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**AN APPARATUS FOR COATING CERAMIC
MONOFILAMENTS VIA CHEMICAL VAPOR DEPOSITION**

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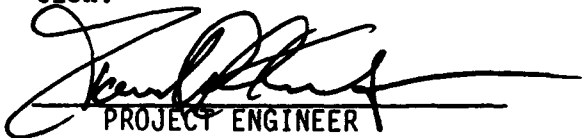
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SUMMARY

A description is given of the design, construction, and operation of an apparatus for the coating of ceramic monofilaments using chemical vapor deposition. Coated filaments are desired in order to investigate issues pertaining to the processing and mechanical properties of ceramic matrix composites. Specific examples are given of processes and results of coating experiments for several different materials including metals and ceramics.

As an example of ceramic coatings, silicon carbide was deposited on carbon rods from a methyltrichlorosilane-hydrogen mixture. Fibers were not coated with silicon carbide but the results of these coating experiments were used to provide an initial check of the operation of the system.

Carbon was deposited on silicon carbide and sapphire monofilaments using a number of reagent gases. The best results were obtained using propylene-argon mixtures. Coatings up to approximately 200 nm can be applied to any fiber. These coatings appear very dense, uniform, and are sufficiently adherent for consolidation into composites. Thicker coatings, up to one micron, are very difficult to apply to sapphire fibers. The two problems encountered in this system are spalling of the coating and the slow growth rate. Coating quality must be sacrificed to achieve fast deposition rates.

Several metals were deposited on silicon carbide fibers by direct chlorination of the metal and subsequent hydrogen reduction of the metal chlorides at the fiber surface. The metals easily deposited include zirconium and tantalum. Metals deposited with more difficulty include molybdenum, cobalt and tungsten.

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1.0 INTRODUCTION

Ceramic materials have found uses in many high temperature structural applications. However, due to the inherent brittleness of most ceramic materials the interest in monolithic ceramics is being replaced by composites incorporating fibers or filaments as reinforcements in ceramic matrices.[1] The design of current ceramic, glass, and glass-ceramic matrix composites is somewhat limited by the scarce number of different types of available fibers and the oxidation behavior of the composite constituents. In recent years it has become evident that weak interfacial strengths are a necessary condition to obtain a tough ceramic composite material.[2] To date, the materials found to best generate such weak interfaces are carbon and boron nitride, usually applied as a coating to the reinforcement fibers.[3,4] Both carbon and boron nitride are easily oxidized at fairly low temperatures. Therefore, it is desirable to find other materials or compounds which are stable in oxidizing environments to above 1000°C, easily applied to fibers or filaments, and lead to a sufficiently weak interface for composite toughening. The purpose of this work is to investigate these first two issues and feed experiments aimed at defining the third.

The systems chosen to investigate the issues mentioned above consist of ceramic monofilaments (SiC and single crystal sapphire) and glass or ceramic matrices. In general, the composites consist of unidirectionally aligned filaments in a matrix densified by hot pressing. To apply coatings to the fibers before consolidation into composites, chemical vapor deposition (CVD) was chosen. The advantages of the CVD method include the wide range of elements and compounds that can be deposited, uniform surface coating that is not line of sight, and the high purity of deposited materials.[5] The fibers of interest are received and coated as single, long

filaments which can be wound on spools and laid-up into tapes for incorporation into composites.

The CVD process involves several general steps as follows:[6,7] Appropriate gases are fed to the atmosphere near the substrate (fiber), gases diffuse to the surface and react leaving atoms of the material to be deposited, product gases diffuse away from the surface and are carried away. The substrate is held at an elevated temperature sufficient for the decomposition of the reactant gases. The process variables - temperature, pressure, and gas composition - necessary to deposit a given material are dependant on the thermodynamics of the particular system. Specific domains of process variables in which it is possible to obtain a given deposit composition may be determined from calculations involving the thermodynamic properties of the components in the system.[8,9]

The hardware requirements for a chemical vapor deposition apparatus include gas control and delivery, pressure/vacuum control, substrate heating, and exhaust gas treatment subsystems. In this case there is also a need for an apparatus to contain and transport the fiber through the coating chamber. These components and their interrelationships will be detailed in the next section.

2.0 DESIGN AND CONSTRUCTION

As there is no *a priori* knowledge of what compound or material will generate a "good" interface material in any given composite system, the CVD system to be constructed was deemed necessary to have as much flexibility as possible for producing a wide variety of coatings. The main process variables which affect the design of a system include temperature of the substrate, pressure in the deposition chamber, and types and quantities of gases passed through the

deposition chamber. Therefore, this system requires three main controlled subsystems in addition to the deposition chamber, fiber handling and transportation device, and the electrical and plumbing interconnections between the various components.

For vacuum generation and pressure control, a mechanical, oil sealed pump was chosen. This pump is equipped with oil filtration, inert gas purging, and filled with an inert oil to withstand pumping corrosive and oxidizing gases. To control pressure at any desired value from approximately 1 torr (133 Pa) to atmospheric, a solenoid driven ballast valve is incorporated in the vacuum line downstream from the reactor chamber. To increase the pressure in the deposition chamber, this valve is opened allowing an inert gas to flow into the vacuum line effectively slowing down the pump. This valve is controlled by the appropriate read-out and control device from which it is possible to select the desired pressure.

In order to achieve deposition onto a fiber, the fiber or a portion of it must be heated to temperatures sufficiently high to cause decomposition or reaction of the precursor gases. Since some of the fibers that are to be used as substrates can not be resistively heated, the most general heat source was deemed to be a tube type resistance furnace. This selection means that the CVD system is a hot-wall type reactor which implies that deposition will also occur on the walls of the deposition chamber. By contrast, in a cold-wall reactor only the substrate is heated and deposition occurs only at the substrate. The cold-wall case typically allows for deposition of cleaner films due to the smaller chance of nucleation in the gas phase and elimination of particles shedding from the chamber walls. The furnace chosen is a single-zone platinum wound resistance furnace 18 inches in length. The temperature is controlled by a pid type

controller receiving input from a set point and a single thermocouple centered in the furnace. The furnace is capable of operating at temperatures up to 1600°C although the limit of the quartz muffle tube is about 1350°C. Temperature profiles were obtained through the length of the furnace and are shown in Figure 1 for three set point temperatures. This profile is obtained after installing a series of shunts across the central sections of the furnace giving a more uniform profile along the center third of the furnace.

In addition to flexibility in temperature and pressure, there is also a need for flexibility in the amount and type of gases to be used for deposition of different materials. A two channel flow system was chosen to allow for the separation of two different precursor gases up to the point of being mixed in the deposition chamber. This will allow for the prevention of condensation reactions in the plumbing and also for the chlorination of metals followed by hydrogen reduction of the metal chlorides further up stream. Many source materials are obtained as compressed gases. These may be used directly from the storage cylinder after pressure control by a regulator. Other source gases must be generated from either liquid or solid compounds such as methyltrichlorosilane or tantalum pentachloride respectively. Specific examples of each of these cases will be given later.

Once the gases of interest are generated and available at sufficient pressures, the flow must be controlled before introduction to the deposition chamber. Electronic mass flow controllers were chosen to measure and control the flow rate of gases. These devices measure the quantity of heat transferred by the flowing gas which is directly related to the mass flow rate of the gas. The readout and control device converts the signal from the mass flow controller to volume flow which is normally stated in standard cubic centimeters per minute (sccm). By measuring the actual flow

and comparing to the set point value, the instrument opens or closes a valve to regulate the flow. These instruments have a very fast response time and good range and resolution of flow rates. Six flow controllers with nitrogen flow ranges of 50, 100, 100, 200, 200, and 500 sccm each are arranged such that three to six channels can flow into one path to the reactor and the remaining three to none can flow into the second path to the reactor. The flow schematic is given in Figure 2. All gas plumbing lines are welded stainless steel except for the vacuum hoses which are PVC.

After passing through the reactor and forming a deposit on the fiber (and tube wall) the gases are passed through the pump and to exhaust treatment before being discharged to the atmosphere. First the exhaust is passed through a scrubber which captures and neutralizes any acid gases and also acts as a filter. The gases neutralized include any halogenated source gases as well as product HCl. After being neutralized, the remaining gases, typically hydrogen and argon, are burned off by passing over a heated SiC burner element. The burner assembly utilizes a redundant burner system so that if one element burns out the second is automatically energized. The temperature is monitored in the burner unit to assure sufficient temperature for safe hydrogen combustion. In the event of under temperature in the burner area an alarm is triggered. A differential pressure guage will also trigger the alarm in the event of no flow due to over or under pressure.

The final part of the coating system is the fiber holding and transporting device. The fiber is stored and wound onto 8 inch diameter spools. The take-up and supply spools are housed in separate stainless steel vacuum chambers. Typically the supply spool is above the vertical reactor tube and the take-up spool is below. The spool chambers are attached directly to the ends of the reaction chamber with

vacuum flange fittings. The size of the orifice between the spool chambers and the coating chamber can be from one inch inside diameter to as small as desired. Typically, an 0.1 inch orifice is inserted to allow for pulling fiber and to prevent gas flow into the spool chamber. Guard tubes can also be inserted which shield the fiber from coating gases in regions outside the furnace hot zone. These fittings also allow for process gas inletting and exhausting as well as for attachment of a pressure guage which feeds back to the pressure monitoring and control device. The supply spool rides on an axle and is turned by pulling the fiber with the take-up spool. Brushes act as brakes to prevent free spinning of the supply spool. The take-up spool is caused to turn on a threaded rod which simultaneously moves the spool laterally such that the coated fiber is not wound on top of itself to prevent damage. The spool is turned by a variable speed DC gearmotor coupled through a vacuum tight rotary motion feedthrough. The tension in the fiber is only controlled by the act of the brushes on the supply spool. No problems have been encountered with either breakage or uncontrolled pay out of the fibers. Figure 3 shows the assembled system except for the pump, scrubber, and controller cabinet.

3.0 OPERATION AND RESULTS

The general operation for all coating experiments is basically the same sequence of steps. The two different cases studied have been batch processes, where only one or several pieces of fiber (or rod, etc) are suspended in the coating chamber, and continuous coating, where lengths of monofilament is pulled through the chamber. The coating chamber used in all the current experiments is a fused silica tube 20mm ID by 25mm OD and 750mm long. The tube is held at the ends by vacuum tight o-ring compression fittings.

Differences in experimental procedures for coating different materials will be given below for three individual cases.

The first step involves assembling all parts that will be required including all electrical and plumbing connections and mounting of the substrate fiber. After all required gases or other source materials are plumbed to the flow meters, the process variables can be selected and input to the various controllers. The entire gas flow path is then purged either by vacuum evacuation or flow of inert gas. The deposition chamber and all piping from gas supply to the pump is evacuated to the limit of the pump, approximately 5×10^{-2} torr (7 Pa), and checked for the absence of leaks by isolating from the pump and monitoring the vacuum gauge for a period of time. If necessary, the chamber and piping is backfilled with an inert gas to the desired operating pressure. It is essential due to the reactive and/or flammable nature of many of the gases used that all oxygen is purged from the system and all leaks eliminated before introducing the flow of any gas.

Once the system is leak checked and the process parameters determined, the coating process can begin. After the desired deposition temperature and pressure are obtained, the coating gas flows can be established first through the pump/scrubber/burner line and then routed to the coating chamber. Typically, 100 sccm of argon is passed into both spool chambers to prevent coating gas intrusion into these chambers. After the desired reaction time for batch processes or the desired length of fiber is coated by being pulled at the desired rate, the reactive gases can then be again emptied to the scrubber/burner line and shut off at the source. The furnace is shut down and the system can again be purged by vacuum evacuation or flow of inert gas and backfilled with argon before the coated fiber is removed. It

is again very important that all process gases be purged from the system before opening to the atmosphere.

3.1 Ceramic Coatings

As a representative example of deposition of a ceramic material, silicon carbide has been deposited from methyltrichlorosilane (MTS).[10,11] In this case, the substrate used was a 3mm diameter graphite rod suspended with graphite yarn. The coated rod can be sectioned to determine the coating thickness at different locations along the chamber as well as radially. The MTS is allowed to flow directly from the storage cylinder through the mass flow controller. Deposition at pressures higher than 100 torr(13.3 kPa) require heating of the MTS cylinder to achieve a sufficiently high vapor pressure. Deposition has been achieved at temperatures between 1200-1300⁰C, pressures from 50-150 torr(6.7-20 kPa) with H₂:MTS approximately 10:1. A representative SEM photomicrograph of a coated rod is shown in Figure 4. It is seen that the coating is very uniform around the circumference of the rod. The thickness along the length of the rod is seen to vary as shown in Figure 5. This information has been used as validation of a model developed elsewhere[12] to predict the coating of fibers by the CVD process.

3.2 Carbon Coatings

As mentioned above, carbon is the coating which has received the most attention and has proven to be effective in creating tough glass and ceramic matrix composite materials. Controlled carbon coatings are desired as part of continuing efforts in studying mechanical behavior of composite materials. In addition, carbon coatings are also being investigated as sacrificial, physical barrier layers that can be removed from the composite by oxidation after processing.

Using this CVD system, carbon has been deposited on both single crystal sapphire and silicon carbide fibers. Several different starting gases have been used to generate carbon coatings including methane [13], acetylene [14], propane [15], and propylene [16]. While dense, smooth, adherent layers can be deposited on stationary fibers to any desired thickness, coatings on moving fibers are generally of lower quality or thickness. In addition, carbon produced from methane decomposition on sapphire fibers easily spalls off. In order to obtain adherent coatings, a lower temperature precursor was needed. Using propylene, carbon can be deposited as low as 850°C at atmospheric pressure, whereas methane requires at least 1050°C. Representative coatings deposited from propylene on sapphire and SiC fibers are shown in Figure 6. In order to obtain long lengths of carbon coated fibers, the coating quality generally must be sacrificed due to the slow growth rate. Alternatively, slow growing, high quality thin films can be applied several times on a given length of fiber to obtain the desired thickness.

3.3 Metallic Coatings

In order to find materials which can withstand oxidizing environments at temperatures higher than carbon or boron nitride, coatings of several different metals have been attempted. Cobalt was studied as a low cost substitute for iridium to examine the feasibility of coating by chlorination of the metal. Tantalum was also deposited on fibers since this method has been used extensively for producing tantalum films.[7,17] Similar conditions were used for coating both cobalt and tantalum. Metal films were deposited by hydrogen reduction of metal chlorides generated within the process tube. In most cases it is possible to obtain metal chlorides or organometallic compounds as the precursor materials.[7,17] Direct chlorination was chosen in this case since a large variety of metals can potentially be deposited with only one

piece of glassware. Also eliminated is the problem of storing, transporting, and disposing of a large number of corrosive or toxic metal compounds.

A schematic of the process tube with chlorinator is shown in Figure 7. Chlorine is passed over the metal foil or sponge held in the heated chlorinator generating volatile metal chlorides which are swept into the deposition region of the process tube. Heating wire is wrapped around the chlorinator and process tube to the end of the coating furnace. The entire process tube is constructed of fused silica tubing with the deposition tube the same dimensions as before and the chlorinator portion approximately 10mm ID by 35mm long.

In the initial experiments, cobalt was chlorinated between 350 and 500°C with Cl_2 flows between 10 and 30 sccm. Very thin cobalt layers were deposited on short sections of fibers at 800 and 900°C and 20 torr (26.7 kPa) with 200 sccm H_2 . The cobalt foil was slow to react and, therefore, very little metal was carried to the deposition chamber. It seems likely that a dense scale is formed preventing further reaction at the cobalt surface after 30 to 60 minutes. Upon removal of the process tube, small amounts of metal films were found at the junction of the chlorinator and main tube, and in the deposition tube at both the top and bottom of the furnace. It is likely that further refinements of the temperature ranges over which the metal is chlorinated and deposited will need to be made before long lengths of fibers can be continuously coated. Tungsten behaves similar to cobalt but with much more of the metal depositing in the tube below the furnace.

Tantalum films of approximately one micron thick were readily formed on long lengths of fibers (2 to 3 meters). Again at 20 torr (26.7 kPa) total pressure, the metal was chlorinated at 450°C with a flow of 5 sccm Cl_2 plus 5 sccm Ar. The

deposition chamber was held at 850⁰C with a 100 sccm flow of H₂. The chlorinator used for these experiments did not have the capacity to hold enough tantalum foil for coating longer lengths of fiber. A larger metal chlorinator will be necessary to coat more than 3 meters of fiber and to insure that there is always an excess of metal in the chlorinator. In some cases the deposition is not uniform along the length of the fiber. This is due to the variability of the area of metal foil in contact with the chlorine gas over time. SEM micrographs of representative Co and Ta coatings are shown in Figure 8. Zirconium and molybdenum were found to behave much like tantalum under similar conditions.

4.0 CONCLUSIONS

It has been shown that the chemical vapor deposition apparatus constructed as detailed above is capable of applying coatings of various materials to small diameter fibers. Coatings other than metals can be easily applied to fibers in lengths long enough to generate tapes for laying up composites. Specifically, a sample 4X4 inches with six layers of fibers could be made using one run of continuously coated fiber. Metallic coatings have not been applied to lengths of fiber more than about 3 meters long. The problems associated with producing longer lengths include the small volume of metal that can fit into the chlorinator used and the uncertainty in the temperature regime over which certain metal chlorides can be generated and transported to the deposition chamber. The first problem may be easily remedied but a solution to the second will require extensive research. When and if a suitable metal is found to help in generating good composites, then an appropriate metal compound (metal chloride or organometallic) can be purchased for use in more reliably depositing metal films on long lengths of fiber.

Uniform, dense carbon coatings (up to approximately 200 nm) which conform to the surface of the fiber can easily be applied. However, thicker carbon coatings cannot be easily produced without sacrificing the quality of the coating. In general, to apply a thick coating (for example 1 micron) in a reasonable period of time, higher temperatures and reactant concentrations must be used. This typically leads to homogeneous nucleation and the incorporation of particles in the growing film as is seen in Figure 6. The thickness and, most likely, density of these coatings is much lower than that of thinner coatings. Only by increasing the residence times of the fiber in the furnace can thicker, smooth carbon coatings be applied. Either a longer furnace or a slower winder motor could be obtained for this purpose.

Silicon carbide is readily deposited from MTS at rates as shown in Figure 5. Coating of fibers with SiC has not been attempted so no conclusions about the uniformity or microstructure of coatings on moving substrates can be drawn. However, it is believed that thick coatings of SiC and similar materials can be readily applied to fibers by the use of this system.

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Appendix 1

Operating Instructions For Coating Tantalum on Fibers

In the text of this report, a generic description was given to illustrate the general operation of the fiber coating system. In this appendix, specific instructions will be given for coating tantalum (or other similar metals) onto a length of fiber. The steps involved include physically assembling the reactor along with the plumbing and electrical connections, ensuring that all reagents are available and plumbed to the system, installing the fiber, setting process variables, coating fiber, shutting down the system, and coated fiber removal.

The first step involves assembling the system with all necessary parts and connections. Referring to figures 2, 3, and 7, the reader can see the arrangement of parts necessary. It is generally easiest to insert the desired amount of metal into the chlorinator portion of the process tube and wrap with heating wire before inserting into the furnace. Glass fiber insulated heating wire or thermocouple extension wire works well for heating the chlorinator. Approximately 12 feet of wire are required and is wrapped as shown in figure 3. It is important to keep fingerprints off any heated portion of the quartz tube to avoid devitrification and weakening of the glass. It is also advisable to wear gloves when handling fiber glass insulated heating wire.

If the system is not at least partially assembled, then it is easiest to start from the top and work down. The supply spool box is set on the rack above the furnace with a length of fiber inside. Below the box is the 5-way KF-flange vacuum tee. The sealing ring for the KF-flange between these two should include the shield tube extending several inches into the top of the furnace. This quartz tube is held in the flange sealing ring with a piece of machined teflon. Next the adaptor KF to 1" Ultratorr fitting is attached to the bottom of the 5-way tee. The 5-way tee is also mounted to

the frame with the machined aluminum collar. The position of the top spool box may be adjusted to align with the tee collar and the furnace. The process/chlorinator tube may now be inserted from the bottom of the furnace (if the take-up spool box is out of the way) and held in the top Ultratorr fitting while the bottom box and fittings are assembled. On the bottom of the process tube, another 1" Ultratorr to KF-flange adaptor is attached and held to the frame with its respective collar. The most difficult part involves aligning and connecting the bottom spool box. In order to slide the lower box in place, the fitting and tube must be pushed as far up as possible. The box with its required sealing ring (already inserted into the bottom of the tube/fitting assembly if a shield tube is used) should slide under the the adaptor fitting with 1/4 inch or less clearance. If this distance is too large or small, then the support for the winder box must be adjusted up or down on the frame. New tubes should be made to close tolerances so as to avoid moving the box support structure. The box can then be centered and leveled before the bottom adaptor fitting is allowed to slide down and be clamped to both the box and frame.

The final connections to the process tube and boxes can now be made. The belt to turn the winder can be gently pressed onto the moving motor pulley after the spool is placed near the right hand edge of its travel. The fiber must be threaded through the tube and attached to the take-up spool with a piece of tape. It is often easier to thread the fiber through the tube before the lower box is installed. The motor should be advanced slowly by applying power to the controller to remove slack from the fiber while making sure that it is aligned properly and following the guides. Each box has one gas line inlet that must be attached if they were previously removed. When attaching the doors to the boxes, ensure that the sealing and o-ring surfaces are clean and tighten the screws evenly. The remaining plumbing

connections are the pressure guage, vacuum hose, blank off flange at the top (5-way KF-flange) and the two gas inlets at the bottom. For chlorination of metal, chlorine flows into the chlorinator tube and is connected using a 1/4 inch Ultratorr fitting. Hydrogen flows into the adaptor fitting below and is connected using a VCR fitting. The other end is connected as shown in figure 2. The open ground glass ball joint is sealed with the other part of the joint and associated clamp. A leak tight seal is made by wrapping the male part of the glass joint with teflon tape. A thermocouple is held against the chlorinator tube in the vicinity of the metal by placing it under the heater wire and tightly winding the wire around the tubing. The ends may be secured by wrapping around a tab on the tube or around a larger piece of wire tightly turned to the tube. The ends of the heater wire are connected to the terminal strip glued to the top of the winder box as are the leads from the variable voltage transformer. The entire chlorinator and process tube up to the bottom of the furnace is wrapped with insulating blanket.

Now that the process tube and boxes are in place, it should be verified that the reactant gases are plumbed to an appropriate mass flow controller(MFC). The system should have been left as depicted in Figure 2 with hydrogen plumbed to MFC's 1 and 3, argon plumbed to MFC2 (to the boxes) and MFC4 (MTS purge line), and with chlorine plumbed to MFC6 to the process line not used by hydrogen. If these gases are not in place, then the gas cylinders will have to be installed and plumbed to an appropriate MFC. The regulator(s) and line(s) from the cylinder to the MFC should be vacuum purged and backfilled with the appropriate gas. This purging should take place after all leaks have been eliminated and the necessary safety systems (scrubber, burner) initialized and operating.

With the exception of the furnace controller, all of the readout and control modules are mounted in a cabinet outside

the fume hood containing the reactor. Gas flows and pressure are set on the 247C and 250B controllers, respectively. In addition, push buttons for operating valves, power supplies, and other electrical connections are mounted in this cabinet. All valves except the butterfly valve (B in figure 2) are normally closed and pneumatically operated. The gas supply for these valves flows into the cabinet and is distributed to the desired valve via a solenoid valve operated by a push button on the front of the cabinet. A light on in the button indicates that the corresponding valve is open. Inside this cabinet is a binder which contains plumbing and electrical schematics, instruction manuals for the various components, and bulletins on spare and replacement parts that may be necessary. The vacuum pump is generally left running unless it is not used for extended periods of time. The pump is energized with a toggle switch on the pump body.

To begin a coating experiment, the system must be evacuated and checked for leaks. First, ensure that a compressed gas supply is on to the cabinet to supply the solenoid valves. The "VAC" valve is opened and then the butterfly valve is slowly opened to vacuum purge the system. As the connections between the fiber spool boxes and the process tube are through fairly small orifices, pump down times are long. Typically, the system will pump down to one torr or less in about 30 to 60 minutes. Further pump down to below 500 microns takes several hours. If very low pressures are needed (the limit of the pump is approximately 40 microns) then overnight pump down may be required. A thermocouple vacuum gauge attached on one of the ports of the 5-way KF flange will make leak checking easier. Once the pressure is down below 500 microns, the "VAC" valve can be closed and the pressure monitored to check for leaks. Two situations may arise that give the impression of a leak when none exists. First, the ballast valve (MKS 248A) usually does not close leak tight so the line leading to this valve must also be purged to the next positive shut-off valve.

Second, if the system is not pumped for a sufficient period of time the boxes will still be at a higher pressure than the process tube and gas will still be flowing out of these.

After all leaks have been eliminated from the system the two exhaust treatment components need to be readied. The first filters and captures any acid gases from the exhaust stream. The second is a burner to safely burn off any flammable gas and prevent the buildup of flammable gases in the room. The scrubber consists of sodium hydroxide suspended on diatomaceous earth particle and must be moistened before use. There is a water reservoir inside through which an inert gas can be directed to moisturize the adsorbent. This will also help purge residual air from the scrubber. Both columns in the scrubber cabinet should be thoroughly purged with an inert gas either by flowing through the pump or the hydration tank to prevent the combustion of hydrogen inside these cylinders. There is a check valve between the scrubber and the burner units to prevent the backflow of air into the scrubber. This should be checked during routine maintenance to ensure that it has not been plugged or stuck open. The hydrogen burner consists of redundant SiC burner elements and a temperature sensor. The controller shows the status of the temperature and pressure to ensure that safe combustion can occur. The burner should be turned on before the start of hydrogen gas flow to ensure that it has reached operating temperature but not before the system is completely purged of air. Manufacturers instruction manuals should be kept in the control cabinet for both of these units.

While the scrubbing equipment is being initialized, the furnace may be turned on and allowed to heat up. It has been found that the temperature overshoots the set point when the furnace is first turned on and that it requires two to three hours for the temperature to stabilize at the set point (for set points of 800-900°C.) After approximately two hours at the set point 800°C, the furnace set point can be changed to

the desired deposition temperature. The current furnace controller has a minimum set point temperature of 800°C, but other controllers may be available which have lower minimum temperatures.

Before starting gas flows to the reactor, the lines from gas cylinders to the MFC's can be purged and backfilled with the appropriate gas. This can be accomplished by opening the valve upstream of the MFC and turning the MFC on while allowing the gas to flow through the pump. The other valves to the process tube can be closed during this purging. Operation of the MFC's is described in detail in the manufacturer's instruction manual.

Now the desired process variables can be input into the appropriate controllers. The furnace (deposition) temperature is usually set first since it requires the longest time to equilibrate. The heater for the chlorinator is turned on next. This requires 1/2 to one hour to equilibrate to the desired temperature. Typical temperatures are 800-900°C and 400-500°C for the furnace and chlorinator, respectively. Gas flows are set on the front of the 247C and pressure is set on the front of the 250B controllers as described in the manufacturers instruction manuals. With the system pumped down to the limit of the pump, an inert gas, usually argon, is allowed to flow first into the boxes (100 ccm through MFC2) and then into the system through the pressure ballast valve (248A) until the pressure matches the desired operating pressure. Again, the small orifices between the process tube and the spool boxes dictate that pressure equilibrium between the two is achieved slowly. Once the pressure is stabilized at the desired setting, the controller can be set on "AUTO". Typical pressures for coating tantalum are 20 to 30 torr.

With everything now operational, the flow of reactant gases can now be started. Typically hydrogen is allowed to flow into the reactor and equilibrate for 10 to 15 minutes. Then the reactant gas(es), in this case chlorine, is(are)

started and allowed to equilibrate while flowing through the pump and not through the process tube. After stabilizing for 5 to 10 minutes, the reactant gas flow(s) are allowed to flow to the process tube by closing the valve between the respective MFC(S) and the pump and opening the valve between the MFC(s) and the process tube. Typically, the gas flows for depositing tantalum are 100 ccm hydrogen through the adaptor fitting below the tube and 5 ccm chlorine plus 5 ccm argon through the chlorinator tube. With gases flowing to the process tube, the winder motor is started (turning in "Reverse") and set to the desired speed. The chlorination reaction will produce heat so the power to the chlorinator heater element may need to be reduced to maintain a constant temperature.

Once the desired length of fiber has been coated the system must be safely shut down. Usually the chlorine cylinder valve is shut off and the regulator pressure bled off through the system. Once the pressure in the regulator is reduced, the MFC can be turned off and the respective shut-off valve closed. Hydrogen flow is then stopped in a similar manner. The system is then again vacuum purged to remove all hazardous and corrosive gases while the furnace and chlorinator heaters are allowed to cool. Argon is left flowing to the boxes to help flush the system. The pump must also be purged of any corrosive gases (byproduct HCl) by opening the valve on the IGS part of the pump and allowing argon to flow through the pump head for at least 1/2 hour. After approximately one hour the entire system is backfilled with argon through the 248A valve to a pressure of about 750 torr. It is now safe to remove the door from the fiber take-up box and remove the coated fiber. The free end of fiber remaining in the furnace can be reattached to the spool and readied for another run if desired.

Subsequent cleaning and maintenance may be required depending on what is to be done with the system next. Typically there will be some residue left on the process

tube. This can include metal chlorides, metal films and/or powders that have condensed or deposited in the tube. If a different material is to be deposited next, the tube should be changed or removed and cleaned. All stainless fittings should be checked and cleaned if dirty before being left unused. Metal chlorides left on the fittings will cause corrosion and failure of the parts. The exhaust scrubber also should be serviced at regular intervals. The adsorbent canisters must be monitored to ensure that they are not completely used up or dried out. Also, as these contain corrosive materials, the fittings before and after the scrubber should be checked and cleaned approximately every other month. If a particular corrosive gas has been used and is not likely to be used for an extended period of time, the lines between the cylinder and the MFC should be purged of this gas and backfilled with argon.

Most of the pieces of equipment used on this system are described by manufacturer literature or instruction manuals which are kept in the control cabinet. The user should become familiar with all of this literature before attempting to use this system. Repair instructions and replacement part information is also available in this literature. Also held in this notebook are Material Safety Data Sheets for the chemicals and gases used to date in this system. These should be read to inform the potential user of hazards associated with the chemicals used. Any subsequent user of the system who uses other chemicals should also see that the MSDS is incorporated in the manual. One additional sheet in the manual is a record of what has been done in this system and which chemicals have been used. This is important in the event that the vacuum pump needs to be rebuilt and so that the contents of the adsorbent canisters are known when they must be disposed of.

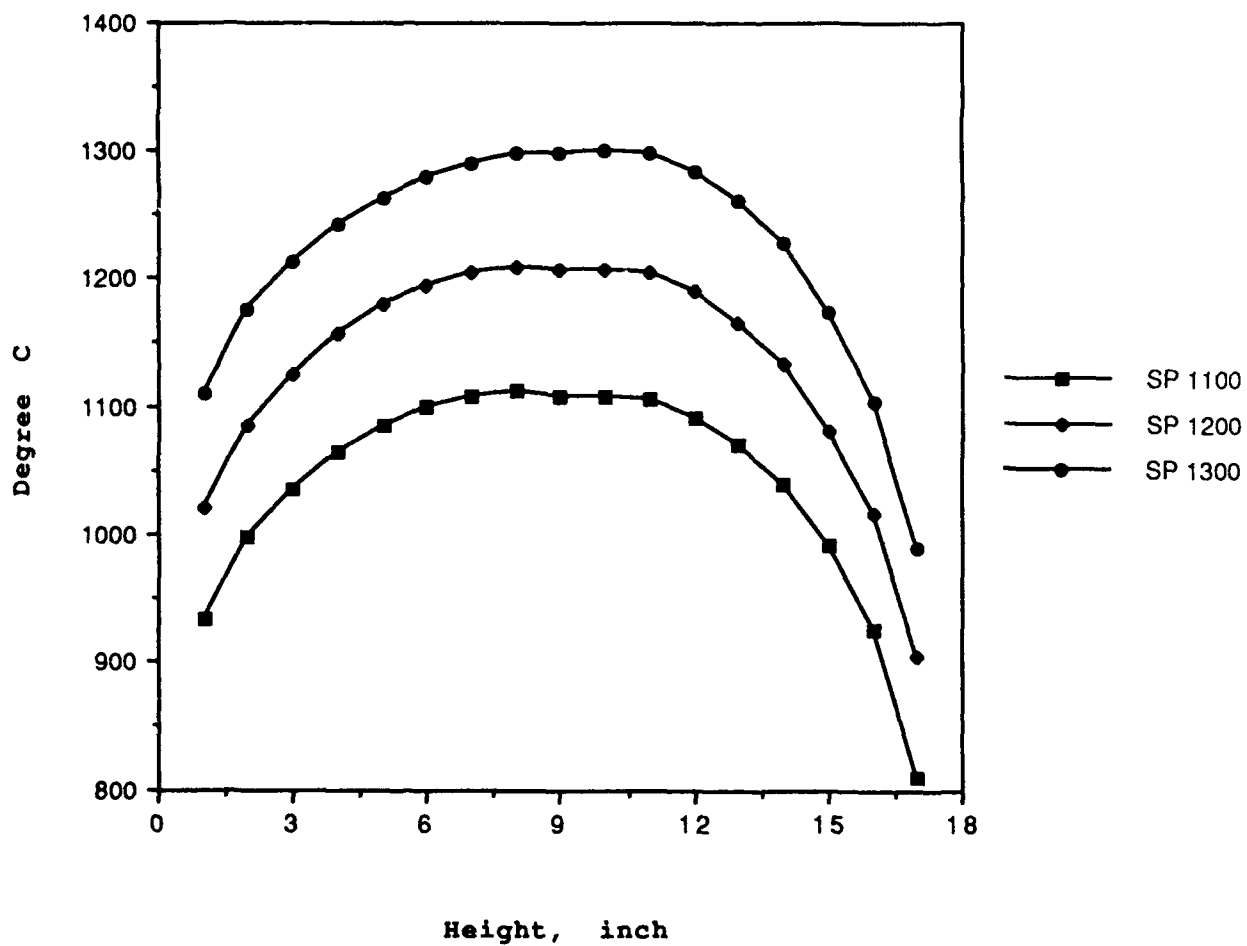


Figure 1. Measured temperature along center line of furnace for three different set points.

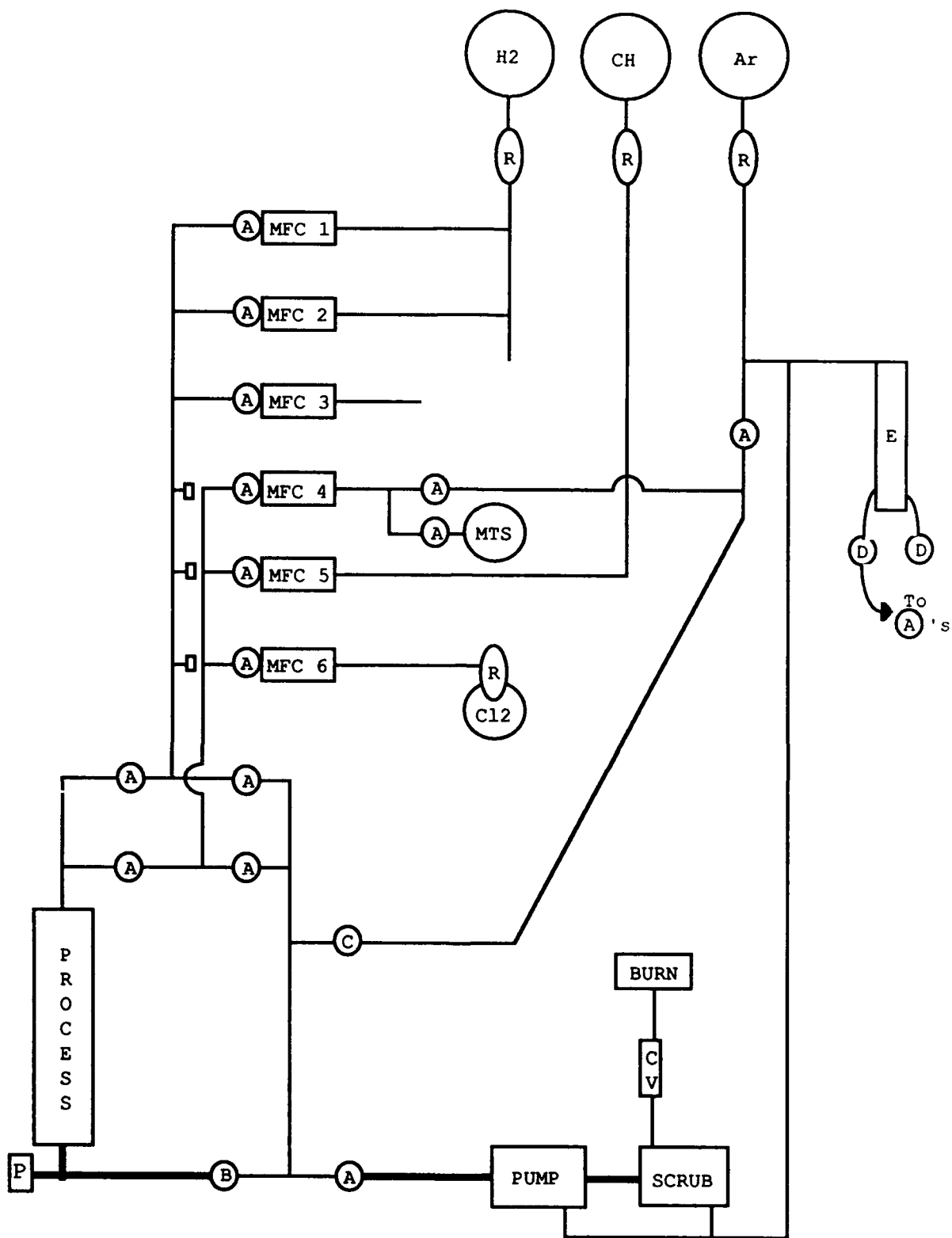


Figure 2. Gas flow schematic

LEGEND

(A)	Nupro 4BK Pneumatic Valve
(B)	MDC Manual Butterfly Valve
(C)	MKS 248A Ballast Valve
(D)	Skinner C3ADK Solenoid Valve
(R)	Gas Regulator
(MTS)	Methyltrichlorosilane cylinder
(Cl2)	Chlorine cylinder
(XX)	Gas Cylinder, High Pressure
(C V)	Nupro Check Valve
(P) —	MKS Baratron Pressure Guage
—	1/4" OD Stainless Steel Tubing
—	Flexible Hose, Vacuum
—	Flexible Tubing
(E)	PVC Tubing Manifold
(MFC)	MKS 1259 Mass Flow Controller

Figure 2. Gas flow schematic continued.

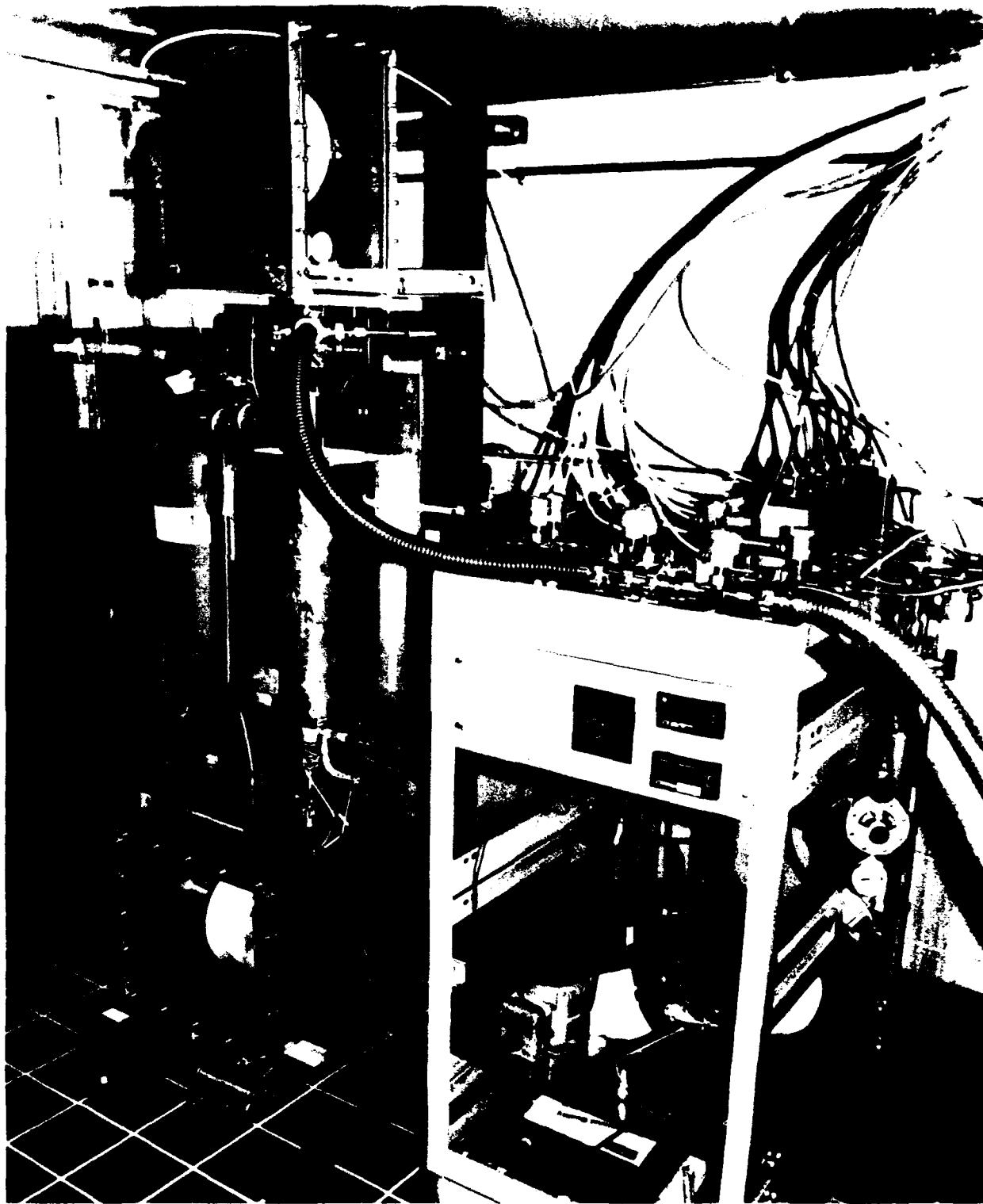


Figure 3. Photograph of the assembled fiber coater showing the furnace and fiber spool boxes (left) and gas flow controllers and plumbing (right).

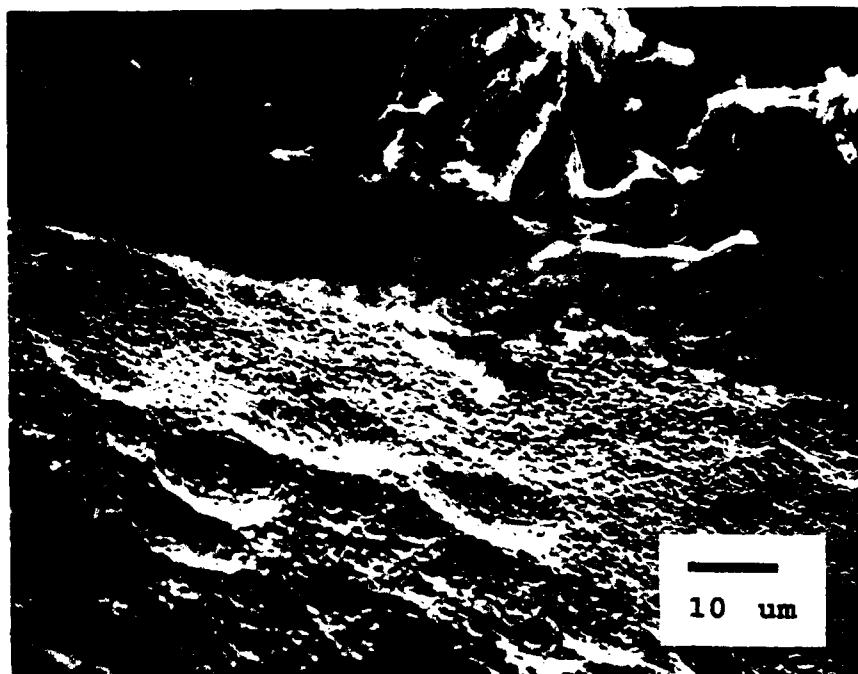


Figure 4. SEM photomicrograph of SiC deposition on a carbon rod. Conditions are: $T_{\text{dep}}=1300^{\circ}\text{C}$, $P=150$ torr, $\text{H}_2\text{:MTS}=10\text{:}1$, 330 sccm total flow.

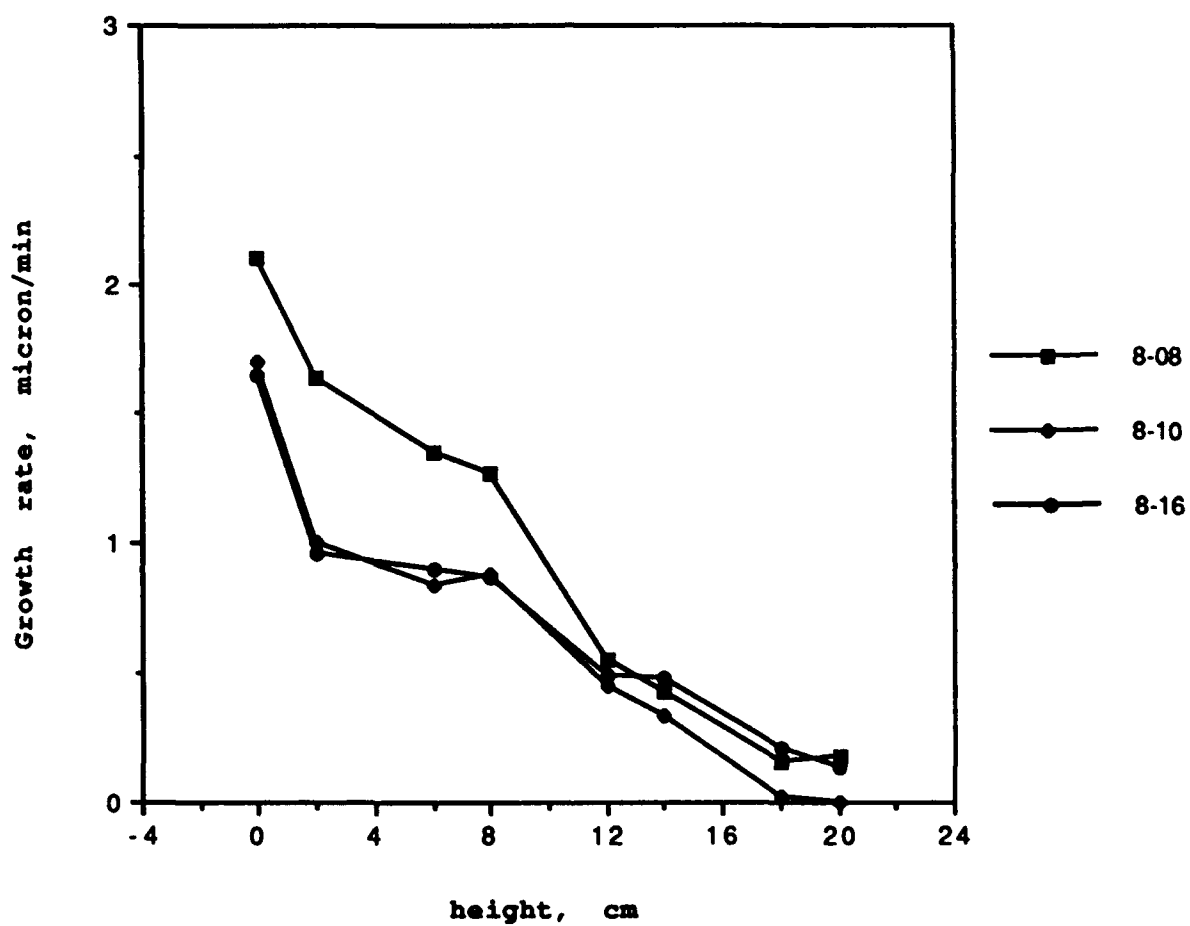


Figure 5. Measured SiC deposition rate versus vertical position in furnace. Conditions are: $T=1300^{\circ}\text{C}$, $P=150$ torr, $\text{H}_2\text{:MTS}=10\text{:}1$, 330 sccm total flow.

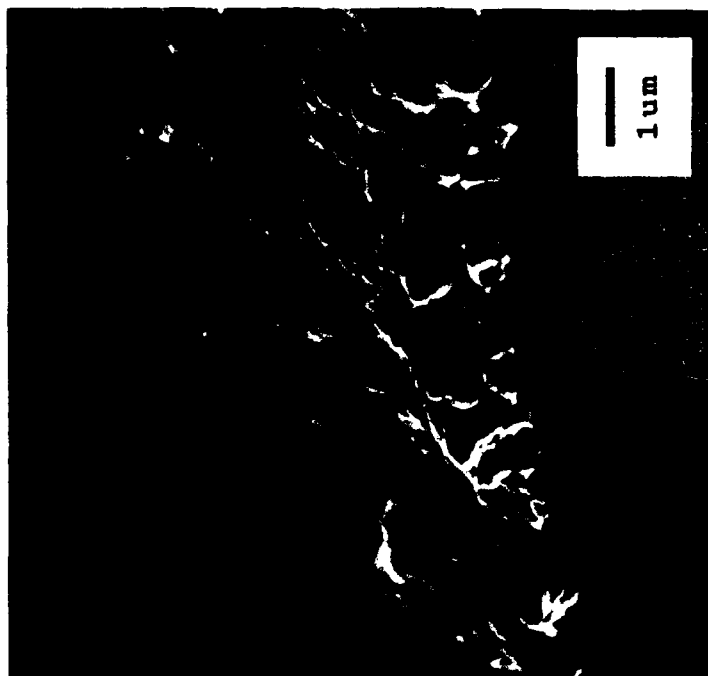


Figure 6. SEM photomicrograph of carbon coatings. Left: on SCS-0 fiber at $T=850^{\circ}\text{C}$, $P=732$ torr, $\text{C}_3\text{H}_6=20$ sccm, $\text{Ar}=200$ sccm. Fiber pull rate 2.6 inch/min. Right: two coats on sapphire fiber. First: $T=850^{\circ}\text{C}$, $P=732$ torr, $\text{C}_3\text{H}_6=15$ sccm, $\text{Ar}=200$ sccm; second: $T=900^{\circ}\text{C}$, $P=732$ torr, $\text{C}_3\text{H}_6=20$ sccm, $\text{Ar}=200$ sccm. Fiber pull rate 1.8 inch/min for each. In all cases argon flowing to boxes at 100 sccm.

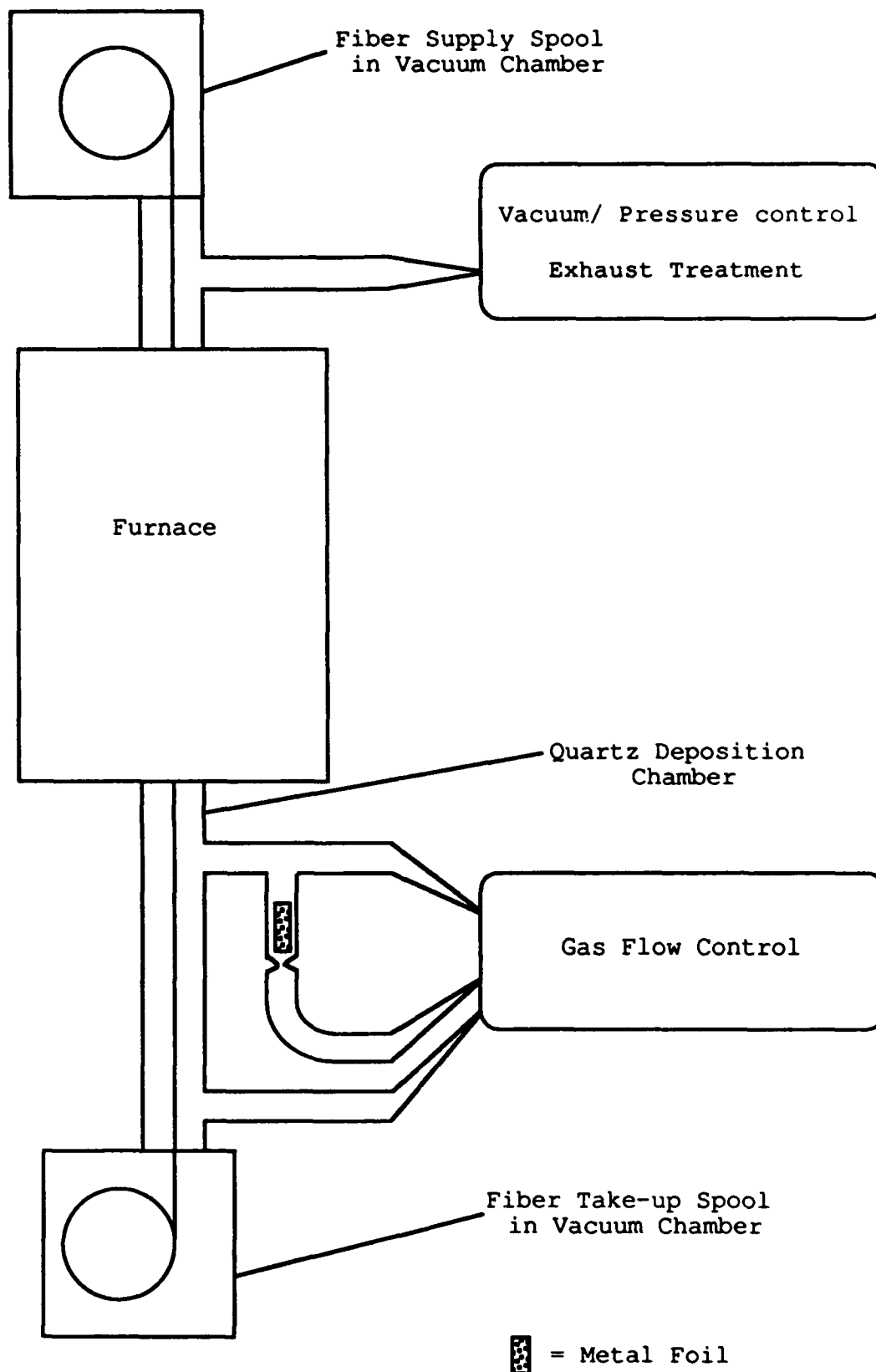


Figure 7. Coater schematic for depositing metals

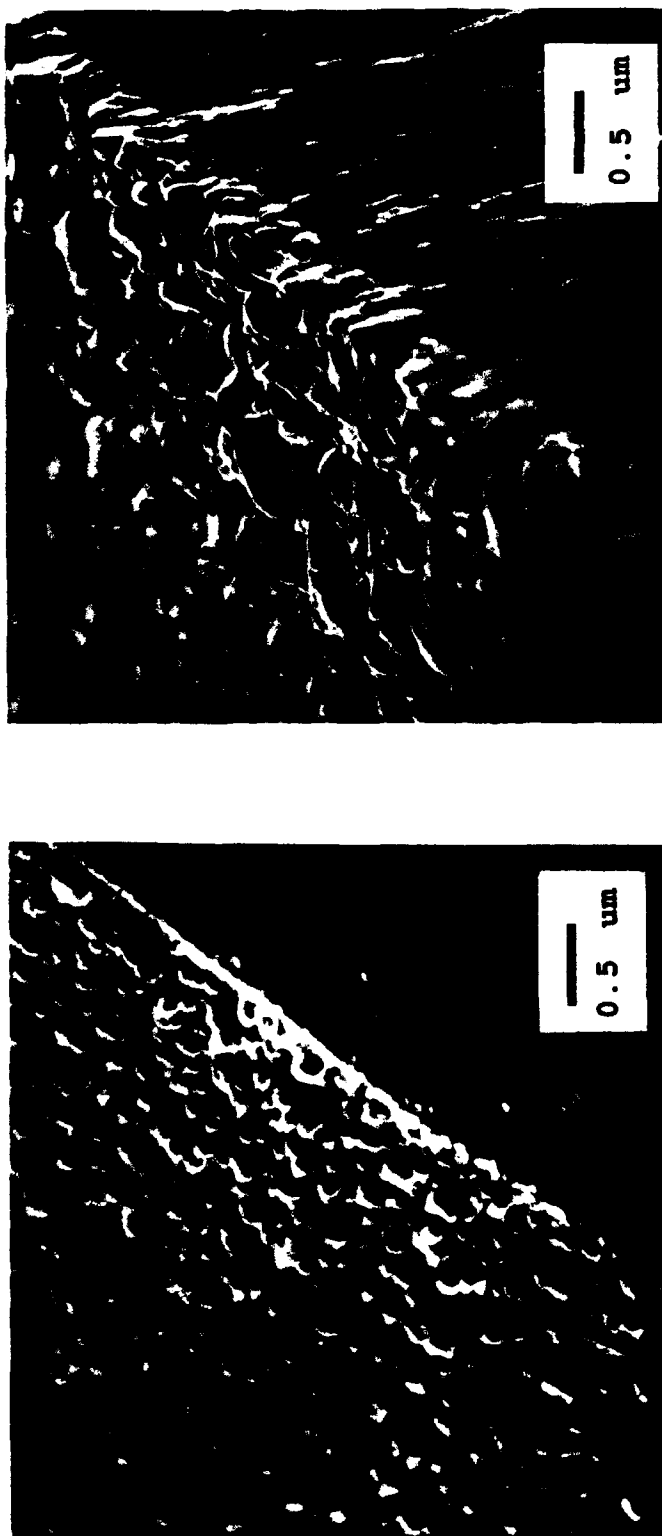


Figure 8. SEM photomicrographs of metal coatings on SCS-0 fibers. Left: Cobalt deposited at $T_{dep}=900$, $T_{Co}=460^{\circ}C$, $P=20$ torr, $Cl_2=20$ sccm, $H_2=200$ sccm. Right: Tantalum deposited at $T_{dep}=850$, $T_{Ta}=450^{\circ}C$, $P=20$ torr, $Cl_2=5$ sccm, $H_2=100$ sccm. Both with 100 sccm of argon to the boxes and 1.8 inch/min fiber pull.