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Semi Annual Progress Report

for

Chemical Vapor Deposition

to

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2 Division of Materials Science and Engineering

University of Utah

Salt Lake City, Utah 84112

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## I. INTRODUCTION

This report summarizes recent activities of the Division of Materials Science and Engineering in chemical vapor deposition. Only a bare indication of the scope of activities is included, with deference to time and space limitations. The final report plus attendant documents (topical reports) will provide a fuller picture.

Of particular satisfaction to the investigators are the results obtained of both scientific and technological nature. As evidence of the first, see Section II-A on Kinetics; of the latter, see Section III-A, particularly Figure 4.

## II. Kinetics and Material Production

### A. Kinetics

Since the annual progress report (October 1960) Mr. H. Huggins has submitted and successfully defended his thesis on the kinetics of C.V.D. tungsten. Important results from this study are: The reaction appears to be second order in  $WF_6$  and first order in hydrogen; The activation energy for the process is 15 kcal, which agrees with the work of Holman and Huegel<sup>(1)</sup> but does not agree with Brecher's work. Brecher reported a value of 30 kcal based on analysis of early work carried on by Brenner et al.<sup>(3)</sup> at the Bureau of Mines.

This thesis work indicates that products other than those given by the simple C.V.D. reaction ( $WF_6 + 3H_2 = W + 6HF$ ) are produced. If the C.V.D. reaction is second order in  $WF_6$  as Huggins' work suggests then complexes such as  $H_3W_2F_9$  may be present on the tungsten surface and as products of the reaction chamber.\* Clearly the process is more complex than we or other workers in the field had thought. A mass spectrometry study of the products of the reaction chamber could prove interesting and valuable. Also a study of the chemisorption of  $WF_6$  or W should prove fruitful. Work along these lines must be performed if our fundamental knowledge of these processes is to increase.

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\*Certainly many other possibilities exist as even a cursory study of transition metal fluorine chemistry shows.

Alloy work has involved the attempt to add Si to C.V.D. tungsten using  $\text{SiCl}_4$  as the carrier. It is hoped that the effects of a chloride on the surface coupled with the presence of a strong fluorine getter will substantially improve the microstructure and properties of C.V.D. tungsten.

This work was halted for some time due to remodeling of the laboratory. However, we are now once again set up and hope to make our initial runs within the month.

### B. Material Production

The apparatus used to produce tungsten tubes is shown schematically in Figure 1. The substrate consisted of a vertical copper tube. The deposition reaction was produced on the inner surface of the copper tube. The hydrogen fluoride, excess hydrogen and any unreacted tungsten hexafluoride passed through a scavenger furnace. The latter consisted of a stainless steel tube at  $850^\circ\text{C}$  and contained iron filings to strip the tungsten from any unreacted tungsten hexafluoride. The hydrogen fluoride was then neutralized in sodium carbonate chemical traps. Cold traps then condensed any remaining hydrogen fluoride gas and all remaining gases were vented to a hood.

Two substrate temperatures  $500$  and  $700^\circ\text{C}$ , and two total gas pressures,  $300$  and  $500$  torr, were evaluated by mechanical testing.

Following deposition, rings were spark cut from the composite copper-tungsten tubes. The interior surfaces of these were either examined by S.E.M. or the entire inner surface electropolished to the desired radius needed for mechanical testing. The outer copper substrate was then etched away with nitric acid. Knoop microhardness measurements were made on all surfaces of the deposited tungsten and conventional metallography was

1.  $WF_6$  TANK
2. ARGON
3. HYDROGEN
4. TEFLON SEATED NEEDLE VALVE
5. KEL-F BODY  $WF_6$  FLOW METER
6. FLOW METERS
7. GAS MIXING CHAMBER
8. MANOMETER
9. FURNACE WITH TAPS
10. SCAVENGER FURNACE
11. IRON FILINGS
12. CHEMICAL TRAPS
13. COLD TRAP (ICE + SALT)
14. SYSTEM PRESSURE CONTROL VALVE
15. VENTILLATION

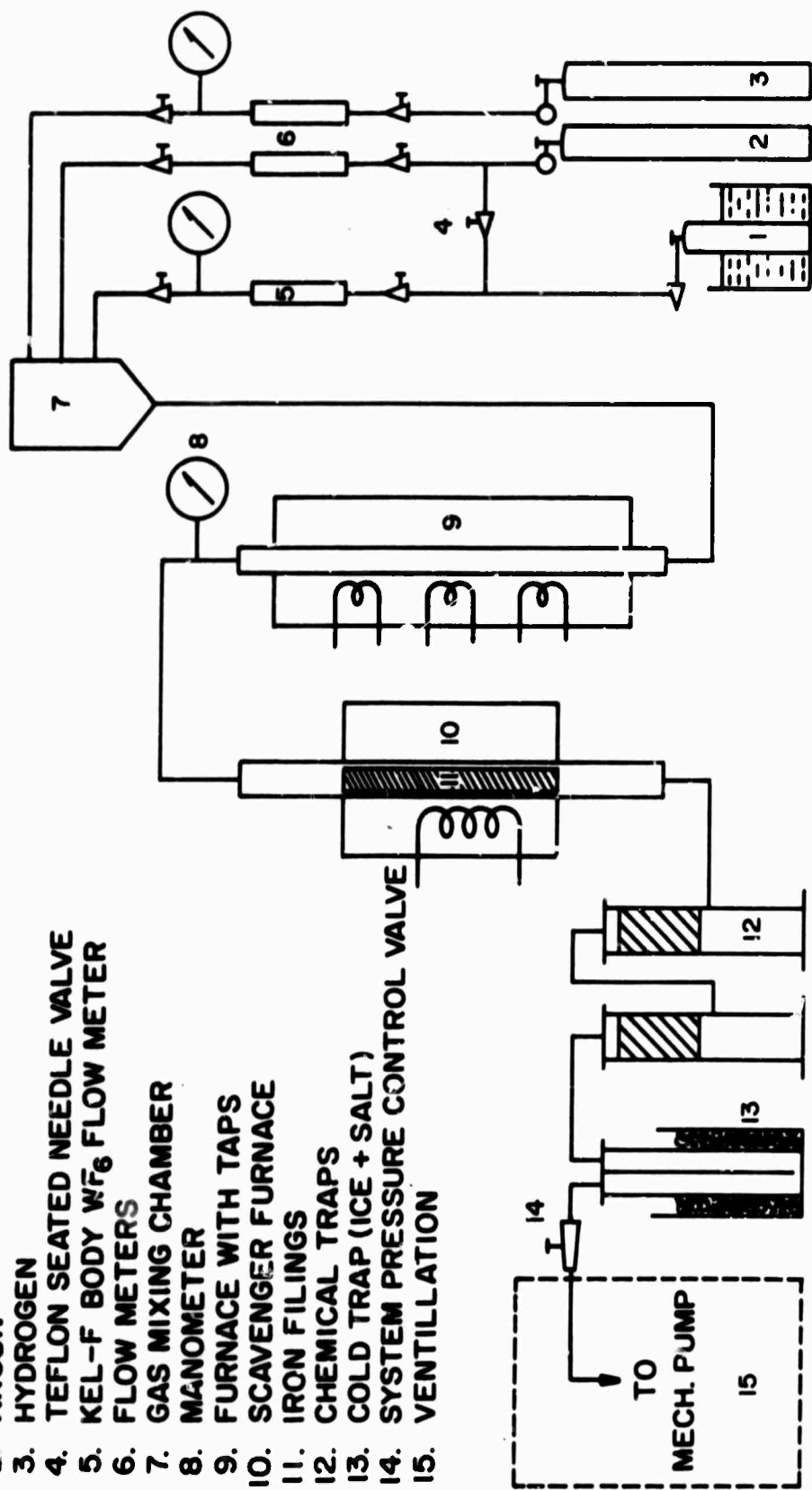


Figure 1. Schematic of Deposition Circuit

performed. Mechanical testing was performed in our special high temperature hoop stress testing apparatus which had been directly calibrated with tensile tests. The test temperatures were 240, 520, 800 and 1000°C. S.E.M. examinations of all fractured specimens were performed. Mechanical and microscopic results will be given in Chapter III.

Through the generous cooperation of the Kennecott Copper Corporation the chemical analysis of fluorine has been carried out for 500°C and 700°C substrate materials. In the prosecution of this work Kennecott has developed some new analysis techniques which will be announced in the near future. The following tables gives the results.

Fluorine Content of C.V.D. Tubes		
Deposition Conditions		P.P.M. Fluorine
Substrate Temperature (°C)	Pressure (torr)	
500	300	1. 23*
		2. 52
		3. 60
500	500	1. 29*
		2. 60
		3. 50
700	500	1. 5*
		2. 18
		3. 43

\*Results of initial attempt - probably all too low. Newer procedures yielded results #2 and #3.

Long straight columnar crystals deposited radially and uniformly on the inner substrate surface. Generally, lower temperatures and pressures favored smoother growth surfaces and slower growth rates. Figure 2 shows the effects not only of temperature and pressure but also flow rates. The maximum growth rates in the current study, designated (s) for Shim in Figure 2, were slightly lower than those of Holman<sup>(4)</sup> although the manometer pressure for both was 500 torr. Salt Lake City has a lower average atmospheric pressure than Livermore, California, which would require a higher absolute pressure to attain the same manometer reading as at our laboratory.

The larger dependence of growth rate on temperature and pressure suggests that surface processes, in which adsorbed species play an important role, are rate controlling. The break in the 500 torr (s) curve in Figure 2, implies that the process becomes reactant supply limited at higher temperatures. The growth rate in this high temperature region is controlled by gas phase diffusion of  $WF_6$ ,  $H_2$  and HF.

The activation energy of approximately 16 kcal/mole (which applies to the lower temperature end of the curve), is in the proper range for surface diffusion, adsorption and desorption, as was pointed out by Holman<sup>(4)</sup>. It is too high for gas phase diffusion and too low to represent chemical reactions at the surface.

Four sided pyramid shapes are typical of C.V.D. tungsten growth interfaces. This structures is similar to the pyramidal structures reported in the electrodeposition of copper single crystals<sup>(5)</sup>. Pyramids developed at 700°C have steeper sides and less crystallographic facets than those

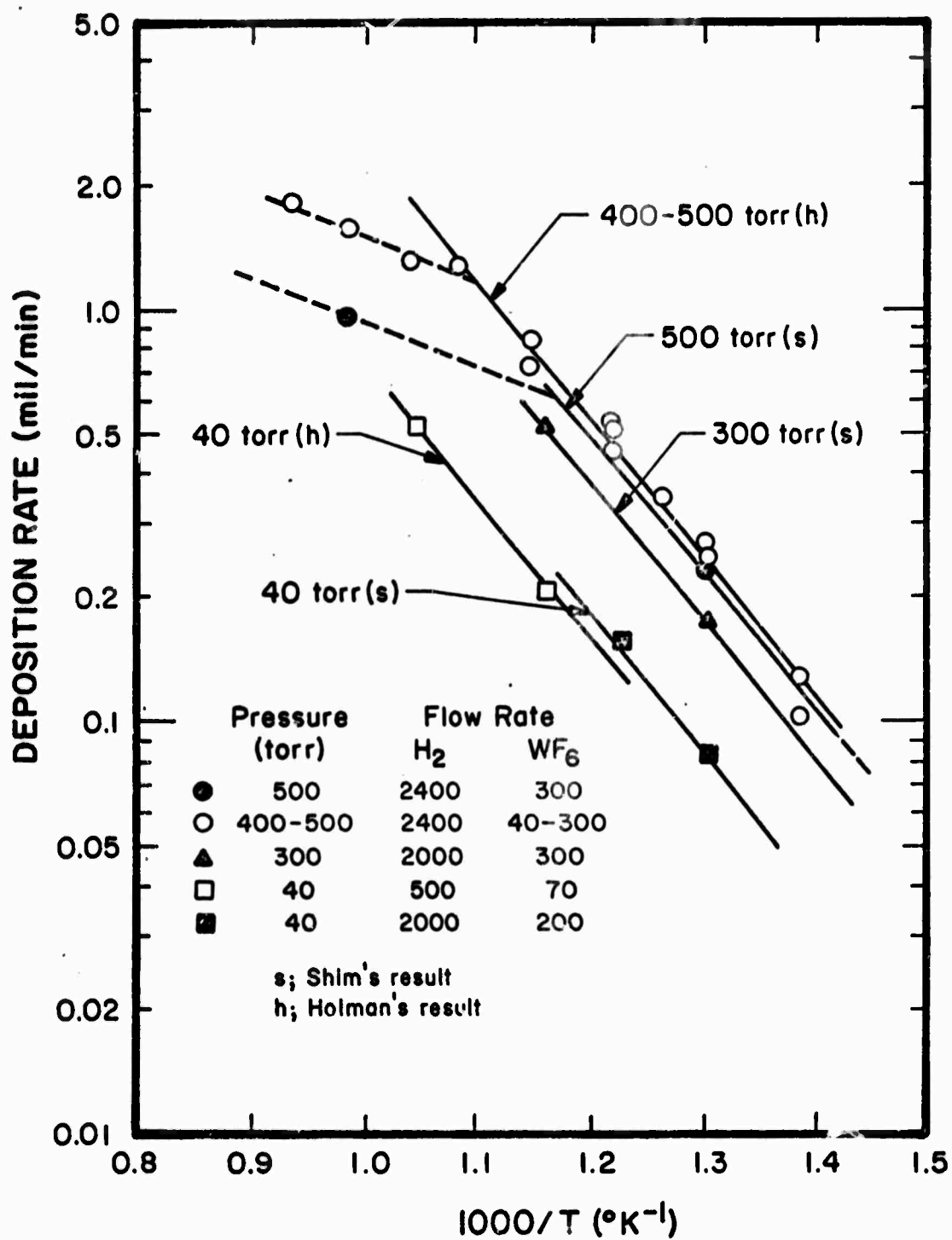


Figure 2. Plot of Deposition Rates versus Reciprocal Absolute Temperature for C. V. D. Tungsten

developed at 500°C. Holman<sup>(4)</sup> suggested that the pyramid faces in C.V.D. tungsten are {111}. This would agree with our earlier pole figure results which indicated largely a  $\langle 100 \rangle$  fiber axis. We feel that the pyramids grow by the advance of ledges on the pyramid faces. The open tops of the pyramids may form when ledges from different pyramid sides intersect. The long dimension of the columnar crystals exhibit more "fanning out" in direction at the 500°C substrate temperature than at the 700°C one for which the crystals are quite straight. They may be one of the "defects" which impart higher strength to test rings grown at 500°C, when they are stressed circumferentially (see Chapter III).

The report discusses the deposition of tungsten at various substrate temperatures. The properties of the tungsten are mentioned.

### III. Mechanical Studies

#### A. Substrate Temperature Effects

Microhardness measurements on material deposited at each of 500 and 700°C are <sup>reported</sup> shown in Figure 3. It is seen that the substrate side of each material (ring O.D.) is harder than the last surface to grow. It is also seen that the lower substrate temperature has the higher microhardness. With this as background let us now consider Figure 4. This represents the yield stress values as determined with our high temperature hoop stress apparatus, as a function of test temperature. Consistent with the microhardness results, the material grown at 500°C is stronger than that grown at 700°C. There is approximately the same temperature dependence for both materials and thus an almost constant 3000 psi difference exists between the curves. Where specimens deposited at 300 torr instead of 500 torr were tested, it is seen that almost no pressure effect on yield strength exists.

The morphologies of the fracture faces for all tests were observed with scanning electron microscopy. <sup>Although no</sup> The most general conclusion one may draw from observing all of these is that material grown at 500°C fractures on a finer scale than that grown at 700°C. This is reasonable if one recalls that straighter and larger crystals (700°C) lend themselves to the larger cleavage surfaces.

The direction of crack propagation was determined by examining river patterns on cleavage facets. In no instance was there evidence for propagation along the long <100> axis of the crystals. All river patterns

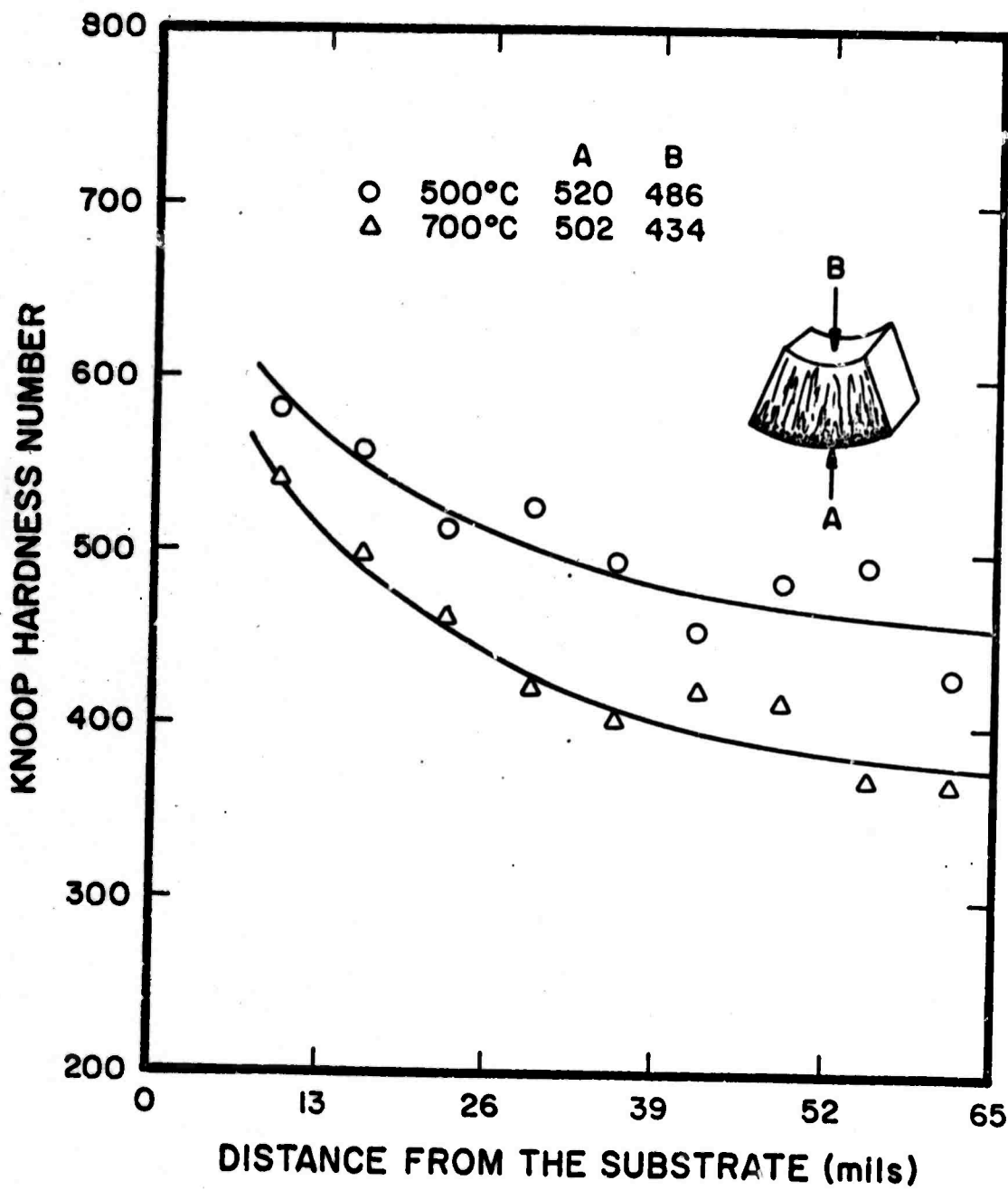


Figure 3. Microhardness versus Distance From Substrate for C. V. D. Tungsten

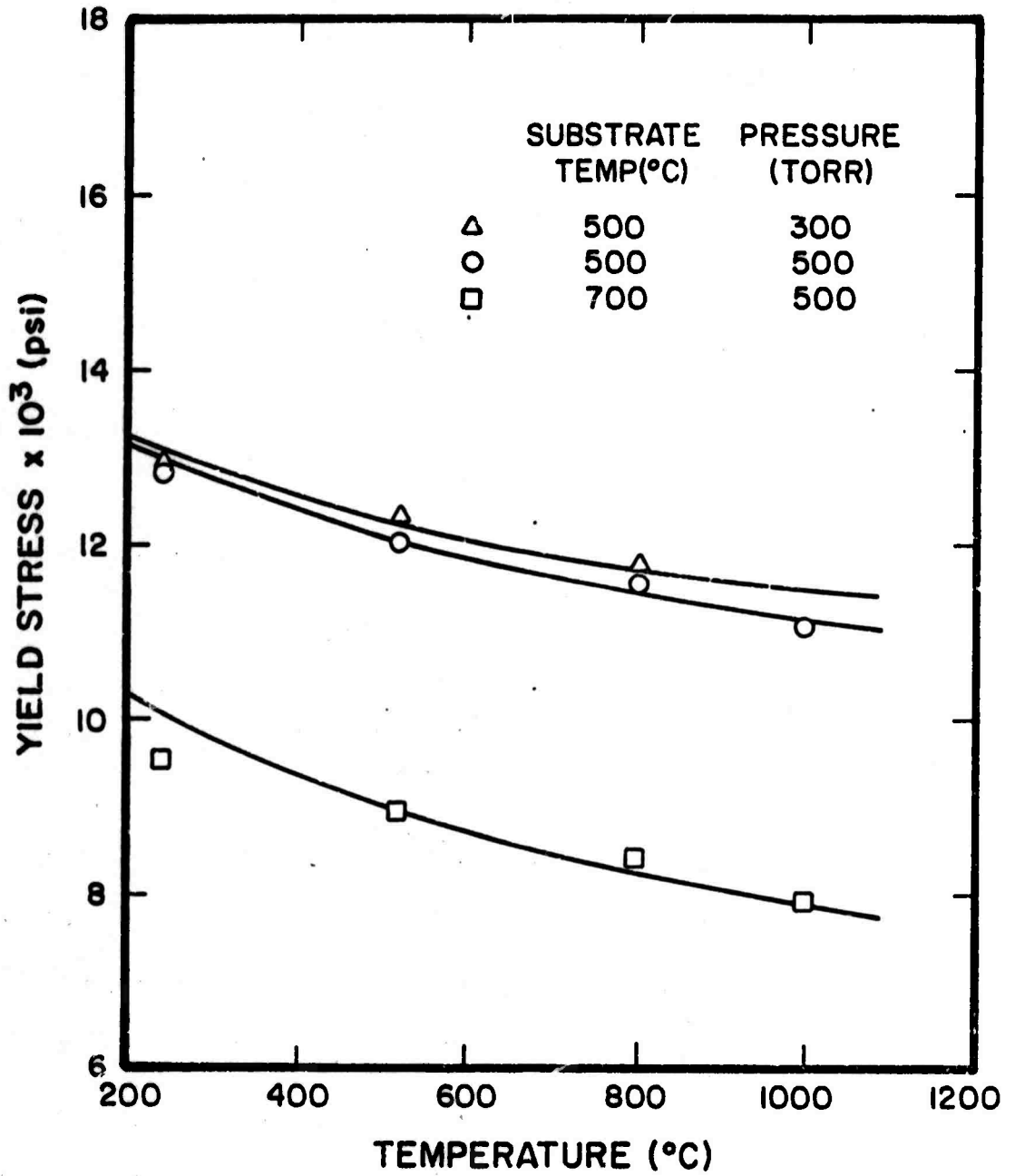


Figure 4. Yield Stress versus Temperature for C. V. D. Tungsten

observed indicated that crack propagation was transverse to the long dimension of the crystals and began in a cleavage mode near the inner diameter of the rings, at either a top or bottom edge, and traveled vertically. The last regions to fracture are toward the outer diameter, where a quasi cleavage mode obtains, undoubtedly because the grain size becomes smaller near the substrate. The latter tendency precludes large surfaces being available for cleavage.

One final observation with respect to S.E.M. observations may be of interest. The degree of both subsidiary cracking in columnar grain boundaries, and the extent of slip is less for 500°C material than for the 700°C substrate material. The stronger 500°C material resists slip and subsidiary cracking better than does the 700°C material. Our conclusions in regard to substrate temperature effects are:

1. Lower growth temperatures lead to higher yield strengths in C.V.D. tungsten films. The main reason for this appears to be the more disturbed microstructure, i.e., the columnar crystals are not as uniformly directed as for higher growth temperatures.

2. Total gas pressure during growth does not have a large effect on film structure or strength.

3. The activation energy value of 16 kcal/mole, for the growth of C.V.D. tungsten, is indicative of control by surface diffusion, adsorption and desorption processes.

4. Four-sided pyramids are found in the growing interface. These are believed to propagate by the advance of ledges up {111} pyramid facets. The pyramids seem to increase in steepness with growth temperature.

5. Fractures in ring specimens propagated by transverse cleavage through columnar crystals. Changes in river patterns on crossing the boundaries between these crystals suggest that the boundaries are of a low angle tilt-twist type.

#### B. High Temperature Hoop Stress Testing

Figures 5, 6 and 7 present the data on our high temperature testing. The upper limit is now 1600°C rather than earlier data up to 1400°C (Semi-Annual Progress Report of April 15, 1970).

Figure 5 shows that the yield strength decreases linearly with increasing temperature. The ultimate tensile strength decreases more rapidly with temperature than does the yield stress because of decreased work-hardening at high temperatures. These dependences are similar to those of powder metallurgy (P.M.) tungsten<sup>(6)</sup>; however, the strength of C.V.D. tungsten is lower than P.M. tungsten at all test temperatures. This was reported earlier by Taylor and Boone<sup>(7)</sup> who believed that void formation during the initial heat treatment of their C.V.D. tungsten accounted for the strength difference. However, in the current investigation specimens which were not heat treated prior to testing also showed lower strength than P.M. tungsten. This suggests that the lower strength is probably more related to the columnar grain structure than to void formation. The current ultimate tensile strength value of 12,000 psi at 1600°C is in good agreement with Taylor's<sup>(7)</sup> result.

The temperature dependence of the elongation is shown in Figure 6. The total elongation increases with increasing temperature up to 1400°C, above which it decreases. This also agrees with Taylor's<sup>(7)</sup> earlier

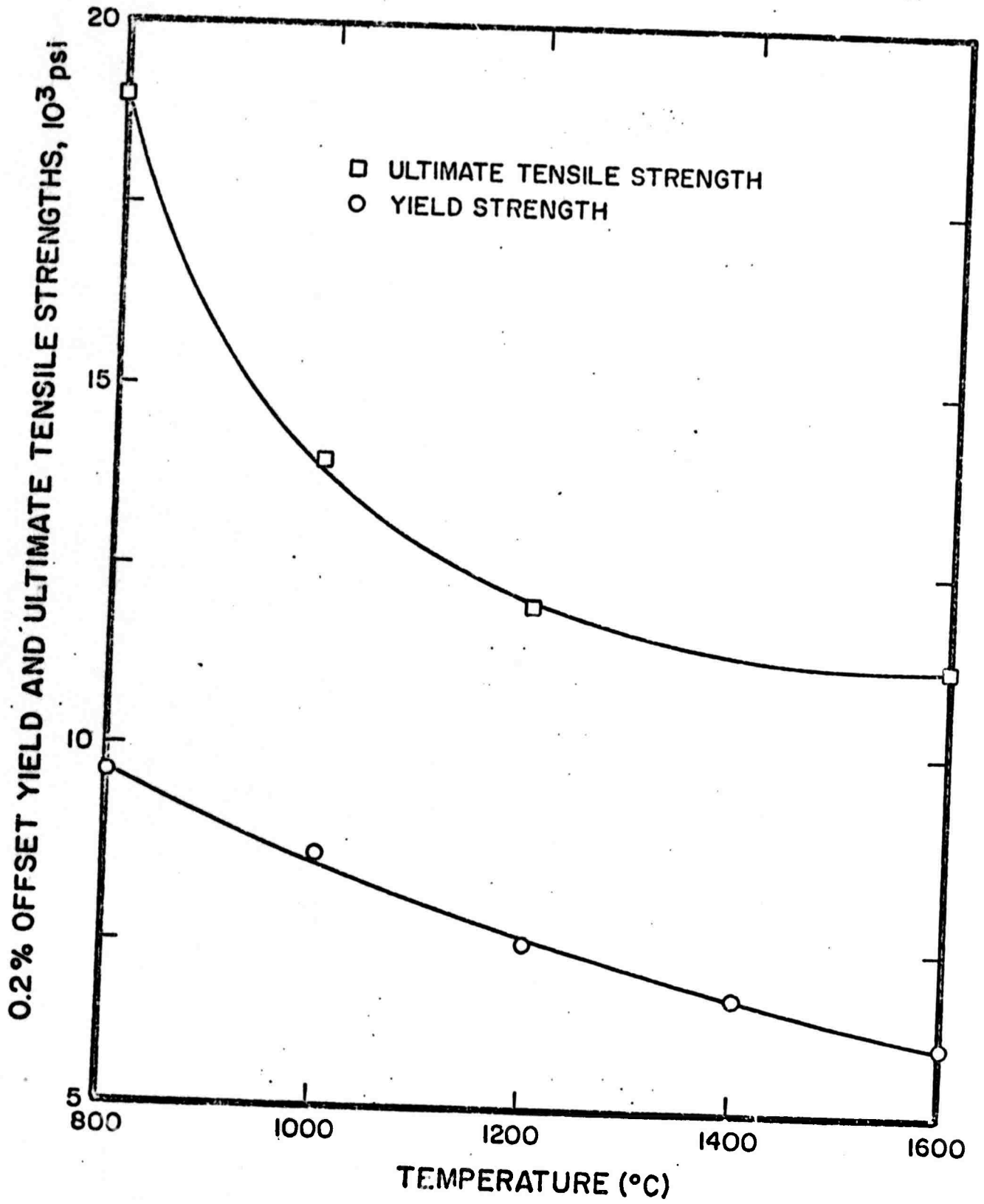


Figure 5. Yield and Ultimate Tensile Strengths versus Temperature for C. V. D. Tungsten between 800 and 1600 $^{\circ}$ C

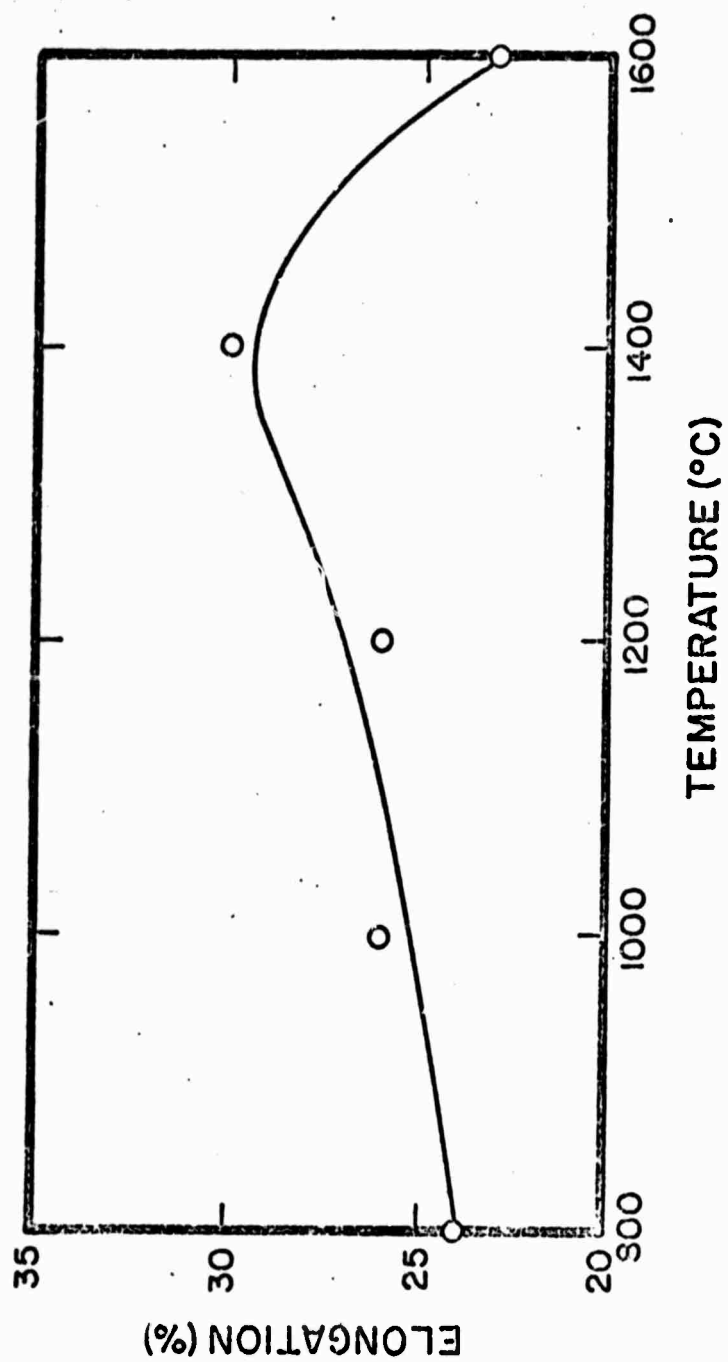


Figure 6. Elongation % versus Temperature for C. V. D. Tungsten

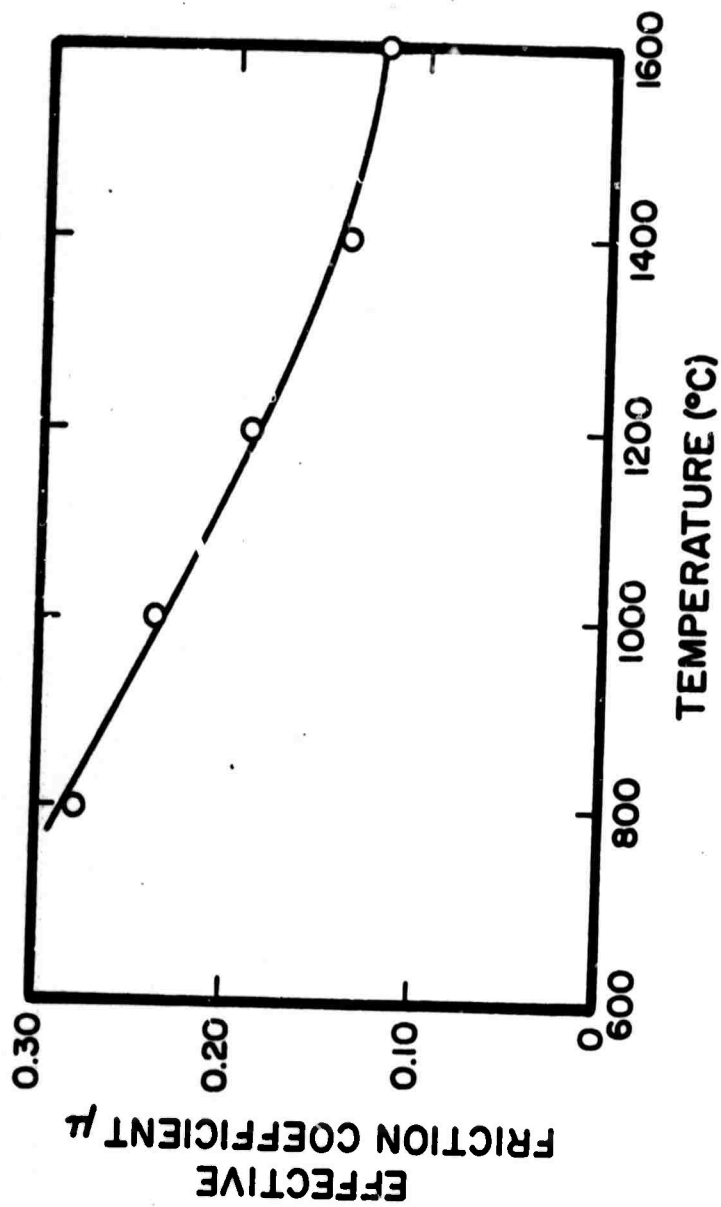


Figure 7. Effective Friction Coefficient versus Temperature for The Hoop Stress Testing Apparatus

polycrystalline results which showed a decrease in elongation above approximately 1380°C. It is important to note, however, that Taylor also tested tungsten single crystals in the same temperature range and these showed a steady increase in ductility with increasing temperature. Like polycrystalline C.V.D. material, powder metallurgy tungsten<sup>(7,8,9)</sup> decreases in ductility beyond a certain temperature. Void formation at grain boundaries followed by intergranular cracking are most likely the cause of the decrease in ductility for both P.M. and C.V.D. tungsten. The current material exhibited void formation during testing at 1400°C and above. All failures were of an intercrystalline type.

It was normally observed that slip was finer on the sides than on the ends of the columnar grains. Another general observation is that only small deviations are found in the directions of slip bands from grain to grain. This merely suggests that a strong crystallographic fiber axis exists.

The intersection angles between the slip bands in most instances were found to be 90°, and occasionally 60°. The 90° intersections no doubt represent {110} slip planes with <100> zone axes. This is in agreement with our fiber axis determinations which were largely <100>. Those few bands found to intersect at 60° represent {110} slip planes with a <111> zone axis. Our conclusions for this section are:

1. The fact that C.V.D. tungsten has lower strength than powder metallurgy tungsten is probably more due to the stressing of its columnar grained structure normal to the long axes of these grains, than to void formation since the latter is found in both materials. Another indication of this is that C.V.D. tungsten has lower strength than P.M. tungsten at temperatures too low for void formation.

2. The decrease in ductility of C.V.D. tungsten above 1400°C is probably related to increased fluorine related void formation.
3. Slip occurs mainly on {110} planes with  $\langle 111 \rangle$  zone axes.
4. The slip band spacing is independent of temperature between 800 and 1600°C and has values between 2 and 20  $\mu$ .

From p 9

#### IV. Annealing Studies

→ Square holes have been observed in transmission electron microscopic observations of sections parallel to the growing interface. These are thought to be caused when the foil is thinned to a section passing through the cavities on the tops of small growth ledges near the base of larger pyramids. Since these small square holes are approximately  $0.1\mu$  wide, they could be sections of such cavities.

→ For W-22% Rh alloy <sup>it is p</sup> <sup>thought</sup> we now think that observed grain growth rate decreases at longer annealing times are caused by the development of bubbles on the grain boundaries. ← The lowest temperature at which this was observed was  $2270^{\circ}\text{C}$ . For temperatures of  $1750^{\circ}\text{C}$  and above log-log plots of the  $D^2 - D_0^2$  vs  $t$  data were useful in examining grain growth behavior after two to five hours at temperature. The impression gathered is that below  $2270^{\circ}\text{C}$  the late time data (beyond two hours) for many temperatures had a slope of about one, whereas above  $2270^{\circ}\text{C}$  the longer annealing time data fell approximately on lines of slope 0.3. This implies that below  $2270^{\circ}\text{C}$  the well known  $D^2 - D_0^2 = kt$  approximation is not too far from the truth (after several hours), but that above this temperature grain growth actually slows down. This, as mentioned earlier, we ascribe to bubbles on the grain boundaries. These bubbles evidently take several hours to become effective.

An Arrhenius slope of 61.7 kcal/mole is obtained for initial grain growth in the alloy. This value is slightly higher than the value of 59 kcal/mole reported earlier for C.V.D. tungsten. This is probably a consequence of the large amount of solute present.

Moon<sup>(10)</sup> just reported 100 kcal/mole for tungsten grain boundary migration. This higher value (than our 59 kcal/mole) may represent events at times longer than one hour in which case bubbles could be increasing the activation energy.

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