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PULSED GAS LOAD PUMPING OF HYDROGEN
BY VAPOR DEPOSITED
TITANIUM FILMS

BY

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PLASMA PHYSICS
LABORATORY

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Pulsed Gas Load Pumping of Hydrogen by Vapor Deposited Titanium Films *

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ABSTRACT

The Princeton Poloidal Divertor Experiment (PDX) plans to use titanium gettering of hydrogen to provide the high pumping speeds required to capture the pulsed gas load which occurs in the region where the diverted plasma is neutralized. Detailed information with respect to hydrogen titanium film interactions under similar conditions was sought so that engineering decisions could be made with greater confidence. Pumping speeds for hydrogen on titanium films were determined by admitting a pulse of gas into the volume enclosed by the substrate and measuring the time constant of the pressure decay. The measurement was made periodically as the film was deposited, and when the maximum sticking coefficient was reached, sublimation was stopped and additional gas pulses admitted to determine the speed vs. hydrogen concentration in the Ti film. The amount of gas per pulse varied from 0.25 to 5 monolayers. Atomic hydrogen produced by thermal dissociation in a continuous measurement gave minimum-values for the sticking coefficient of 0.3 for a room temperature film. A summary of results is shown in Table I. Titanium film peeling tests were perfomed and sublimation sources were test operated.

EXPERIMENTAL METHOD

The experiment consisted of pulsing varying amounts of molecular hydrogen into a volume formed by a copper liner located within an aluminum tank. This liner acts as the substrate for the vapor deposition of a titanium film. The rate at which this film pumps the gas admitted into it is measured and the sticking coefficient calculated by means of the following analysis.

$$-V \frac{dP}{dt} = S_L P \tag{1}$$

V = Liner volume
S_L = Liner speed
P = Liner pressure
t = time

$$\ln \frac{P}{P_o} = - \frac{S_L}{V} t \tag{2}$$

S_L is determined graphically from a semi log plot of P/P_o vs. time. The sticking coefficient is found from S_L by the expression

$$s = \frac{S_L}{A(Sb)} \tag{3}$$

s = Sticking coefficient
A = Geometric area of titanium film
Sb = Speed per unit area for unity sticking coefficient

A schematic of the vacuum system is shown in Fig. 1. The pulse valve admits the gas in approximately 5×10^{-4} sec into the liner with a volume of 148 liters and a surface of $1.56 \times 10^4 cm^2$. The interior of this liner is coated with a sublimed film of titanium coming from a centrally located sublimator. A cooling tube is soldered to the .030" thick copper, which forms the wall of the

liner, to regulate the temperature. Four copper constantan thermo-couples monitor temperature. Liner temperature was varied between $160^{\circ}C$ and $-195^{\circ}C$. A fast ion gauge, with a time constant of 250 μsec for room temperature hydrogen follows the rapid changes in pressure. The ion current signal drives an oscilloscope whose trace is photographed. The RC of the input to the oscilloscope is 379 μsec. A second coil located between the liner and the aluminum vacuum tank is cooled with liquid nitrogen to control the partial pressure of water. A quadrapole mass spectrometer monitors the ambient vacuum. The vacuum tank is sealed with viton "o" rings and pumped with a standard oil diffusion pump with a Freon refrigerated baffle.

The gross speed S_L is corrected for a measured 2500 l/sec aperture conductance, for room temperature H_2, from the liner to the vacuum tank due to the clearance around the penetrations shown in Fig. 1.

The term monolayer will denote a surface cover - 5×10^{14} particle/cm^2. The area referred to here is the geometric surface of the substrate.

The variable experimental parameters were substrate tempera-ture, rate of sublimation, quantity of gas per pulse, and film thickness.

For the results plotted in Fig. 2, we find that between 500 and 1000 monolayers of titanium were required to reach an equilibrium value for the sticking coefficient. The slower rate of increase for the first run was probably due to the initially higher background pressure at start-up.

The substantial film thicknesses required to achieve the highest capture coefficients require that an essential step in the capture process be the formation of atoms whose removal from the surface depends on unobstructed diffusion into the film.

Long term saturation effects are shown in Fig. 3.

Films of various thickness are laid down, sublimation is terminated, and the concentration of hydrogen is increased by exposing the film to a sequence of gas pulses. Results show that film thickness is the dominant factor, and that the sublimation rate is secondary as long as the background pressure is such that the film deposited is $\geq 75\%$ titanium. The poor performance of the thicker films indicated that surface concentrations become high enough to restrict diffusion before all of the film can participate.

Short term saturation effects were investigated by varying the amounts of gas contained in a given pulse. Fig. 4 shows the results.

Approximately a 40% decrease in sticking coefficient is found as the gas load is increased by an order of magnitude. The sticking coefficient does not change during a particular pulse of gas. It would appear that the initial flux of gas to the film determined the surface concentration, and the sticking coefficient, which remains unchanged as the balance of the gas in the pulse is pumped. Although titanium is being continuously sublimed, the measurements occupy such a short time that, for practical purposes, titanium deposition can be ignored.

Figure 5 gives the results obtained for elevated substrate temperatures. The background, almost exclusively H_2 pressure, is also shown.

Upon recooling the substrate, the initial conditions were restored. The pressure in the liner during the measurement is at least an order of magnitude greater than the hydrogen background pressure, so the decrease in the capture coefficient is real and not merely the difference between what is captured and what is released thermally. Adequate cooling of the substrate is essential for performance.

When the substrate was cooled to liquid Nitrogen temperature (77^OK) sticking coefficients of ≥ 0.6 were obtained for gas pulses of ≤ 0.5 monolayer. Since the gas pulse is introduced in approximately 0.5×10^{-3} sec, the sticking coefficient for times shorter than this is unobtainable. For a 0.9 sticking factor the τ of this system is 0.5×10^{-3} sec for H_2 at 77^OK . As monolayer coverage is approached, saturation is observed and the sticking coefficient is sharply reduced. Figure 6 gives the dependence of the sticking coefficient as a function of the cumulative gas admitted.

To examine long and short time recovery effects, the time between pulses is varied from 5 min to 15 sec. For low coverages the capture efficiency appears high and constant, with a substantial reduction as monolayer coverage is reached. No recovery of the capture coefficient is seen for coverages of less than 0.5 monolayer, slight recovery at ≈ 0.75 monolayer, and complete recovery at lower capture efficiencies

from $\approx$ 0.75 to monolayer coverages, 75% of which occurs
within 15 sec with $\approx$ 25% additional recovery over a 5 min
period. When two monolayers of gas are admitted in a single
pulse, the capture coefficient decreases at a more rapid
rate. However, even after 10 millisec of pumping it has
not fallen to zero, but remains 0.03. This suggests a low
efficiency pumping mechanism which does not saturate.

The theoretical model capable of explaining some of these
observations is developed from the following assumptions:
the sticking coefficient is unity for an unoccupied active
site; these sites are dense forming a monolayer; as sites are
permanently occupied they become inactive, and the sticking
coefficient decreases as the coverage increases, going to
zero with monolayer coverage.

$$f = \frac{V(n_o - n)}{KA} \qquad (4)$$

V = volume
n_o = the initial density
n = density
K = particles/unit area required to form a monolayer

$$s = (1-f) \qquad (5)$$

s = sticking coefficient

$$-V \frac{dn}{dt} = s \frac{A\bar{v}}{4} n \qquad (6)$$

$\bar{v}$ = average velocity

From these equations we obtain

$$\frac{n}{n_o} = \frac{1 - \frac{Vn_o}{KA}}{\exp\left[(1 - \frac{Vn_o}{KA}) \frac{\bar{v}}{4} \frac{A}{V} t\right] - \frac{Vn_o}{KA}} \qquad (7)$$

when $KA = Vn_o$

$$\frac{n}{n_o} = \frac{1}{\frac{\bar{v}}{4} \frac{A}{V} t + 1} \qquad (7a)$$

and

$$s = 1 - \frac{Vn_o}{KA}\left[1 - \frac{n}{n_o}\right] \qquad (8)$$

Eq. (7), (7a), and (8) are plotted in Figs. 7 and 8 for three values of the parameter Vn_o/KA. This model predicts successfully some of the observed features, high initial speed, rate of decrease in speed, and saturation as a function of time and amount of gas admitted. Recovery effects are ignored as is the low speed pumping mechanism.

Five experimental runs to measure H_2 capture rates of titanium films at 77^oK were made during the course of eight months. The first run, made after several room temperature sublimations, saturated at a coverage of 5×10^{14} monecules/cm^2 (i.e., monolayer coverage). The second measurement made ten weeks later, after considerable titanium sublimation, required about four times as much gas to produce the same saturation effect. Subsequent measurements at 77^oK showed no further change. This indicates a fourfold increase in the real physical surface with respect to the apparent geometric surface.[1] The

geometric surface has been used in Eq. (3) and to calculate all values of the sticking coefficient. The one sticking coefficient result obtained before the first liquid N_2 run was 35% lower than the average values obtained after the increase in physical surface had occurred. The high speed performance of the film at 77°K could be completely restored by subliming an additional 10 monolayers of titanium indicating that only surface processes are involved.

In the course of making measurements, the background gas was monitored with a quadrapole mass spectrometer and an ion gauge. Typical starting pressures of 5×10^{-7} to 2×10^{-6} torr were observed. After sublimation of several hundred monolayers the pressure falls to 5×10^{-8} - 1×10^{-7} torr. When 1000 layers of titanium were deposited the pressure was typically $1-2.5 \times 10^{-8}$ torr. Pressure measurements were made with 600 to 750 watts of power being applied to the sublimator. With the sublimator off, pressures fell to 5×10^{-9} - 1×10^{-8} torr. Except for the 160°C substrate experiment with its high H_2 background pressure, the background gas mass scans were quite unremarkable. Mass 28 accounted for the majority of the background with lesser amounts of H_2, H_2O, and methane. Some oil peaks were seen before sublimation began.

In Fig. 9 the effects of admitting oxygen (0.5 torr) and N_2 (0.4 torr) are shown. The chemical reaction at the surface appears to block the diffusion of hydrogen atoms, formed at the surface, into the film.

ATOMIC HYDROGEN EXPERIMENT

Atomic hydrogen interactions with titanium films were studied using a steady-state method. A continuous flow of hydrogen was introduced into an oven, see Fig. 1, which thermally dissociated some fraction of the incoming gas into atoms. For a given gas flow rate, the liner pressure was first measured without dissociation and then again with dissociation in progress. The following analysis was used:

For <u>no dissociation</u>

$$\frac{Q_M}{S_M} \equiv P_o \qquad (9)$$

Q_M = mass flow rate H_2

S_M = total speed for H_2

P_o = initial pressure

<u>with dissociation</u>

$$\frac{Q_A}{S_A} + \frac{Q_m}{S_M} = P \qquad (10)$$

P = pressure during dissociation

Q_m = mass flow of H_2 with dissociation

Q_A = mass flow of atoms with dissociation

if "f" is the fraction of H_2 dissociated we have

$$Q_A = 2 \, f Q_M \qquad (11)$$

$$Q_m = (1-f) Q_M \qquad (11a)$$

the factor 2 is due to the fact that 2 atoms are produced from each molecule.

$$S_A = \frac{2 S_M}{1 - \frac{1}{f} \left(\frac{P_o - P}{P_o} \right)} \qquad (12)$$

from (3) we obtain:

$$s_a' = (\frac{1}{\sqrt{2}}) \frac{2s_m}{1 - \frac{1}{f}(\frac{P_o-P}{P_o})}$$

(13)

s_a = sticking coefficient atomic hydrogen

s_m = sticking coefficient molecular hydrogen

"f" is not available since the pressure in the oven and the conductance from the oven to the liner are not known. If "f" is assumed to be unity, the minimum value of s_a is obtained. If 0.04 is used for s_m at 300^OK, the experimental results predict that $s_a \geq 0.3$ (i.e., $(P_o-P)/P = 0.8$) .

The oven used to dissociate the hydrogen was formed from a 0.002" thick sheet of tungsten rolled into a tube about 4 cm long and 1 cm in diameter with the ends crimped closed and connected to the supporting current leads. Gas is introduced through a 0.125" tantalum tube which enters the tungsten tube at the edge of one of the crimped ends. The highest temperature achieved was about 2100^OK. Hydrogen pressures in the liner were varied from 1 to 5×10^{-7}torr during the measurements.

When pulsed gas measurements indicated that maximum film performance has been reached, the atomic measurements were begun.

Pulsed gas measurements were made during the continuous atomic measurements to obtain the values for s_m used. Results obtained at film temperatures of 77^OK gave values ≥ 0.6 for the atomic sticking coefficient.[2] During these measurements titanium was continuously sublimed at a rate of 800 monolayers per hr. The lowest value of s_m obtained from the pulsed

measurement was used to calculate s_a . No saturation effects for atom capture efficiencies were seen, and atoms appeared to be able to diffuse into the interior of the film at $77^O K$. In view of the conservative value chosen for "f" and the greater value of s_a at $77^O K$, one suspects that the atomic hydrogen capture coefficient is close to unity. Titanium films sublimated on the ATC vacuum vessel[3] strongly suppressed neutral recycling and the particles escaping from the plasma are for the most part, atoms or protons.

DISCUSSION AND CONCLUSIONS

Simonov et al,[4] proposed a capture mechanism described as "dissociative" for the capture of molecular hydrogen at room temperature. Double bonding of the molecule is required for capture with dissociation and diffusion following. The low efficiency arises because suitably spaced or paired and therefore, rare, active sites to capture and dissociate the molecule are required. The atoms diffuse to the interior and the sites again become available. At $77^O K$ they propose that a single bond is sufficient to bind the molecule and that no dissociation, and hence, no diffusion, occurs. This capture process is fast since all sites are now effective. Saturation is expected as the sites become occupied.

The experimental results previously described are by and large in agreement with the above model. However, one modification is suggested. The surface coverage

(5×10^{14} particles/cm^2) at saturation for 77°K films implies

that the active sites are numerous enough to be "densely

packed" (i.e., a monolayer) so that active pairs should occur

with high probability. To explain the low probability of dis-

sociative capture at room temperature when many paired sites

exist, another hypothesis must be sought. The orientation

of the axis between the atoms could also restrict the capture

efficiency if it is assumed that this axis must be relatively

parallel to the film surface so that "simultaneous" bonding

and, therefore, capture and dissociation can occur.

The dependence of capture efficiency upon film thickness

and purity strongly support the suggested dissociative capture

process at room temperature since only by diffusion can the

bulk of the film interact with the surface. The diffusion

rate of atoms into the interior, diluting the surface concentra-

tion, is required to achieve maximum capture efficiencies. The

decrease in capture rates, observed experimentally, produced

by increasing the amount of gas contained in a pulse is also

compatible with this model.

The fact that atoms formed in the oven by thermal dis-

sociation still diffuse readily at 77°K into the film, supports

the hypothesis that molecules captured by means of a single

bond do not dissociate. It could have been supposed that dis-

sociation occurred at 77°K, but that the diffusion rate of

atoms into the film is so reduced that the surface saturates.

The recovery of $\approx$ 20% of the surface area of a 77°K film within 15 sec probably occurs as the result of "limited" dissociation and absorption into the film by diffusion, since this gas is not detected in the volume. However, the experimental accuracy is not sufficient to be positive. This process clears only $\approx$ 20% of the surface in 15 sec and only 5% more after 5 minutes. At least 50% of the surface remains permanently blocked. Further sublimation of $\approx$ 10 monolayers is required to restore full capture efficiency. During surface recovery measurements, no titanium is sublimed.

The capture efficiencies for atoms and molecules are summarized in Table I.

The capture efficiencies dependence upon hydrogen concentration indicate that thick films are wasteful, and that after the maximum capture efficiency has been reached, a ratio of 2 atoms of titanium sublimed for each molecule of hydrogen captured will maintain it.

The pulsed gas method of measuring sticking coefficients extends the surface flux by three orders of magnitude at which sticking coefficients can be measured. It minimizes the effect of titanium evaporation during measurements, and induced gas disorption phenomena. Only ratios of ion gauge currents are needed instead of absolute values and signal to noise ratios are high, at room temperature, measurements can be made without affecting the film being deposited appreciably. Saturation and recovery phenomena are readily examined. Rapid surface processes can be examined.

ENGINEERING TESTS

Film peeling tests were made using molybdenum, aluminum, tantalum, titanium, copper and stainless steel substrates (see Fig. 10). Strips of these materials about 30 cm long and 10 cm wide, mechanically clamped at each end to water-cooled heat sink, were coated with a film equivalent in amount to that expected to develop in PDX over an eight-month period. One half of each strip was sandblasted, the remainder was untreated. All were acetone rinsed.

Sandblasted areas were markedly superior with respect to film adhesion. Titanium and aluminum gave the best results with titanium having a slight edge. Hydrogen loaded films were also tested and gave similar results (see Fig. 11 and 12).

The various sublimators (i.e., Ti Balls) were also subjected to interrupted operation required when the magnetic fields are operated. The current to the sublimators is turned off while magnetic fields are on. The 10 to 20 sec off-period thermally cycles the Ti Ball which could shorten its life by promoting crystal growth which damages the ball structure. Ten and fifteen second interruptions have no effect. Twenty second interruptions reduced ball life by $\approx$ 20% (see Fig. 13).

The sublimators at operating temperature were subjected to a sudden inrush of air. The tungsten heaters were destroyed but the titanium did not burn. When air is admitted suddenly the titanium film which has peeled, or that is in poor thermal contact with a heat sink, becomes hot enough to burn. Excessive loose film should be avoided.

In operation, gas pulses of up to $\approx 5 \times 10^{20}$ particles per pulse will be admitted to form the plasma. Up to 10^3 pulses a day are to be expected. The gettered surface must be capable of pumping each pulse of gas in 50 to 200 millisec. The plan is to use 80 Ti Balls (35 gm of available titanium each) as vapor sources to deposit a film of titanium over a getter surface of some 60 M^2, 60 kW of power will be required for operation. The film substrate is to be 0.125" aluminum plates, mechanically clamped to water-cooled heat sinks. The aluminum plates may be removed for servicing from the fully assembled device. The Ti Balls may also be serviced from within the assembled vacuum vessel.

The room temperature capture coefficients for molecular hydrogen are somewhat lower than those obtained by others;[5,6] however, they are sufficient to give the required PDX performance if the magnetic throats through which the plasma escapes can be baffled sufficiently. If atoms predominate, high performance is anticipated.

ACKNOWLEDGMENTS

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TABLE I

Sticking coefficient for atomic and molecular hydrogen on vapor deposited titanium

Temperature	Sticking coefficient	
	H_2	Atomic (H)
$160^{O}C$	0.005	
$100^{O}C$	0.03	
$20^{O}C$	0.04	≥ 0.3
$-195^{O}C$	$>0.6^{*}$	≥ 0.6

* coverage $\leq$ 0.5 monolayer
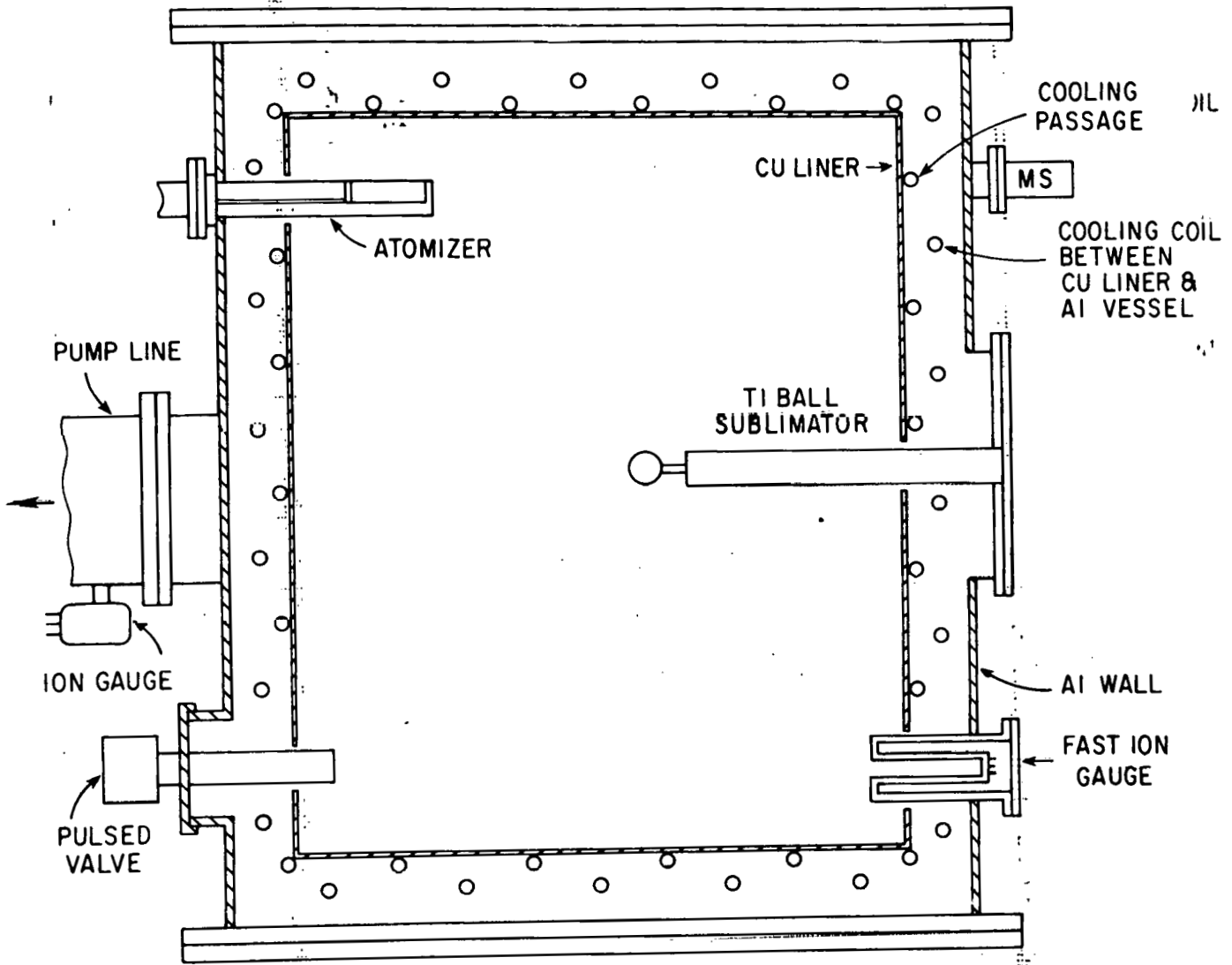
Fig. 1. Schematic of experimental system.
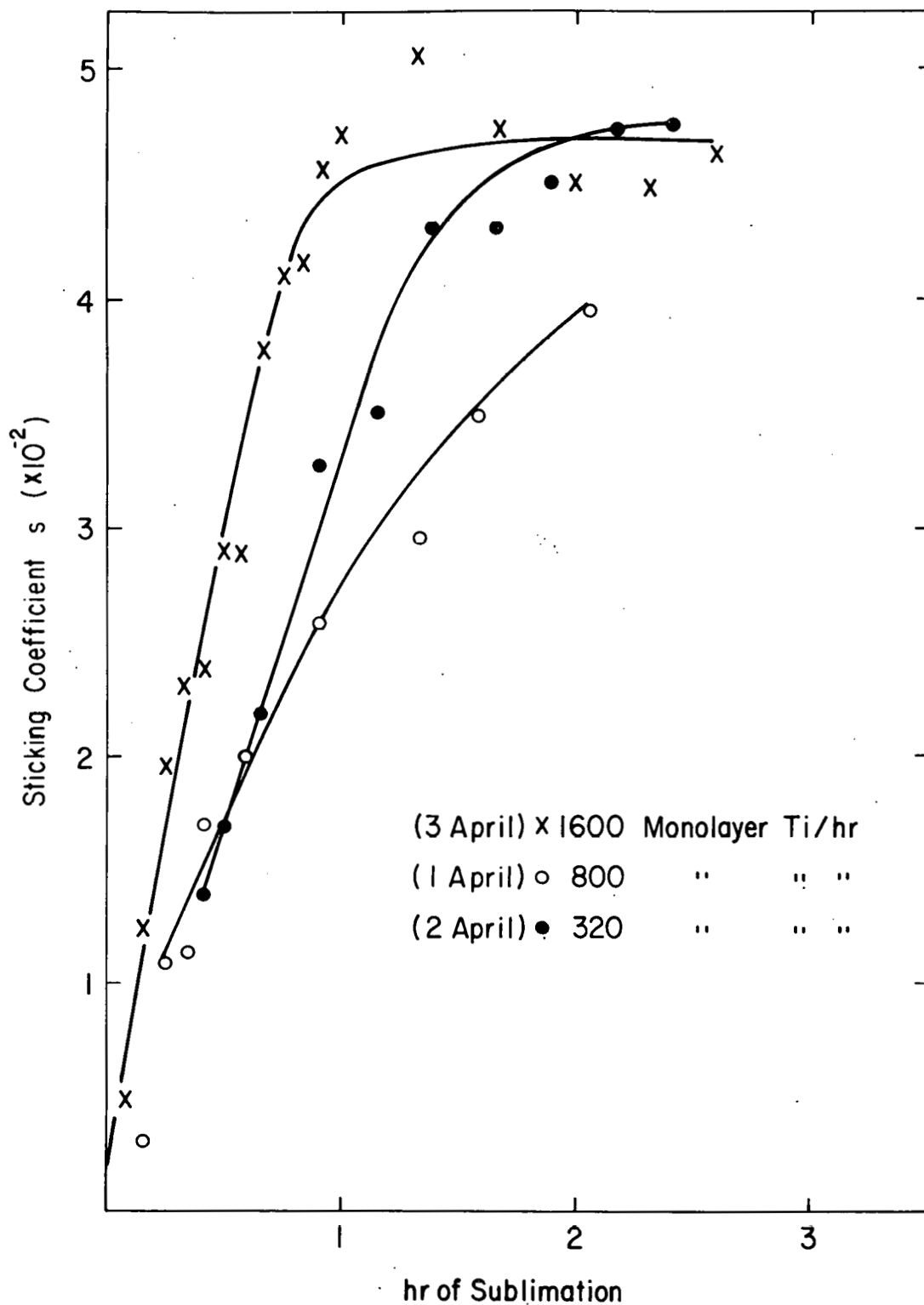
Fig. 2. Sticking coefficient vs. time for three successive runs at different sublimation rates, two monolayers H_2 per pulse. The substrate is at room temperature and sublimation is continuous.

754798
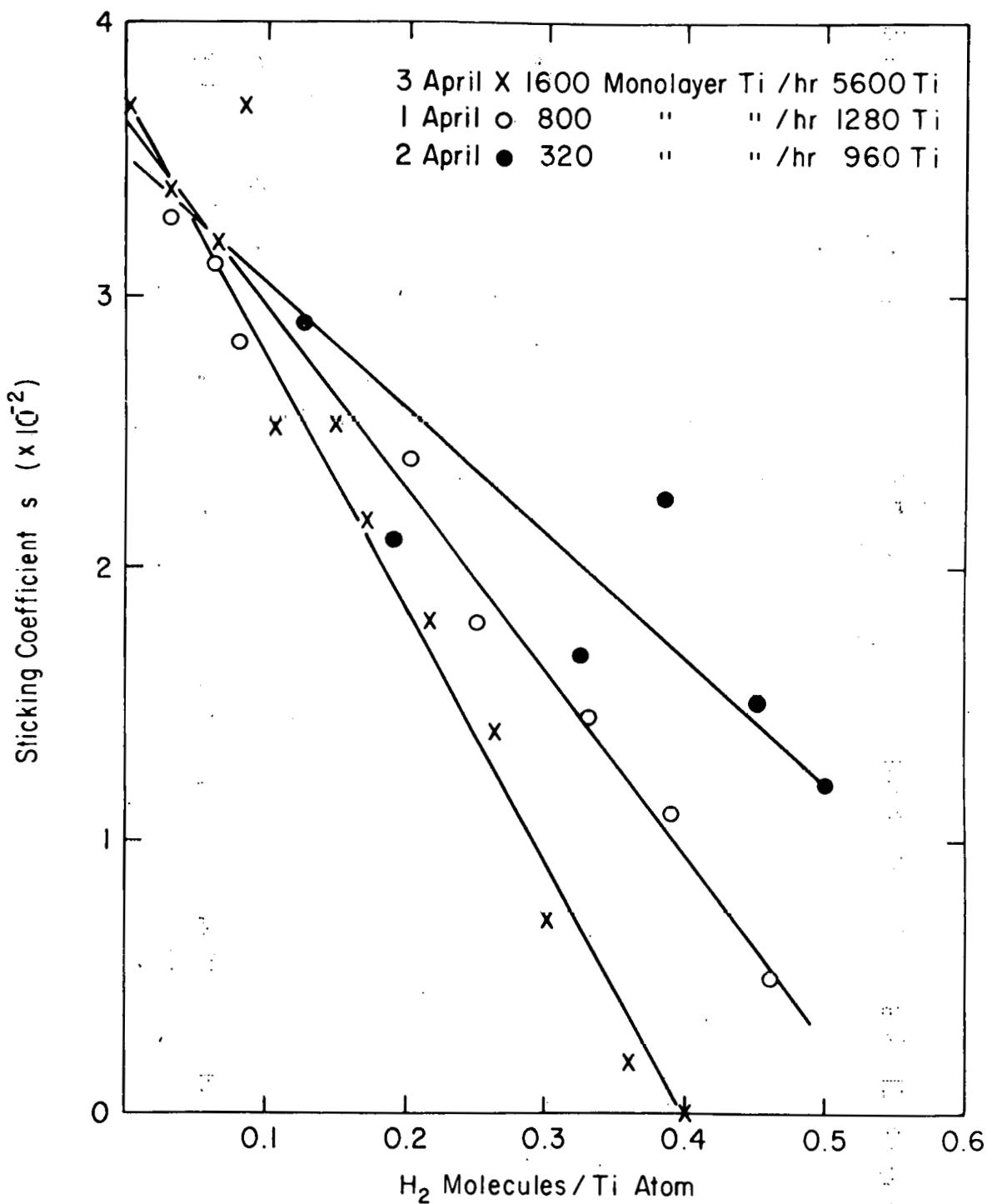
Fig. 3. The dependence of the sticking coefficient as a function of the amount of hydrogen pumped for film thicknesses of 5600, 1280, and 960 monolayers of titanium. The substrate is at room temperature and sublimation is continuous.
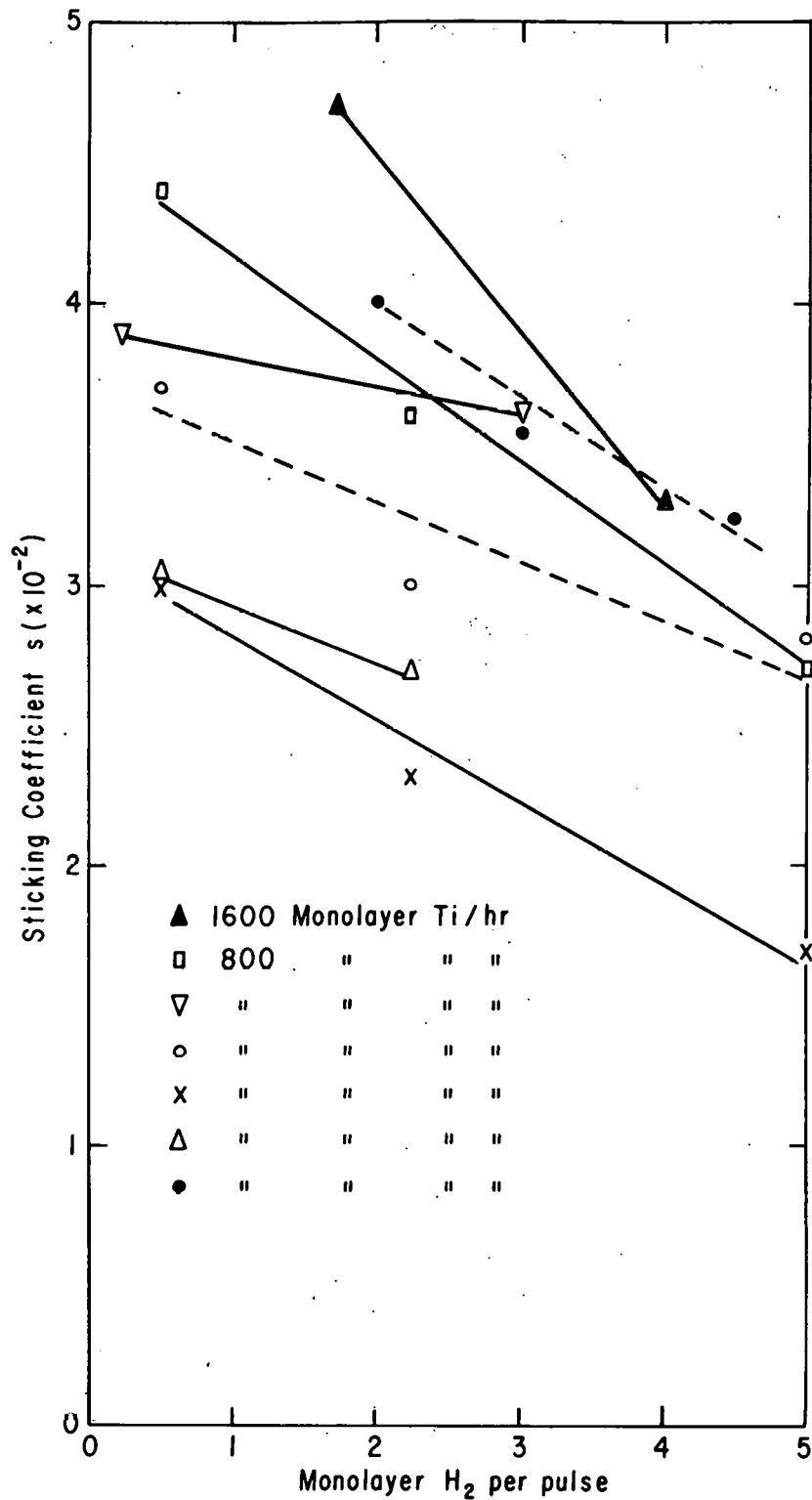
754791

Fig. 4. Short term dependence of the sticking coefficient as a function of the amount of gas contained in a single pulse. The substrate is at room temperature and sublimation is in progress.
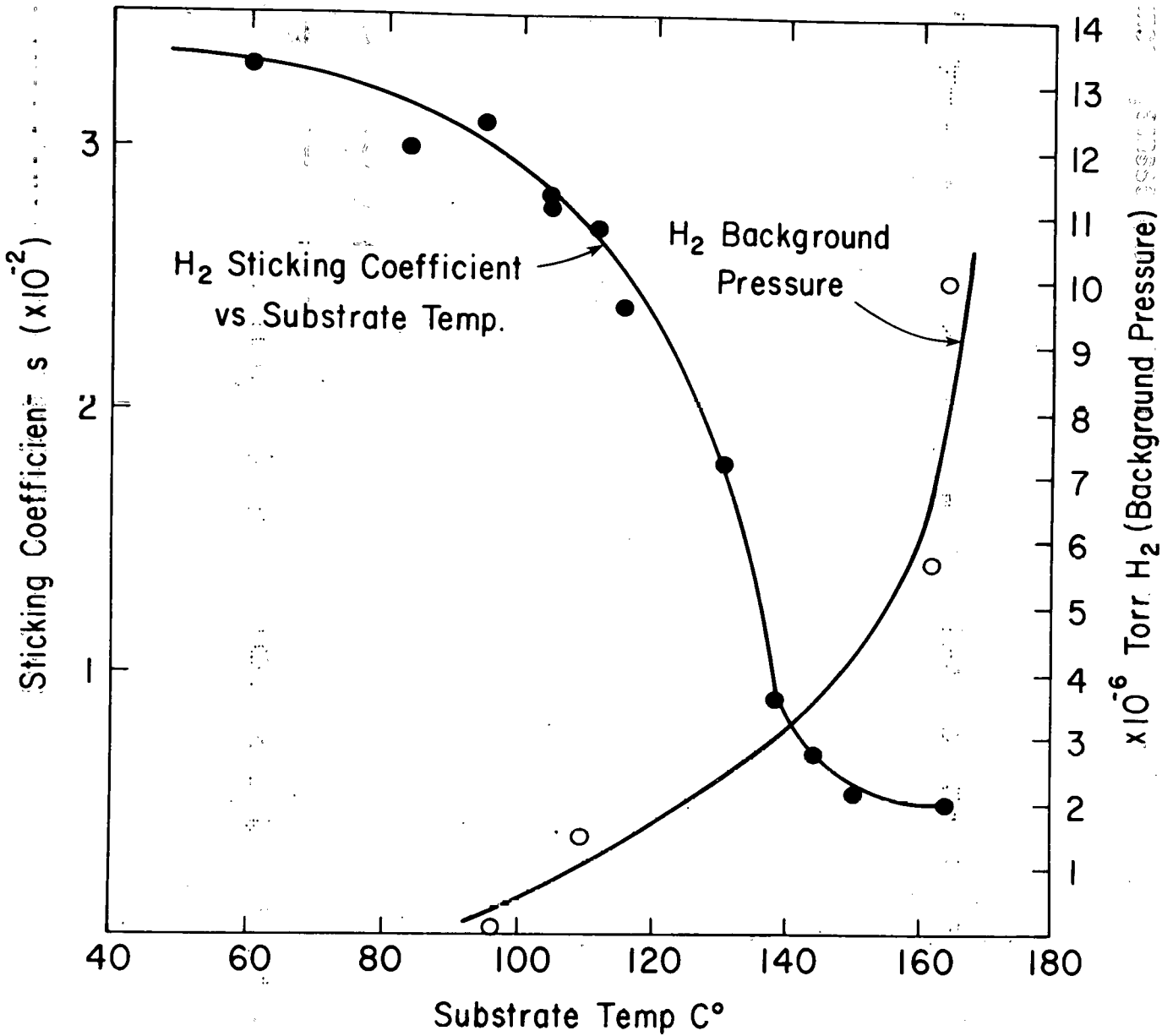
Fig. 5. Sticking coefficient dependence on elevated substrate temperature. Continuous sublimation in progress at 800 Monolayer per hr rate. 0.5 Monolayers of H_2 admitted per pulse.

754796
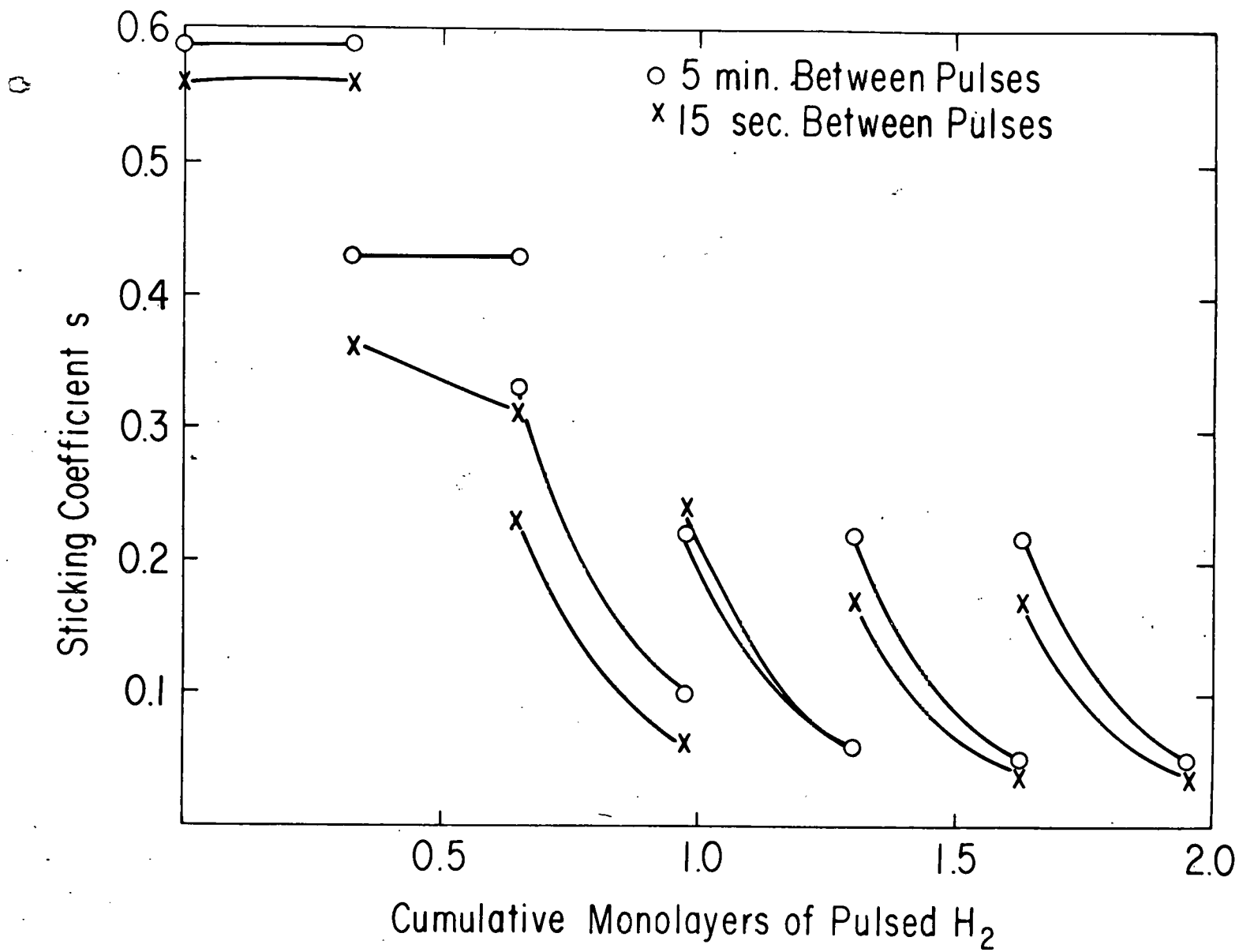
Fig. 6. Sticking coefficient dependence on surface coverage with substrate at liquid nitrogen temperatures. 0.325 Mono-layers of H_2 are admitted by each pulse.
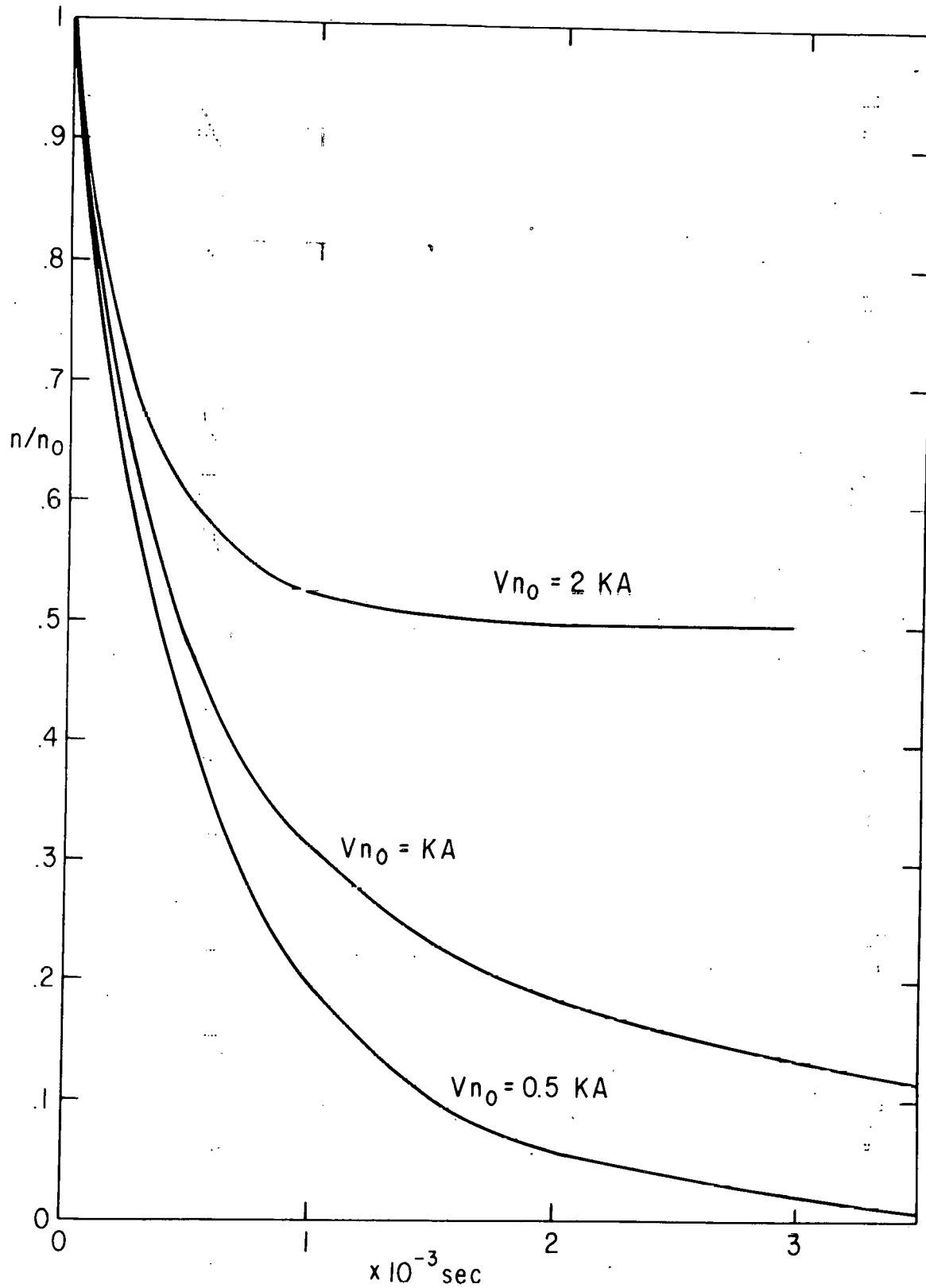
Fig. 7. The dependence of n/n_0 as a function of time, for different quantities of gas admitted at $t = 0$, using Eq. (7) and (7a).
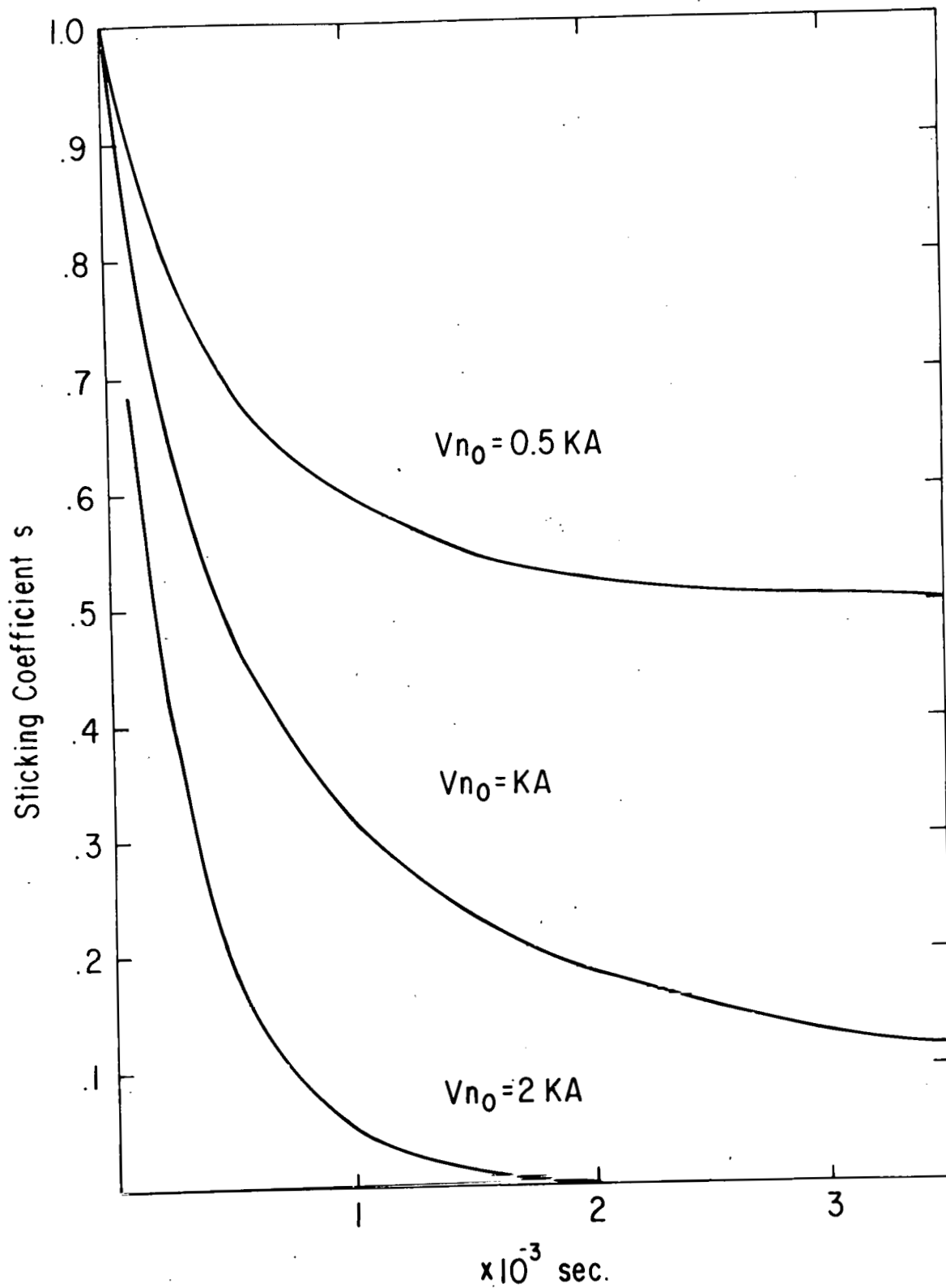
756238

Fig. 8, The time dependence of the sticking coefficient
for different quantities of gas admitted at t = 0 predicted
from Eq. (8).
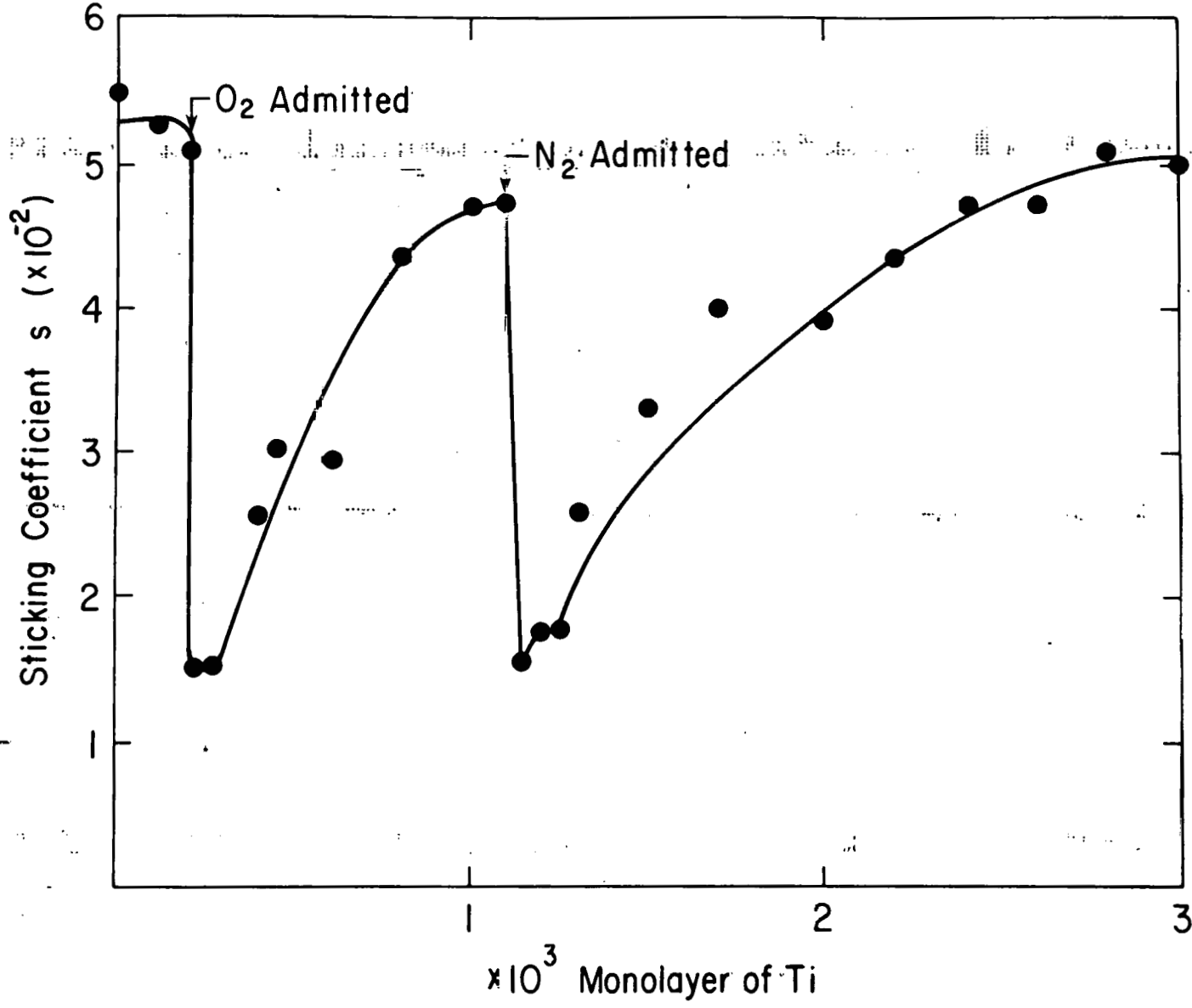
Fig. 9. The effects of exposing titanium films to oxygen and nitrogen are displayed. The sticking coefficient reduction and recovery are shown. The sublimation was continuous at 800 monolayer of titanium per hr. The substrate was at room temperature.

7754794
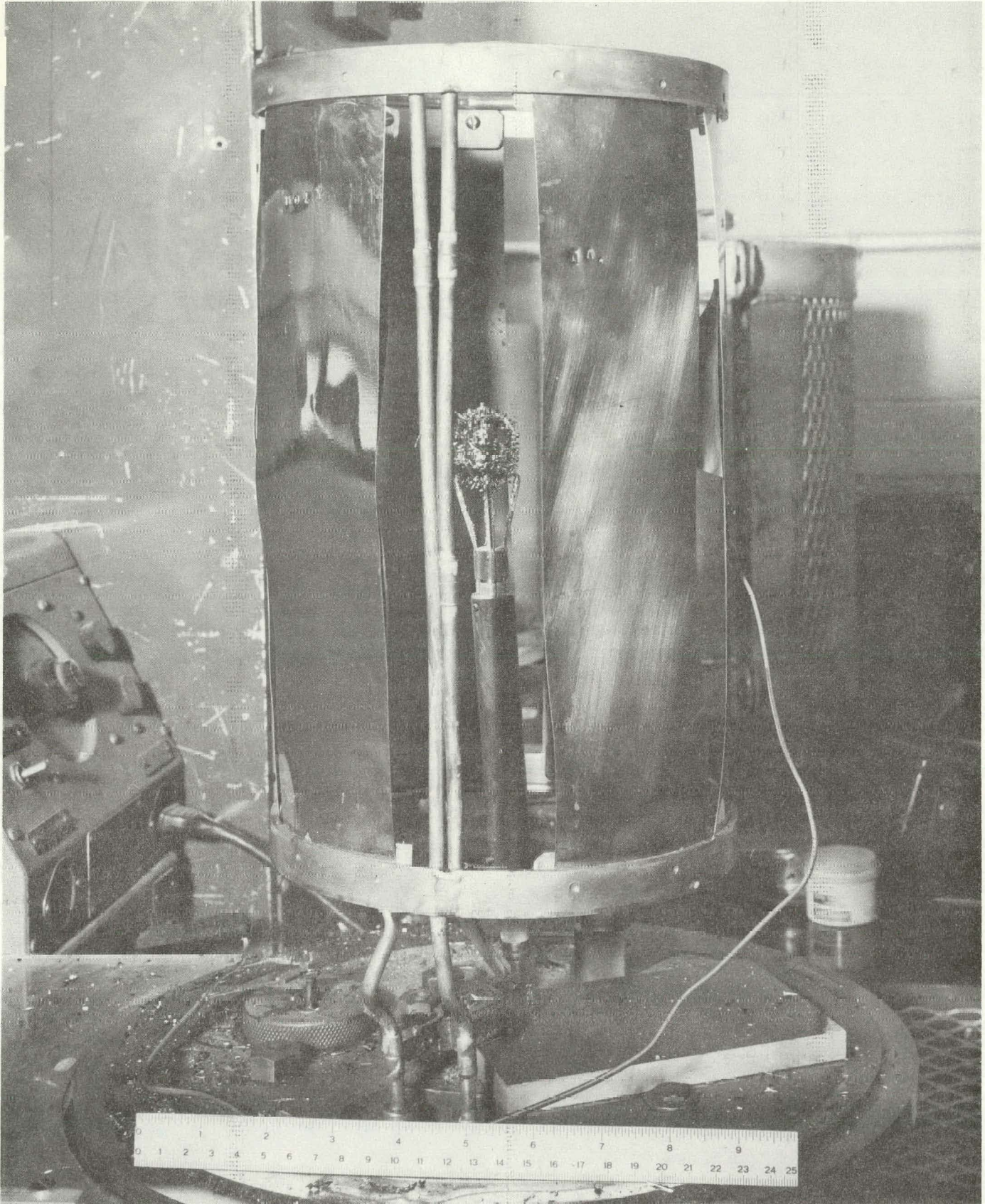
SIDE VIEW OF TITANIUM PEELING TEST STAND.
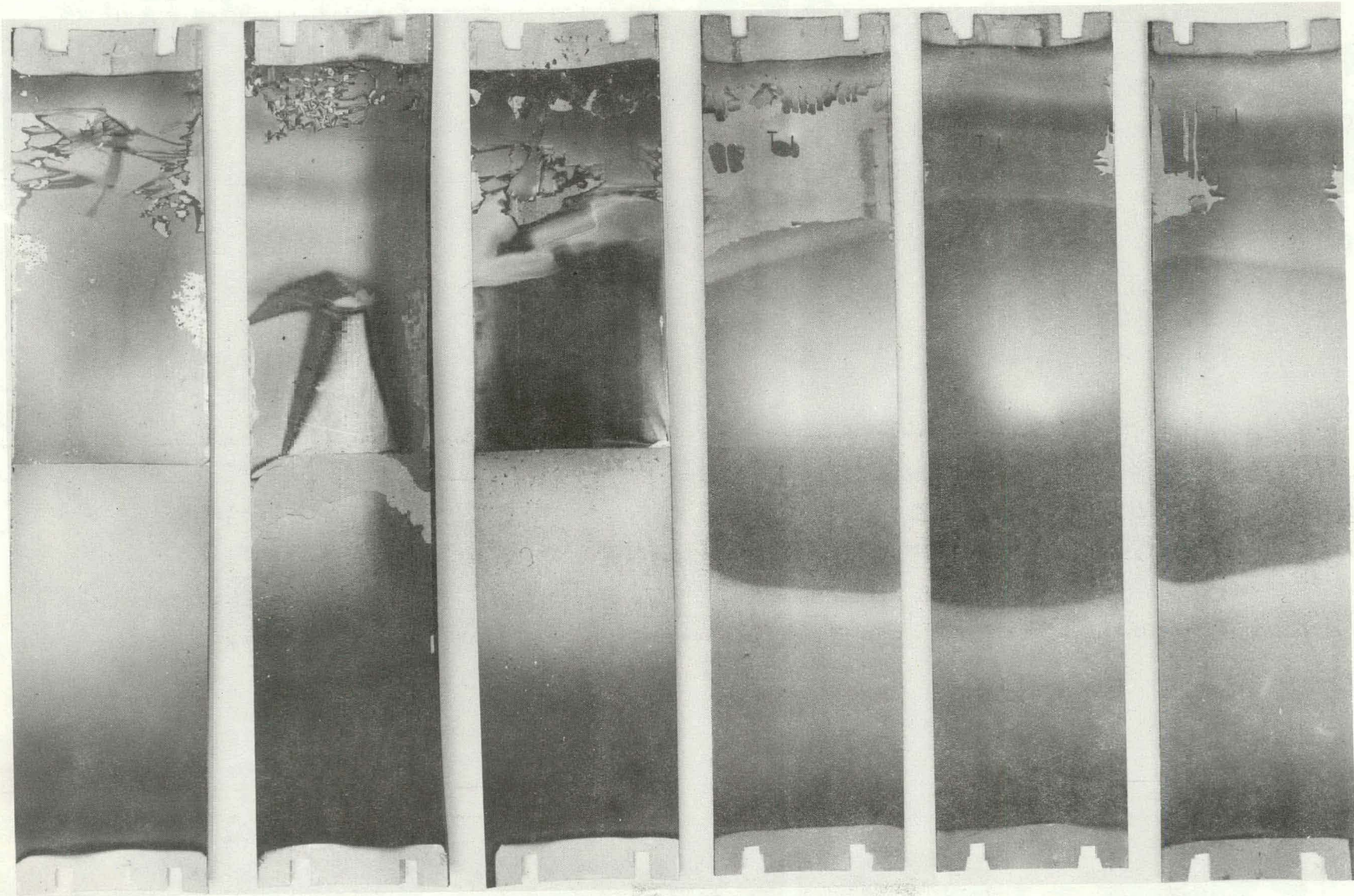PHOTO TAKEN JAN. 29, 1975.

753118
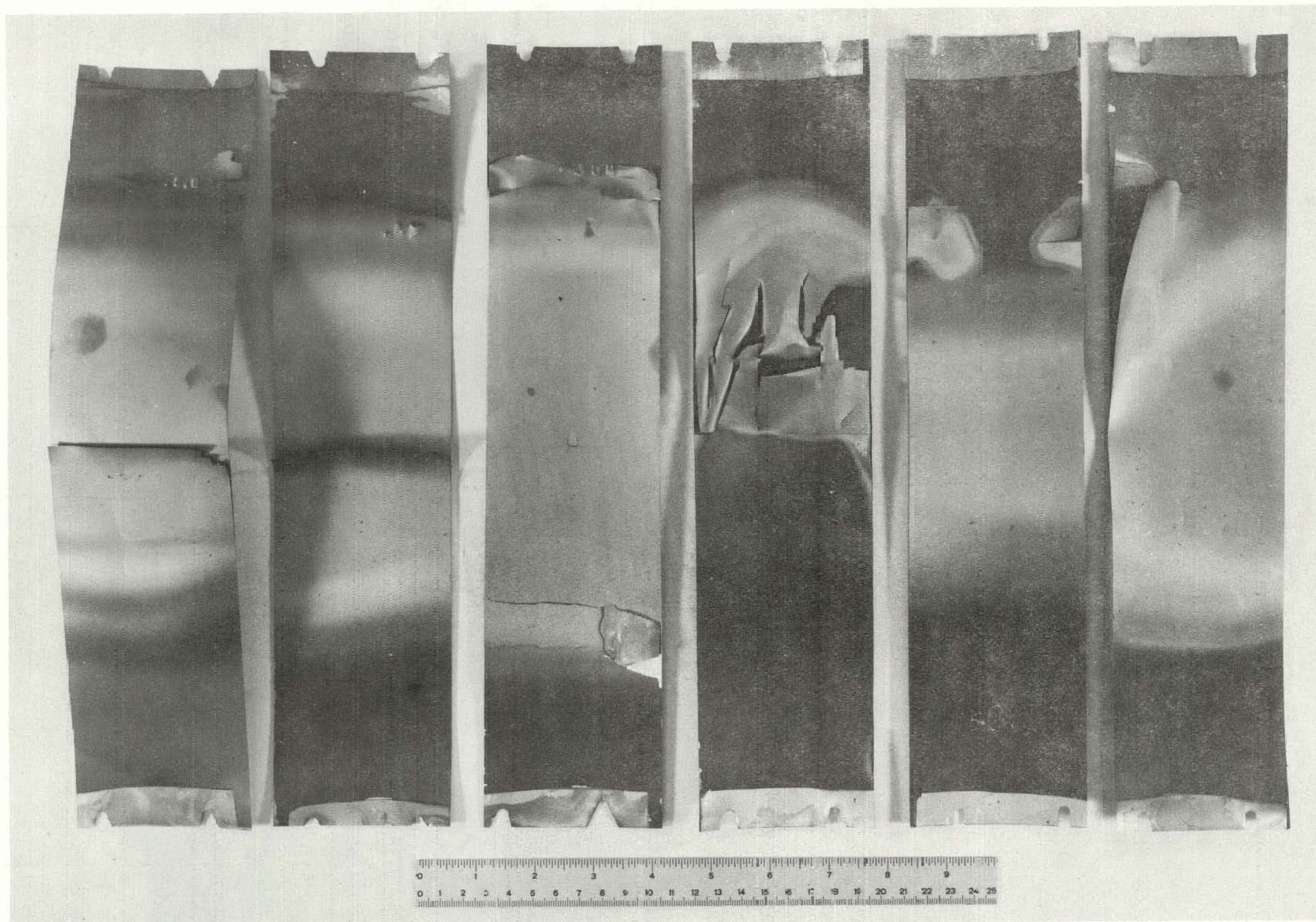
PEELING TEST FOR SUBLIMED TI LOWER
HALF SAND BLASTED LEFT TO RIGHT
S.S., TA, MO, CU, AL, AND TI
MAX. FILM THICKNESS 0.009"
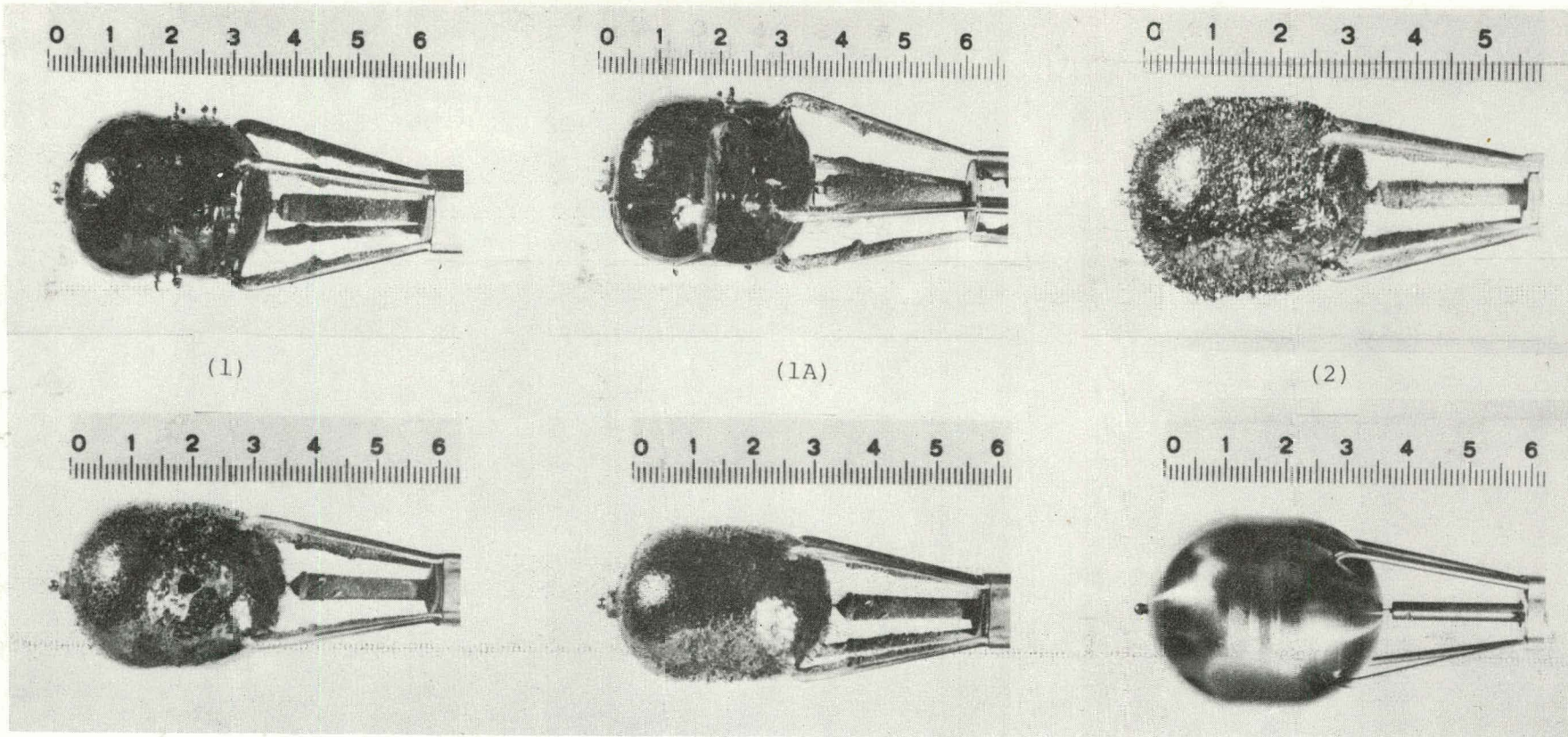   PHOTO TAKEN JULY 3, 1975.

PEELING TEST FOR TITANIUM HYDRIDE
ON ALUMINUM & TITANIUM SUBSTRATES
(SEPT. '75). LOWER HALF SAND
BLASTED. TWO TI BALLS EVAPORATED.
FROM LEFT TO RIGHT AL(0.020"),
AL(0.125"), AL(0.020"), 3TI(0.020")
PHOTO TAKEN SEPTEMBER 23, 1975

(1) (1A) (2)

(3) (4) (5)

(1) TI BALL SUBLIMED AT 750 W FOR ONE MINUTE
    OFF 20 SEC. FOR 4,000 CYCLES. 28 GRM TI
(1A) SUBLIMED.

(2) 750 WATT FOR 1 MINUTE 15 SEC OFF 7200
    CYCLES. 31 GRM TI SUBLIMED.

(3) 750 WATT FOR 1 MINUTE 10 SEC. OFF 3600
    CYCLES. 31 GRM TI SUBLIMED.

(4) 750 WATT CONTINUOUS OPERATION 70 HR. AT
    0.5 GRM TI/HR. SUBLIMATION RATE STANDARD
    OPERATION. 35 GRM SUBLIMED.

(5) TI BALL SOURCE BEFORE SUBLIMATION.

PHOTO TAKEN OCTOBER 17, 1975

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