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"Hydrogen Transport in Alpha Titanium"

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Signed Donald L. Johnson

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Introduction

A semi-annual progress report was submitted in January outlining the results of permeation experiments after nitriding the inlet surface of a hollow cylindrical membrane. In this report, permeation data on two additional specimens given pre-oxidation or pre-nitriding treatments at both inlet and outlet surfaces are presented in terms of Arrhenius plots. Additionally, an analysis of geometry dependence on permeation rate was made for several specimens including the ones mentioned above. For simplicity in this report, the term as-polished is used to refer to a specimen which is either as-polished or is as-polished, pre-oxidized and annealed.

Experimental

Geometry Dependence

Permeation can be defined by

$$J = 2\pi \ell D C_2 \, [\ell n(b/a)]^{-1} \tag{1}$$

for the case where diffusion through the metal is slow and surface reactions are relatively fast (ref. 1). A plot of J versus $[\ell n(b/a)]^{-1}$ is linear in such a case. However, if the surface reactions are slow and diffusion through the metal is relatively fast, the relationship is non-linear. In the latter case, it is also expected that J would not necessarily be constant for a constant value of the b/a ratio. For example, if the surface at a were more important than b in controlling the rate, the permeation rate would be more sensitive to change in a with b constant than it would be to change in b with a constant.

To observe how equation (1) would apply to the data, hydrogen flow rate was plotted in terms of $[\ell n(b/a)]^{-1}$ in Figure 1. The profile is non-linear, thus confirming that surface reactions are important during the transport process in α-titanium. As expected for the case where surface reactions are important, values of J appear to increasingly vary as $[\ln(b/a)]^{-1}$ increases at a particular b/a ratio. For example, at $[\ln(b/a)]^{-1} = 7$ the spread in $J \times 10^8$ (mol s^{-1}) is about 13. At $[\ln(b/a)]^{-1} = 9.0$ the spread in $J \times 10^8$ is about 31. Because of the limited number of specimens studied, it is impossible to determine which surface predominates in controlling the hydrogen flow rate. A systematic study of geometry dependence is planned using about 20 additional specimens.

Geometry dependence may also be characterized in a different way using equation (2). Setting a constant in equation (1) and putting the resulting equation in linear form:

$$1/J = \frac{\ln(b)}{2\pi \ell D C_2} - \frac{\ln(a)}{2\pi \ell D C_2}$$

$$= K\ln(b) - K' \qquad (2)$$

If permeation is diffusion controlled, equation (2) is linear just as it would be in equation (1). However, if diffusion is not controlling, a plot of 1/J versus $\ln(b)$ is non-linear. At this point, equation (2) has no advantage over equation (1) in the analysis unless a similar plot is made between J and 1/a where b is constant according to equation (3):

$$1/J = K\ln(1/a) + K'' \qquad (3)$$

If the plot of equation (3) is less linear than equation (2), then the surface at a is more important than the surface at b in controlling the rate and the location of the important surface reaction is established. Due to a lack of data on specimens of constant b/a ratios for various b and a values, an interpretation based on equations (2) and (3) cannot be made at this time.

Another way that geometry dependence can be characterized is from Fick's second law solution for hydrogen transport through hollow cylindrical membranes.

Lag-time expressions have been developed for (1) diffusion controlled transport, (2) phase boundary reaction control at the inlet surface, and (3) phase boundary reaction control at the outlet surface (ref. 2). These expressions yield lag-time equations of the general form:

$$1/t_L = \alpha D \tag{4}$$

where (a) α is defined as α_D (functional radii dependence for diffusion control applies).

(b) α is defined as α_a (functional radii dependence for inlet surface control applies).

(c) α is defined as α_b (functional radii dependence for outlet surface control applies).

If equation (4) is valid for the properly selected value of α, a log-log plot of $1/t_L$ versus $1/\alpha$ yields a straight line of slope $n = -1$. The correct functional value of α then identifies the predominant controlling mechanism and its location. Again, an attempt was made to apply equation (4) but the results were inconclusive because of the limited lag-time data available for varying geometries.

Oxide Films

A modified form of Richard's equation is given by

$$J = Kp_{H_2}^{n} \quad (0 < n \leq 1) \tag{5}$$

Taking the logarithm of both sides, a plot of log J versus log p_{H_2} yields a straight line of slope n where $n = 1/2$ for diffusion control and $n = 1$ for surface reaction control. The effect of inlet surface pre-oxidation and pre-nitriding on pressure dependence is shown in Figure 2. Comparison with the as-polished condition shows both the decrease in permeation rate and the typical first power pressure dependence normally observed before pre-oxidation. Permeation rate is markedly influenced by the location of the oxide film. As can be seen in Figure 3, oxide film at the outlet surface results in a permeation rate increase, whereas at the inlet surface, pre-oxidation results in a permeation rate decrease. In the latter case, activation energy increases relative to the as-polished condition as illustrated on the Arrhenius plot in Figure 4. Such an observation was observed on a different pre-oxidized specimen and was reported on earlier (ref. 3). In Figure 4, a very thin oxide film (∿ 50A) on the inlet surface is effective in reducing the rate whereas about the same film on the outlet surface increases the rate. Above 500 - 600°C the permeation rate decreases to the value it would have if the specimen had not been pre-oxidized at the outlet surface. After annealing at about 700°C, the process was repeated and the data reproduced.

As observed in both Figures 3 and 4, an increase in permeation rate was observed after pre-oxidation at the outlet surface. The same observation is noted in Figure 5, except that the permeation rate is slightly less for a thicker oxide film at the outlet surface. Figures 5 and 6 show that first power pressure dependency is maintained regardless of the pre-treatment.

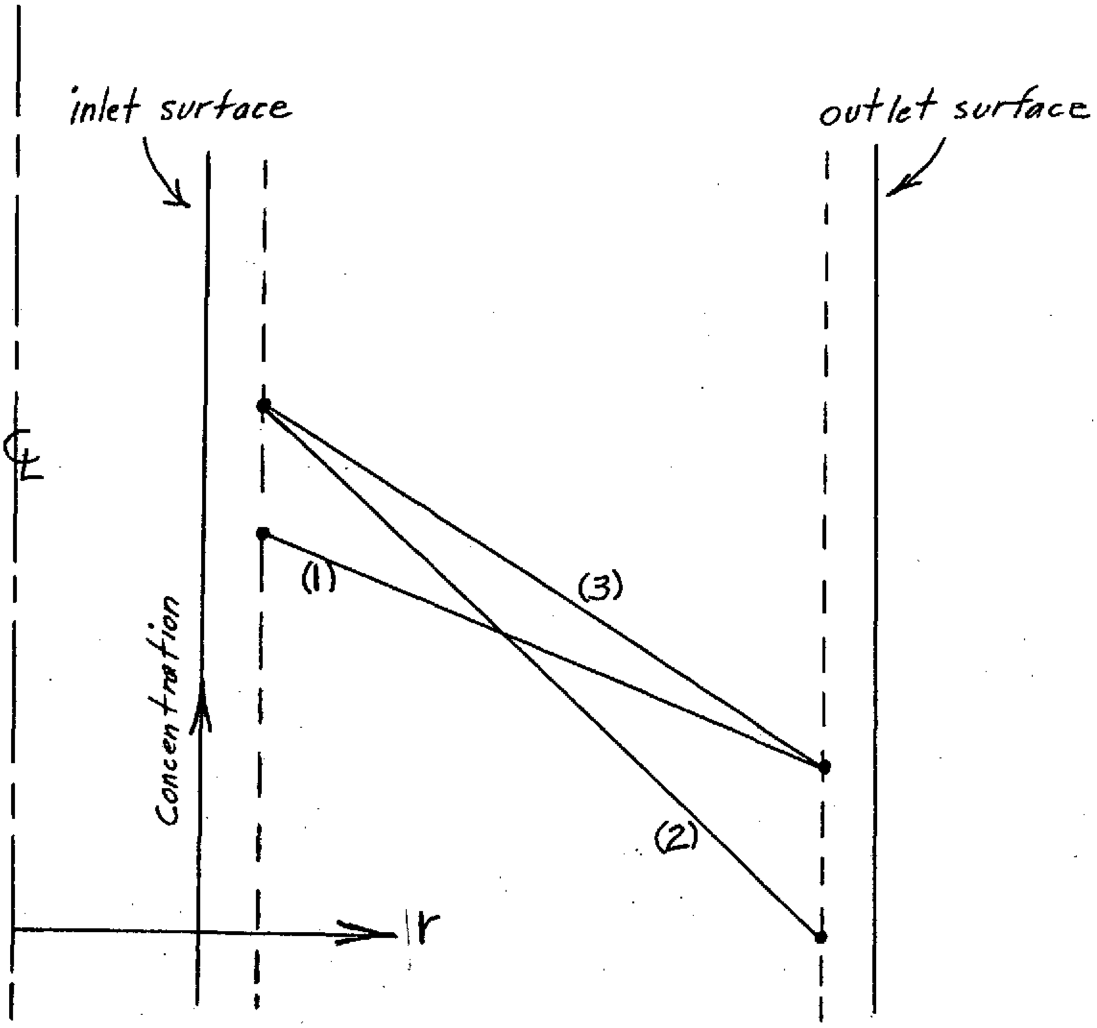
Nitride Films

The permeation rate is much more sensitive to nitride film at the inlet surface than it is at the outlet surface. Figure 7, presented earlier in the semi-annual report, is an Arrhenius plot of the permeation rate through progressively thicker nitride films on the inlet surface. As the film thickness increases, the permeation rate decreases. Permeation is first power dependent upon pressure as shown in both Figures 7 and 8. Very thin nitride films (∿ 1-2Å) at the inlet surface are effective in reducing the rate as shown in Figure 8. Figures 9 and 10 represent two different sets of data that compare the effect of pre-nitriding at inlet and outlet surfaces. Pre-nitriding at the outlet surface promotes only slight change in the rate.

Discussion

The decrease in permeation rate in the presence of oxide at the inlet surface is consistent with an interpretation put forth that steady state is established between gas-phase molecular hydrogen, a discontinuous layer of TiH_2 and atomic hydrogen in the titanium lattice (ref. 4.) It is suggested that this steady state condition is modified by oxygen in such a way that partial filling of available chemisorbed sites by oxygen reduces the number of sites available to hydride. Therefore, the actual concentration of hydrogen in α-phase titanium is lower than it was for the case where the surface was not pre-oxidized. While the process is surface controlled, this decrease in concentration is equivalent to a reduced concentration gradient across the membrane and a reduced hydrogen flow rate. Other information which adds credibility to this explanation is noted in the literature. Caskey interprets lack of hydride formation on titanium as due to the formation of a stable oxide film (ref. 5). Reichardt comments on the inhibiting effect of contaminants on reaction between hydrogen and titanium (ref. 6) and Schoenfelder and Swisher account for their results in terms of the retarding effect of oxide films on the rate of hydriding (ref. 7). Wasilewski and Kehl recognized the effect of oxide on reaction rates in titanium in 1953 (ref. 8).

This interpretation of surface controlled permeation of hydrogen through α-titanium is consistent with experimental observations assuming hydride forms as an intermediate product at the inlet surface. This interpretation can be used to explain the permeation mechanism at the outlet surface if it is assumed that hydride forms at this location also. That this is a logical assumption can be explained in terms of Barrer's interpretation of surface dependent permeation (ref. 9). Since the actual concentration just inside the inlet surface is below equilibrium, much of the hydrogen is removed by diffusion to the outlet surface. At this surface, the slow rate of transfer across the interface but relatively high diffusion rate through the solid leads to an accumulation of hydrogen just inside the outlet surface. The actual concentration is therefore greater than the equilibrium (zero) concentration expected at the outlet side in contact with vacuum. Thus, at the outlet surface, it is logical to expect hydride formation and a permeation mechanism identical to that described for the inlet surface. When the outlet surface is preoxidized, the available sites for hydride decrease, and the concentration just inside the outlet surface decreases just as it did at the inlet surface. However, contrary to the decrease in the concentration gradient and equivalent decrease in hydrogen flow rate after oxidation at the inlet surface, the concentration gradient now increases and the equivalent result is an increase in the hydrogen flow rate after oxidation at the outlet surface. The gradients (greatly magnified) for the three cases (1) Inlet oxidized (2) Outlet oxidized and (3) As-polished are depicted in the following sketch:



First power pressure dependence has been consistently observed regardless of pre-treatment, temperature or pressure. This suggests that the boundary reactions at each surface are identical to what they are in the as-polished condition and the only variable is the degree of surface coverage by hydride. First power pressure dependence results, not because the process is surface dependent, but because molecular hydrogen dissolves in the TiH_2 on a 1:1 basis. This is equivalent to solution as molecular hydrogen for the purpose of this discussion. The process is first power pressure dependent regardless of the location of the surface treatment since in the above interpretation TiH_2 exists at both surfaces. It is quite possible that the controlling surface switches from one surface to another depending upon the contaminant on the surface and its relative thickness. As mentioned earlier, for example, oxide at the outlet is more effective than nitride in varying the rate whereas the opposite is true at the inlet surface.

It is interesting to note that Smithells and Ransley observed differences in the hydrogen permeation rate through aluminum depending upon which surface was abraded (ref. 9). Abrasion of the outlet surface reduced the permeability whereas abrasion of the inlet surface increased permeability.

Conclusions

1. Pre-oxidation, pre-nitriding, and film thickness have no effect on the usual dependence observed between permeation rate and first power of pressure.
2. Irrespective of location, thicker oxide and nitride films reduce the permeation rate.
3. Hydrogen flow rate is more sensitive to nitride film at the inlet surface than the outlet surface whereas the opposite is true for oxide film.
4. Analysis of geometry dependence and effects of oxide-nitride films provides further evidence that permeation of hydrogen through α-titanium is surface reaction controlled.
5. Nitrogen is more effective as a hydrogen "barrier" than oxygen under the same conditions of pressure and temperature.

Nomenclature

J - Hydrogen flow rate or permeation rate

ℓ - Reduced gage section length

C_2 - Hydrogen concentration just inside inlet surface

b - Outlet radius

a - Inlet radius

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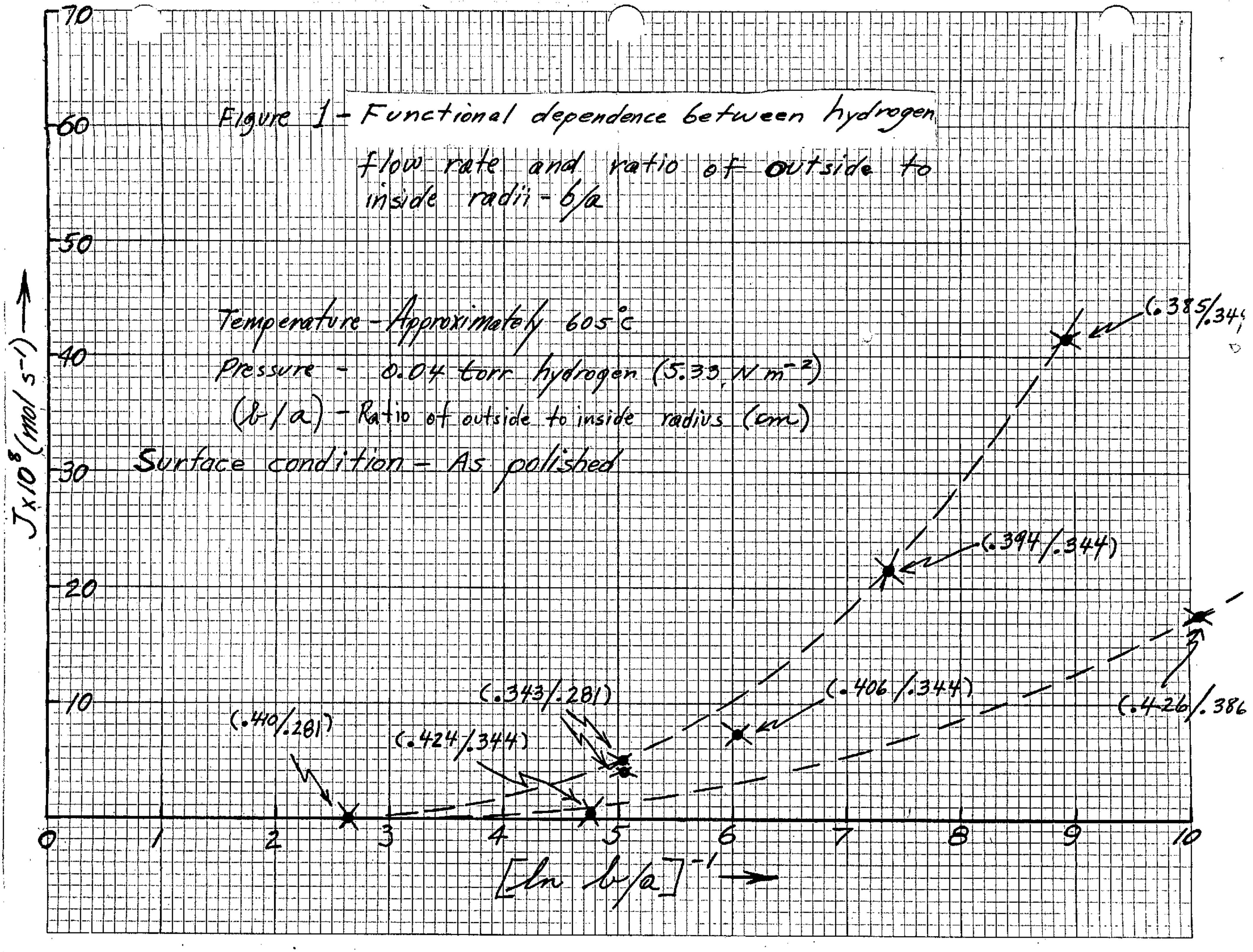

Figure 1 - Functional dependence between hydrogen flow rate and ratio of outside to inside radii - b/a

Temperature - Approximately 605°C

Pressure - 0.04 torr hydrogen (5.33 N m^{-2})

(b/a) - Ratio of outside to inside radius (cm)

Surface condition - As polished

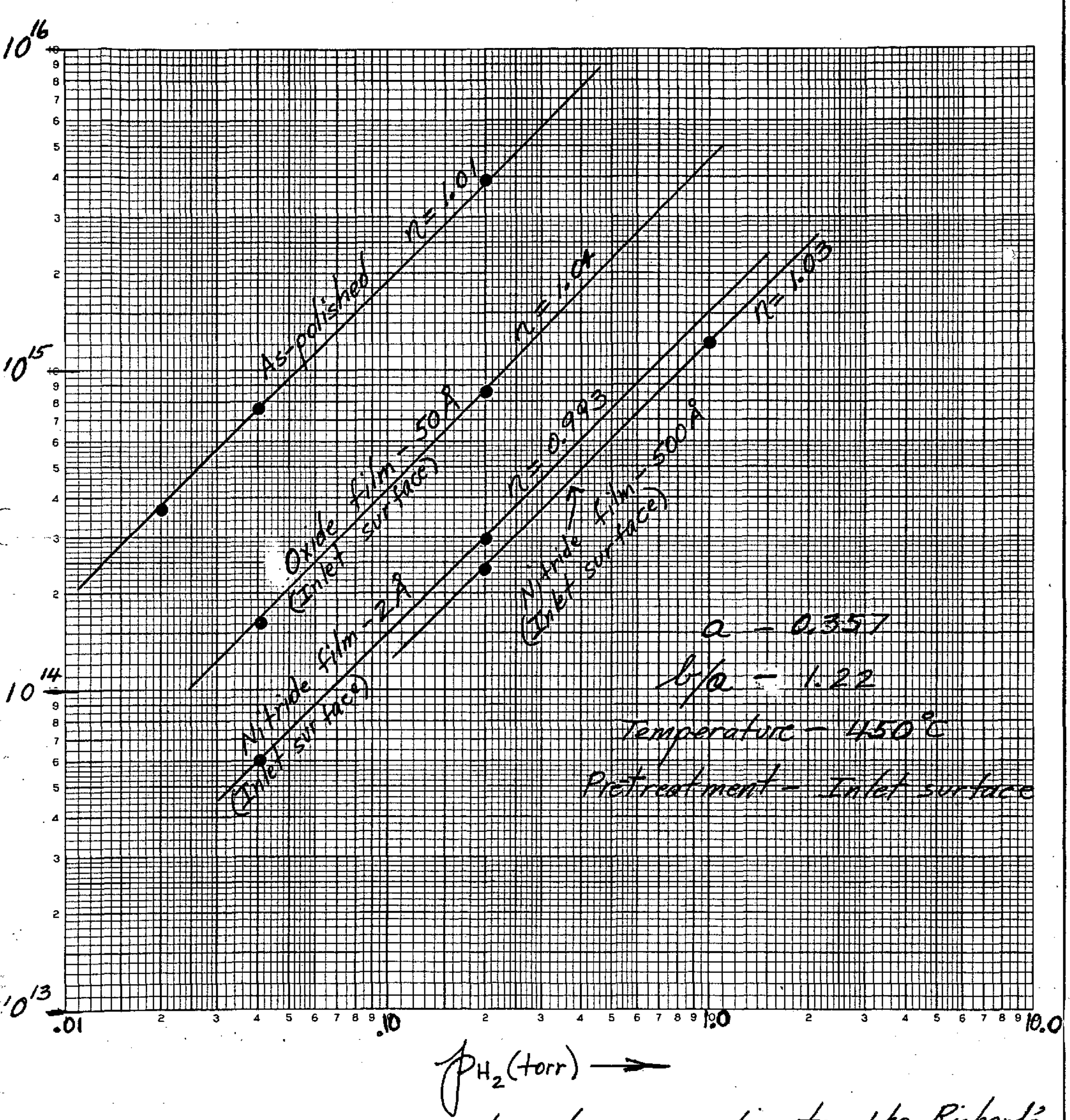

Figure 2 - Pressure dependence according to the Richard's equation $P = K p_{H_2}^{n}$ for as-polished and pre-treated condition at inlet surface

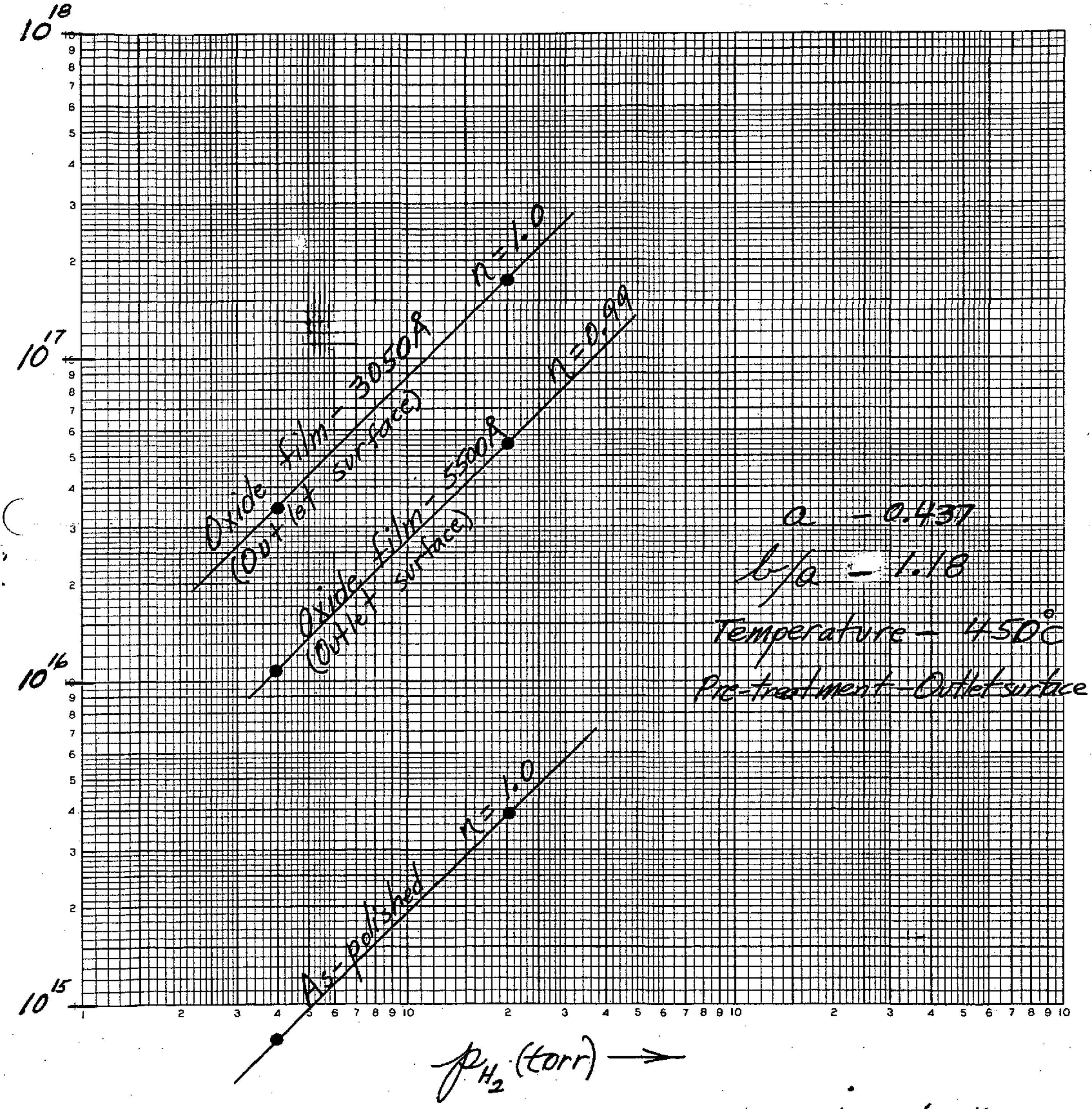

Figure 3- Pressure dependence according to Richard's equation, $P = K p_{H_2}^{n}$ for as-polished and pre-treated condition at outlet surface

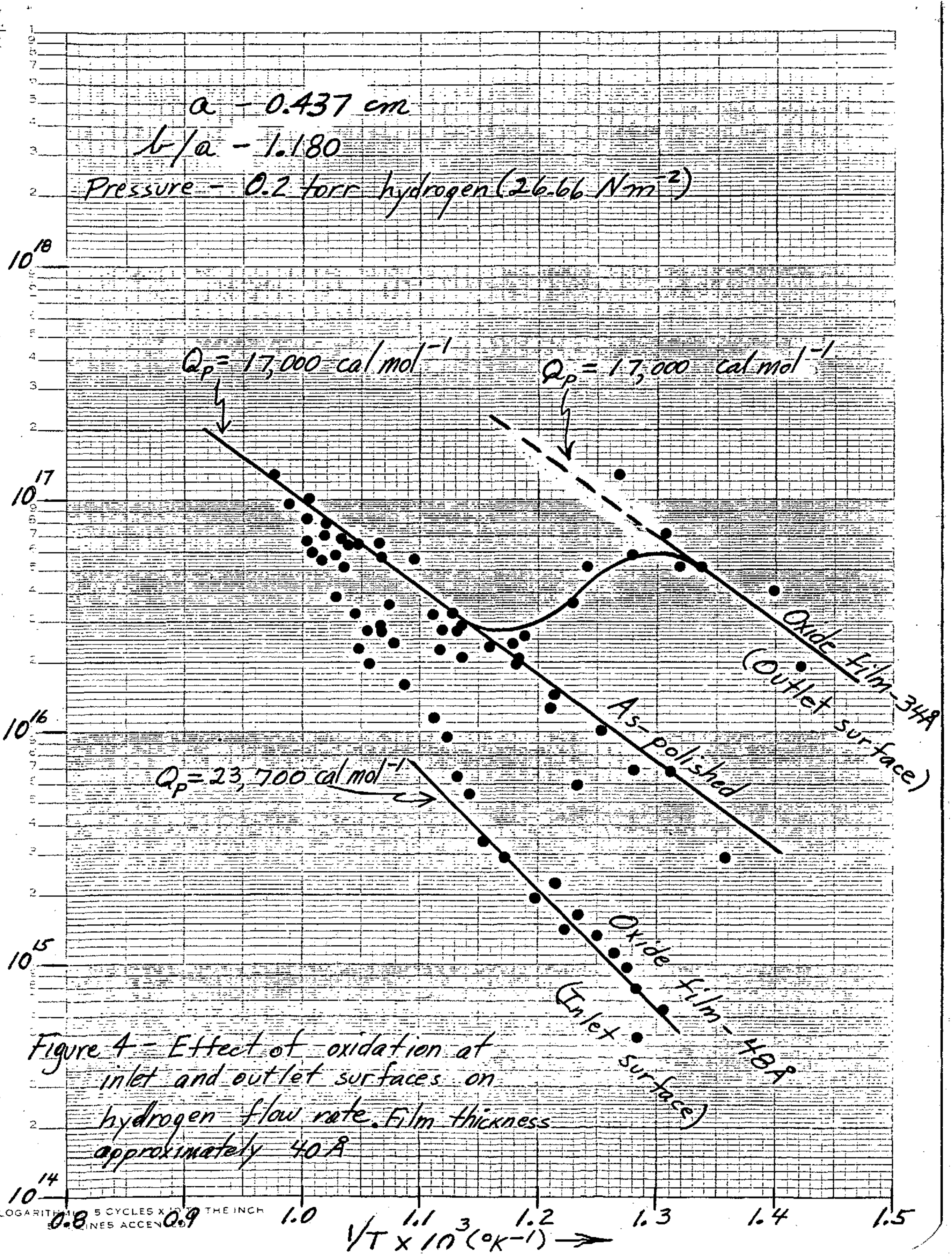

Figure 4 - Effect of oxidation at inlet and outlet surfaces on hydrogen flow rate. Film thickness approximately 40 Å

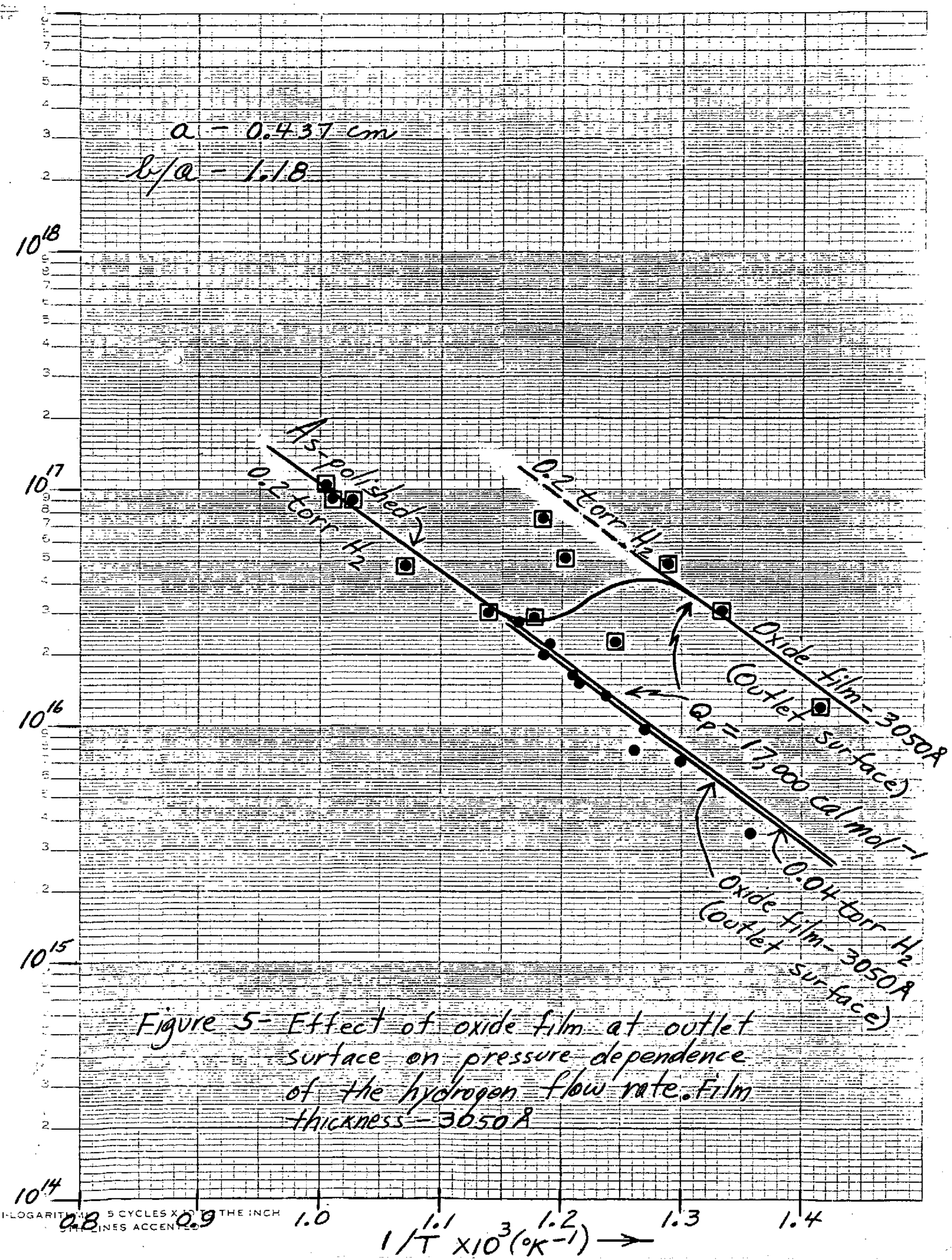

Figure 5- Effect of oxide film at outlet surface on pressure dependence of the hydrogen flow rate. Film thickness - 3050 Å

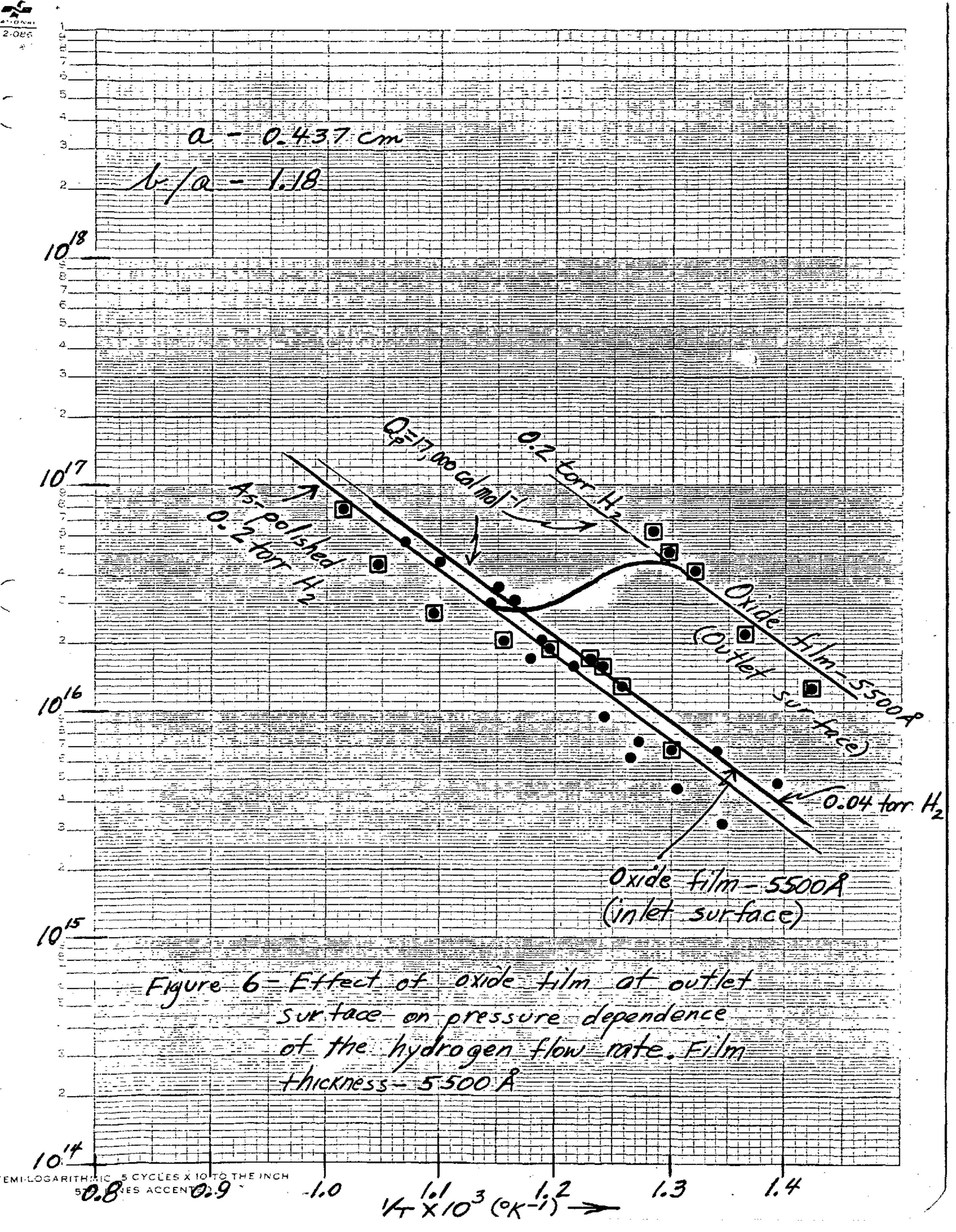

Figure 6 - Effect of oxide film at outlet surface on pressure dependence of the hydrogen flow rate. Film thickness - 5500 Å

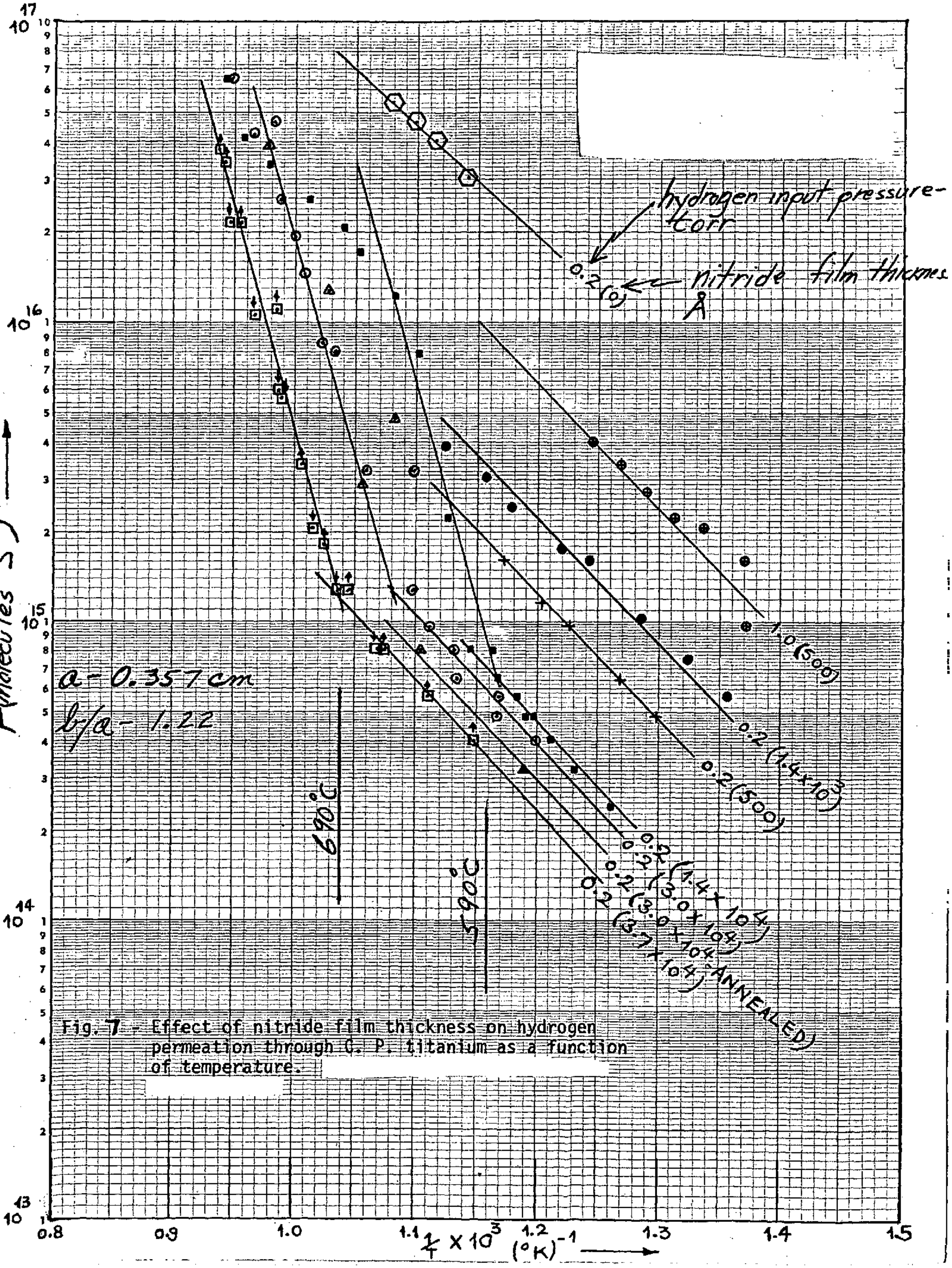

Fig. 7 - Effect of nitride film thickness on hydrogen permeation through C. P. titanium as a function of temperature.

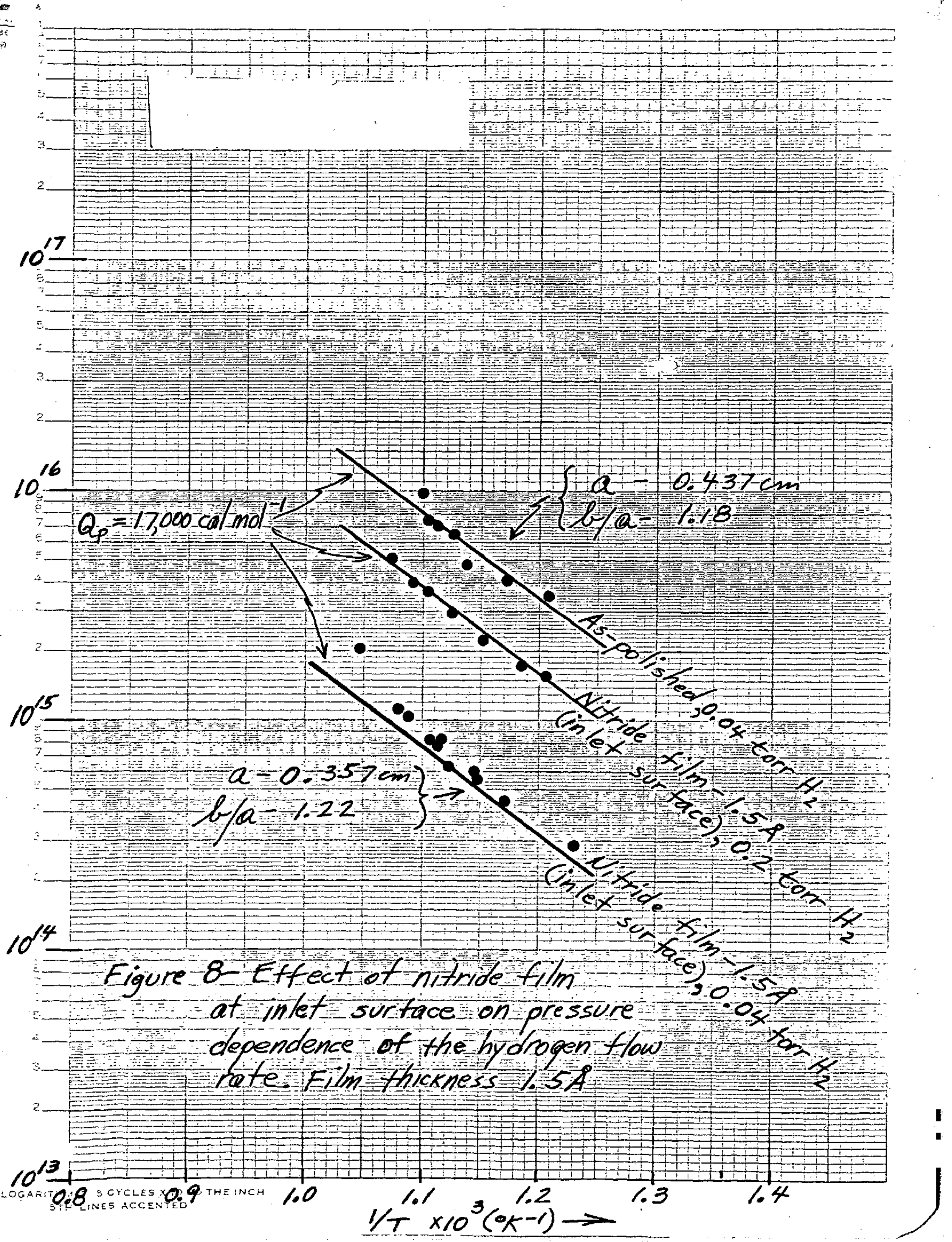

Figure 8- Effect of nitride film at inlet surface on pressure dependence of the hydrogen flow rate. Film thickness 1.5Å

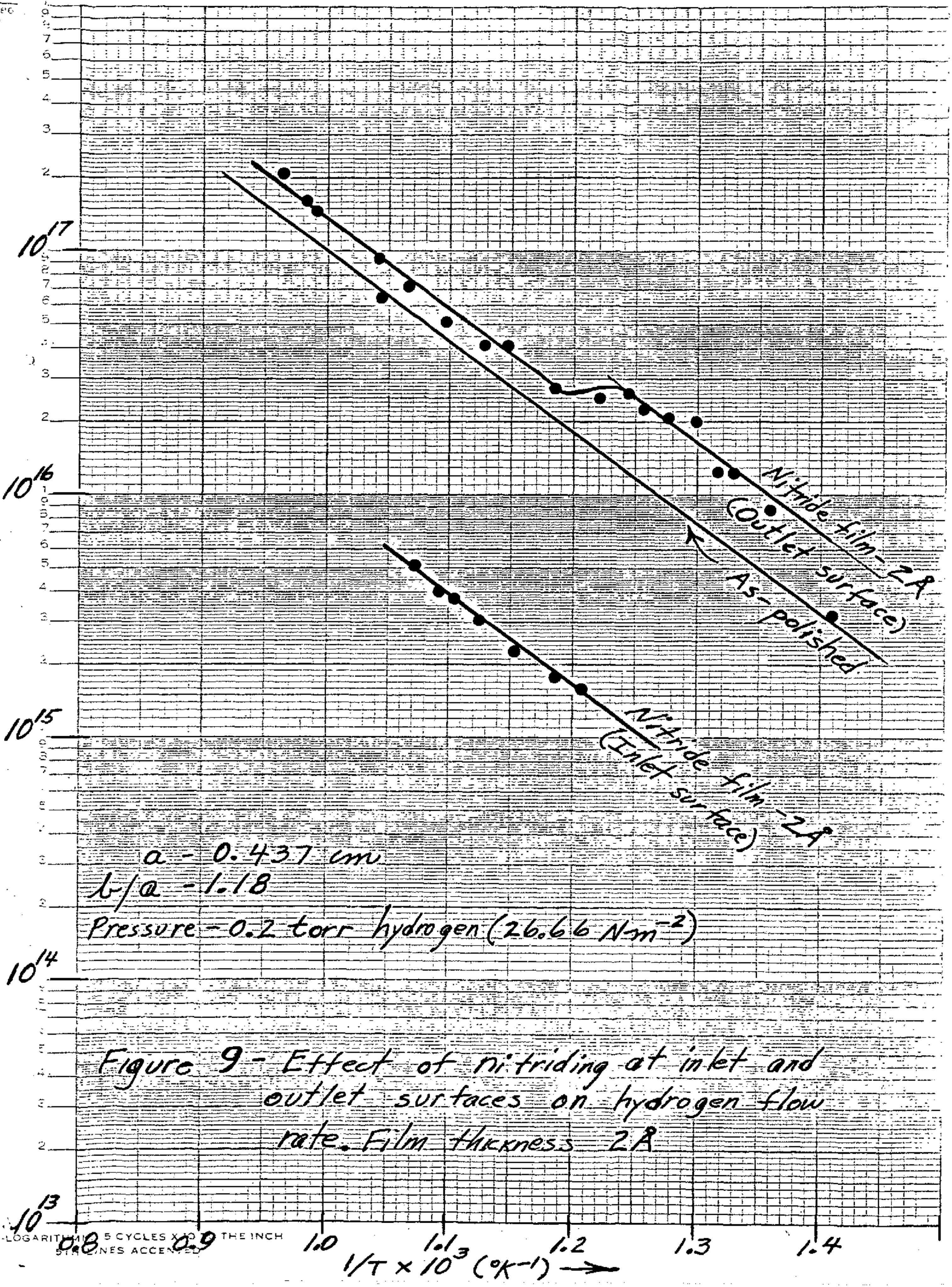

Figure 9 - Effect of nitriding at inlet and outlet surfaces on hydrogen flow rate. Film thickness 2Å

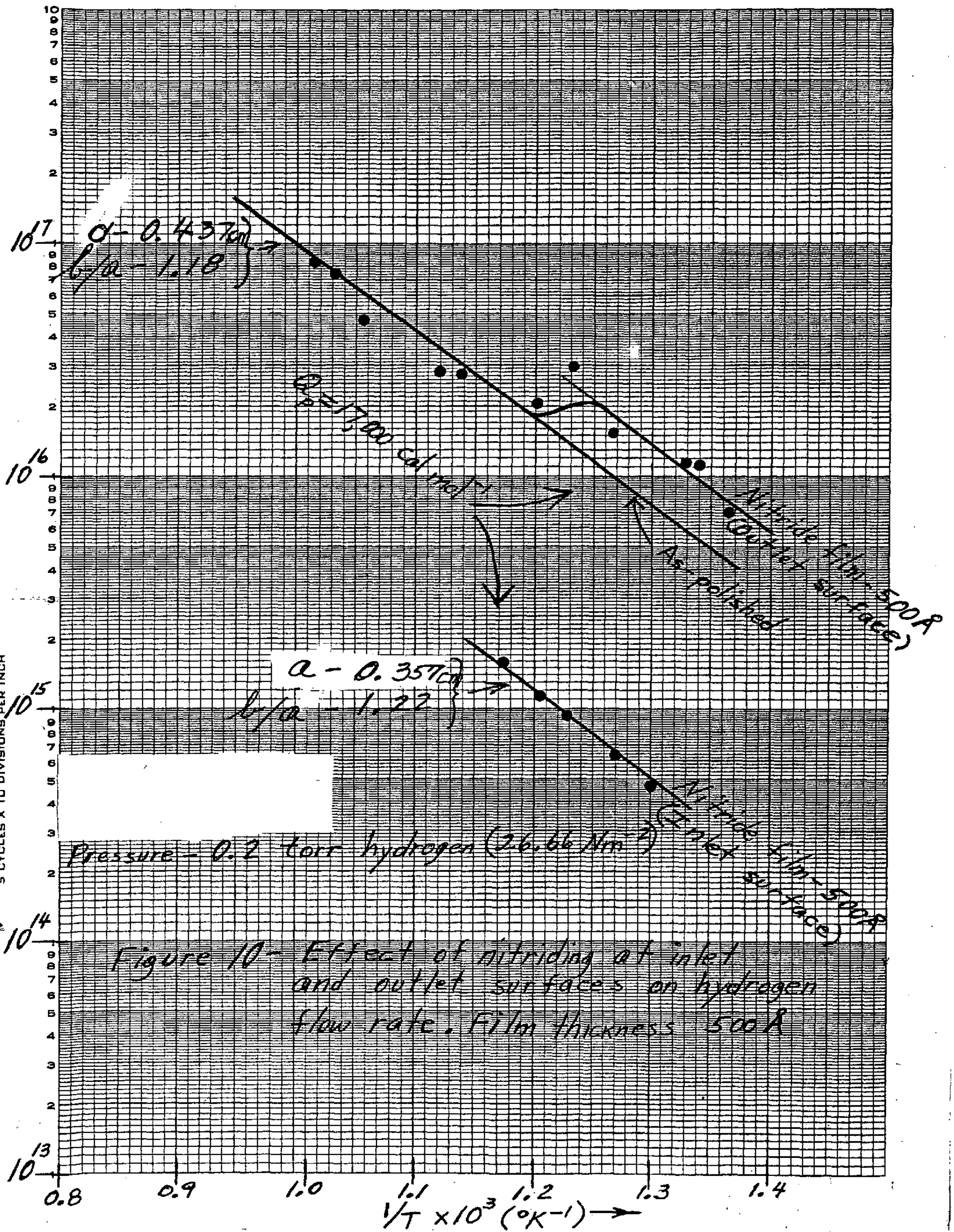

Figure 10- Effect of nitriding at inlet and outlet surfaces on hydrogen flow rate. Film thickness 500Å