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DEVELOPMENT AND STUDY OF CHEMICALLY VAPOR DEPOSITED TANTALUM BASE ALLOYS

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ABSTRACT

A technique for the chemical vapor deposition of alloys has been developed. The process, termed "pulsing", involves the periodic injection of reactant gases into a previously-evacuated reaction chamber where they blanket the substrate almost instantaneously. Formation of alternating layers of the alloy components and subsequent homogenization allows the formation of an alloy of uniform composition with the composition being determined by the duration and relative numbers of the various cycles. The technique has been utilized to produce dense alloys of uniform thickness and composition (Ta- 10 wt % W) by depositing alternating layers of Ta and W by the hydrogen reduction of $TaCl_5$ and WCl_6. A similar attempt to deposit a Ta - 8 wt % W - 2 wt% Hf alloy was unsuccessful because of the difficulty in reducing $HfCl_4$ at temperatures below those at which gas phase nucleation of Ta and W occurred.

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Summary

One of the greatest problems associated with the formation of alloys by CVD is the achievement of compositional uniformity. In a typical deposition apparatus, wherein reactant gases are made to flow over the substrate in a continuous manner, this non-uniformity is inherent for two reasons. The composition of the gas stream changes as a function of its distance of travel over the substrate and, inevitably, one of the reactant compounds is more easily reduced than the other(s). This problem has been overcome in the present work by the development of a process termed "pulsing". In it reactant gases are periodically injected into a previously evacuated reaction chamber where they cover the substrate almost instantaneously. By this technique gas composition at any point in time is not dependent upon distance along the substrate. Formation of alternating layers of the alloy components and subsequent homogenization allows the formation of an alloy of uniform composition with the composition being determined by the duration and relative number of the various cycles. This technique has been utilized to produce dense alloys with the composition Ta -10 wt.% W by depositing alternating layers of Ta and W by the hydrogen reduction of $TaCl_5$ and WCl_6. The alloys were uniform in thickness and composition over lengths in excess of 20 cm. and the target composition was attained. A similar attempt to deposit a Ta - 8 wt. % W - 2 wt. % Hf alloy was unsuccessful because of the difficulty in reducing $HfCl_4$ at temperatures below those at which gas phase nucleation of Ta and W occurred (1200 and 1175°C respectively).

I. Introduction

The objective of the research described in this report was to develop a chemical vapor deposition (CVD) technique for producing dense tantalum-base alloys of uniform thickness and composition. The alloys considered were T-111 (Ta-8 wt% W-2 wt% Hf) and Ta-10W (Ta-10 wt% W). The description of the technique and its evaluation will be preceded by a brief introduction to the thermodynamic, kinetic, and morphological factors influencing CVD processes and a review of previous attempts to deposit alloys by CVD.

A. Thermodynamics of CVD

For a deposition reaction to be thermodynamically possible at constant temperature and pressure the Gibbs free energy change (ΔF) must be negative. For example, in order for the production of hafnium (Hf) by the hydrogen reduction of $HfCl_4$ to be feasible ΔF for the reaction

$$HfCl_4(g) + 2H_2(g) = Hf(s) + 4HCl(g) \qquad (1)$$

must be less than zero. The overall free energy change may be written

$$\Delta F = \Delta F^o + RT \ln \frac{a_{Hf} p_{HCl}^4}{p_{H_2}^2 \; p_{HfCl_4}} \qquad (2)$$

where ΔF^o is the standard free energy change for Eqn.(1), a_{Hf} is the activity of hafnium in the deposit; p_{HCl}, p_{H_2} and p_{HfCl_4} are the partial pressures of HCl, H_2 and $HfCl_4$ in the reaction systems (ideal gas behavior has been assumed in replacing activities by partial pressures for these species); and RT has its usual significance. Clearly, ΔF for almost any reaction may be made negative, regardless of the sign of ΔF^o, if appropriate values of the parameters in the second term on the right-hand-side of Eqn.(2) are established within the system, e.g. for Eqn.(1) these would include low values for a_{Hf} and p_{HCl} and large values for p_{H_2} and p_{HfCl}. In practice, however, there are limits to the actual values which can be established for these parameters and deposition reactions for which ΔF^o is much greater than zero are generally unfavorable.

The partial pressures in a CVD reactor can be calculated as follows. Assume a certain value for the fraction of $HfCl_4$ reacted. If, for economic reasons (this compound is relatively expensive), it is essential that most of the $HfCl_4$ be reacted, assume a large value for this fraction. If deposition efficiency is less important than achieving a reaction at either a more easily attained temperature or a faster flow rate (to possibly increase the rate of deposition), then assume a low fraction of conversion. From the stoichiometry of the reaction, the starting molar ratio of hydrogen to $HfCl_4$ (it need not be the stoichiometric ratio) and a value for the pressure it is possible to calculate the needed partial pressure values from which ΔF can be determined. An example calculation demonstrating this procedure is given in Appendix A.

A caution is necessary. Some deposit-bearing gaseous compounds exist which have stable compounds of lower valence. The formation of these compounds can greatly limit the range of operating conditions over which a deposit of the desired material can be realized. In addition, if complete conversion of the higher valence compound is not thermodynamically possible, any attempted study of the kinetics of deposition will be invalidated since the rate will be thermodynamically rather than kinetically limited. Thus, a thermodynamic analysis must be made to determine the ranges of parameters for which complete conversion is possible. This procedure is illustrated for the hydrogen reduction of $TaCl_5$ to tantalum metal in Appendix B.

Furthermore, Loonam (Ref. 1) has shown that, for cases in which lower valent compounds of the deposit-bearing reactant have sufficient stability in the gaseous state, not only will the deposition efficiency experience a maximum as a function of this reactant's partial pressure but at sufficient partial pressure and temperature the deposition efficiency will go to zero and eventually assume a negative value. In this latter situation, the formation of the stable, gaseous lower valent compound is so favored that its formation occurs by reaction of the deposit with the higher valent reactant gas.

Once, by thermodynamic analysis, it has been established that a given deposition reaction is possible for a range of parameters, it is still necessary to determine whether or not the reaction is kinetically favorable.

B. Kinetics of CVD

Unfortunately, for the vast majority of CVD systems, kinetic data are not available in a form that lends itself to ready prediction of deposition rates as a function of deposition parameters. (Ideally this form consists of mathematical relations, one for each range of parameters for which a different rate limiting mechanism is associated.) This void leaves the investigator several courses of action.

One course is to search the literature for data on deposition rates. If these are available, however, they will likely be limited to a specific reactor geometry and size, be limited to a narrow range of operating conditions, will apply strictly only to the gas composition at zero percentage reactant conversion and could possibly represent conditions which are far from optimum.

A preferred approach is to perform and analyze the results of several experiments. By keeping constant the pressure, flow rate, and starting gas composition and varying only the deposition temperature for a deposit produced under conditions of low reactant conversion (for instance by employing a substrate of small surface area), data can be obtained from which conditions conducive to yielding a reasonable rate can be ascertained. These data are best analyzed by plotting the logarithm of the deposition rate as a function of the reciprocal of the absolute deposition temperature. A plot of these data will be similar to the hypothetical plot of Figure 1.

The regions of this plot labelled A, B, and C represent (assuming no thermodynamic limitation) respectively rate control by a reaction occurring at or near the substrate surface, rate control by mass transport in the gas and finally rate limitation due to homogeneous gas phase nucleation of product. The possible surface reactions which can control the process rate (and which are seen to be very temperature dependent) include

(b) adsorption of reactant(s) onto the substrate surface, (c) chemical reaction on the surface (this could also include surface diffusion) and (d) desorption of product gas(es) from the surface. These reactions are collectively referred to as kinetic steps in the overall process.

Mass transport includes the two steps of (a) transport of reactant(s) to the substrate and (e) transport of product gas(es) away from the substrate. The total process of chemical vapor deposition is generally assumed to consist of these steps occurring in the sequence (a), (b), (c), (d) and (e).

To maximize the deposition rate, those conditions producing mass transport control should be utilized. These conditions may also be determined by a method alternate to the one just described. Where, for some reason, it is necessary or desirable to maintain a relatively constant deposition temperature, data on rate as a function of pressure (with constant starting gas composition and flow rate) can be used. Transport control, and hence maximum rate, is indicated by a relative independence of rate on pressure.

Variations of deposition rate with respect to substrate position must be considered in addition to the overall rate. In attempting to deposit a single element over a substrate of considerable surface area by the standard procedure of continually flowing the reactant gases over the substrate, a deposit thickness profile such as that shown schematically in Figure 2 is likely obtained. This non-uniformity of deposit thickness is caused by the continual depletion of reactants and formation of product gas as the stream moves over the substrate. Experimental data on the deposition of tungsten by the hydrogen reduction of WF_6 showing this variation of gas composition are given in Figure 3.

This steady state variability of gas composition with respect to location on the substrate can be eliminated by the application of a CVD process refinement (Ref. 2) known as "pulsing". In this technique known quantities of reactant gases are injected into a previously evacuated reaction chamber where they almost instantly blanket the substrate with a gas of uniform composition. Naturally, the composition changes during the time in which the gas is confined to the reaction chamber but the composition at any time is likely invariant with respect to position on the substrate. During evacuation of the spent gases, fresh reactant gases are being accumulated in reservoirs of known volume for the next injection. Successive repetitions of the evacuation-injection cycle are used to form a deposit of uniform thickness. Further details of this technique will be given in subsequent sections of this report.

C. Morphology of CVD Deposits

Deposits form by a nucleation and growth mechanism. In addition they often exhibit a high degree of preferred crystallographic orientation. This orientation develops, in the absence of epitaxy, by growth from the randomly oriented nucleation layer first formed on the substrate. Growth proceeds by the more rapid growth of preferentially oriented grains with the result that less favorably oriented grains are prevented from further growth. Thus, as a deposit thickens, a columnar grain structure is developed.

The degree of preferred orientation is controlled by process variables and the selection of deposit-bearing reactant. The effects of process parameters on orientation in tungsten deposited by the hydrogen reduction of WCl_6 have been most recently discussed by Wahl and Batzies (Ref. 3). Numerous observations have been made on preferred orientation in WF_6-produced tungsten (Refs. 4-7) and in rhenium produced from several rhenium-bearing reactants (Refs. 8-10). This form of structural anisotropy is highly desirable for applications involving thermionic emission but can be detrimental where strength in a direction normal to the growth direction is important.

Where the substrate is crystalline, an epitaxial relation will often exist between it and the deposit. Where the substrate is amorphous, the oriented deposit is often referred to as oriented overgrowth. Epitaxy is favored by low substrate temperature and a low supersaturation of deposit-bearing reactant gas (Ref. 11). At greater supersaturations the epitaxial relation is lost while at even greater supersaturations it is possible to have nucleation occur homogeneously in the gas phase to produce a powdery deposit.

The normal columnar structure can be prevented. With the continued introduction of "impurities" to provide new nucleation sites, an equiaxed structure can be formed. This has been demonstrated by Holzl (Ref. 12) who produced equi-axed CVD tungsten by purposely injecting small quantities of oxygen into the reactant gas stream to react with WF_6 and produce particles (presumably WOF_4) which serve as nucleation sites. Continuous mechanical deformation of the deposit has also been shown to produce equiaxed structures (Ref. 13). During the deposition of tungsten by the hydrogen reduction of WF_6 mechanical energy was imparted to the deposit by having it stroked with tungsten wires. This allowed the nucleation of new grains and produced a more random microstructure.

The growth of CVD deposits on substrates of small surface area is typically 25-1500 μm/hr (1-60 mils/hr) with rates between 75 and 250 μm/hr being most commonly encountered (Ref. 14). Maximum growth rate is not always desirable since, at higher growth rates, grains become discontinuous with one another resulting in large mounts of in-grown porosity (Ref. 15). Densities approaching theoretical are obtained with proper control of deposition variables.

D. CVD Alloy Formation

The deposition of alloys requires knowledge and control of all the factors discussed in Sections A-C plus additional ones, particularly those affecting composition. In all likelihood the deposition kinetics of the separate elements are sufficiently different that besides a thickness variability found in the standard, flow-through process there will also be a compositional variation across the dimension of the deposit paralleling the direction of gas flow. This variability of composition is illustrated for a tungsten-rhenium alloy in Figure 4. Attempts have been made to improve the flow-through process to produce a more homogeneous alloy. These attempts include periodically reversing the gas flow direction (Ref. 16), rotating the substrate (Ref. 13), combining gas flow reversal with substrate rotation (Ref. 17), stirring the reactant gases as they enter the reaction chamber (Ref. 18), and flowing the reactant gases in a direction normal to the direction of translation of a moving substrate (Ref. 19). None of these modifications has been totally successful.

Successful deposition of alloys should, however, be possible with employment of the "pulse" technique. With simultaneous injection of all reactants, uniform thickness and uniform composition can be expected. The attainment of the target composition in this manner requires considerable experimental effort since no means of theoretically fixing the composition of reactant gas is available.

Some of the problems peculiar to alloy deposition can perhaps be better appreciated by considering some known features of efforts to co-deposit tungsten and rhenium. One might, for example, assume that in the formation of this alloy by hydrogen reduction of the appropriate fluorides the rates of deposition of the separate elements (and hence the final composition) would be in the same proportion that their fluorides occur in the reactant gas for the stipulation that the free energies of each deposition reaction were comparable. That this assumption is a poor one was confirmed by calculations made using the data of Holman and Huegel (Ref. 13). By making the reasonable assumption that the fraction of reacted fluorides in their system was 0.1, free energies per mole of HF formed were found to be -37,000 cal and -30,500 cal for the rhenium-producing and tungsten-producing reactions respectively. Even though these free energy values are similar, the deposition rate of tungsten was not 13 times as great as that of rhenium (based on the rates being assumed to being linear with reactant concentration). Instead, the tungsten formation rate was only about 4 times that of the rhenium rate for the investigated temperature of 600°C. Obviously, not both of these rates are linear functions of reactant concentration if indeed even one of them is. It is suggested that the reduction of ReF_6 is enhanced by the presence of tungsten, possibly by means of a displacement reaction.

At temperatures greater than 600°C, the rate of tungsten deposition was found to increase significantly with temperature while that of rhenium increases only slightly (Ref. 17). These results are supported by other data (Refs. 18,20). This suggests that different mechanisms are controlling the separate depositions. It was further noted (Refs. 20-22) that the rate of tungsten deposition was essentially independent of the presence of ReF_6 for temperature in excess of 600°C.

The work on a tungsten-rhenium-molybdenum alloy (Ref. 17) showed too that rhenium deposition rate was essentially independent of temperature above 600°C while the rates for both tungsten and molybdenum were significantly affected by temperature. Thus, again we see an example in alloy deposition where the rate for one element is mass transport controlled while for the other element(s) control is due to one of the so-called kinetic steps in the process. This sort of behavior greatly complicates the formation of CVD alloys by co-deposition.

A possible alternative to co-deposition is provided by the "pulse" process in which elements can be sequentially deposited to produce a layered structure that is subsequently homogenized to form an alloy. The sequential approach avoids some of the complexities of co-deposition but possesses possible disadvantages in the forms of increased deposition time and the potential for formation of Kirkendall voids during homogenization.

In certain instances there is no alternative to co-deposition since a temperature may not exist which is conducive to deposition of each of the elements. (The pressure and reactant gas composition can, however, be tailored to the particular element.) Co-deposition, with its potential for enhancement of a slower reaction by the presence of other reactants or products, is, for this situation, the only method for preparing a CVD alloy.

Clearly the versatility of the "pulse" process permits alternative approaches to be considered in the deposition of alloys. Therefore, this technique was chosen for the present study of chemical vapor deposition of tantalum alloys (T-111 and Ta-10W). The remainder of this report describes the application of this technique to CVD of alloys and the analysis of the factors required for establishing deposition parameters.

II. Experimental

A. Preliminary Analysis

The pulsing technique was chosen for the deposition trials because it offered the best possibilities for achieving deposits of uniform thickness and composition. However, prior to designing a deposition apparatus it was necessary to evaluate a number of factors such as the most suitable reactants, the injection-evacuation time cycle, and assuring compositional homogeneity of deposits. Because these evaluations are essential to the development or modification of a CVD technique for alloy deposition they will be briefly reviewed.

1. Choice of Reactants and Deposition Processes

Thermal decomposition of metal halides was not considered as a potential deposition process since, for any given compound, a considerably greater temperature is required than is normally associated with hydrogen reduction (Ref. 23). The hydrogen reduction of TaF_5 has not been reported as a CVD process since this compound is very stable (Ref. 24, p. 281). $TaBr_5$ and TaI_5 would appear to offer no advantage over $TaCl_5$, and thus all were considered as possible reactants for hydrogen reduction in the temperature range 800°C to 1400°C (Refs. 25-27). However, $TaCl_5$ was chosen since it was the only tantalum-bearing halide used in commercial practice and was thus likely to be most readily available.

The thermal decomposition of carbonyls or organometallics of the subject metals were not considered since, in general, these processes, although permitting low deposition temperatures, produce deposits highly contaminated with carbon.

Because of the temperature range required for the reduction of $TaCl_5$ at a reasonable rate, the use of WF_6 as a source of tungsten was prohibited because of the likelihood of gas phase nucleation of tungsten at temperatures above 900°C. Tungsten iodide was rejected because of its instability (Ref. 28). Tungsten hexachloride (WCl_6) was chosen over the other possibility, WBr_6, in order to eliminate side reactions between WBr_6 and $TaCl_5$ owing to their different anions. The temperature range over which WCl_6 may be hydrogen reduced is compatible with that for $TaCl_5$ (Ref. 26). A minimum temperature of about 880°C has been reported for WCl_6 reduction (Ref. 3).

Hafnium tetrachloride ($HfCl_4$) was chosen for the deposition of hafnium because of the desirability of a common anion and because thermodynamic calculations using the data of Glassner (Ref. 29) showed the hydrogen reduction of this compound would be at least as favorable as that of any of the other halides of hafnium. However, these calculations also showed that, because of the high stability of the hafnium halides, extensive reduction is only possible at temperatures greater than 1500°C even for low reaction chamber pressures of about 10 torr and high $H_2/HfCl_4$ ratios of about 100. These conditions of pressure and reactant ratio would result in unacceptably slow deposition rates and the high temperatures are not compatible with those for the deposition of tantalum and tungsten.

Therefore, while it was clear that Ta-10W could be deposited by sequentially depositing layers of Ta and W, the deposition of T-111 could not be accomplished in this manner because of the impossibility of obtaining compatible deposition parameters for elemental Hf. It was decided to attempt to obtain Hf in deposits by codepositing it with Ta because of the possibility of displacement reactions between the respective chlorides and because the activity of Hf would be less than unity in such a deposit. Several steps can be taken to enhance the deposition of hafnium. The deposition temperature must be as high as possible within the constraints described previously. In this way the standard free energy of $HfCl_4$ is reduced and the diffusion rate of hafnium into tantalum is increased to provide a low hafnium activity at the surface. A concentration of $HfCl_4$ in the gas phase which is greatly in excess of the desired concentration of hafnium in the deposit can be employed.

The final choice of deposition parameters was the temperature range above 900°C but below that at which gas phase nucleation of Ta or W occurred and system pressures above 20 torr in order to obtain significant reaction rates. The further specification of these two parameters and the partial pressures of reactants could only be determined experimentally.

Successful operation of the "pulse" process requires that reactant gases be accumulated in their respective reservoirs prior to their injection into the reaction chamber. To affect this accumulation, sufficient vapor must be generated within a vaporizer and transported to the reservoir in the time allowed by the evacuation portion of each injection-evacuation cycle. This reasonably requires only a few seconds. Vapor pressure and transformation temperature data (Ref. 24, Table D) for the compounds of interest are given in Table I. To assure an adequate flow rate of gaseous reactant to a reservoir, a vapor pressure of 400 torr was judged to be sufficient based upon the work of others with both WCl_6 and $HfCl_4$ (Ref. 30). To realize this vapor pressure, vaporization temperatures of 211°C, 306°C and 297° are required for $TaCl_5$, WCl_6 and $HfCl_4$ respectively.

2. Choice of Injection-Evacuation Time Cycle

Without available kinetic data, the length of time required for the injection portion of the cycle cannot be predicted. Long times will more fully permit utilization of reactants but will also cause increased total deposition time since the deposition rate drops off once significant depletion of reactants occurs. Past experience with the "pulse" deposition of tungsten from WF_6 (Ref. 2) indicated that a residence time for gases of 10 to 15 seconds was sufficient to permit considerable reduction of metal-bearing reactant in a chamber of the anticipated size. Considering the proposed size of the reaction chamber, the approximate deposition pressure range, and the capacity of the vacuum pump, it was reasonable to expect that evacuation to well below one torr could be accomplished in just a few seconds. Thus, the total injection-evacuation cycle could reasonably be expected to require between 15 and 30 seconds.

3. Assurance of Compositional Homogeneity and Structural Integrity

As initially deposited, the alloys would consist of layers of tantalum (or tantalum plus hafnium) separated with layers of tungsten. As deposition proceeded, the first material deposited would be undergoing homogenization while that material just recently deposited would have a layered structure. For the purpose of calculation, this layered structure was presumed to consist of tungsten layers of 16Å thickness separated by 184Å thick layers of tantalum. By considering a single solute layer of tungsten in an infinite solvent of tantalum, it was calculated (Appendix C) that essentially complete homogenization would occur during the course of deposition for even the lowest anticipated deposition temperature of 900°C. Complete homogenization of the several last-deposited layers would require a post-deposition hold, for the temperature of 900°C, of a maximum of 5 hours. For the case in which the thickness of each type of layer is increased by a factor of 10, homogenization at 900°C would take a prohibitively long time. However, at a deposition temperature of 1200°C, homogenization should require only a fraction of an hour.

The very thin alternate layers of tungsten are desirable for another reason besides the one of favoring homogenization. With this as-deposited structure, the possibility for Kirkendall void formation is minimized. This is an important consideration since void formation, which could otherwise form on the tantalum (or tantalum-hafnium) side of each interface, could seriously disrupt the integrity of the alloy's structure. Elimination of these voids is favored by higher deposition temperatures. Thus, even though 900°C is sufficient for homogenization in certain instances, the temperature required for void elimination could be considerably higher.

B. Equipment Design

The basic form of the equipment is shown schematically in Figure 5. The essential components are vaporizers (1), reservoirs (2), air-operated valves (x), reaction chamber (3), vacuum pump (4) and a programming device (not shown) to control the operation of the valves. For example, in the proposed scheme to form T-111 from alternately deposited layers of tantalum-hafnium and tungsten, it would be necessary to deposit sufficient tantalum-hafnium layers for each tungsten layer to form, upon homogenization, the T-111 composition. A tungsten layer would be formed as follows. Valves x_3 and x_5 remain closed to confine $TaCl_5$ and $HfCl_4$ to their respective vaporizers. Upon signal from the programmer, valves x_1 and x_7 open while valve x_2 and x_8 close to permit filling of hydrogen and WCl_6 reservoirs. Simultaneously valve x_9 opens to permit exhaustion of the reaction chamber and reactant feed lines. This sequence constitutes the exhaust portion of the deposition cycle. After completion of the programmed time allotted for exhaustion, the programmer initiates the injection portion of the deposition cycle by signalling the simultaneous opening of valves x_2 and x_8 and the closing of valves x_1, x_7, and x_9. All the while valves x_3 and x_5 remain closed. The reactant gases and the formed product gas remain in the reaction chamber for a predetermined period of time. Once this time has elapsed a single tungsten layer has been deposited. Similar operation for $TaCl_5$ plus $HfCl_4$ (with WCl_6 injection being prohibited) would permit formation of a tantalum-hafnium layer. The amount deposited per cycle and hence the number of each type of cycle required for the formation of layers of thickness appropriate to yielding the target composition must be determined experimentally.

The chlorides are solids at room temperature where their vapor pressures are slight. It is not until the vaporizers containing the chlorides are heated to temperatures which produce a vapor pressure of approximately 400 torr that this portion of the system is operable. To prevent condensation of these vapors during transport to the reaction chamber the feed lines must be kept hotter than the temperature of the vaporizer. This is also a precaution to prevent the condensation of sub-chlorides possibly formed by reaction with feed lines and vaporizers. Thus a minimum temperature must be maintained for which the partial pressure of sub-chloride in the feed gas is less than the vapor pressure of this substance at the same temperature. For $TaCl_5$ this minimum temperature has been reported to be 242°C (Ref. 31) while the vaporization temperature to produce a vapor pressure of 400 torr is 211°C.

No information on the feed line temperature for $HfCl_4$ is available. The feed line temperature for WCl_6 must be kept between 350°C and 400°C (Ref. 32). To further minimize the possibility of sub-chloride formation all components of each feed system were constructed from either 304 or 316 type stainless steel, both of which are known to possess excellent resistance to attack by dry chlorides.

Figure 6 shows a more detailed schematic drawing of the deposition apparatus. The three feed system portions of the apparatus are each contained in a separate, temperature-controlled furnace, designated (12). The furnace controller is designated (13). For the sake of simplicity, only one of the three chloride feed systems is shown in this figure. All three are identical in their construction differing only in the size of reservoir contained in each. To maintain those portions of a feed system other than the vaporizer (14) hotter than the vaporizer, heating tape (15) was wrapped about each and controlled at the required temperature by a variable transformer (16). These portions of a feed system include a reservoir (17) whose ends terminate in double-acting, air-operated bellows valves (18) capable of operation to about 500°C.

A four-way solenoid valve (19) controls the action of the air operators in such a manner that one valve is always open while its counterpart at the opposite end of the reservoir is closed and vice-versa in accordance with the previous description of the principle of operation of the "pulsing" technique. The hand operated bellows valve (20) affixed to the vaporizer operates only as an on-off valve to permit removal of the valve from the system for loading with reactant.

A nickel diaphragm gage (21) reacts to the pressure within the vaporizer and transmits its deflection through a silicone liquid filled line to a Bourdon tube vacuum gage (22) located outside the furnace. As noted from Figure 6, the air operator portions of the bellows valves also lie outside the confines of the furnace. Removal and replacement of the vaporizer and reservoir is facilitated by the furnace being supported on jacks which permit its being lowered to expose the components of the feed system and their support structure.

Chromel-alumel thermocouples are used to monitor the temperatures of the vaporizer, diaphragm, reservoir and several locations on the feed lines leading to the reaction chamber. The volume of the reservoir is fixed to provide a certain molar quantity of reactant to the reaction chamber during each injection in accord with the desired molar ratio of reactants. This volume is calculated from the ideal gas law. The desired number of total moles of reactants to be injected is determined by the chosen deposition parameters.

The operation of the hydrogen injection system is similar to that for the chlorides except that it operates at ambient temperature. Its reservoir (23) is sized to produce the ratio of hydrogen to total chloride required by the selection of deposition parameters. As a safety precaution, its air-operated bellows valves (24) are both of the normally closed type to prevent passage of hydrogen should there be a failure in either the accompanying electrical or compressed air circuit. Reservoir pressure is read from a Bourdon tube gage (25). Valve operation is initiated by a four-way solenoid valve (26). Safety from explosion due to hydrogen leakage from any portion of the equipment is provided by a detection alarm system (32) which automatically shuts off the supply of hydrogen at its source by means of a solenoid valve (33) once the level of hydrogen in the laboratory's atmosphere reaches a small percentage of that concentration known to be potentially explosive.

The outer portion of the reaction chamber (2) is contructed of Inconel 601 alloy. This alloy was selected for its excellent oxidation resistance at expected temperatures of operation. The substrate upon which the deposition occurs is a 6 1/3 cm tube of 304 type stainless steel which is concentric with the wall of the reaction chamber. That center portion of the substrate which reaches a fairly uniform temperature has a relatively large surface area and thus approximates that of hardware items which might conceivably be formed in the equipment. The substrate can be replaced for each experiment.

Both ends of the reaction chamber are water cooled to permit sealing of the end ports by "O"-rings. Prior to the start of deposition experiments, a stainless steel thermocouple well (4) projects through the entrance port (3) by means of a compression fitting contained in the outer component of the port. This arrangement permits the insertion of a platinum/platinum-13% rhodium thermocouple to various distances along the axis of the substrate in order that the temperature profile which exists there can be determined for a number of settings of the control pyrometer (28) for the Globar furnace which heats the reaction chamber. During deposition the thermocouple well is removed and its compression fitting is replaced by a plug.

Reaction pressure is measured by means of a diaphragm gage (6). A 2 cm air-operated bellows valve (7) controls exhaustion of the reaction chamber. This valve is capable of operation to about 650°C. It is controlled by a two-way solenoid valve (30). A dry ice - acetone cold trap (9) is situated upstream from the 1.4m^3/min. (50CFM) mechanical vacuum pump (10) to remove condensable vapors which would otherwise contaminate the pump. Exhaust gases from the pump are made to flow through a water scrubber (11) where the last traces of HCl are removed. Unreacted hydrogen in the exhaust stream is burned by directing it into the flame of a Bunsen burner which is situated under a hooded exhaust fan.

The apparatus is equipped with a thermocouple vacuum gage (8) which allows the apparatus to be leak checked.

Operation of the solenoid valves and hence the air-operated bellows valves is controlled by the action of a pre-punched tape which is driven by a synchronous motor through a tape reader (29). All electrical circuits stay closed as long as their respective conductive brushes within the reader maintain contact with the tape driving drum by protruding through holes punched in the non-conducting tape. These holes are spaced at regular intervals, each corresponding to one second of elapsed time, the period for which a brush can maintain contact with the drum. For a period for which it is desired to break a circuit, no holes are punched in that circuit's channel of the tape. In this manner the operation of all the solenoids for reactant feed and reaction chamber exhaustion are completely programmable. Numerical tabulation of the number of complete deposition cycles is kept by a cycle counter (31) whose operation is also controlled by the tape reader.

C. Experimental Procedure

The deposition parameters of temperature and pressure were first chosen. A hydrogen to total chloride ratio of 10 was used throughout the T-111 studies but was reduced to 4 in the work on Ta-10W. Reservoirs having volumes consistent with the appropriate amounts of reactant gases were fabricated and installed. (This volume included the dead space within the air-operated valves that comprised the ends of the reservoirs.)

Acetone-cleaned and weighed stainless steel tubing was used as the deposition substrate. This substrate was 115 cm long by 6 cm inside diameter. Once the substrate was positioned, the deposition chamber was heated under vacuum to the desired nominal temperature. The temperature profiles corresponding to several nominal temperatures had been previously determined. Cooling water was continually circulated through the end ports of the deposition chamber.

A known amount of each reactant chloride to be used was charged to a separate vaporizer inside a helium-filled glove bag. Following installation of a vaporizer to the appropriate feed system, the transport lines within the system were evacuated prior to opening the vaporizer's shut-off valve. The entire apparatus was then leak checked. Thermocouples were affixed to the feed lines and heating tapes were wrapped about them and connected to variable transformers. The feed system's pre-heated furnace was raised until it enclosed the vaporizer, the reservoir and the line connecting these components.

A tape, pre-punched to produce the chosen injection-evacuation cycle, was installed in the programmer. Once all the temperatures had reached their target values and the hand valve located at each vaporizer had been opened, the programmer was activated to begin the deposition process.

Deposition was continued for the pre-determined number of cycles, whereupon the hand valve located at each reactant source was closed. Several additional cycles were made to exhaust the feed lines of gases before the programmer was finally stopped and power to the vaporizing furnaces and heating tapes was interrupted.

For purposes of calculation, the entire substrate weight gain was used in the calculation of deposition rate. To be strictly correct, only the weight gain from that portion of the tube which corresponded to the region of uniform temperature should be used in this calculation. However, since the majority of the tube is at or near the nominal (maximum) deposition temperature and the remainder of the tube is at lower temperatures, this procedure was not felt to introduce serious error into the calculation.

Ta-10W alloy specimens were retained in the deposition chamber for an additional period of one hour, at the temperature of deposition, for the purpose of providing in situ homogenization. Once removed from the furnace, all alloy specimens were freed from their stainless steel substrates by dissolving the latter in a mixture which included 6 parts hydrochloric acid to 1 part nitric acid and a minimal amount of acetic acid. Tantalum-hafnium specimens were then homogenized at 1200°C for approximately 20 hours. This time period was chosen merely on the basis of convenience.

When sufficiently cooled, the vaporizer(s) and substrate tube were removed from the system and weighed. With this information (coupled with the results of microprobe analysis of the specimen deposit where applicable) the percentage conversion of chloride reactant and the deposition rates were determined.

III. Experimental Results

A. Element Deposition

Initial efforts were directed at studying the deposition of pure tantalum under conditions most suitable for subsequent formation of CVD T-111. These results are summarized in Table II. It is evident that the first two trials each provided a significant result. From trial #1, which employed a nominal deposition temperature of 1300°C, it was learned that tantalum could not be deposited at a system pressure of 40 torr at any temperature above 1200°C. Since subsequent tantalum-hafnium binary deposits would require as high a temperature as possible (to favor the reduction of $HfCl_4$), further tantalum trials were conducted at 1200°C.

In trial #2 it was learned that feed line temperatures of less than 250°C produced plugging. This result is in agreement with that reported in Reference 31. Presumably the plugging is caused by condensation of lower chlorides of tantalum formed by reaction between $TaCl_5$ and the stainless steel of the feed system. It was also learned in this trial that deposition efficiency was greatly increased by going to a 23 second deposit plus 7 second exhaust cycle.

In these first two trials the deposition rate was about 1.8 micron per hour. This low rate was expected since the reaction chamber pressure was low and the substrate area (about 500 cm^2) was purposely made very large to simulate the substrate mandrel that would be required to produce articles such as heat pipes. To increase the deposition rate the deposition pressure was increased to 60 torr for trials #4 and #5 by increasing the vaporization temperature of $TaCl_5$ to provide more of this reactant to its reservoir and by increasing the hydrogen pressure. At this vaporization temperature of 227°C the $TaCl_5$ powder sintered and thus became incapable of providing the necessary quantity of $TaCl_5$ vapor for each filling of the reservoir. To avoid any sintering the vaporization temperature was increased to 238°C to 244°C (above the melting point of $TaCl_5$) and a smaller reservoir was used to maintain the deposition pressure at 60 torr. In these trials (#6 through #10) feed line plugging prevented the achievement of any significant quantity of deposit. At the time it was felt that the higher vaporization temperatures produced increased quantities of tantalum oxychloride ($TaOCl_3$) vapor that could cause condensation of some substance in the feed lines. However, the use of average feed line temperatures as great as 385°C failed to prevent the plugging. To reduce the partial pressure of $TaOCl_3$ the vaporization temperature was reduced to 216°C to 218°C (trials #11 through #13) but line plugging persisted. A further decrease in vaporization temperature to 207°C (trial #14) also failed to eliminate this problem.

From the results of some published work (Ref. 33) on the chlorides of tantalum it was reasoned that high feed line temperatures could have been promoting the dissociation of $TaOCl_3$ to $TaCl_5$ vapor and solid tantalum oxide. The lines could thus have been plugged by formation of the oxide. By reducing the feed line temperature to about 290°C while maintaining a vaporization temperature of about 210°C, successful operation to produce a tantalum deposit, having a uniform thickness over that portion of the substrate which was at 1200°C, was achieved. As expected, operation at 60 torr produced a greater rate of deposition than did the previous operation at 40 torr. In addition, use of the higher pressure resulted in the achievement of improved deposition efficiency.

The resultant microstructure is shown in Figure 7. The grains are typically columnar. Deposit thickness measurements, taken at locations on the substrate tube corresponding to the 25 cm long region of uniform temperature were all very near a value of 25 microns.

A further increase in pressure (trial #19) to 100 torr produced a powdery deposit. Changing the deposition cycle to 33 second deposit plus 7 second exhaust had little effect on efficiency while it served to reduce the deposition rate.

In summary, a near-optimum process for preparing the tantalum portion of CVD T-111 by the "pulse" technique was found to have these parameters.

Average feed line temperature	290°C
Vaporizer temperature	210°C
Deposition temperature	1200°C
Deposition pressure	60 torr
Hydrogen to chloride ratio	10
Pulse cycle (deposit+exhaust)	23 + 7 seconds

The results of deposition trials for pure tungsten are shown in Table III. This element was readily deposited and no feed line plugging was encountered. However, to avoid the formation of deposits having areas of low density (areas where the deposit flaked off), the deposition temperature was reduced to 1175°C. The alternative remedy of lowering the deposition pressure much below 40 torr, while maintaining a hydrogen to chloride ratio of 10, was not considered since this approach would likely have had much less effect in retarding gas phase nucleation.

The grain structure of the deposit is shown in Figure 8. A uniform tungsten thickness of about 25 microns was achieved over the uniformly-heated portion of the substrate. The deposition rate of 1.2 microns/hr corresponds to 100Å thickness being deposited in each pulse cycle.

The results for tungsten deposition dictated that a new set of parameters be established for depositing the tantalum portion of the alloy. A further trial for tantalum deposition at 1175°C and 40 torr was conducted. Values for the other parameters were identical to those listed for the near-optimum process. The efficiency of $TaCl_5$ utilization was calculated to be 51% while the deposition rate was found to be 1.6 microns/hour. This rate corresponds to a thickness deposited of 131Å per pulse cycle.

Before binary deposits of tantalum and hafnium could be attempted, it was necessary to establish temperature conditions for realizing the transport of $HfCl_4$ to the reaction chamber. A vaporizer temperature of 300°C (the value required to achieve a vapor pressure of about 400 torr) and an average line temperature of about 400°C were found to be acceptable. (As expected, no deposition of hafnium occurred on the substrate which was heated to 1175°C.)

B. Tantalum-Hafnium Deposition

Based on the difficulty expected in reducing $HfCl_4$, the first binary trial was made using a 1/4 molar mixture of $HfCl_4$ and $TaCl_5$ (see Table IV). The hydrogen to total chloride ratio was maintained at 10. The optimum levels of the other parameters, including the reaction chamber temperature of 1175°C, were employed. Homogenization was carried out in the deposition chamber at 1200°C for a time of 20 hours. The long time period was chosen based on convenience. Essentially, no hafnium was found in the deposit by microprobe analysis. Increasing the molar ratio of $HfCl_4$ to $TaCl_5$ to 1/1 (Trial 2) and subsequently to 4/1 (Trial 3) failed to produce a deposit containing hafnium. Increasing the deposition temperature could not be considered because of the aforementioned limit established by gas phase nucleation of tungsten. Decreasing the total pressure (at constant hydrogen/chloride ratio) was not possible because of the minimum size restriction of the chloride reservoirs. More specifically, the reservoir volume for the chloride of lower partial pressure could not be made smaller for to do so would have made the dead space in the reservoir valves a significant fraction of this volume. Reducing the total pressure slightly by reducing the amount of hydrogen relative to the sum of the fixed partial pressures of chlorides was not felt to offer hope for any significant improvement and thus was not attempted.

In each case the microstructure was very similar to that of the elemental tantalum shown previously. Since no hafnium was deposited, the overall deposition rates were considerably less than that previously determined for elemental tantalum under similar conditions. Based on the results of these trials the deposition of T-111 was abandoned and study was concentrated on deposition of Ta-10W.

C. Tantalum-Tungsten Alloy (Ta-10W) Deposition

Before preparing the Ta-10W alloy (by alternate injections of hydrogen plus $TaCl_5$ and hydrogen plus WCl_6) effort was directed at increasing the deposition rates of the elements. By lowering the hydrogen to $TaCl_5$ ratio from 10 to 4, while maintaining the partial pressure of $TaCl_5$ at its previous value (3.6 torr for a total system pressure of 40 torr), a rate of 2.5 microns/hr (Table V) was obtained. This rate corresponds to a thickness deposited per pulse cycle of 194Å.

In similar fashion (again by lowering the hydrogen to chloride ratio to 4 while maintaining the chloride partial pressure at 3.6 torr) tungsten was deposited at 1.8 microns/hr (Table V) or 162Å per pulse cycle. For neither metal was any change in microstructure noted from that produced at a hydrogen to chloride ratio of 10.

If the rates for tantalum and tungsten deposition had been equal, deposition of the alloy could have been accomplished by permitting a repetition of 9 cycles of hydrogen plus $TaCl_5$ followed by a single cycle of hydrogen plus WCl_6. However, as shown, this was not the case. The desired ratio, based on actual deposition rates, was 7.53 hydrogen plus $TaCl_5$ pulses to each one of hydrogen plus WCl_6. Since there can obviously be only integral values for the number of pulses the ratio was rounded off to 15/2. A programmer tape was prepared which produced the sequence 8Ta + 1 W + 7 Ta + 1 W + 8 Ta, etc. The parameters shown previously to be optimum for the separate elements were used. No separate homogenization step was employed. The deposit was merely held within the reaction chamber at the deposition temperature (1175°C) for one hour following the cessation of reactants injection.

Following dissolution of the stainless steel strips, microprobe results on the concentration of tungsten in the alloy were obtained. These data are given in Table VI. The average tungsten concentration was calculated to be 10.09 weight percent. Compositional uniformity was checked by performing an analysis of variance on the data for time periods required for the microprobe counter to receive 10^4 counts of tungsten. (These data are directly related to the tungsten content in the alloy.) The 54 individual readings (6 readings at each of the 9 locations) for this trial ranged from 9.45 to 10.70 weight percent. These values are well within both the 3σ limits (Table VI) and the specification limits (8.5 to 11.0) for weight percent tungsten.

Further evidence for the compositional uniformity of the alloy, on a scale of about one micron (the beam diameter of the electron microprobe), is provided by the X-ray scanning images taken for both tungsten and tantalum (Figures 9 and 10).

The microstructure of the alloy is shown in Figure 11. It is evident from this figure that, over the portion of the substrate tube (50 to 75 cm measured from the inlet end) which was at uniform temperature, the deposit is of uniform thickness. A grain count of $13 \times 10^3/\text{mm}^2$ was estimated by comparing a photomicrograph, Figure 12 (taken in a direction normal to the growth direction), to photomicrographs at equal magnification of similar structures of known grain size.

No porosity was observed by optical microscopy performed at magnification of 1000 times. This observation was verified by scanning electron microscopy investigation of a fracture surface at magnifications up to 4000 times. A typical fracture surface is shown in Figure 13.

The ductility of the alloys was not directly investigated but no evidence of brittleness was found either in removing the alloys from the substrate or in subsequent handling.

A further Ta-10W deposition trial was made to demonstrate the reproducibility of the "pulse" process to form an alloy of uniform composition. That this end was achieved is shown by the results of Tables V and VI. Once again no porosity was noted by examination either by SEM or optical microscopy and the deposit was of uniform thickness over the zone of uniform substrate temperature.

Further lowering of the hydrogen to chloride ratio to the stoichiometric values might possibly increase the rate somewhat as might a change from the injection - evacuation cycle used for tungsten deposition. These changes would be expected to have only a minor effect, however, and the deposition conditions given in Table V are considered essentially optimum for the deposition of dense Ta-10W alloys of uniform thickness and composition.

IV. Discussion

The present study is the first work, of which the authors are aware, in which an alloy prepared by chemical vapor deposition has uniformity of thickness and composition over an extensive surface area (about 500 cm^2). This would seem to indicate the superiority of the "pulse" process over any modification of the flow-through process for depositing alloys. This superiority is a direct consequence of the manner in which the composition of the gas phase varies in each process. In "pulsing" the variation is a function of time and thus, within the restriction of uniform temperature, each portion of the substrate is exposed to the same conditions of deposition. In a flow-through process, unless the substrate is made very small or the concentration of metal-bearing reactant made very low, separate portions of the substrate are coated under a condition of different gas composition. Even where the elements in the alloy are deposited in separate, alternate layers by a flow-through process, a high degree of compositional uniformity would not be expected because of thickness variations of the layers with distance along the substrate. In addition to demonstrating both the ability of the "pulse" process to achieve a target composition and to affect compositional uniformity, the results of the present work further demonstrated the ability of this process to form deposits of uniform thickness. These results also strongly suggest that deposit thickness uniformity could possibly be realized over substrates having dimensions considerably greater than those employed to date.

No void formation during homogenization, as the result of vacancy migration and coalescence by the Kirkendall mechanism, was observed in the Ta-10W alloy. For the interdiffusion of two elements, this mechanism postulates a net flux of vacancies into the element of lower melting point. This flux equals the difference in fluxes of atoms of the two elements. If the rate of arrival of these vacancies at a location within the lower melting temperature element is greater than the rate of vacancy dispersal by normal vacancy motion and entrapment at grain boundaries and dislocations, voids will form there. The absence of voids in the homogenized Ta-10W deposits can be attributed to a single factor--the extreme thinness of the layers of the constituent elements made possible by application of the "pulse" process. As shown by the analysis of Appendix C, this factor permits homogenization in a short time and at low temperature. Low homogenization temperature is related to low net vacancy flux. Homogenization periods of duration less than the time required for an accumulation of vacancies sufficient to initiate coalescence will also prohibit void formation. The homogenization parameters used in the present study are well within the limits for the onset of void formation. Arcella (Ref. 34) found no voids to have formed in macro-size tantalum-tungsten diffusion couples held at 1200°C for 2000 hours. However, void formation was noted following interdiffusion at 1500°C for the same time period.

The displacement reaction between $HfCl_4$ and tantalum, upon which the deposition of hafnium was predicated, failed to materialize to a sufficient degree at 1175°C. Whether or not utilization of a higher temperature would have produced the desired concentration of hafnium in tantalum is open to conjecture. It is important to remember in this regard that deposition temperature refers to the temperature of the substrate. It is this temperature which is referred to in the reporting of maximum deposition temperatures. For substrates of small surface area (for example a wire in a cold-walled chamber), these maximum temperatures can be employed without promotion of gas phase nucleation. However, in the present study, the gas temperature would be expected to much more nearly approach that of the substrate and, thus, increase the possibility of gas phase nucleation.

The success in preparing CVD Ta-10W, coupled with the inability to deposit T-111, suggests that only alloys whose metal-bearing reactant compounds are fairly similar in their values for standard free energy of formation should be considered for formation by chemical vapor deposition. This restriction, however, is not overly confining. CVD alloys should be readily formed within the groups titanium-zirconium-hafnium, molybdenum-tungsten, niobium-tantalum, iron-cobalt-nickel and platinum-rhodium-iridium rhenium. Vanadium and chromium, by virtue of their typical deposition parameters (Refs. 26,35), could be added to the first group. The formation of many inter-group alloys should also be possible as evidenced, for example, by the present work on tantalum-tungsten and reported results on tungsten-rhenium (Refs. 18-21,36,37), niobium-vanadium (Ref. 38), and cobalt-tungsten (Ref. 39). The results of the present investigation indicate that many of these systems would be worthy of further study.

It should not be presumed, however, that the formation of other alloys by "pulsing" will be readily accomplished as was the formation of Ta-10W in the present study where the individual rates of deposition for both tungsten and tantalum were essentially the same for both alloy and single element deposition. Some experimental effort, in addition to establishing deposition rates for the separate element or alloy layers, may be necessary to form other alloys by the demonstrated process.

The early problems experienced with feed line plugging during the work on tantalum deposition are felt to be the result of impurity oxygen contained in the as-received $TaCl_5$. If undetected leaks in the deposition apparatus were present or the chlorides were improperly handled during loading of the vaporizers then plugging problems would likely have also been experienced with the chlorides of tungsten and hafnium. However, such was not the case. A possible solution to the problem of impurity pickup is to chlorinate chips of the appropriate metal in a chlorination unit which is an integral part of the deposition apparatus. In this manner the need for a vaporizer is eliminated and with it the necessity for handling hygroscopic powder of generally fine particle size.

The authors are unaware of any reported value for the grain size of either CVD tantalum or CVD Ta-10W. Thus, no comparison can be made with that of the "pulse"-produced CVD Ta-10W. The ease with which this alloy was homogenized precluded the possibility of formation of a coarse grain structure which could otherwise have resulted had a high temperature post-deposition homogenization treatment been necessary. The grain size of the "pulse" deposited tungsten (Fig. 8) was not measured quantitatively but is considerably less than 50 microns which is typical of chloride tungsten produced by flow-through techniques (Ref. 40). The "pulse" technique may, therefore, offer additional possibilities in the area of grain refinement.

V. Conclusions

Tantalum and tungsten can be deposited at high temperature with the formation of a dense, columnar grain structure. Respective maximum deposition temperatures of 1200°C and 1175°C for low pressure (40 torr) operation were fixed by the onset of homogeneous gas phase nucleation. The feasibility of preparing uniformly thick deposits of these elements by a "pulsing" modification of CVD was demonstrated.

The extension of these results to the verification of the process' ability to form a T-111 alloy was hindered by the inability to sufficiently reduce $HfCl_4$ to hafnium metal in a range of parameter values dictated by the successful deposition of the other two elements. The extreme thermodynamic stability of $HfCl_4$, relative to that of $TaCl_5$, made its reduction essentially impossible.

The similar thermodynamic stability of $TaCl_5$ and WCl_6 did make the deposition of Ta-10W possible by the "pulse" technique. This work marks the first successful attempt to prepare this alloy by chemical vapor deposition.

The improvement in CVD alloy preparation provided by the success of the "pulse" process suggests that many other alloys, having a controlled and uniform composition, might also be deposited by this method.

The ability of the "pulse" process to blanket a uniformly heated section of substrate with a mixture of gases (whose composition varies not with position on the substrate but instead with time of residence in the reactor) enables metal of uniform thickness to be deposited. The further ability of the process to limit the thickness deposited per injection cycle to values of only several hundred angstroms enhances the formation of homogeneous, pore-free CVD alloys.

APPENDIX A

CALCULATION OF PARTIAL PRESSURES OF GASES IN CVD REACTIONS

For an assumed starting reactant gas composition of 10 parts hydrogen to one part $HfCl_4$, reaction (1) can be re-written as

$$\begin{array}{ccccccc} HfCl_4(g) & + 2\ H_2\ (g) & = & Hf(s) & + 4\ HCl\ (g) \\ (1-x) & (10-x) & & (x) & (4x) \end{array} \qquad (A\text{-}1)$$

where x is the fraction of $HfCl_4$ reacted. For the purpose of calculation, x is assigned the value of 0.1. The system pressure is assumed to be 10 torr. Thus, the total moles of all substances present is 11.2 and the partial pressures of the gaseous species, p, are found to be

$$p_{HfCl_4} = (0.9/11.2)\ 10\ \text{torr} \approx 0.8\ \text{torr} \qquad (A\text{-}2)$$

$$p_{H_2} = (9.8/11.2)\ 10\ \text{torr} \approx 8.8\ \text{torr} \qquad (A\text{-}3)$$

$$p_{HCl} = (0.4/11.2)\ 10\ \text{torr} \approx 0.4\ \text{torr} \qquad (A\text{-}4)$$

These partial pressure values are substituted into equation (2), the value of J is determined and finally a value for $_{\Delta}F$ of the deposition reaction is found. For the gas constant, R, having the value 1.99 cal/$^{\circ}$K · mole, the partial pressure values must be converted to units of atmospheres.

APPENDIX B

DETERMINATION OF THERMODYNAMIC LIMITATION TO COMPLETE CONVERSION OF $TaCl_5$

The thermodynamics of the $TaCl_5$-H_2-HCl system were studied to determine the conditions of pressure and temperature required to assure the possibility of complete conversion of $TaCl_5$ to tantalum metal. The reduction of $TaCl_5$ was considered to consist of the following steps.

$$TaCl_5 + 1/2\ H_2 = TaCl_4 + HCl \qquad \text{(B-1)}$$

$$TaCl_4 + 1/2\ H_2 = TaCl_3 + HCl \qquad \text{(B-2)}$$

$$TaCl_3 + 1/2\ H_2 = TaCl_2 + HCl \qquad \text{(B-3)}$$

$$TaCl_2 + H_2 = Ta + 2\ HCl \qquad \text{(B-4)}$$

At all temperatures for which a significant deposition rate would be expected, that is greater than about 1000°K but less than about 1500°K (Ref. 25), $TaCl_5$ and $TaCl_4$ are gases while $TaCl_3$ and $TaCl_2$ are condensed phases. Within this temperature range the standard free energy of each reaction step (Ref. 29), with the exception of reaction (B-4) is sufficiently low that equilibrium composition would lie far to the product side and, assuming favorable kinetics, result in near 100% conversion of the tantalum-bearing reactant being attainable. Thus, if any step in the sequence is to prevent 100% conversion of $TaCl_5$, it would be the last step. To determine if this step could produce a thermodynamic limitation to complete conversion, the percentage conversion of $TaCl_2$ was calculated as a function of temperature and pressure for a starting gas composition of 0.9 mole fraction hydrogen.

These data are presented in Figure 14. At temperature in excess of 1200°K, complete conversion of $TaCl_2$ is expected for any system pressure up to one atmosphere. Since powder formation by homogeneous nucleation is favored by high system pressure, the maximum pressure to be studied was chosen as 100 torr. A corresponding minimum temperature for study that would assure the possibility of complete conversion was estimated as 800°C.

APPENDIX C

CALCULATION OF HOMOGENIZATION TIME FOR CVD Ta-W ALLOY

The homogenization time for the layered structure may be calculated as follows. By considering a single solute tungsten layer in an infinite solvent (tantalum), a solution for the solute concentration $C_{y,t}$ as a function of time (t) and distance (y) from the centerline of the solute layer is given by (Ref. 41)

$$C_{y,t} = \frac{C_o}{2}\left[\operatorname{erf}\frac{(h+y)}{2(Dt)^{1/2}} + \operatorname{erf}\frac{(h-y)}{2(Dt)^{1/2}}\right] \qquad \text{(C-1)}$$

where C_o is the initial concentration of tungsten (100%), h is the half thickness of the tungsten layer (assumed 8Å) and D is the diffusion coefficient for tungsten (assumed to be constant with concentration). Since the ultimate concentration of tungsten in the solvent is low (10 weight %), it is this value for D that will control the process and thus be used in the analysis.

An approximate value for D is found by considering available data on the interdiffusion coefficient for tungsten and tantalum, $\tilde{D}$, and assuming the amount of hafnium in the tantalum is negligible. This interdiffusion coefficient, where D* is an intrinsic diffusivity, is

$$\tilde{D} = X_{Ta}\, D_W^* - X_W\, D_{Ta}^* \qquad \text{(C-2)}$$

However, since the mole fraction of tungsten, X_W, is considerably less than that of tantalum, X_{Ta}, this equation reduces to

$$\tilde{D} \approx D_W^* = D \qquad \text{(C-3)}$$

The value for $\tilde{D}$ (and hence for D) at 900°C is near 10^{-16} cm^2/sec.

Thus the concentration of tungsten at the centerline of the solute layer (y = 0) and at the centerline of the solvent layer (y = 92Å) can be determined. The results are given in the following table.

TABLE C-1 Calculated Homogenization Data for CVD T-111

time (hours)	C_W at y = 0 (%)	C_W at y = 92Å (%)
0	100 (C_o)	0
0.1	26.3	0.10
0.5	11.8	4.30
1.0	8.3	5.40
5.0	3.7	2.3
10.0	2.6	1.5

These results indicate that within 5 hours at 900°C tungsten concentration at the location $y = 0$ would fall to 3.7% or well below the target alloy composition of 10%.

If the layered structure were to contain layers each 10 times as thick (i.e. 160Å thick tungsten layers alternated with 1840Å thick layers of tantalum plus hafnium) deposition at 900°C would require a follow-up homogenization treatment at increased temperature. A post-deposition hold at 900°C would take approximately 100 hours to lower the tungsten concentration at $y = 0$ to less than 10%.

For deposition at 1200°C, where $\tilde{D}$ is now $6 \times 10^{-4} cm^2/sec$ (Ref. 34) this thicker layered structure would require a post-deposition hold of only a fraction of an hour to complete homogenization. (The tungsten concentration at $y = 0$ is 9.6% at 0.1 hour and 2.4% at 1.0 hour.) At the lowest considered deposition temperature of 900°C, homogenization would require a post-deposition hold time of less than 100 hours. Should this time prove to be impractical, increasing the temperature following deposition can be resorted to.

Since the real system has a solvent whose thickness is much less than the assumed infinite thickness, these calculated times for complete homogenization are conservative. In addition, diffusion in the actual case would produce even more rapid homogenization since tungsten would be supplied to the tantalum areas from two sides instead of only one as assumed in the analysis. It is concluded that for a deposition temperature of 1200°C, a post-deposit hold at temperature of only a small fraction of an hour should be sufficient to produce a homogeneous alloy.

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TABLE I. Vapor Pressures and Transformation Temperatures Of Metal-Bearing Reactants

COMPOUND	LOG P (torr)	TEMPERATURE RANGE (°K)	MELTING POINT (°K)	BOILING POINT (°K)	SUBLIMATION POINT (°K)
$HfCl_4$(solid)	$\frac{-5197}{T} + 11.71$	476-681	705	----	589
WCl_6(solid)	$\frac{-4080}{T} + 9.73$	500-557	553	611	----
WCl_6(liquid)	$\frac{-3050}{T} + 7.87$	553-611	553	611	----
$TaCl_5$(solid)	$\frac{-4654}{T} + 12.197$	--------	473	487	----
$TaCl_5$(liquid)	$\frac{-2865}{T} + 8.54$	473-487	473	487	----

TABLE II. Summary of Results for Tantalum Deposition

TRIAL	DEP TEMP (°C)	VAP TEMP (°C)	AVG LINE TEMP (°C)	DEP CYCLE (DEP-EXH) (sec)	DEP PRESS (torr)	DEP EFFIC (%)	DEP RATE (μ/hr)	RESULT
1*	1300	210	260	12 + 3	40	32	1.8	Successful operation for 6 hours---Plugged at Location where temp. not known---No deposit for temp.>1200°C
2	1200	210	249	23 + 7	40	52	1.7	Successful operation for 4 hours---Plugged
3	1200	210	280	23 + 7	40	--	---	No deposit even though no plugging-Suspect $TaCl_5$ powder sintering
4*	1200	227	274	23 + 7	60	--	---	Plugged when heating tape failed
5	1200	227	271	23 + 7	60	--	---	No deposit even though no plugging-Suspect $TaCl_5$ powder sintering
6	1200	238	271	23 + 7	60	--	---	Plugged when heating tape failed
7	1200	244	269	23 + 7	60	--	---	Plugged---No failures in system
8	1200	244	304	23 + 7	60	--	---	Plugged---No failures in system
9	1200	244	371	23 + 7	60	--	---	Plugged---No failures in system
10*	1200	238	385	23 + 7	60	--	---	Plugged---No failures in system
11*	1200	216	390	23 + 7	60	--	---	Plugged---Leak found in valve
12*	1200	218	393	23 + 7	60	--	---	Plugged---No failures in system

TABLE II. Summary of Results for Tantalum Deposition (Cont.)

TRIAL	DEP TEMP (°C)	VAP TEMP (°C)	AVG LINE TEMP (°C)	DEP CYCLE (DEP-EXH) (sec)	DEP PRESS (torr)	DEP EFFIC (%)	DEP RATE (μ/hr)	RESULT
13*	1200	216	385	23 + 7	60	--	---	Plugged---No failures in system
14*	1200	207	385	23 + 7	60	--	---	Plugged---No failures in system
15*	1200	210	288	23 + 7	60	--	---	No deposition---Suspect incomplete removal of plug from previous trial
16*	1200	213	288	23 + 7	60	--	---	No deposition---Reservoir valves found to be nearly completely plugged
17*	1200	210	288	23 + 7	60	--	---	Successful operation for 4 or 5 hours ---heating tape failed
18*	1200	213	294	23 + 7	60	61	1.9	Successful operation
19*	1200	211	292	23 + 7	100	--	---	Powdery deposit formed
20*	1200	210	289	33 + 7	60	64	1.6	Successful operation

---

*Indicates that the vaporizer was loaded with fresh $TaCl_5$ for this trial

TABLE III. Summary of Results for Tungsten Deposition

TRIAL	DEP TEMP (°C)	VAP TEMP (°C)	AVG LINE TEMP (°C)	DEP CYCLE (DEP+EXH) (sec)	DEP PRESS (torr)	DEP EFFIC (%)	DEP RATE (μ/hr)	RESULT
1	1200	302	406	23 + 7	60	--	---	Powdery deposit formed in some areas
2	1200	303	408	23 + 7	40	--	---	Aborted---Exhaust pressure not low enough
3	1200	303	406	23 + 7	40	--	---	Powdery deposit formed in some areas
4	1175	300	409	23 + 7	40	48	1.2	Successful operation
5	1175	302	408	23 + 7	60	--	---	Powdery deposit formed in some areas

TABLE IV. Summary of Results for Tantalum-Hafnium Deposition

TRIAL	$HfCl_4$/ $TaCl_5$ RATIO	DEP TEMP (°C)	VAP TEMP(°C) $TaCl_5$	VAP TEMP(°C) $HfCl_4$	AVG LINE TEMP(°C) $TaCl_5$	AVG LINE TEMP(°C) $HfCl_4$	DEP CYCLE (DEP + EXH) (sec)	DEP PRESS (torr)	DEP EFFIC (%)	DEP RATE (μ/hr)
1	1/4	1175	212	302	288	404	23 + 7	40	42.6	1.3
2	1/1	1175	210	303	290	402	23 + 7	40	32.0	1.0
3	4/1	1175	209	299	290	401	23 + 7	40	25.6	0.7

TABLE V. Summary of Results for Tantalum - Tungsten Deposition

TRIAL	H_2/ CHLOR RATIO	TEMP (°C)	VAP TEMP (°C)		AVG LINE (°C)		DEP CYCLE (DEP+EXH) (sec)	DEP PRESS (torr)	DEP EFF (%)		DEP RATE (μ/hr)		RESULT
			$TaCl_5$	WCl_6	$TaCl_5$	WCl_6			Ta	W	Ta	W	
1	4	1175	210	---	291	---	23 + 7	18	62.7	----	2.5	---	Ta deposited*
2	4	1175	---	302	---	407	23 + 7	18	----	68.5	---	1.8	W deposited**
3	4	1175	208	302	289	406	23 + 7***	18	63.0	69.1	2.4	1.8	Alloy deposited
4	4	1175	211	304	288	409	23 + 7***	18	64.0	70.4	2.5	1.8	Alloy deposited

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*$TaCl_5$ plus hydrogen injection only

**WCl_6 plus hydrogen injection

***Ratio of number of $TaCl_5$ injections to number of WCl_6 injections was 15/2

TABLE VI. Concentration of Tungsten in CVD Ta-10W

		WEIGHT PERCENT TUNGSTEN					
TRIAL	POSITION*	FIRST DEPOSITED SURFACE	MID-THICKNESS OF DEPOSIT	LAST DEPOSITED SURFACE	TOTAL DATA RANGE	TOTAL DATA 3σ RANGE	$\bar{X}$
3	20	10.1	10.1	10.2	9.45 - 10.7	9.2 - 11.15	10.09
	25	10.05	10.25	9.9			
	30	9.9	10.2	10.2			
4	20	10.3	10.35	10.25	9.5 - 10.6	9.2 - 10.95	10.94
	25	10.0	10.2	10.2			
	30	10.35	10.05	9.95			

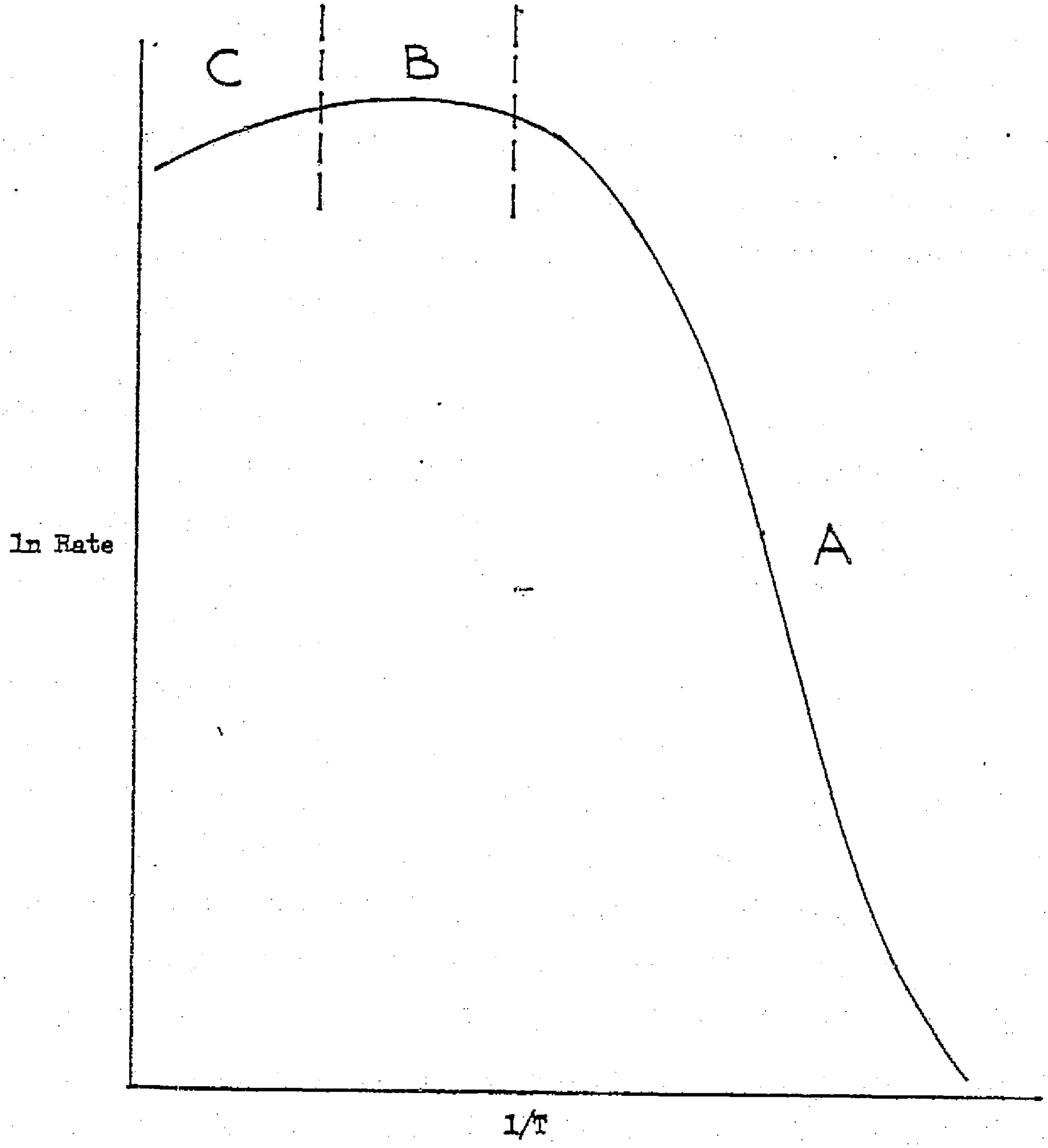


Figure 1. Suggested Form of Plot to be Used in Analyzing Deposition Rate Data.

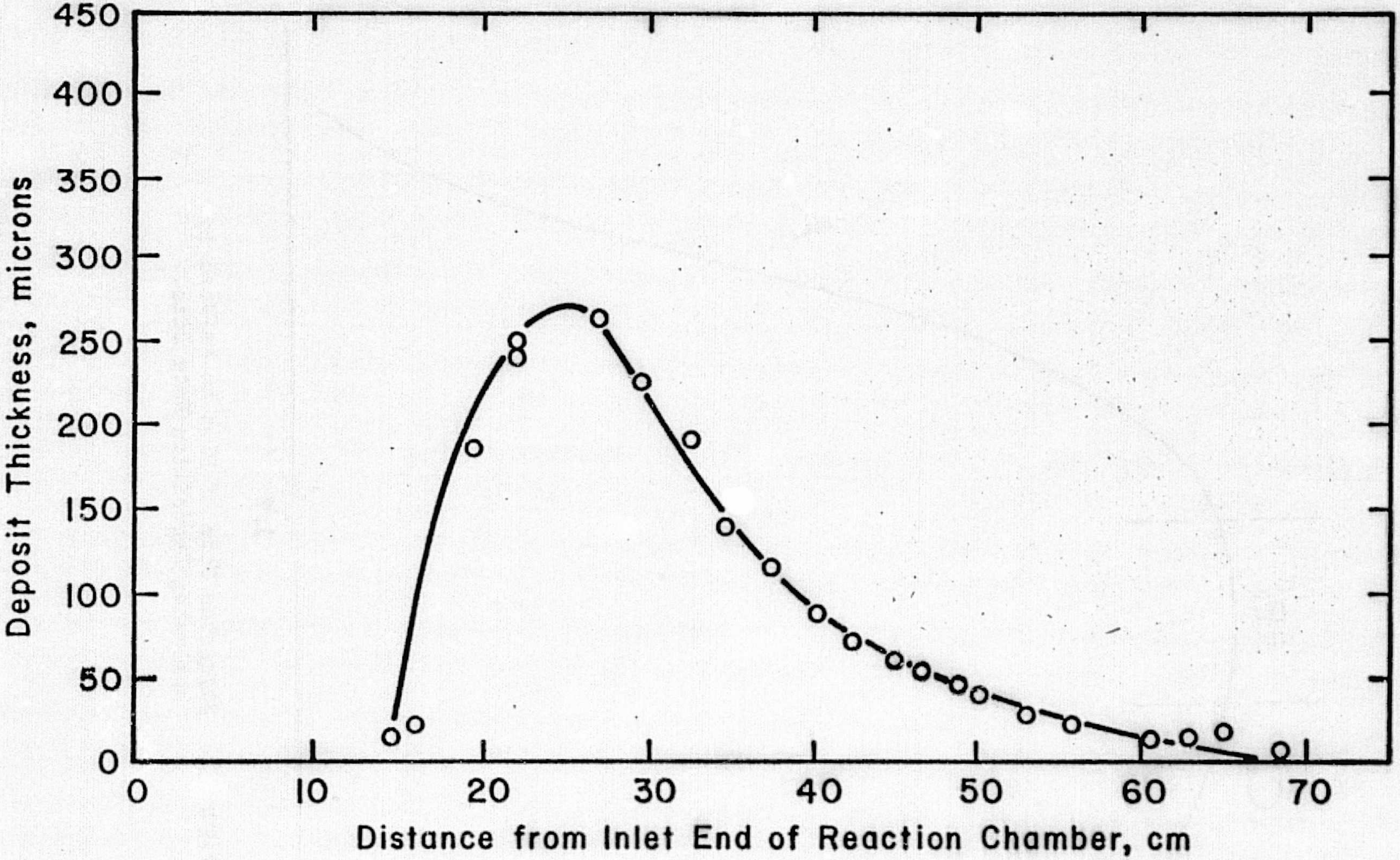


Figure 2. Typical Deposit Thickness Profile

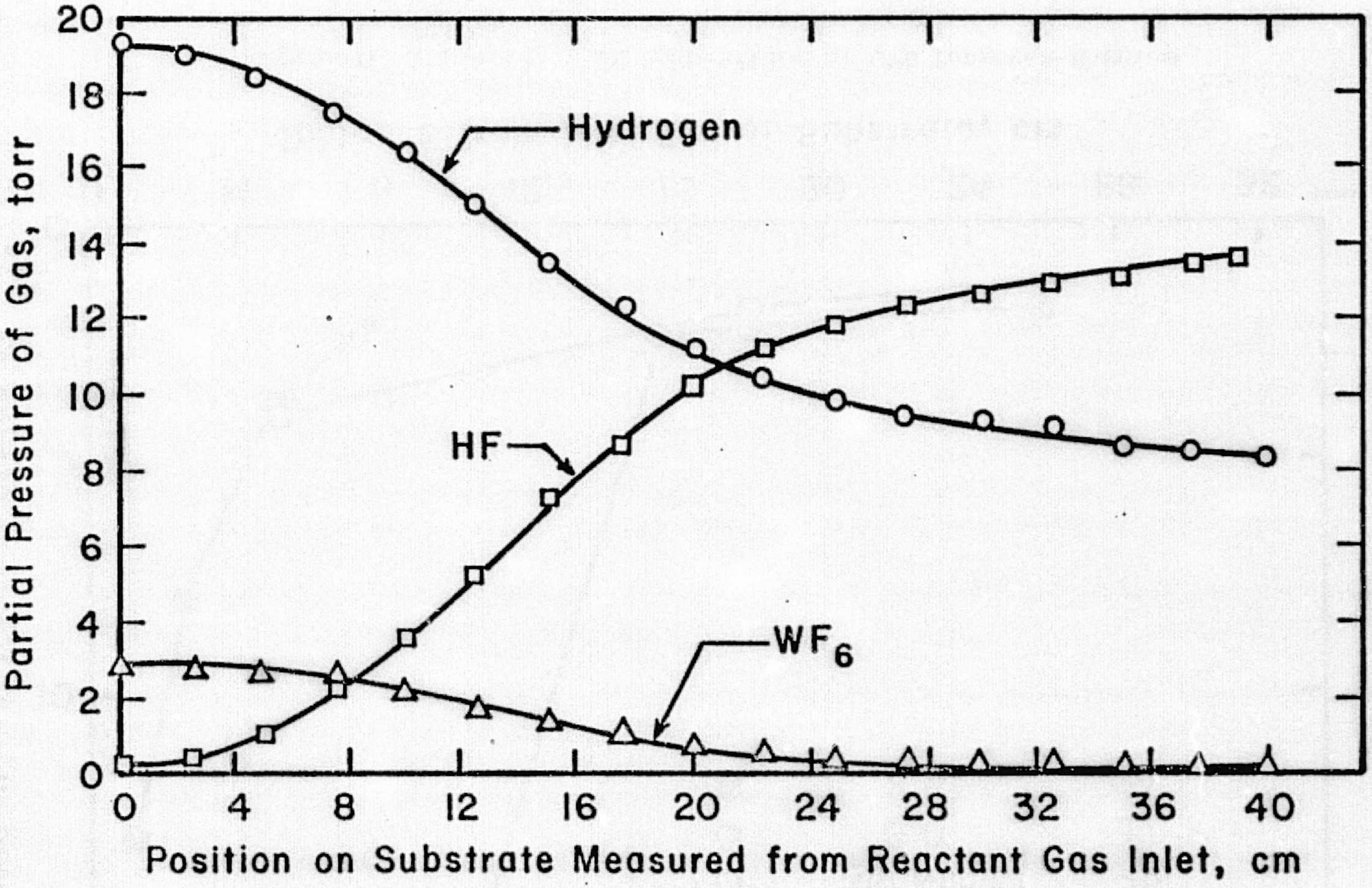


Figure 3. Gas Composition as a Function of Position on Substrate

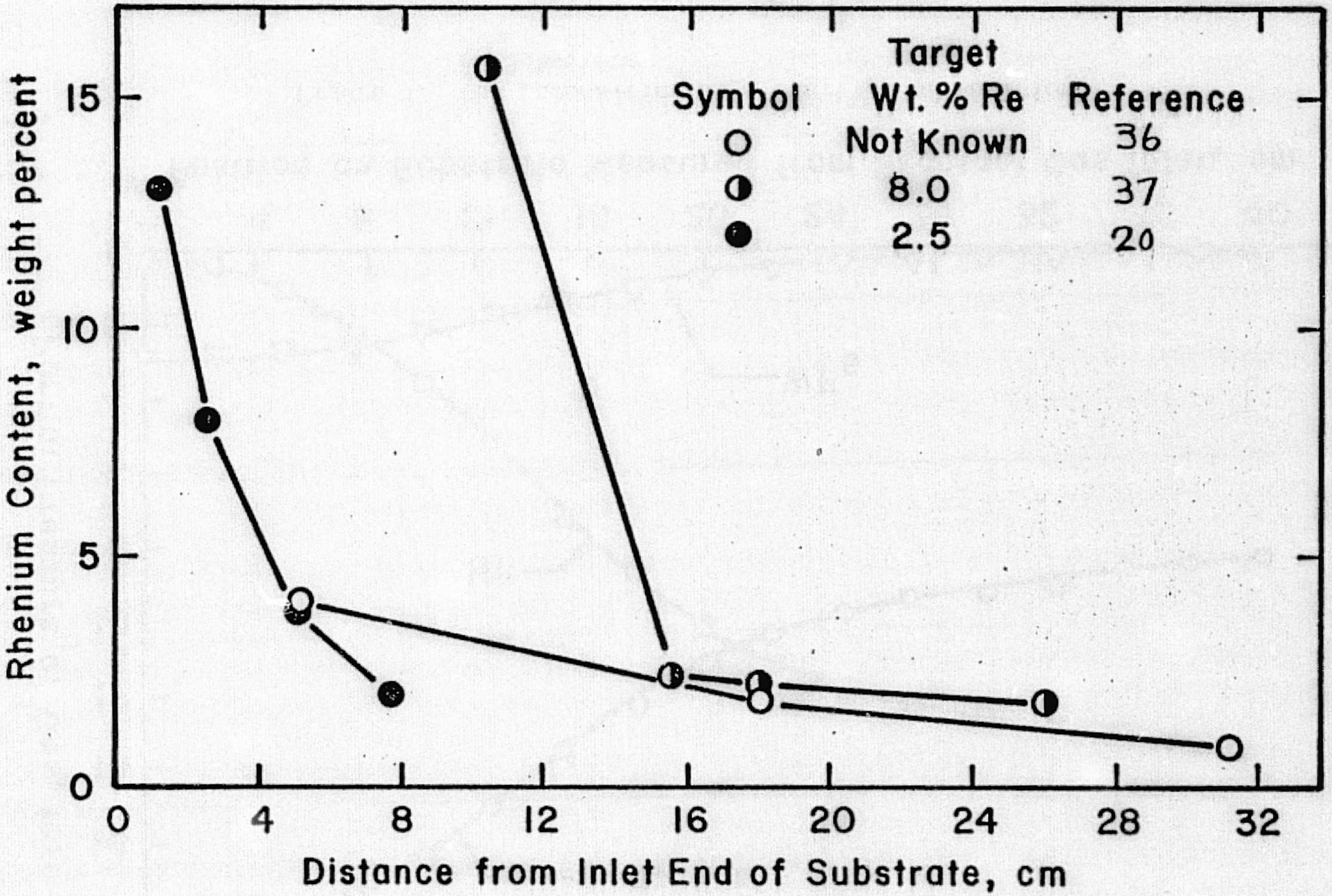


Figure 4. Variability of Composition of CVD Tungsten-Rhenium Alloys

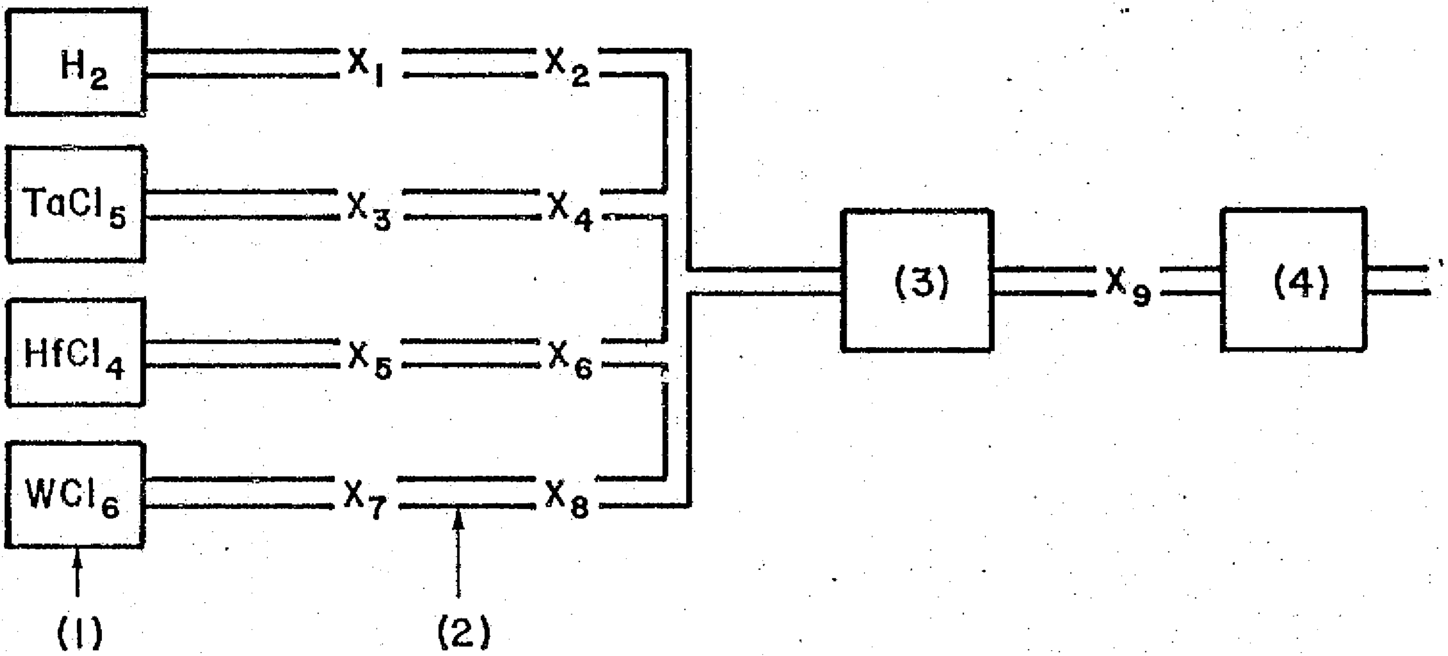


Figure 5. Basic Components of Equipment used in "Pulse" Process

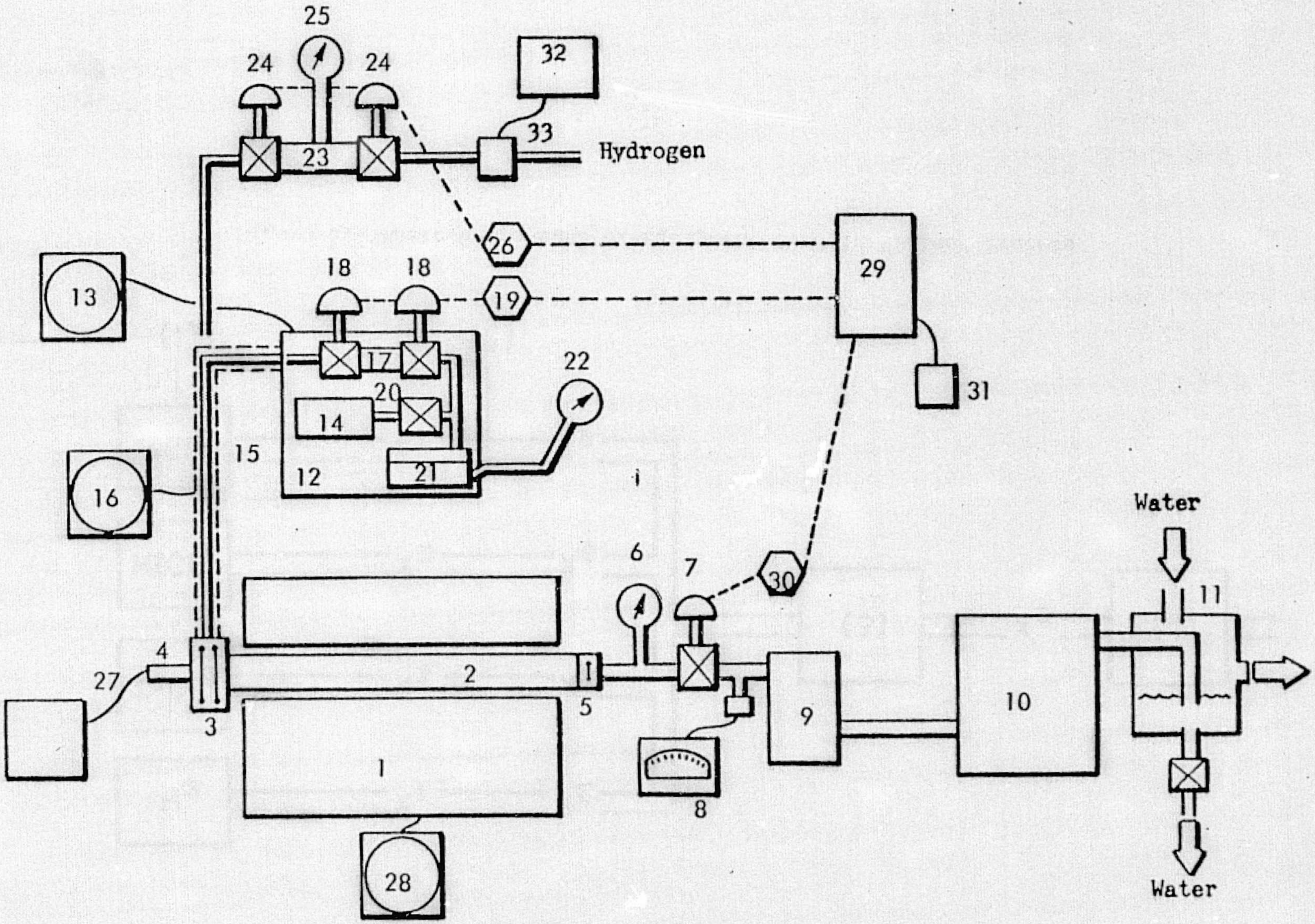
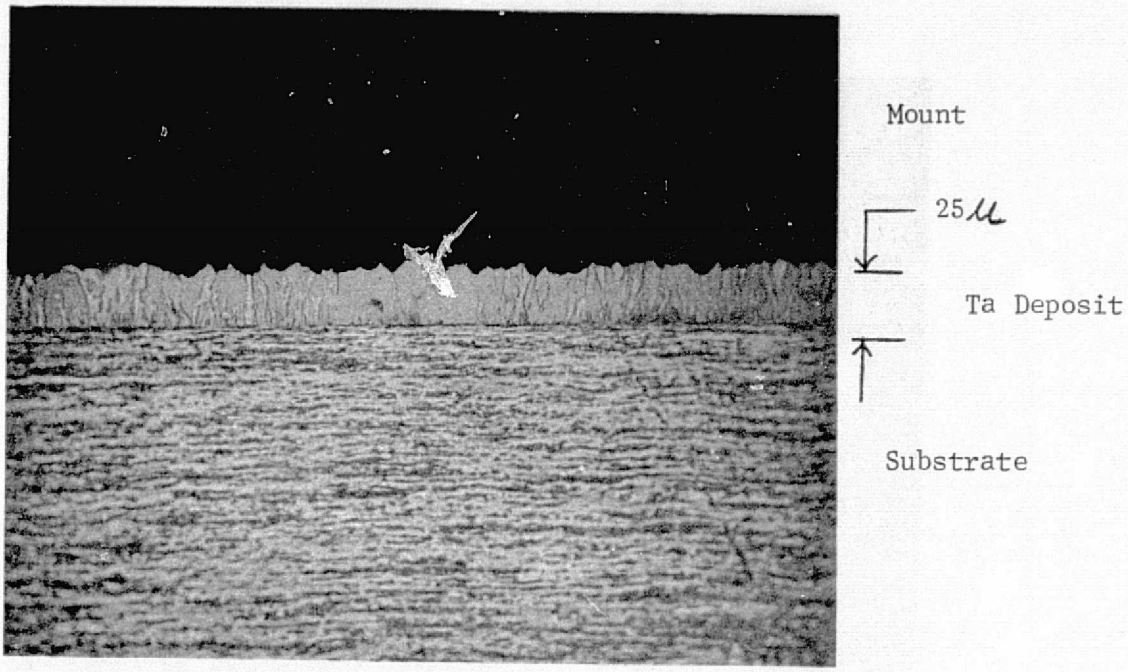
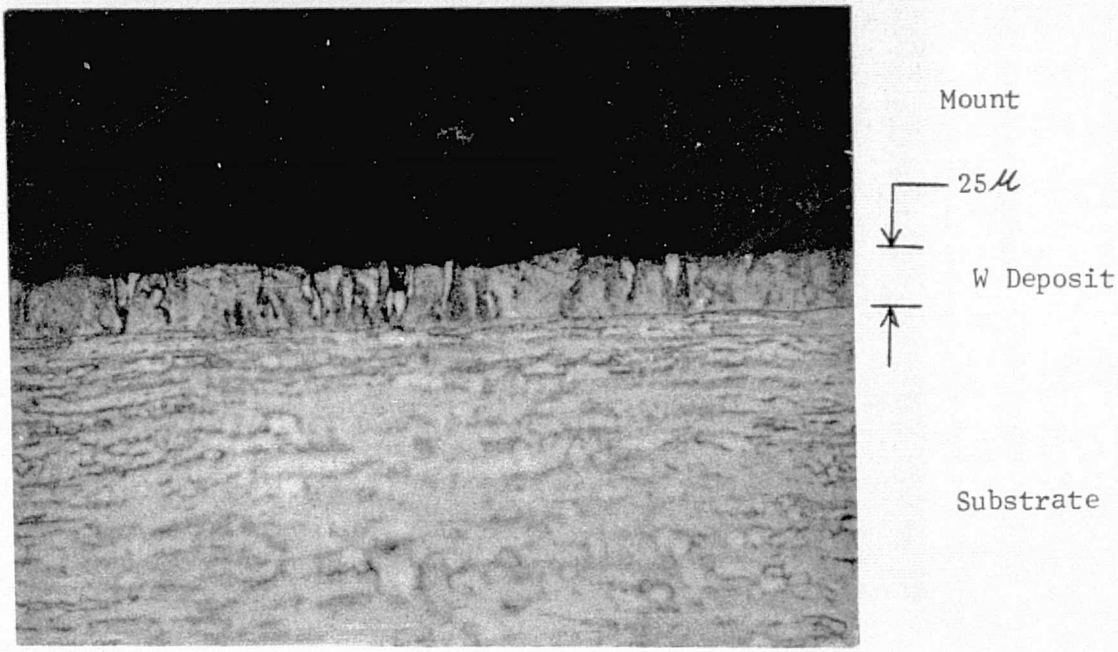


Figure 6. Detailed Schematic Drawing of Equipment Used in "Pulse" Process



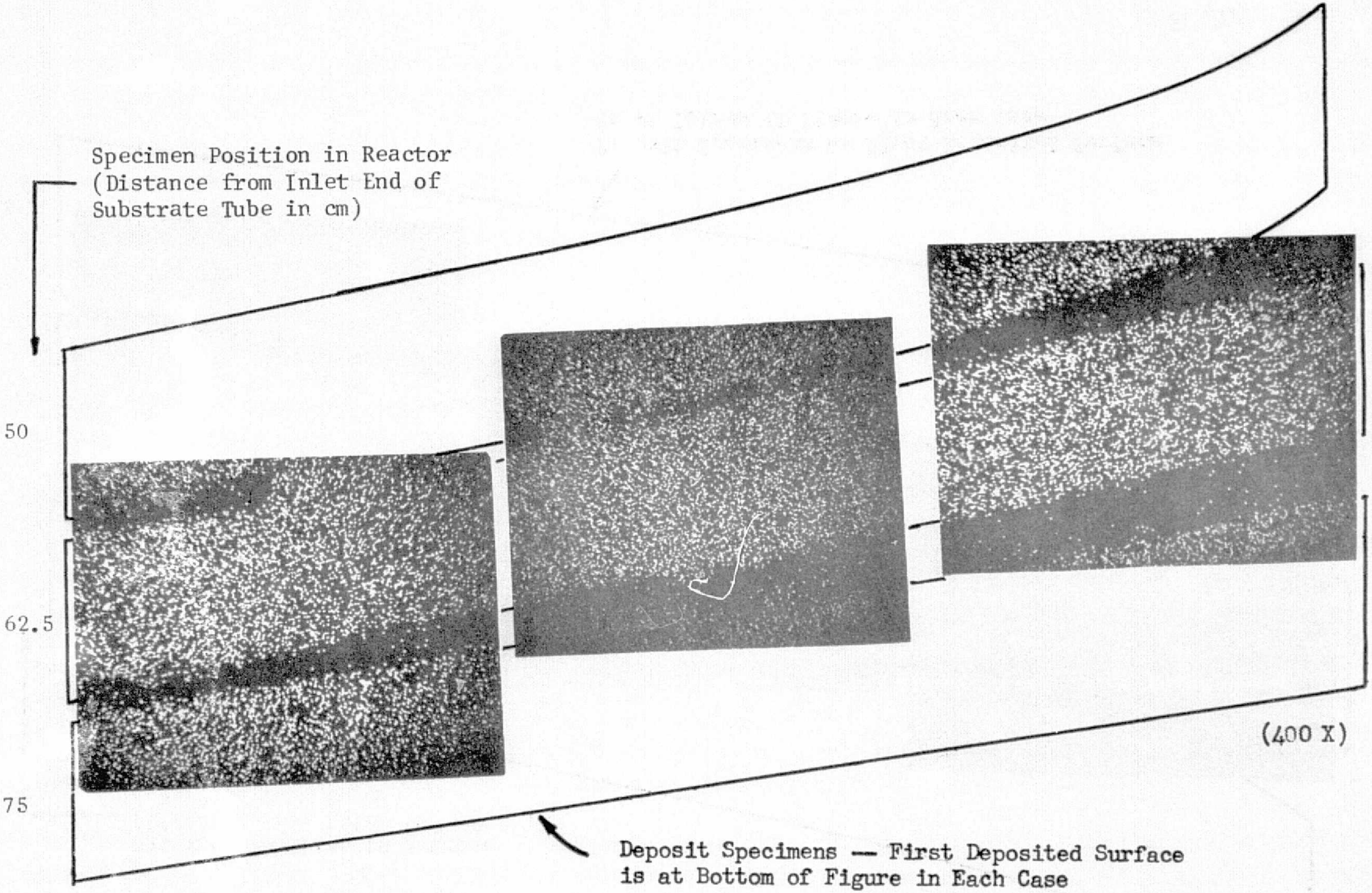
(400 X)

Figure 7. Microstructure of CVD Tantalum Produced by "Pulse" Process



(400 X)

Figure 8. Microstructure of CVD Tungsten Produced by "Pulse" Process



Specimen Position in Reactor (Distance from Inlet End of Substrate Tube in cm)

Deposit Specimens — First Deposited Surface is at Bottom of Figure in Each Case

Figure 9. X-ray Scanning Image for Tungsten in CVD Ta-10W

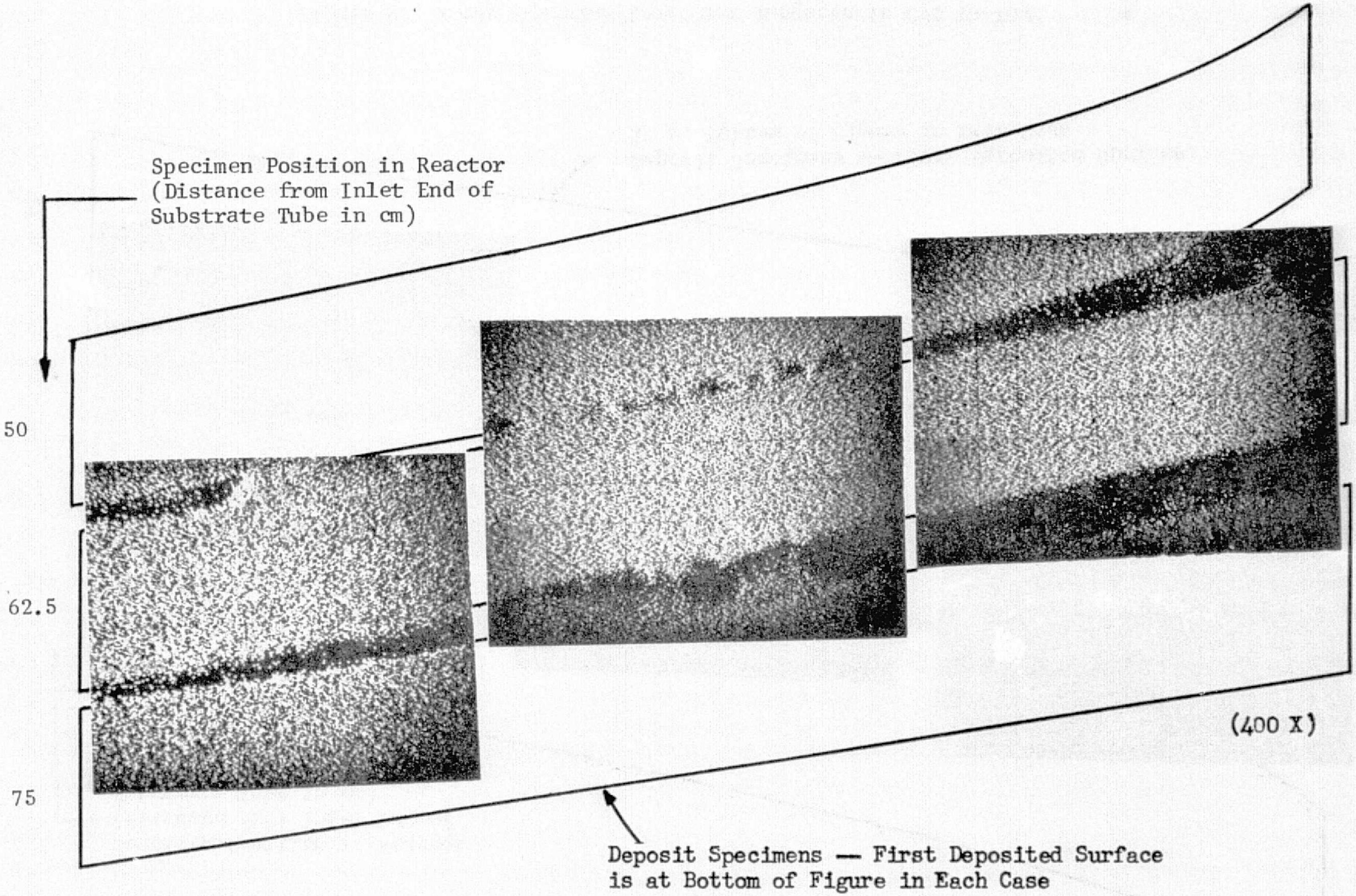
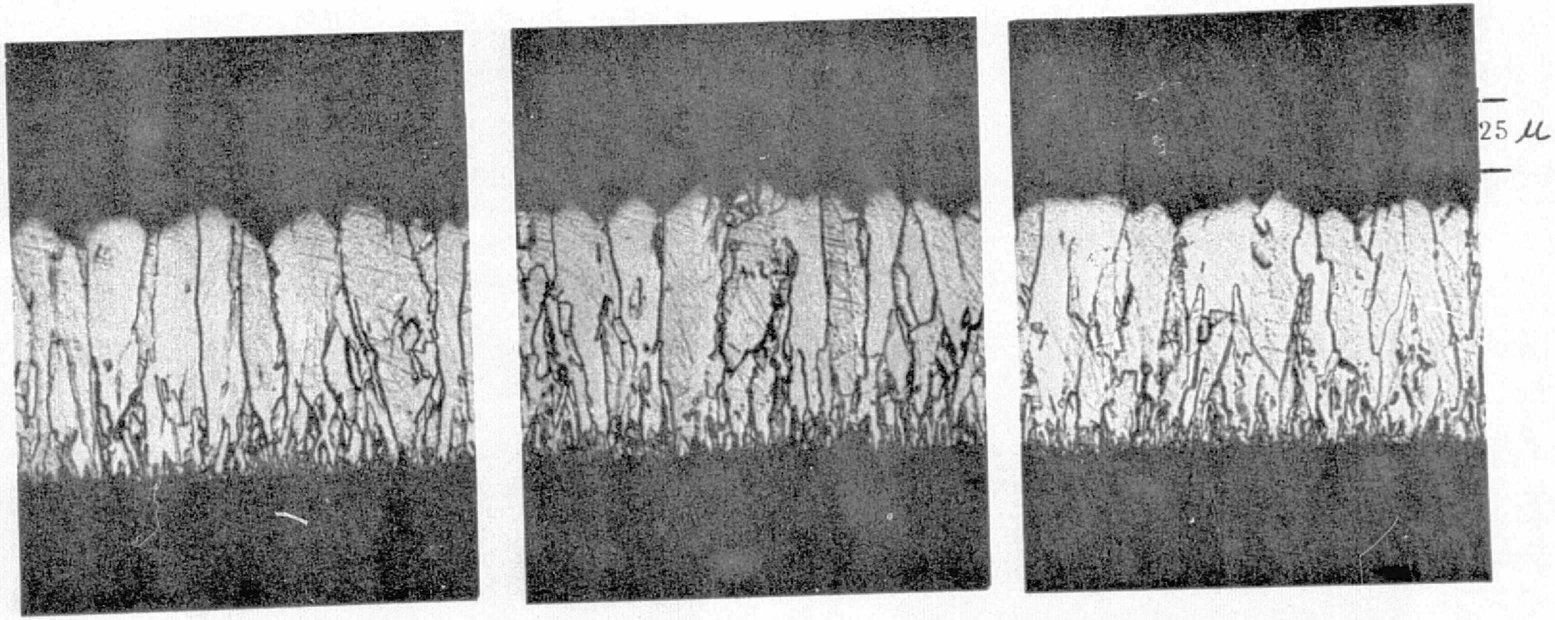


Figure 10. X-ray Scanning Image for Tantalum in CVD Ta-10W



50 cm

62.5 cm

75 cm

Distance from Inlet End of Substrate Tube

Figure 11. Microstructure and Deposit Thickness Uniformity of Ta-10W Produced by "Pulse" Process

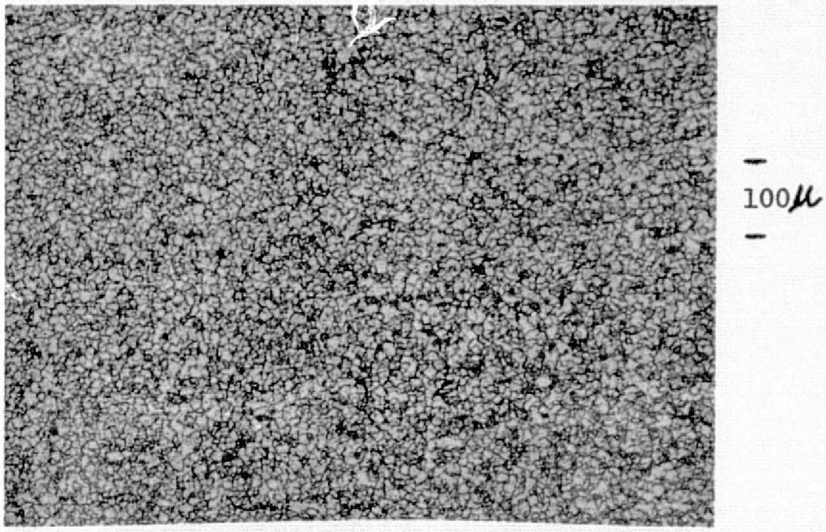


Figure 12. Microstructure of CVD Ta-10W in Plane Parallel to Substrate

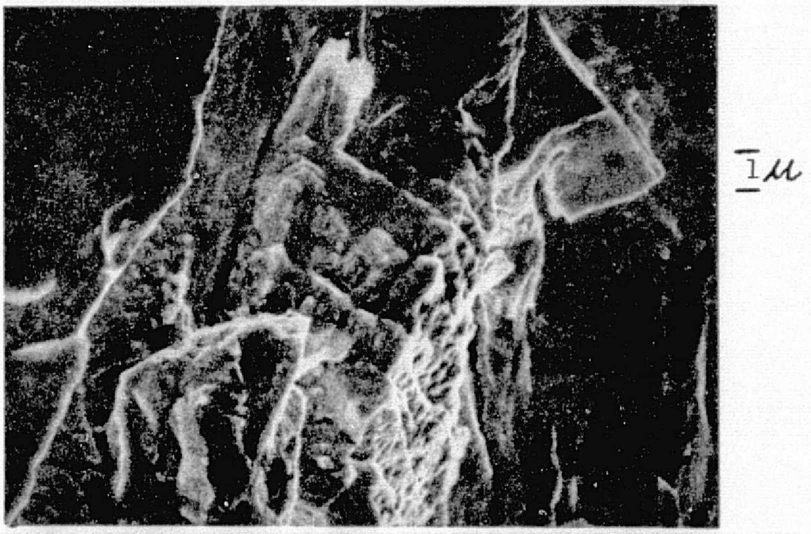


Figure 13. Fracture Surface of CVD Ta-10W

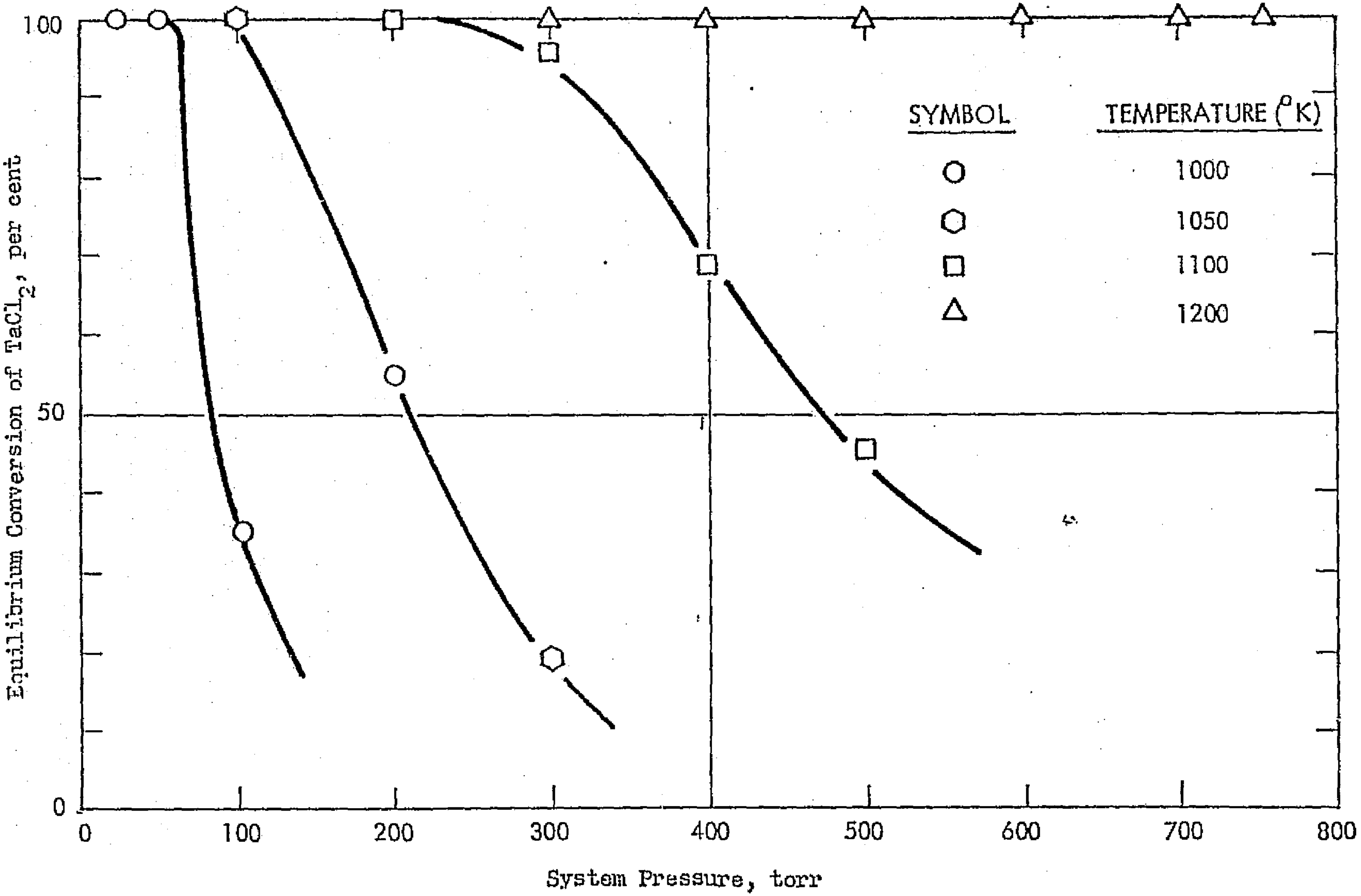


Figure 14. Equilibrium Conversion of $TaCl_2$ for Initial $H_2/TaCl_5$ Ratio of 9.0