrogen Temperature, −195°C

The high vacuum deposition of titanium onto substrates at liquid-nitrogen temperatures produces films which have a metallic appearance, small crystallite sizes, and high sorption rates. The results of sorption measurements during continuous deposition are given in Fig. 14.[37] Figure 15 is a plot of s, the sticking fraction, vs Q, the quantity of previously adsorbed gas, for sorption onto films after their preparation. Note the marked improvement in s obtained as the result of deposition in a baked system. Figure 16 shows data for the sorption of hydrogen, deuterium, and nitrogen onto films deposited in a 2.5×10^{-3} torr pressure of helium with the substrate at liquid-nitrogen temperature. These latter films had the greatest sorption rates for hydrogen of all of the films tested and had a velvety black appearance and small crystallite sizes similar to those observed in films deposited at 10°C.

Correlation of Sorption Characteristics with Film Structure

The electron-microscope and electron-diffraction apparatus were used to study evaporated titanium films in an effort to correlate structural features of the films with their pumping characteristics. Films were studied in which substrate temperature and evaporation environment were varied to produce films of the types used in the sorption measurements.

Typical structures of the replicas are shown in Figs. 17–23. It is immediately evident that both the low substrate temperature and the helium environment have the effect of increasing the surface roughness. Figure 17, taken from the film deposited at room temperature in a high vacuum, is the smoothest one of the group. The large black pieces casting the long shadows are dust particles which were present on the sodium chloride before it was inserted in the vacuum. The large, continuous

---

[37]The temperature of the incident gas must be considered in the calculation of pumping speed. The subscripts on the F values in Table 2 indicate the temperature for which the conversion factor is to be used.
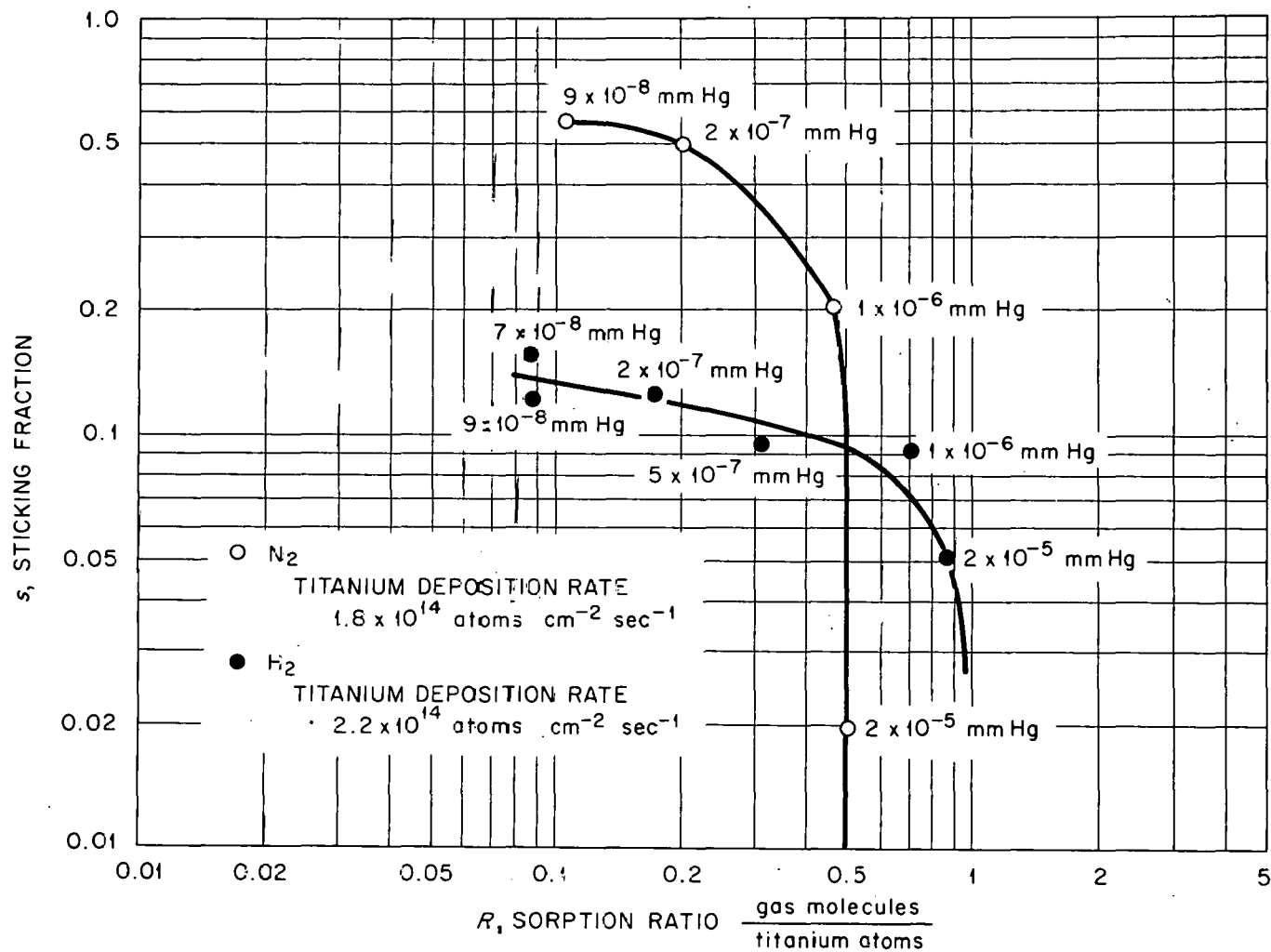
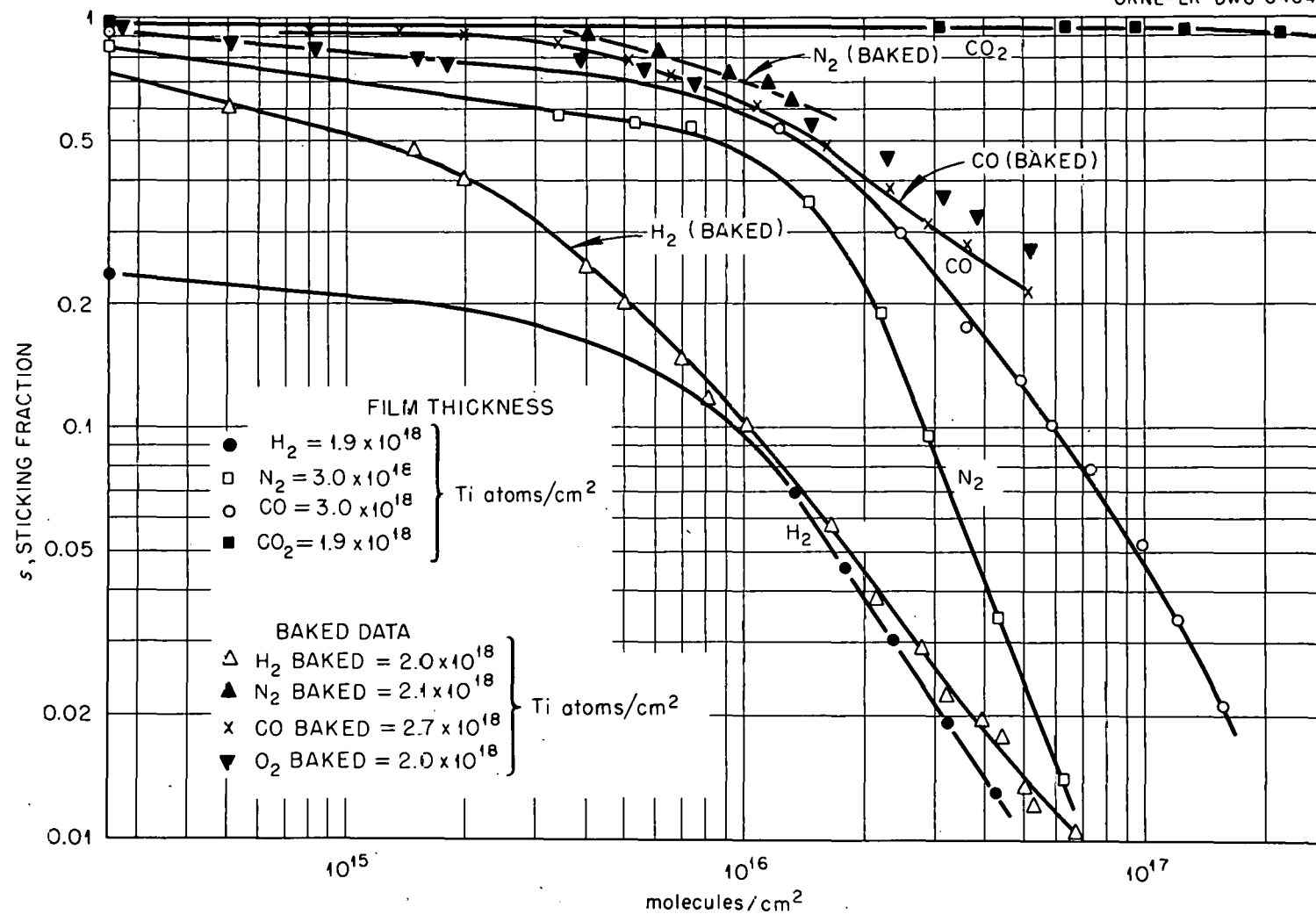Fig. 14. Sorption of Gases onto Films Formed During Continuous Evaporation of Titanium onto a Surface at −195°C.

Fig. 15. Sorption of Gases onto Films Formed by Titanium
Evaporation in High Vacuum onto a Surface at −195°C.

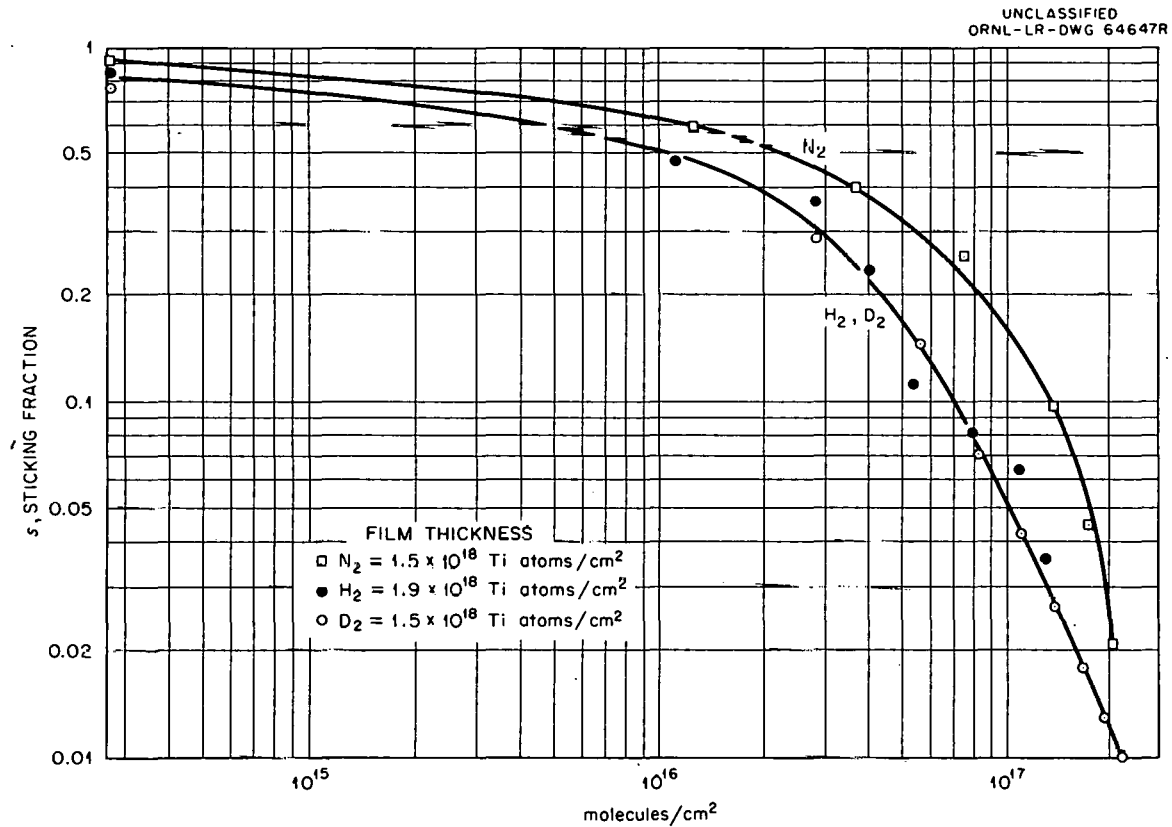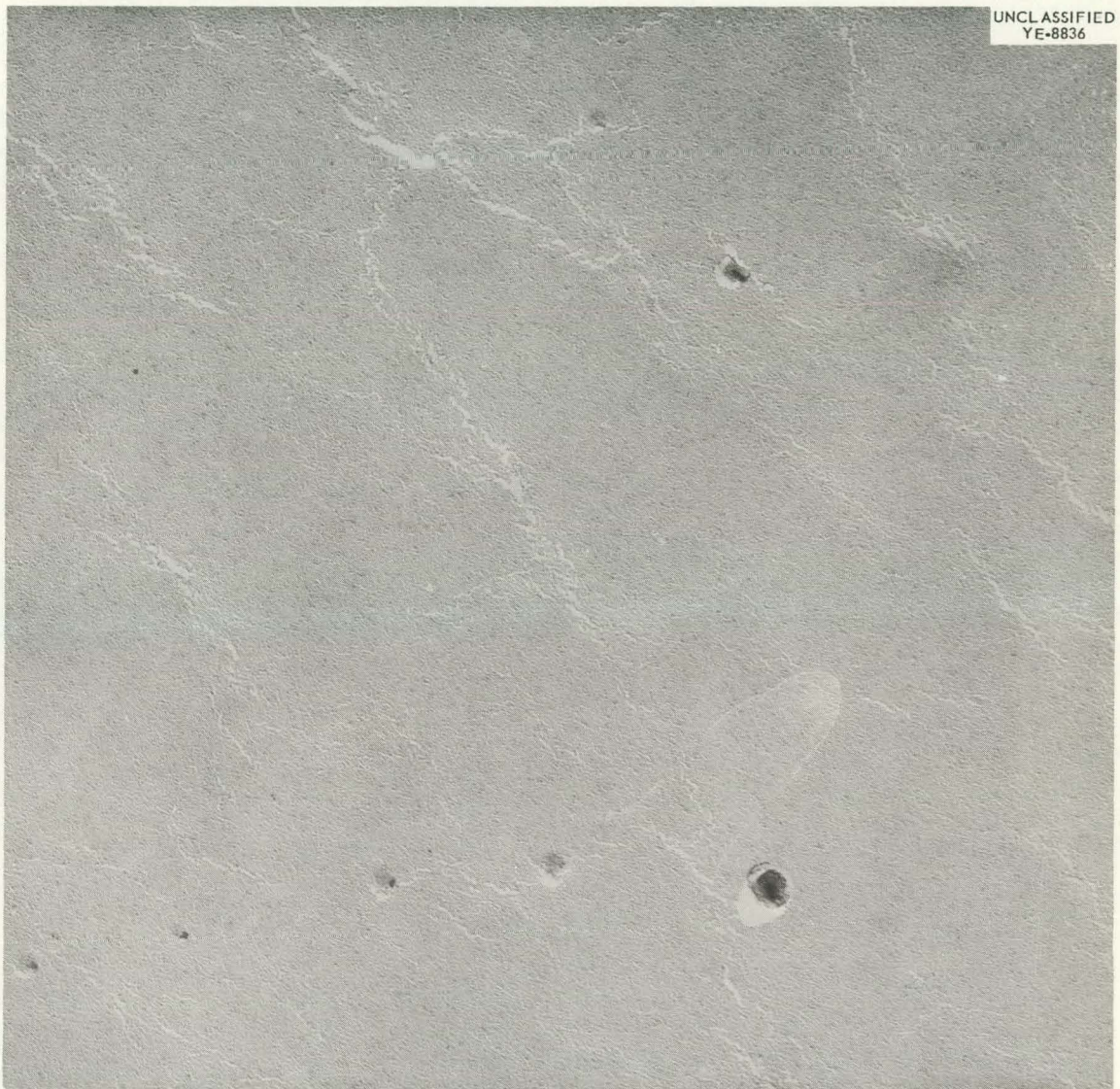Fig. 16. Sorption of Gases onto Films Formed by Titanium Evaporation in the Presence of 2.5×10^{-3} torr Pressure of Helium onto a Surface at $-195°C$.

Fig. 17. Replica of Titanium Film Prepared by 10-min Evaporation in High Vacuum at Room Temperature. 35,000×. Reduced 18%.

Fig. 18. Replica of Titanium Film Prepared by 1-hr Evaporation in High Vacuum at Liquid-Nitrogen Temperature. 7,500×. Reduced 20%.
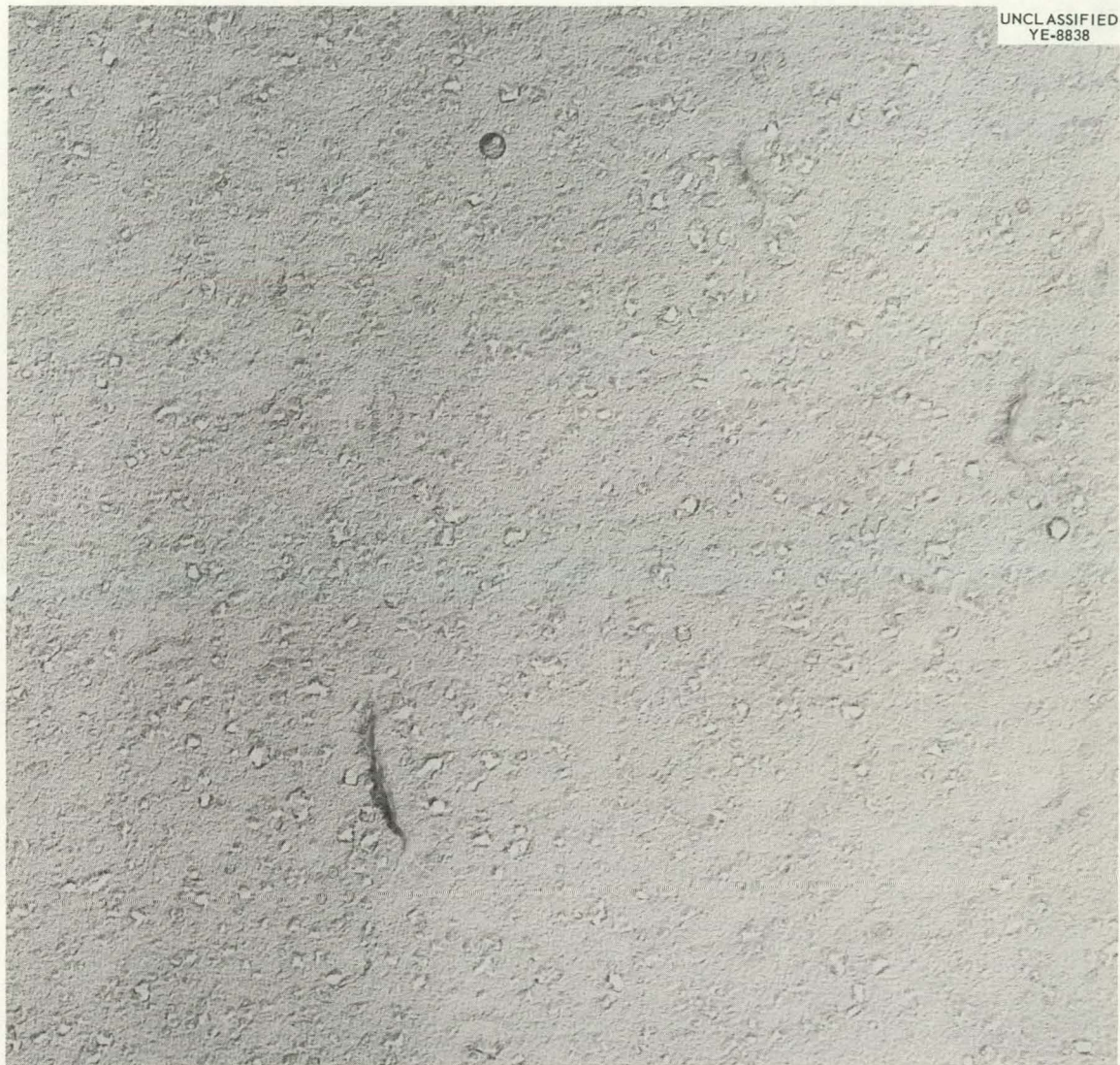
Fig. 19. Replica of Titanium Film Prepared by 1-hr Evaporation in High Vacuum at Liquid-Nitrogen Temperature. 35,000X. Reduced 20%.
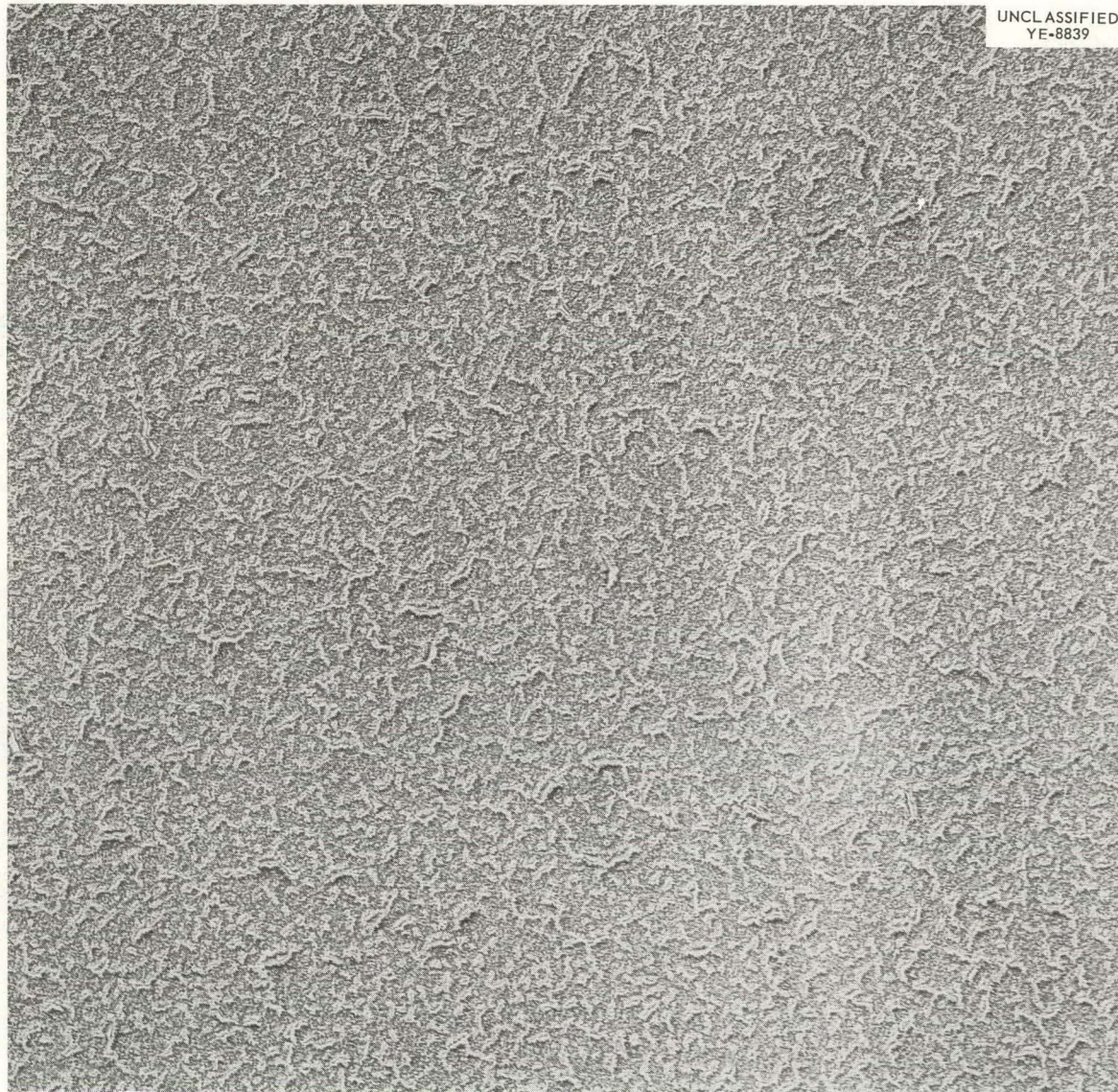
UNCLASSIFIED
YE-8839

Fig. 20. Replica of Titanium Film Prepared by 1-hr Evaporation in High Vacuum at Liquid-Nitrogen Temperature. 35,000X. Reduced 17%.

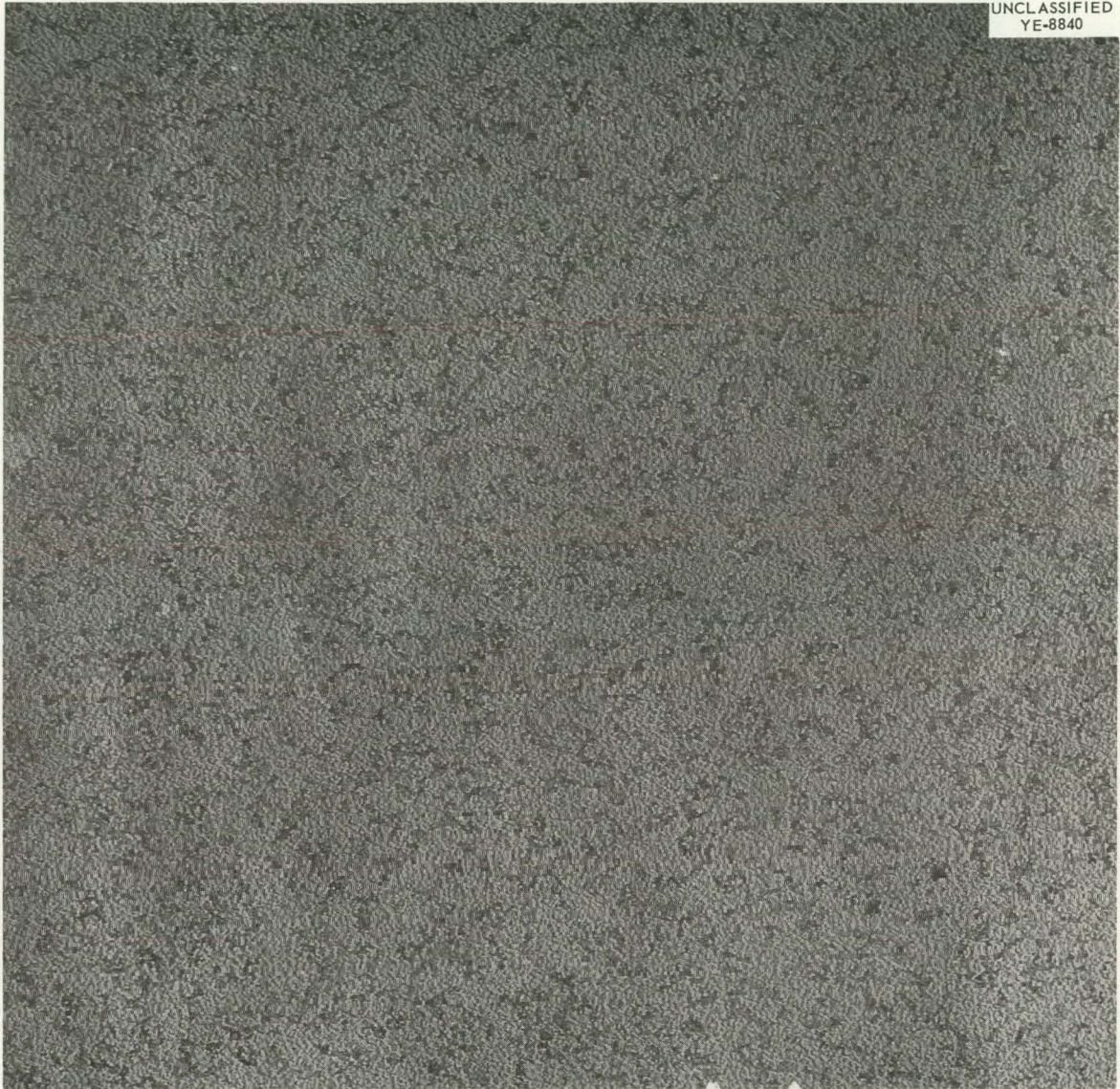Fig. 21. Replica of Titanium Film Prepared by 10-min Evaporation in a Helium Atmosphere of 2.5×10^{-3} torr at Room Temperature. 35,000×. Reduced 17%.
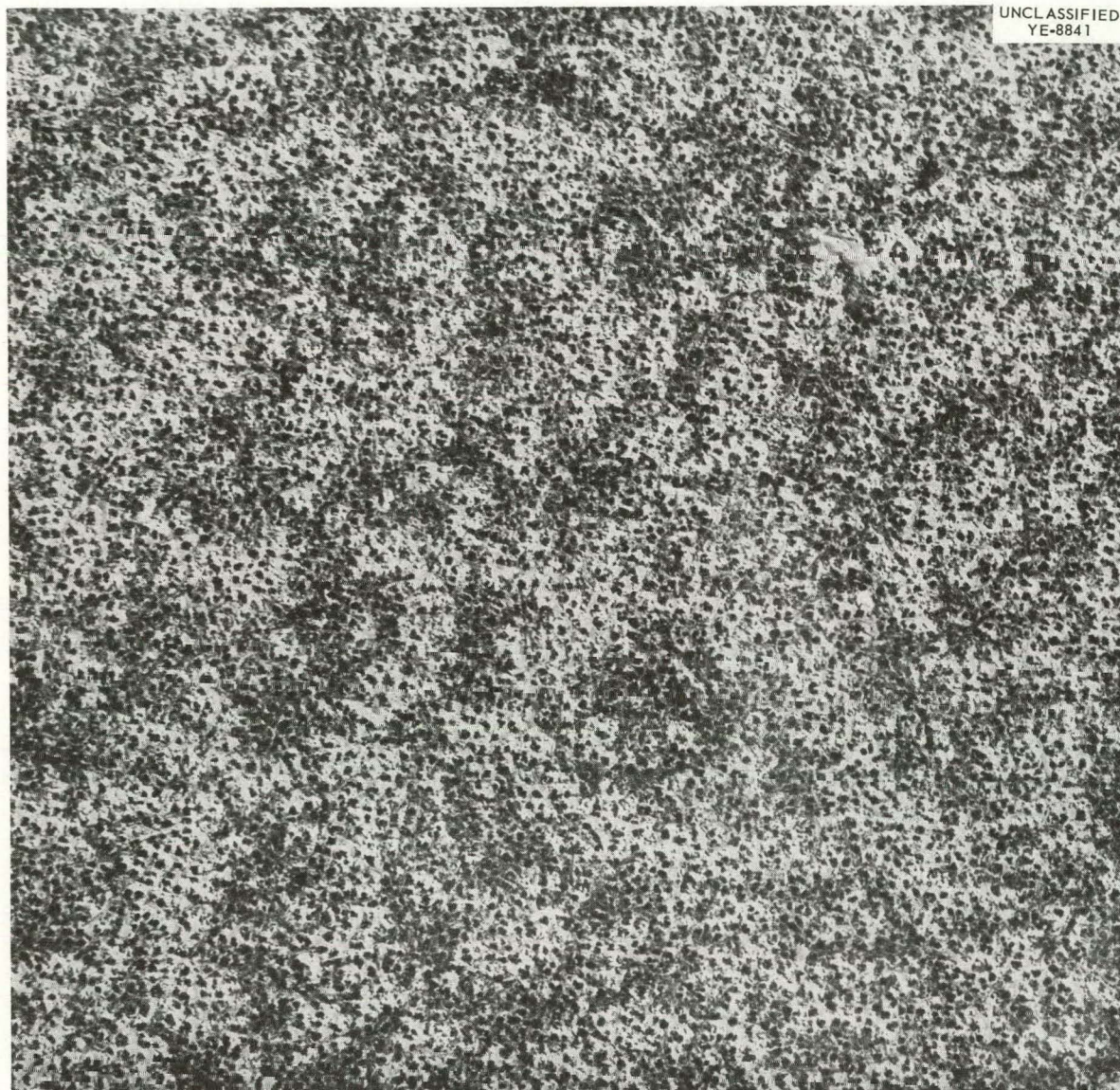
UNCLASSIFIED
YE-8841

Fig. 22.   Replica of Titanium Film Prepared by 1-hr Evaporation in a Helium Atmosphere of 2.5×10^{-3} torr at Liquid-Nitrogen Temperature. 35,000X.   Reduced 17%.
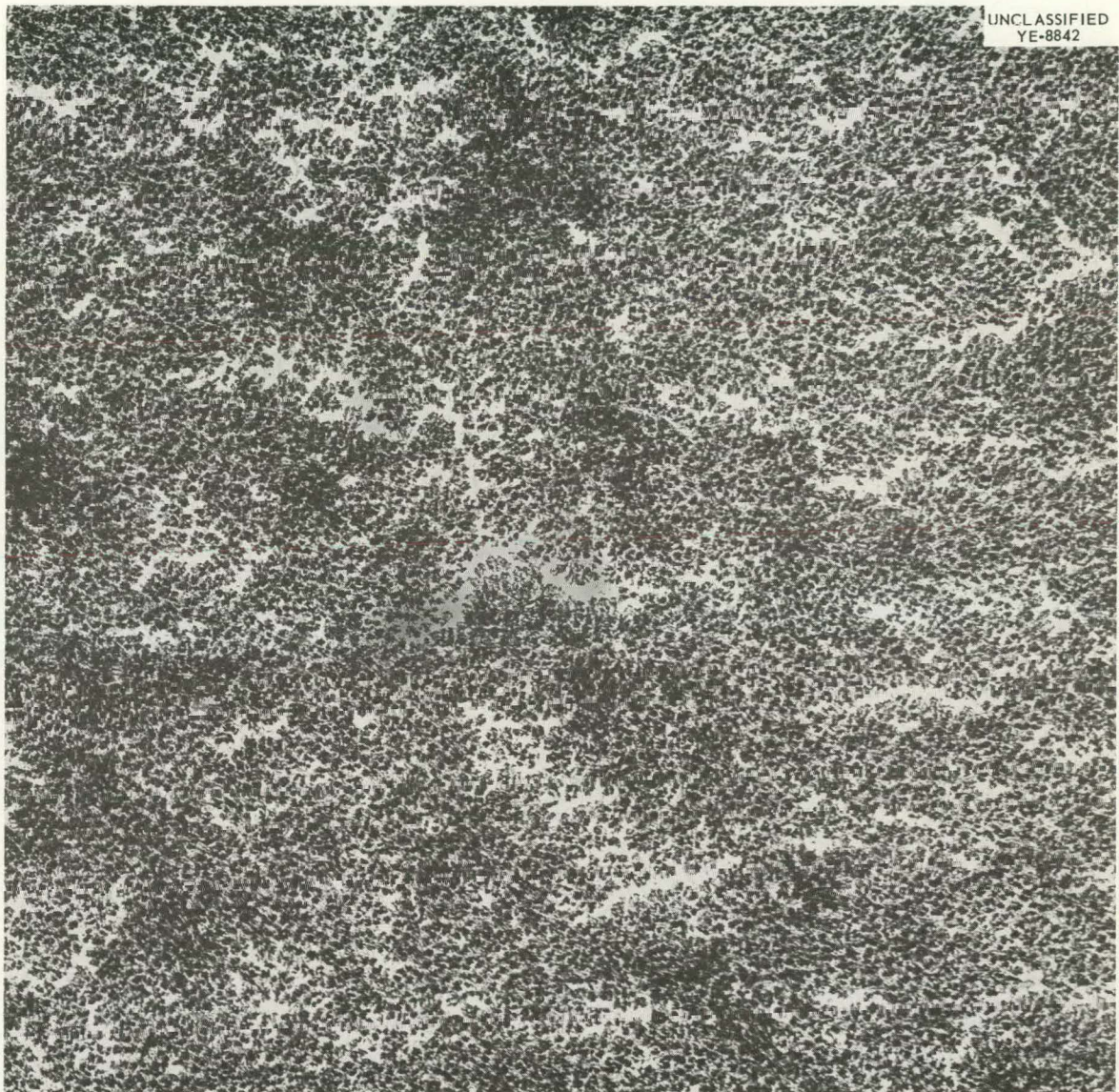
Fig. 23. Replica of Titanium Film Prepared by 1-hr Evaporation in a Helium Atmosphere of 2.5×10^{-3} torr at Liquid-Nitrogen Temperature. 35,000X. Reduced 17%.

white bands which run across the micrograph are cleavage steps on the
sodium chloride crystals. The very tiny white bands could correspond
to smaller cleavage steps. They could also arise if the titanium were
not evaporated at normal incidence. The first titanium atoms on the
surface cluster together and effectively shadow the region behind them
which ultimately leads to a structure of this same type. This structure
becomes more pronounced as the evaporation angle decreases.

Films prepared in high vacuum on liquid-nitrogen temperature sub-
strates contained many large, unconnected cracks as is shown in Fig. 18.
The cracks probably occurred on heating the film and substrate to room
temperature, or later. If such large eruptions on the surface existed
at liquid-nitrogen temperature, they certainly would have cast large
shadows. A higher magnification view of the region between the cracks
is shown in Fig. 19. The surface is quite rough and contains a large
number of randomly located protrusions. The results of two evaporations
under nominally identical conditions are not completely reproducible, as
is demonstrated by the specimen shown in Fig. 20 which was prepared under
the same conditions as that of Fig. 19. This specimen showed fewer of
the large cracks and more of the coarser surface structure.

Specimens prepared in the low-pressure helium environment showed a
fine-scale surface roughening resembling the texture of an orange peel,
Figs. 21—23. The specimen evaporated at liquid-nitrogen temperature was
considerably rougher on both a large and a fine scale, but this could be
due in part to a longer evaporation time (1 hr against 10 min for the
room-temperature evaporation). The dark regions in Fig. 21 do not cast
shadows and, therefore, do not correspond to surface perturbations. They
probably result from a component of the films insoluble in the acids
used, or from an etching product which was deposited on the films. There
is not enough of it present to allow identification by electron diffraction.

Electron-diffraction patterns from each of the specimens showed the
presence of titanium metal. The specimen formed at room temperature in
a helium environment gave one additional ring corresponding to a "d"
value of approximately 1.55 A which could not be indexed as either
titanium or aluminum. Since only one ring was present, it could not be
used to identify the component responsible for it. The intensity of the

ring was weak and no other rings corresponding to the component were
observed; therefore, it was apparently present in only very small amounts
and may have been introduced during handling. A few isolated spots were
also observed on some of the diffraction patterns. They could not be
indexed on known titanium compounds and were probably from small dirt
particles on the surface.

Titanium metal was identified in all the diffraction patterns even
though there were remarkable differences in the optical properties of
the films. The films formed in high vacuum have a metallic appearance,
while the films formed in the helium atmosphere appear dark and dull.
Diffraction patterns of films of nominally the same thickness gave strong
titanium patterns for films prepared in high vacuum but showed only
diffuse scattering for films prepared in helium. Very small particle
size or lattice strain in the latter films could cause this. The line
widths of very thin films prepared in the helium atmosphere did not
differ appreciably from those of the thicker films prepared in a high
vacuum, however. The explanation for this effect is not obvious but
might be related to problems of nucleation and growth or lattice strain
in the thicker films.

The preceding observations suggest a relationship between the struc-
ture of the films and their pumping properties. The specimens with much
diffuse scattering produced the highest sorption rates. Surface roughness
differs greatly among the specimens and appears to be related directly
to sorption rates.

Comparison of the Performance of Systems Using a Combination of Titanium Getter Pumping and Oil-Diffusion Pumping with Systems Depending Entirely on Diffusion Pumps

The sorption performance of titanium-getter films shows that, in an
experimental system consisting of a right cylindrical container 36 in.
high and 36 in. in diameter (with a small diffusion pump attached) and
coated on its inner surfaces with a suitable titanium film, hydrogen
released in the center of the container could be removed at a rate of
more than 1,000,000 liters/sec. This speed is equivalent to that obtain-
able from 30–35 nominal 32-in. oil-diffusion pumps with liquid-nitrogen

baffles. (Each of these pumps is rated at 72,000 liters of hydrogen per second without a baffle, but baffles normally cut pump speed by a factor of 2 or more.)   The so-called 32-in. oil-diffusion pumps are 35-in.-ID so that a 32-in. pump is roughly equivalent in diameter to the hypothetical getter-pumped chamber. One diffusion pump and its cold trap would, thus, occupy a considerably larger volume than the complete getter-pumped system.

Even if it were possible to connect 30 or more 32-in. diffusion pumps onto the experimental chamber, both the diameter and length of the chamber would have to be more than doubled just to provide a surface area equal to the area of the entrances to the diffusion pumps. This is a manifestation of the relatively poor speeds of diffusion-pumped systems compared with the arrival rate of gas molecules. In this case the diffusion-pumping speed is only about 13% of the gas-arrival rate as compared with a more than 80% sticking fraction achieved for sorption onto titanium films.

The advantages of the combination of getter pumping and diffusion pumping over diffusion pumping alone for applications requiring very high speeds at low pressures are very great. Requirements for low maintenance systems operating continuously at pressures above 5×10^{-6} torr (where the gas loads may be large) most frequently will be best satisfied by diffusion-pumped systems since high gas loads require large titanium evaporation rates and, therefore, frequent attention to the evaporator. Cryopumping offers advantages similar to those of titanium sorption pumping and does not suffer from the throughput limitations at high pressures. Cryopumping will not satisfactorily handle any appreciable quantities of hydrogen or helium with the present state of the art, however.

CONCLUSIONS

Data obtained and techniques developed in the course of this investigation have established the feasibility of large-scale getter pumping with vapor-deposited titanium films. A system combining a small diffusion pump and a large titanium film getter has demonstrated the sorption of

more than 80% of the hydrogen molecules on each contact with the getter surface. Nitrogen, oxygen, carbon monoxide, carbon dioxide, and water vapor are also efficiently sorbed.

The measuring technique developed for this investigation provides accurate data, particularly when the sticking fraction approaches unity. The use of very large getter deposits is useful in minimizing errors due to the perturbing influence of instrumentation and evaporation apparatus, and also reduces the effect of outgassing and small gas leaks in the system.

The sticking fraction for chemically inert gases including methane on titanium films at room temperature is very small (less than 0.01).

The sticking fractions for the chemically active gases, hydrogen, oxygen, nitrogen, carbon monoxide, and carbon dioxide, can be made very high (that is, approaching unity) through adjustment of the film deposition and sorption conditions. Lower substrate temperatures, faster deposition rates, and/or the presence of inert gases during deposition produce films having larger sticking fractions.

Considerable evidence in the form of electron photomicrographs, electron-diffraction patterns, and visual examination indicates that changes in the structure of the titanium film are largely or perhaps entirely responsible for the increased sticking fraction observed. Due to equipment limitations (that is, the long-time periods required to change the liner temperature), it has not been possible to completely separate the effects of film structure and the kinetics of low-temperature sorption.

Sorption measurements with hydrogen during continuous deposition at 10°C indicate the sticking fraction remains usefully large until the ratio of hydrogen molecules sorbed to titanium atoms deposited approaches 1 (indicating that TiH_2 is formed). Nitrogen behaves in a similar manner but in this case TiN is formed at a limiting ratio of 1/2.

Hydrogen diffuses into the titanium films quite rapidly at room temperature so that the entire film thickness (up to several thousand angstroms) is available for sorption with only slight decreases in sticking fraction. This is not true at −195°C for hydrogen or for any of the other gases tested at either temperature.

Sorption of small amounts of oxygen or nitrogen onto a freshly deposited film apparently decreases the subsequent sorption rate for hydrogen. This observation is in accord with the increased hydrogen sticking fractions found on films deposited in better vacua, that is, to 5×10^{-9} torr as compared with 5×10^{-8} torr.

ACKNOWLEDGMENT

ORNL-3481
UC-25 – Metals, Ceramics, and Materials
TID-4500 (26th ed.)

INTERNAL DISTRIBUTION

1–3.	Central Research Library	90.	C. F. Leitten, Jr.
4.	Reactor Division Library	91.	A. P. Litman
5–6.	ORNL – Y-12 Technical Library	92.	H. G. MacPherson
	Document Reference Section	93.	A. P. Malinauskas
7–16.	Laboratory Records Department	94.	H. F. McDuffie
17.	Laboratory Records, ORNL R.C.	95.	D. L. McElroy
18.	ORNL Patent Office	96.	C. J. McHargue
19.	Russell Baldock	97.	M. L. Picklesimer
20.	J. O. Betterton, Jr.	98.	J. D. Redman
21.	Charles Butler	99.	H. W. Savage
22.	J. G. Carter	100.	R. L. Shipp
23–72.	R. E. Clausing	101.	C. S. Shoup, Jr.
73.	J. L. Cook	102.	I. Spiewak
74.	C. W. Cunningham	103.	L. E. Stanford
75.	J. H. DeVan	104.	R. L. Stephenson
76.	J. R. DiStefano	105.	J. O. Stiegler
77.	D. A. Douglas, Jr.	106.	J. A. Swartout
78.	J. H Frye, Jr.	107.	W. C. Thurber
79.	R. G. Gilliland	108.	G. M. Watson
80.	H. W. Godbee	109.	A. M. Weinberg
81.	George Hallerman	110.	W. J. Werner
82.	R. L. Heestand	111.	J. C. Wilson
83–85.	M. R. Hill	112.	A. A. Burr (consultant)
86.	H. Inouye	113.	J. R. Johnson (consultant)
87.	G. W. Keilholtz	114.	C. S. Smith (consultant)
88.	Lawrence Landau	115.	R. Smoluchowski (consultant)
89.	C. E. Larson		

EXTERNAL DISTRIBUTION

116.	C. M. Adams, Jr., MIT
117–118.	David F. Cope, ORO
119.	Research and Development, ORO
120.	D. E. Baker, GE, Hanford
121.	Ersel Evans, GE, Hanford
122.	J. L. Gregg, Cornell University
123.	J. Simmons, AEC, Washington
124.	Lawrence M. Slifkin, University of North Carolina
125.	E. E. Stansbury, University of Tennessee
126.	Donald K. Stevens, AEC, Washington
127–707.	Given distribution as shown in TID-4500 (26th ed.) under Metals, Ceramics, and Materials category (75 copies – OTS)