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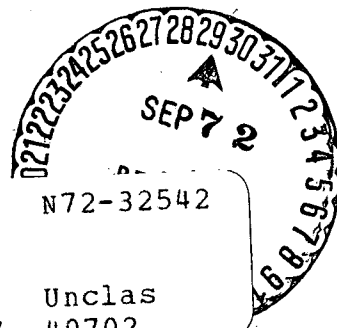
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ACCESS TO UNCOMBINED TITANIUM THROUGH AN INHIBITING FILM IN SUBLIMATION PUMPING OF DEUTERIUM

by Robert Steinberg and Donald L. Alger
Lewis Research Center
Cleveland, Ohio

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National Aeronautics and Space Administration
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ABSTRACT

In principle, titanium bulk sublimator pumping should be ideal for removing large quantities of deuterium from a vacuum system. In practice, much of the deposited titanium remains uncombined and is wasted. We have demonstrated, through a series of experiments, that it is possible (by the addition of a thin layer of titanium to an apparently occluded surface) to gain access to previously deposited sublayers of uncombined titanium in spite of the presence of an inhibiting film (such as an oxide) on the surface.

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INTRODUCTION

Titanium bulk sublimator (TBS) pumping has found application in many different types of vacuum systems; however, it only recently has been considered for use in small neutron generators where sublimation pumping offers major advantages in reducing the tritium hazard and increasing system reliability (ref. 1). Tritium is radioactive and decays by beta emission, with a half-life of 12 years. More efficient use of the available titanium would provide extended pump life, thus further reducing the necessity of handling tritiated components.

Unlike getter ion pumps, the pumping speed of a TBS is independent of pressure in the low-pressure ranges. As a result, control of the sublimation rate becomes an important consideration. This is normally a manual operation and a considerable amount of titanium is usually wasted. During the operation of our 300-kilovolt positive-ion accelerator incorporating sublimation pumping, we became aware of the fact that it was possible, under certain circumstances, to gain access to previously-deposited uncombined sublayers of titanium. This ability to penetrate the inhibiting surface film could allow us to utilize the available titanium more efficiently; however, it may also have significance in other applications such as hydrogen pumping with sputter ion pumps and improved loading for tritiated neutron-generator targets.

This paper describes a set of experiments which was conducted in order to obtain a better understanding of the phenomenon observed and to attempt to determine the mechanism involved.

ADSORPTION OF DEUTERIUM BY TITANIUM

Several processes take place during the interaction of deuterium with titanium: physical adsorption on the surface, activated adsorption, diffusion, absorption, and chemical interaction through the formation of chemical compounds. Our primary concern here is with physical adsorption which depends mainly on the state of the titanium surface. We know that this process occurs very rapidly until a monomolecular layer of the gas has been adsorbed on the surface. At this stage the gas molecules have not yet dissociated into atoms (ref. 2).

Physical adsoprtion is just the first phase in the total sorption process of deuterium in titanium and is followed by activated adsorption which is a much slower process and requires considerable time for the establishment of an equilibrium condition. Until now, it had been assumed that in activated adsorption the gas molecules dissociate into atoms which facilitate the diffusion of deuterium into the bulk titanium. Recently, this assumption that deuterium does diffuse into metals in the atomic and not the molecular form was experimentally confirmed (ref. 3). Moreover, it has been established that the deuterium also ionizes and diffuses rapidly as a deuteron (ref. 4). The condition of the surface has a considerable effect on the rate of diffusion. If both physical and activated adsorption are reduced, then the dissociation of molecules into atoms and, therefore, the diffusion of deuterium into titanium will also be limited. We know that the rate of diffusion decreases sharply in the presence of an oxide (ref. 5). Under such conditions, the rate of diffusion is independent of the deuterium pressure and

is determined solely by the condition of the oxide film on the surface.

If the inhibiting film is strictly a surface phenomenon, then the process of physical adsorption could be the controlling factor in restricting access to bulk titanium. Although we do not know the nature of this inhibiting film formed in the sublimator system nor its depth nor the extent to which it covers the titanium, we have made the following assumptions: (1) The inhibiting film is very thin; and (2) it does not completely cover the titanium surface. Based on these assumptions, if the processes of physical and activated adsorption could be initiated, thus enhancing the formation of deuterons, it seemed reasonable to expect that diffusion through the surface film could be increased. This hypothesis could easily be verified by depositing a thin layer of titanium onto a surface which (1) had many previously deposited layers of uncombined titanium and (2) had reduced pumping speed due to an inhibiting film on the surface.

APPARATUS

The accelerator system used for the measurements is described elsewhere and, therefore, will only be briefly mentioned here (ref. 6). Figure 1 shows the vacuum system of the 300-kilovolt 15-milliampere ion accelerator which served as a vacuum chamber for the measurements. Roughing down the system is accomplished with the aid of three sorption pumps. The TBS consists of a 400-gram rod of titanium which is heated by electron bombardment to approximately $1500^\circ C$, causing the titanium to sublime onto the surface of a water-cooled chamber surrounding the

rod. The fresh titanium forms stable solid compounds with the chemically-active gas molecules that strike the surface, resulting in high pumping speeds for active gases such as oxygen, hydrogen, nitrogen and water vapor. The inert-gas load and the hydrocarbons are pumped by a 270-liter/sec sputter ion pump. The system base pressure is approximately $2x10^{-8}$ torr. As vacuum systems go, the accelerator system is fairly "dirty." It is not designed for bakeout; it has a large ceramic surface exposed to the vacuum (the high voltage section is 56 cm in length by 53 cm in diameter) and uses vinyl seals for the high-voltage section and the source. All measurements were made within this system. The deuterium gas leak for all measurements was restricted to 27 atm cm^3/hr* which is the flow rate required to maintain a 15-milliampere beam of deuterons on target, and the pressure range of interest was limited between $2x10^{-8}$ and $1x10^{-5}$ torr which is the normal operating range. The sublimator was set to sublime at 1.0 grams/hr.*

EXPERIMENT I

In order to determine if we could penetrate the inhibiting surface film, the following experiment was performed. With the system at an equilibrium pressure of $6.5x10^{-7}$ torr (See fig. 2.), deuterium gas with a leak rate of 27 atm cm^3/hr was introduced into the system. The broadened lines in figure 2 indicate when deuterium gas is flowing. In less than 3 minutes, the system pressure had passed $1x10^{-5}$ torr. The deuterium leak was then closed and the TBS turned on for 0.5 minutes to deposit 0.008 grams of titanium on the sublimation surface.

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*Measured value.

After 20 minutes, the system reached an equilibrium pressure of approximately 4×10^{-7} torr. Deuterium gas was again introduced and the pressure again rose rapidly. However, at approximately 9×10^{-6} torr, the rate at which the pressure rose showed a marked decrease, and pressure then held constant at approximately 1×10^{-5} torr for 110 minutes. At this point in time, unfortunately, a low-flow safety switch on the accelerator heat exchanger shut the system down, cutting off the deuterium gas. Instead of re-establishing the gas leak, we elected to sublime again, only this time for 5 minutes depositing 0.08 grams of titanium. After the system reached a base pressure of approximately 1×10^{-7} torr, we again introduced deuterium. The leak was maintained for 1578 minutes before a pressure of approximately 1×10^{-5} torr was reached, after which the experiment was terminated. Based on a sublimation rate of 1 gram/hr, a deuterium flow rate of 27 atm cm^3/hr, and the formation of titanium deuteride ($TiD_{1.5}$),[*] a total of 5.5 minutes of sublimed titanium should have been completely used up in about 73 minutes. The ability to pump a volume of gas significantly larger than could be consumed in the freshly deposited layer tends to confirm that the inhibiting film can be penetrated.

EXPERIMENT II

In order to try to determine the dominant limiting process, the following experiment was conducted. As in the previous case, a deuterium gas leak of 27 atm cm^3/hr was established. Figure 3 shows the rise in pressure with time. In 13 minutes the pressure rose

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[*]See Run #5, Table I.

from 4.1×10^{-8} to 1×10^{-6} torr (figure 3, curve #1). A layer of titanium was then sublimed onto the substrate for 5 minutes (0.08 grams). The system was allowed to establish an equilibirium pressure of 2.5×10^{-8} torr and deuterium was again introduced (figure 3, curve #2). A system pressure of 1×10^{-6} torr was reached in 426 minutes. In this case, the 300 seconds of sublimed titanium should have been consumed in 67 minutes. Curves #3, #4, and #5 represent repeats of the sequence used for curve #2 except no titanium was sublimed. (A period of 11 hours elapsed between the end of measurements for curve #2 and the beginning of measurements for curve #3.) In each case an equilibrium pressure was established before another run was begun. Finally, titanium was sublimed for an additional 300 seconds (0.08 grams) and then the pressure change with time for the standard deuterium gas leak was again measured (See curve #6.).

EXPERIMENT III

In order to determine if the 300-second sublimation time was sufficient to cover the entire sublimation chamber, it was decided to increase the sublimation time. The results of 7 separate runs are shown in figure 4. As was the case in previous runs, deuterium was leaked into the system at 27 atm cm^3/hr. The pressure rose from 3×10^{-7} to 5×10^{-6} torr in 52 minutes (curve #1). The leak was closed off allowing the system to come to equilibrium, and then a 5-minute deposit of titanium (0.08 grams) was placed on the substrate and the process repeated (curve #2). Figure 4 shows additional curves generated with sublimation times of 15, 30, 60, 60 and 5 minutes (curves #3-7).

These results, obtained sequentially in one continuous time period lasting over 80 hours, are compared with calculated values and presented in Table I.

EXPERIMENT IV

If indeed it was the oxygen which is responsible for the formation of the deuterium inhibiting film, it should be possible to form a deuterium barrier by introducing oxygen to the system and then perhaps to penetrate the barrier by means of an added layer of titanium. The results of experiment IV shown in figure 5 represent an attempt to produce and to penetrate such a barrier. The system was initially at an equilibrium pressure of $2x10^{-7}$ torr. Titanium was then sublimed onto the chamber wall for 60 minutes (1 gram) in order to build up a thick layer of titanium. After equilibrium pressure was again established, high-purity oxygen was admitted to the system in order to form a barrier. The pressure was allowed to rise to approximately 10^{-4} torr and then the oxygen leak was closed. (The ion pump was only cracked open to the system in order to reduce its effect on this operation.) This procedure was repeated about 15 times during a 30-minute time interval in order to form a complete barrier to deuterium. Each time the deposited titanium pumped the oxygen introduced into the system. Deuterium gas was then leaked into the system (27 atm cm^3/hr - See broadened line, figure 5.) resulting in the pressure reaching $5x10^{-6}$ torr in 2 minutes; the barrier was effective. After subliming for 5 minutes (0.08 grams) and re-establishing an equilibrium pressure, 150 minutes were required for the pressure to reach $5x10^{-6}$ torr with the deuterium gas leak

open. Once again titanium was sublimed for 5 minutes and, after establishing a pressure equilibration at 6×10^{-8} torr, deuterium was again admitted to the chamber; 375 minutes were required to reach 5×10^{-6} torr. In theory 0.16 grams of titanium (10 minutes of subliming) should have removed about 60 atm cm^3 of deuterium. Instead, 236 atm cm^3 were adsorbed. The barrier appears to be penetrable.

DISCUSSION

Our main concern in these experiments is with physical adsorption and barrier and bulk diffusion processes. The addition of a thin layer of titanium to an apparently occluded surface has the effect of providing an increase in the physical adsoprtion rate. The results obtained in experiment I (figure 2) indicate quite dramatically our ability to penetrate the inhibiting surface film. Based on the formation of $TiD_{1.5}$, the 0.09 grams of titanium which was deposited on the chamber surface should have been completely used up in 73 minutes; instead it took a total of 1688 minutes. The reduction in the rate of change of system pressure with time at 100 minutes represents a condition under which the leak rate of deuterium into the system is matched by the physical adsorption and diffusion of the deuterium into the substrate. The gradual decrease in the slope after 600 minutes indicates that diffusion through the barrier and into the bulk titanium is occurring quite readily.

Experiment II was performed in order to determine if the physical adsorption rate was limiting the amount of deuterium diffusing into the bulk titanium. After curve #2 in figure 3 was measured, a period

of 11 hours elapsed before the measurements for curves #3, #4, and #5 were made. The large change in slope between curve #2 and curves #3, #4, and #5 at 1×10^{-6} torr indicates that the surface physical adsorption rate could have changed significantly during the 17-hour period between the start of the measurement of curve #2 and curve #3. This result was verified by the deposition of another layer of titanium (same as for curve #2) and the admission of deuterium gas. Curve #6 (figure 3) indicates that the surface film is again being penetrated and is not greatly limited by physical adsorption, nor does it appear to be diffusion limited. The 0.08 grams of titanium deposited before the measurement of curve #6 should have maintained the system pressure for only about 67 minutes. The fact that it lasted for 247 minutes indicates that a previously deposited sublayer of titanium was being utilized and that indeed curves #3, #4, and #5 were physical-adsorption limited.

The results of experiment III indicate that a 5-minute deposition of titanium is not sufficient to make most of the titanium sublayer accessible. The chamber is cylindrical (68.5 cm in length by 45.6 cm in diameter) and a monolayer should be formed in about 5 seconds. In practice it would seem from the results of figure 4 that in order to be totally effective in our chamber, a thickness of about 180 mono-layers (15-minute sublimation) would be required. This does not seem unreasonable since the source is not isotropic nor is it symmetrically positioned in the chamber, and much more surface is available for sub-limation than the chamber geometry would indicate. The irregularity

of the surface can be seen in figure 6 which shows a typical uneven titanium deposition. The curves for the 15, 30, and 60-minute sublimation runs also show a reversal in slope which indicates a limited amount of bulk titanium available. Verification of this is shown in Table I where it can be seen that runs #5, #6, and #7 have used only the deposited titanium. Run #7 which represents a deposition for 5 minutes on a surface with no bulk reserve lasted for about 60 minutes which is in good agreement with calculations.

Experiment IV was supposed to indicate that oxygen present in the system could indeed be responsible for the formation of an inhibiting film. A 60-minute layer (1 gram) of titanium was deposited to supply the source of bulk titanium and an amount of oxygen was admitted which should have covered the entire surface of the sublimator chamber with at least a monolayer. As can be seen from figure 5, at first it was not possible to penetrate the inhibiting oxide film. Only after deposition of a newly formed thin film did the bulk titanium become available. The important result of this experiment is that we were able to penetrate an oxide barrier with a thin layer of titanium after the surface was closed. While these results do not prove conclusively that oxygen is responsible for the formation of the inhibiting film in the normal operation of our system, it does seem a likely candidate since the decomposition of water vapor in the vacuum system supplies a continuous source of oxygen.

It should be made clear that the primary purpose of this vacuum system was not to conduct research into the penetration of inhibiting

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films on titanium substrates. The system was not designed to meet this function and, as a result, the accuracy of some of the measurements leaves something to be desired; however, the overall results are valid and suggest many interesting possibilities for incorporating this concept in the design of sputter ion pumps and the formation of titanium tritide targets.

SUMMARY

We have shown that it is possible to gain access to sublayers of uncombined titanium in spite of an inhibiting film (such as oxygen) on the surface. While we have not demonstrated that the film must be an oxide, we have shown that if it is, then it can be penetrated. Although most of the work presented here was directed toward more effective utilization of titanium in bulk sublimation pumping for small positive-ion accelerators, these results should be of considerable interest to others concerned with hydrogen pumping in general and the problems associated with inhibiting films.

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TABLE I

Results of Experiment III

Run No.	Sublimator On Time Rate: 1 gram/hr. (Min)	Time to Rise to 5×10^{-6} torr (Minutes)	Deuterium Gas Leaked Into System (Atm cm^3)	Grams of Titanium Used	Calculated Deuterium Consumed in Freshly Deposited Layer (Based on Formation of TiD$_{1.5}$) (Atm cm^3)
1	0	52	23	0	0
2	5	335	151	0.08	30
3	15	1245	560	0.25	89
4	30	1280	576	0.50	178
5	60	790	356	1.00	357*
6	60	810	364	1.00	357
7	5	63	28	0.08	30

*The results of run #5 indicate that there was no bulk titanium sublayer available for diffusion and that all of the physical adsorption and subsequent diffusion were occurring in the freshly deposited titanium. This is again verified in run #7. A titanium deuteride ratio of 1:1.5 was based on run #5 and the measured deuterium gas leak of 27 atm cm^3/hr. A recent measurement of sublimator surface material using a mass spectrometer showed good agreement with this value. The fact that TiD$_{1.5}$ was formed rather than the stoichiometric value of TiD$_2$ is not surprising when the "cleanliness" of the vacuum system is considered.
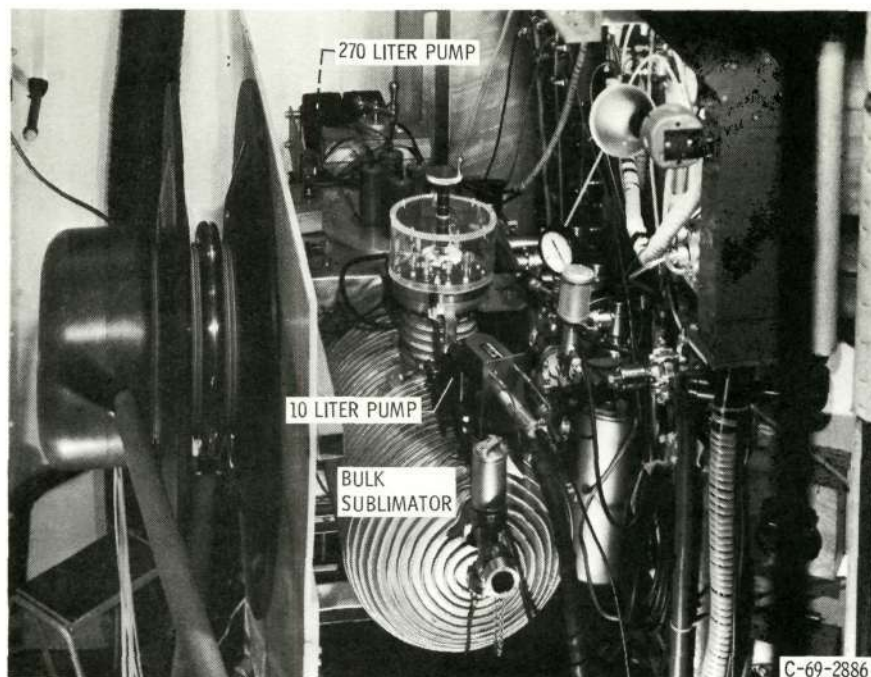
Figure 1. - 300 Kilovolt ion accelerator which served as vacuum chamber for all the measurements.
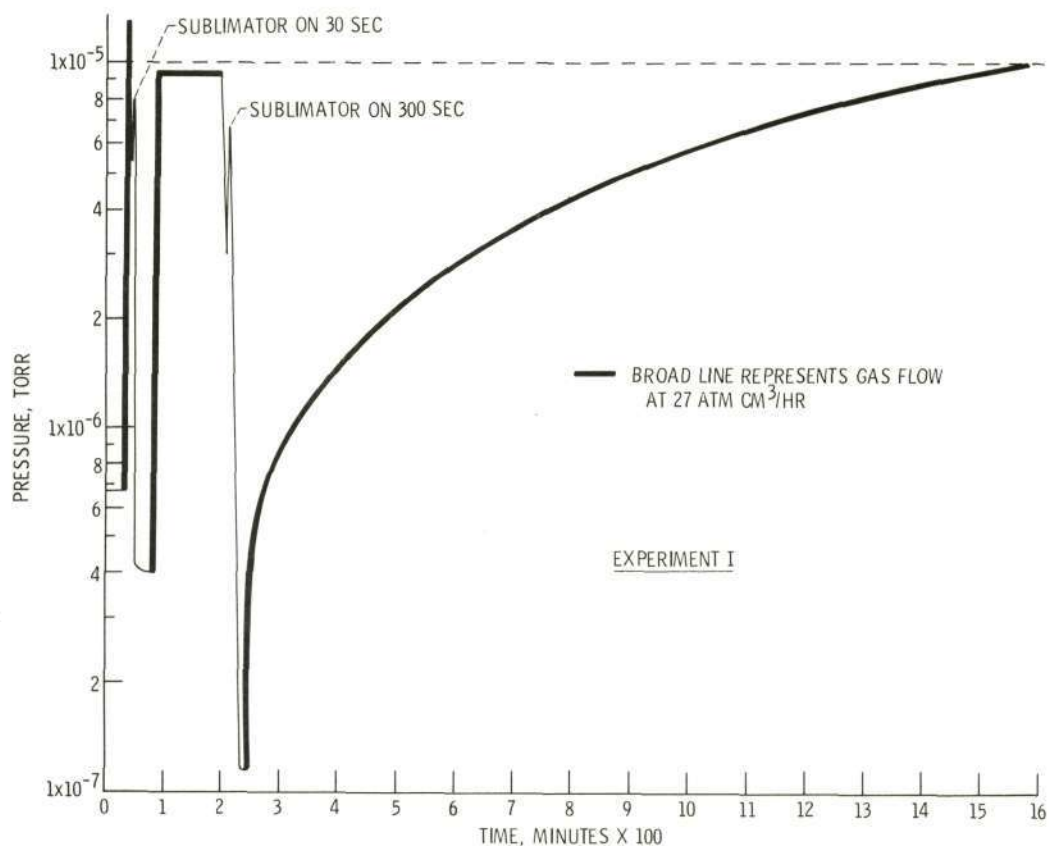

Figure 2. - Shows a plot of the variation of system pressure for various deuterium gas load conditions and demonstrates ability to penetrate the inhibiting film.
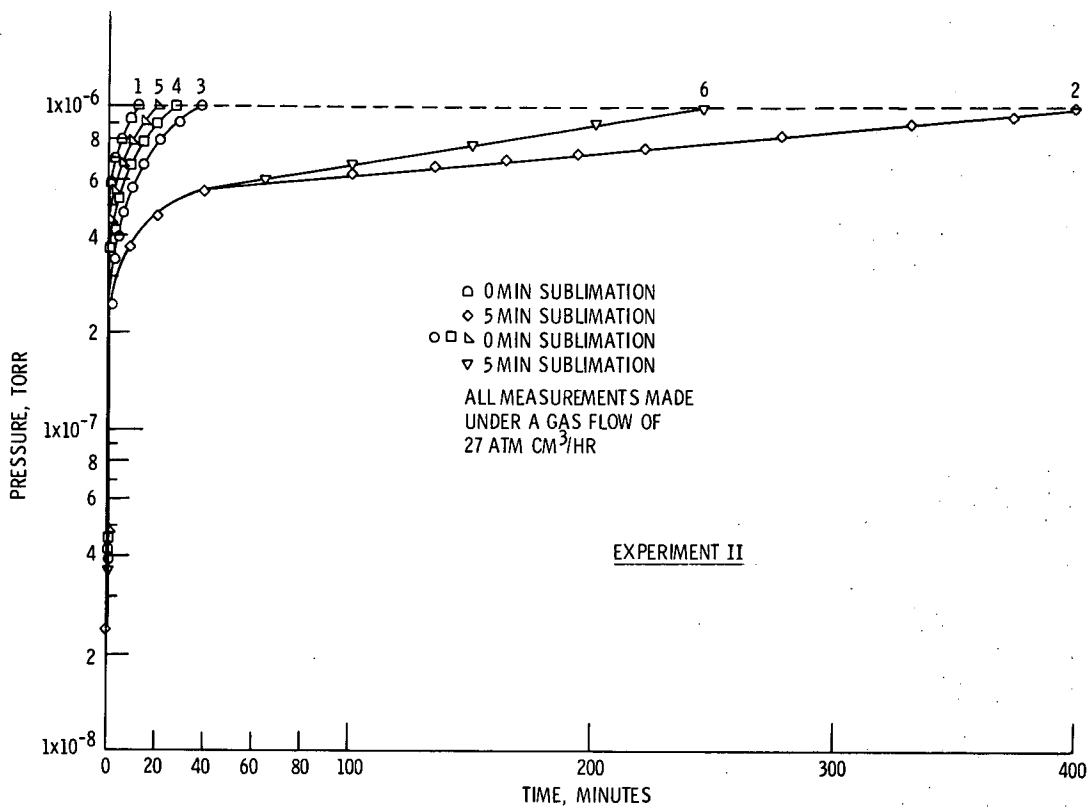
Figure 3. - Shows the effect of physical adsorption on the system pressure under a deuterium gas load.
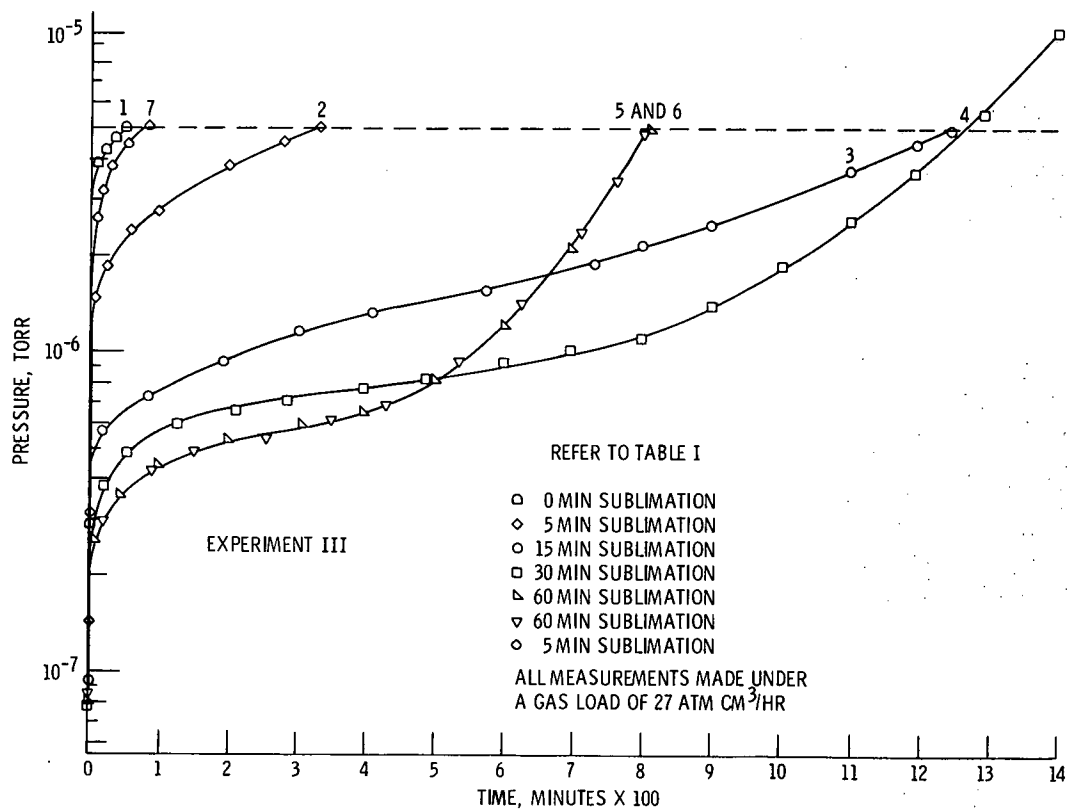

Figure 4. - Shows the effect of the variation in sublimation time on system pressure and indicates the need for multimonolayer deposition to penetrate inhibiting film.
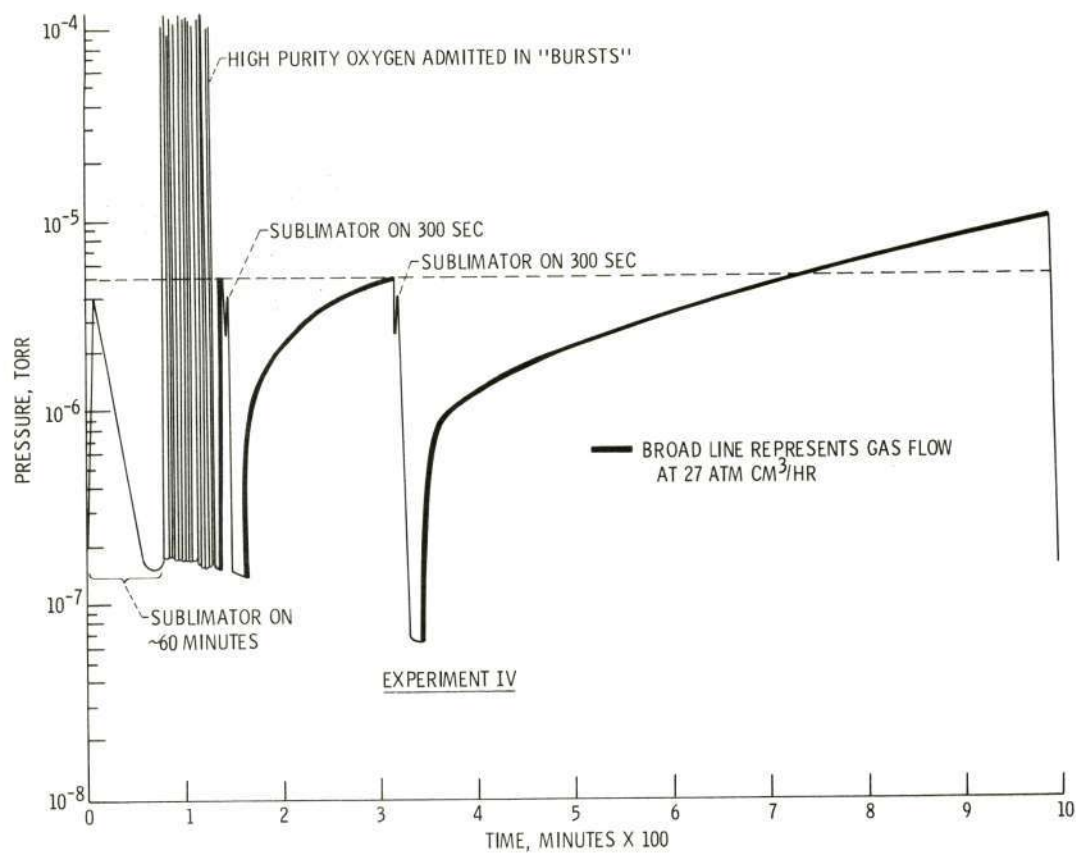
Figure 5. - Shows the effect of an oxide barrier on system pressure (under gas load) and demonstrates the ability to penetrate this barrier.
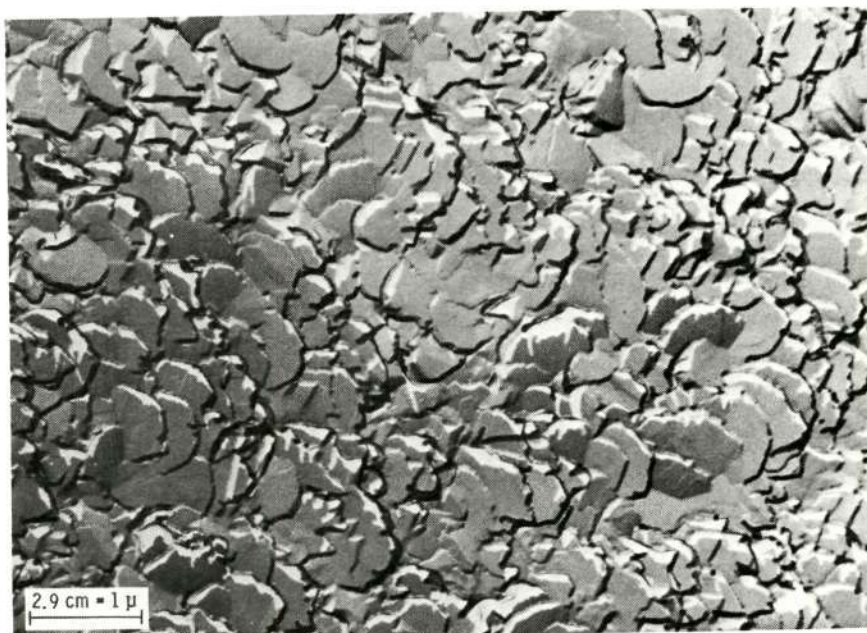

Figure 6. - Magnified view of a typical sublimated surface.