UNCLASSIFIED

AD NUMBER

ADB211185

NEW LIMITATION CHANGE

TO

Approved for public release, distribution unlimited

FROM

Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; 01 DEC 1967. Other requests shall be referred to National Aeronautics and Space Administration, Washington, DC.

AUTHORITY

NASA TR Server website

THIS PAGE IS UNCLASSIFIED

AD D411542

N68-28440

NASA CR-72016
TEI-TP 293

"DTIC USERS ONLY"

IMPROVED ABLATIVE MATERIALS

by

Gordon H. Miller and Joseph A. Haefling

PREPARED FOR

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS3-7948

DEPARTMENT OF DEFENSE
PLASTICS TECHNICAL EVALUATION CENTER
PICATINNY ARSENAL, DOVER, N. J.

19960607 123

TEXACO

DTIC QUALITY INSPECTED 3

TEXACO EXPERIMENT INCORPORATED

11595

UNLIMITED

NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the National Aeronautics and Space Administration (NASA), nor any person acting on behalf of NASA:

A.) Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

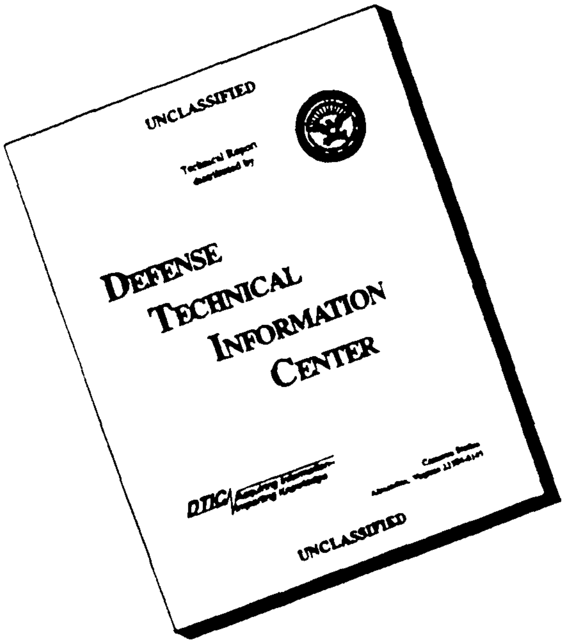
B.) Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method or process disclosed in this report.

As used above, "person acting on behalf of NASA" includes any employee or contractor of NASA, or employee of such contractor, to the extent that such employee or contractor of NASA, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with NASA, or his employment with such contractor.

Requests for copies of this report should be referred to

National Aeronautics and Space Administration
Office of Scientific and Technical Information
Attention: USS
Washington, D.C. 20546

DISCLAIMER NOTICE



THIS DOCUMENT IS BEST QUALITY AVAILABLE. THE COPY FURNISHED TO DTIC CONTAINED A SIGNIFICANT NUMBER OF PAGES WHICH DO NOT REPRODUCE LEGIBLY.

NASA CR-72016
TEI-TP 293

Final Report

IMPROVED ABLATIVE MATERIALS

by

Gordon H. Miller and Joseph A. Haefling

Prepared for
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

December 1, 1967

Contract NAS3-7948

Technical Management
NASA Lewis Research Center
Cleveland, Ohio
Liquid Rocket Technology Branch
Stephen M. Cohen, Project Manager

TEXACO EXPERIMENT INCORPORATED
Richmond, Virginia 23234

#11595

ABSTRACT

The factors which govern the design of a chemical vapor plating reactor for preparing TiB_2 and TiC continuous filaments are described herein.

Uneven substrate heating was found to be a major problem in reactors where resistance type substrate heating was employed. This problem was found to be related to the electrical conductivity of the TiB_2 and TiC deposits, but was overcome by the use of radiofrequency power to heat the substrates. A reactor design incorporating radiofrequency heated substrates for continuous filament preparation is presented, and its operation during preparation of TiB_2 filament is discussed. Extraordinary problems associated with TiC filament preparation resulted in its elimination from the current program. An evaluation of the prepared TiB_2 filament is also given.

author, modified)

TABLE OF CONTENTS

TABLE OF CONTENTS (Cont'd)

LIST OF FIGURES

FIGURES (Cont'd)

LIST OF TABLES

SUMMARY

Work carried out at TEI under a previous contract (1), where ablative tests were run at high temperatures in fluorine-containing oxidizing atmospheres on samples of several bulk materials, indicated that TiB_2 and TiC, as well as pyrolytic graphite, B_4C, ZrO_2, ZrB_2, and tungsten coated boron were promising as ablative reinforcement materials. Attempts were then made by a batch chemical vapor plating (CVP) process to prepare a number of these materials in the form of high strength fibers. Methods of preparation were accomplished for fibers of TiB_2 (up to 370 kpsi tensile), pyrolytic graphite (up to 104 kpsi), TiC (up to 63 kpsi but which held up well in ablative tests), and tungsten coated boron.

The program reported herein was undertaken to study the conversion of batch to continuous processing and to prepare three fibers on a continuous basis so as to be able to evaluate their ablative characteristics at another contractor site. By agreement with NASA, TiB_2 and TiC were chosen as the fibers for initial study, and subsequently ZrB_2 was investigated briefly.

The first phase was the development of a CVP reactor for preparing continuous filaments. Construction of two CVP units and the initial operation of the equipment to identify and solve operability difficulties were included in this development. The systems involved preparation of TiB_2 by the H_2 reduction of BCl_3 and $TiCl_4$; and of TiC by the H_2 reduction of $TiCl_4$ and the thermal decomposition of n-C_4H_{10}.

DESIGN CRITERIA

The following design criteria for the reactor were identified and evaluated in the development of a suitable design:

(1) The reactor must be heated to about 450° to 500°C to prevent condensation of $TiCl_3$ and other low volatility reaction products on the walls of the reactor.

(2) In direct electrical resistance heating of the substrate, the distance between the electrode and the point where the deposition begins must be held to a minimum (less than 1/8 in.) to avoid overheating of the substrate in this region.

(3) There must be unobstructed visibility of the filament so that the temperature can be monitored over its entire length.

(4) Any electrode material must have low volatility at operating temperatures and either be chemically resistant to or separated from the plating gases.

(5) The reactor should be capable of satisfactory operation for substantial periods of time because it will be used ultimately for production as well as process development.

(6) Design features which will increase production rates should be emphasized.

TEMPERATURE GRADIENT PROBLEM

In the initial stages of this program, a heated cross-flow type reactor was designed and constructed which partially satisfied the above criteria. Water-cooled mercury standpipe electrodes were used to supply dc power to the substrate. The most pressing operability problem was the formation of a severe temperature gradient on the substrate after deposition began.

Although considerable improvement was made, the temperature gradient problem could not be sufficiently eliminated in the cross-flow reactors, and since uniform substrate heating is of prime importance in CVP reactions to obtain a uniform deposit, it was decided to investigate other means of substrate heating. Success of radiofrequency (rf) substrate heating in other programs in this laboratory led us to consider this means of substrate heating for TiB_2 and TiC filament preparation. Four advantages of rf over resistance heating of substrates were believed to exist: longer uniform heat zones, single chamber design, faster substrate speeds for a given temperature and filament size, and elimination of contact electrodes.

TiB_2 FIBERS: INITIAL PRODUCTION

Preliminary experiments confirmed these advantages and indicated that uniform heat zones up to 18 in. long could be obtained on substrates during TiB_2 filament preparation. At substrate speeds of 6 in./min., 5-mil diameter TiB_2 filament was prepared on 1-mil wire.

Two rf heated substrate reactors were designed, constructed, and placed into operation in the CVP units. The reactors were of the split-flow type (plating gases enter at opposite ends of the reactor and leave at a common exit at the center) and were surrounded by ovens which maintained temperatures of 400° to 500°C on the reactor walls. The entire CVP unit was enclosed in a double screened framework to minimize rf radiation outside the enclosure. Eventually it was necessary to place enclosure filters on all electrical lines passing through the framework and to add screening behind the units to meet Federal Communications Commission regulations in regard to the intensity of the emitted radio signal.

Operability of the units for preparation of TiB_2 was initially very low; most breakdowns were due to substrate burnouts which were usually caused by wall deposits falling on the substrate. Temperature readings became difficult shortly after the start of a run due to deposition on the chamber walls. With experience, the operability was improved: uniform temperature zones up to 32-in. long were obtained on the substrate, and filaments up to 3.8 mils in diameter were prepared at 12 in./min and 3.2 mils diameter at 20 in./min. In an initial production effort, a total of 3090 ft of TiB_2 filament with tensile strengths in the general range of 100 to 200 kpsi was prepared in the two units.

BATCH STUDIES, TiB_2 AND TiC

During the period when the CVP units were being converted for rf substrate heating, a heated batch CVP reactor was operated for further parameter studies on TiB_2 and TiC fiber preparation. The results of the TiB_2 fiber-preparation experiments helped determine the limitation of substrate temperature and of gas flows of each chemical used in the reaction. From the results of experiments on the preparation of TiC fibers, it became apparent that preparation of these filaments in a heated reactor has two major drawbacks: the reactor walls become clouded regardless of wall temperature, and the fiber quality is extremely poor.

In another batch reactor, attempts were made to prepare TiC fibers using CH_3TiCl_3 as the TiC precursor. High strength fibers were obtained with a diameter less than 2 mils on 1 mil W substrates, but the CH_3TiCl_3 is difficult to handle due to its instability at room temperature.

At this point in the program, it was decided to drop further work on TiC continuous-filament preparation, therefore, the remainder of the program was devoted to improved TiB_2 continuous-filament preparation.

ZrB_2 FIBERS

A few experiments were run on the preparation of ZrB_2 fibers, but none of the resulting fibers was of good quality. The chief problem was keeping the $ZrCl_4$ in the gaseous state as it was transferred through the system.

TiB_2 FIBERS: SUPPLEMENTAL PRODUCTION

A supplemental effort was made to prepare 12,000 ft of TiB_2. With increasing experience and close control of operating conditions, the unit operability was improved: daily production rose from about 150 ft/day to over 400 ft/day. The longest day's run (8 hr day) was 625 ft. Product appearance was smooth and shiny. Tensile strength of more than two thirds of the material was in the range of 200 to 300 kpsi; about 6 percent was between 300 to 400 kpsi, and the highest individual pull was 502 kpsi. The average diameter of the filament was 2.6 mils, and its density was about 4.45 g/cm^3. Elastic modulus values averaged about 71 x 10^6 psi for the filament.

I. INTRODUCTION

Ablative liner materials, used to cool the thrust chambers of liquid-propellant rocket engines, permit simplification of design and operation by eliminating the requirement for pumping liquids to provide regenerative or transpiration cooling. Current liner materials appear to be marginal with propellants such as N_2O_4/50 percent N_2H_4-50 percent UDMH or LO_2/LH_2. The more-energetic propellant systems, using fluorine or FLOX, demand more-effective ablative composites to function satisfactorily. This is because of their higher flame temperatures, more-corrosive combustion products and, in some cases, increased erosion due to the presence of solid particles.

Ablative resins currently used, or improved resins now being developed, are capable of absorbing the heat from the motor, but they require reinforcing fibers with properties such that the resulting composites will have adequate strength to endure the physical demands. This means that the majority of liner improvements must come from new and improved fibers. Accordingly, this program was concerned with the development of reinforcing fibers that will lead to more-effective ablation composites for use in advanced liquid-fuel rocket-engine thrust chambers.

The specific objectives of this investigation were: 1) to scale up the preparation of selected fibers from a batch to a continuous process, and to delineate the important operating parameters to provide fibers of uniform quality; and 2) to fabricate 12,000 ft of three fibers on a continuous basis so that they could be composited elsewhere, and studied as ablative fiber reinforcements.

The experimental work was carried out during the periods January 1966 to February 1967 and July 1967 to December 1967.

The fiber materials were selected from those materials recommended in a previous investigation (1). By agreement with NASA, TiB_2 and TiC were chosen as the fibers for initial study, and subsequently ZrB_2 was investigated briefly.

Successful preparation of TiB_2 and TiC in fiber form had been achieved by batch-type chemical vapor plating (CVP) using $TiCl_4$ as the titanium precursor, BCl_3 as the boron precursor, and n-butane, neopentane, or ethyl bromide as the carbon precursor (1). On the basis of these successes, continuous chemical vapor plating from these precursors was selected as the general approach to be investigated in this program. It was recognized, however, that scale-up from batch to continuous methods would not be straightforward because of certain unique problems. These include the need for high temperature plating-chamber walls to prevent condensation of reaction products, substrate temperature gradients, low plating rates, and the use of low volatility plating compounds.

The use of $TiCl_4$ as a precursor for titanium imposes two important design criteria for the CVP apparatus. First, $TiCl_4$ is a liquid at standard temperature and pressure (STP) and, therefore, must be vaporized before it is introduced into the CVP reactor. The boiling point of $TiCl_4$ at 760 mm Hg is 136°C (2). Thus, it is necessary for the temperature of the walls of the equipment handling $TiCl_4$ to be maintained above 137°C to prevent condensation. Good control of $TiCl_4$ vapor flow is possible only if condensation is prevented. Second, in the hydrogen reduction of $TiCl_4$, intermediate compounds $TiCl_3$ and $TiCl_2$ (which are solids at STP) are produced. Unless the walls of the plating chamber and effluent gas equipment are heated, these intermediates will also condense on the cool surfaces and eventually completely obscure the fiber, thus preventing measurement of its temperature. Another consequence of the wall deposits is that when they develop to a certain thickness, they spall off and fall upon the fiber, frequently causing hot spots and perhaps even influencing the CVP process in the vicinity of each impinging particle.

Titanium trichloride apparently sublimes at a temperature of about 425°C in a vacuum (3) but, at 760 mm Hg pressure, $TiCl_3$ disproportionates to $TiCl_4$ and $TiCl_2$ at 440°C (2) or $>$475°C (3). Titanium dichloride disproportionates to $TiCl_4$ and Ti metal above 600°C at 760 mm Hg pressure. These data suggest that the temperature of the CVP reactor should be maintained above about 425°C to prevent condensation of $TiCl_3$ but below 440° to 475°C to prevent disproportionation of $TiCl_3$ to the less volatile $TiCl_2$ which, apparently, is a stable solid up to at least 600°C.

The above findings are at least partially substantiated by results of experiments reacting BCl_3 and Ti metal in sealed capsules (4). With increasing temperature up to 450°C, violet colored crystals ($TiCl_3$) appeared in increasing quantity. At 475°C, the walls of the capsule became coated with Ti metal, and black crystals ($TiCl_2$) appeared. At 500°C, the $TiCl_2$ was present in larger quantities. Looking at the overall composite of the information available, it appears that the plating chamber temperature should be controlled between 450° to 475°C.

The plating chambers designed and built in the first part of this investigation were a cross-flow type using resistively heated tungsten substrate. CVP chamber development for another program at this laboratory had developed a chamber that would give high plating rates. This is a chamber in which the plating gas is premixed and flows at right angles across the substrate. Such arrangement provides "fresh" gas to each portion of the substrate and avoids the tendency, most pronounced at low gas-flow rates, for gas depletion to occur as it may in parallel-flow chambers. These units were satisfactory in practice except for a severe temperature gradient on the resistively heated substrate and fiber. The causes of the temperature gradient and methods attempted to overcome it are discussed below. The gradient posed a serious obstacle to good fiber preparation.

When difficulties were encountered with TiB_2 and TiC filament preparation due to the temperature gradient problem, it was decided at a meeting on May 20, 1966 at Richmond, Virginia, (with the NASA Project Manager and the NASA Headquarters Representative) to concentrate work on preparation of two fibers instead of three. It was also decided that, due to the problem of temperature gradient with resistance heating of electrically conducting fibers (such as TiB_2, TiC, and ZrB_2), a study be made of the feasibility of using rf substrate heating. In a later consultation with the NASA Project Manager, it was agreed that TiC workwould cease and studies on the preparation of ZrB_2 be undertaken.

When the feasibility study showed the rf heating to work better than resistance heating, the CVP units were redesigned for rf heating. Both CVP units were used for TiB_2 filament preparation only, to produce as much TiB_2 filament as possible during the remainder of the program. In this production period, 3090 ft of TiB_2 filament was made and shipped. In a supplemental period, 12, 060 ft of TiB_2 filament was made and shipped.

The authors wish to acknowledge the contributions of Barbara G. Fox, Jr. Chemist, and Pauline S. Crowling, Jr. Chemist, who performed the X-ray analyses, metallography and etching studies; and of Leigh R. Middleton, Research Technician, and George T. Inge, Assistant Technician, for their work in assembling the equipment and operating the plating units. We also wish to acknowledge the help of the analytical section under Dr. J. H. Alsop and of the Instrument Department under Dr. J. E. Goodwin. We wish to thank Mr. George Furman of the Texaco Research Center, Beacon, New York for special micro-hardness measurements on certain TiB_2 samples. Of special recognition are the accomplishments of George C. Robinson, Jr., Research Metallurgist, who worked on this program before his death on October 13, 1966. His absence was keenly felt during the remainder of the program.

II. CVP UNITS WITH CHAMBERS UTILIZING RESISTANCE-HEATED SUBSTRATES

A. DESIGN CONSIDERATIONS

When electric resistance heating is used to heat the substrate, the electrical properties of the substrate and deposit have an important effect on the design of the plating chamber. As the substrate moves through the plating chamber, the thickness of the deposit increases. If the resistance of the deposit is much higher than the resistance of the substrate, heat is generated mostly in the substrate at a nearly constant rate along the length of the chamber. However, if the resistance of the deposit is low and approaches that of the substrate, the heat generation rate at a given current decreases as the deposit thickens so that, inherently, the temperature of the fiber decreases from the entrance electrode to the exit electrode. This temperature gradient is very undesirable because the plating efficiency (mass of deposit laid down per unit length of chamber for a given substrate speed) is low and the variable deposition temperature could cause a radial variation in the composition and properties of the fiber.

The specific resistances of several substrate materials and deposits are presented in Table I. In some instances, the values given are the only values found in the literature. Where two values were found for a given material, one of the values was selected on an arbitrary basis. Note that the specific resistances of ZrB_2, TiB_2, and TiC are appreciably lower than the resistances of B, SiC, and B_4C. These last three materials have been successfully prepared as fibers by CVP on a continuous basis. The resistivities of the first group, as well as the carbides and borides of the substrate materials, are all characteristic of metallic conductors. They are generally of the same order of magnitude as the metals both at room temperature and at elevated temperatures. The B, SiC, and B_4C are characteristic of semiconductors that have very high resistivity at room temperature and, although resistivity decreases at elevated temperature, it is still about 1000 times higher than the metallic conductors.

The data presented in Table I were used to compute the percent of total power per unit length of fiber which is generated in the core, and the ratio of the resistance of the substrate to the resistance of the fiber for several fiber materials. The results of these computations are given in Table II. Note that for TiB_2, ZrB_2, and TiC fibers, most of the power is generated in the deposit even when the substrate area constitutes 25 percent (2-mil substrate) of the total fiber area. Because the deposits are relatively good conductors, it is apparent that the temperature of TiB_2, ZrB_2, and TiC fibers will decrease from the entrance electrode to the exit electrode for a given current. This factor must be

Table I

ELECTRICAL RESISTANCE OF FIBER MATERIALS

Material	Ref.	Specific Resistance μ ohm-cm at 20°C	Coefficient of Electrical Resistance $\mathrm{deg}^{-1} . 10^3$	Specific Resistance μ ohm-cm at 1000°C
Substrates				
W	6-3	5.5	-	30
W_2B_5	7	43	4.26	200[b]
WC	7	19.2	0.5	30[b]
W_2C	7	75.7	1.95	200[b]
Ta	11	12.4	-	54
TaB	7	100	-	-
TaB_2	7	37.4	-	-
TaC	9	42.1	-	90
Conductive Deposits				
TiB_2	7	14.4	2.78	50[b]
ZrB_2	7	16.6	1.76	50[b]
TiC	8	76[a]	1.16 (Ref. 7)	200[b]
Semi Conductive Deposits				
B	7, 10	1.7×10^{12}	-	25,000
SiC	7	1.3×10^{7}	-	>50,000
B_4C	7	1×10^{6}	-	30,000

[a] Average of six reported values (90, 70, 65, 84, 78) μ ohm-cm

[b] Computed

Table II

ELECTRICAL RESISTANCE SUMMARY

			R_s/R_f[a] at 1000°C			Percent of Total Power Per Unit Length of Fiber Generated in Core		
			Substrate Diameter, mils			Substrate Diameter, mils		
Substrate	Deposit	Core	0.5	1.0	2.0	0.5	1.0	2.0
W	TiB_2 or ZrB_2	W	38	10	2.8	2.6	10	36
W	TiB_2 or ZrB_2	W_2B_5	38	9	2	0.4	1.6	8
W	TiC	W or WC	11	3	1.5	9.5	31	69
W	TiC	W_2C	9.6	2.4	0.5	1.3	1.6	2
W	B	W_2B_5	0.15	0.15	0.15	~100	~100	~100
W	B_4C	WC	1	1	1	94	98	~100
W	B_4C	W_2C	0.21	0.17	0.15	70	91	~100
W	SiC	W	1	1	1	97	99	~100

[a] $R_s/R_f = \frac{\text{Resistance of Unit Length of Substrate}}{\text{Resistance of Unit Length of Fiber}}$

Note: Fiber Diameter is 4 mils.

considered in the design of the plating chamber so that appropriate steps can be made to minimize the temperature gradient.

In conventional resistance heating of the substrate and fiber where current is supplied through mercury "T" electrodes, the substrate must be capable of carrying the current required to heat the fiber. In Table II it is noted that the resistance of a 0.5-mil diameter substrate is an order of magnitude higher than the resistance of 4-mil diameter fibers of TiB_2, ZrB_2, or TiC. This means that the heat generation rate in that part of the substrate lying between the entrance electrode and the point where deposition begins is an order of magnitude greater than the heat generation in the 4-mil diameter fiber itself. Since the current requirements are based on maintaining the fiber at a temperature of 1000° to 1200°C, the temperature of the lead-in substrate will be significantly higher. As Table II shows, this effect can be minimized by using larger diameter (lower resistance) substrate but this is not considered desirable from an overall standpoint because of the potentially greater influence the large volume of substrate would have on the properties of the fiber. We would anticipate that the fiber would be weaker and would have lower metallurgical stability at higher temperatures. Another possible aid would be to use a substrate material which has a lower specific resistivity than tungsten. Unfortunately, all of the other metals that have significantly lower resistivities are not suitable substrates, primarily because of their low melting temperatures (~ 1000°C).

Experiments were conducted to determine if the substrate between the electrode and plating zone could be gas cooled: Fig. 1 shows the experimental set-up. The flow of hydrogen required to keep the substrate temperature at 1000°C for various current ratings was determined. The results are shown below:

Current, Amps	Without Cooling Gas, °C	With Cooling Gas, °C	Cooling Gas Flow, cc/min
0.30	1100	1000	395
0.33	1200	1000	770
0.35	1400	1000	1800

It has been established experimentally (1) that it takes about 1.5 amps to heat a 4-mil diameter TiB_2 fiber to 1100°C in a plating gas flow of 1000 to 2000 cc/min. It is obvious from these data that the cooling gas flow for 1.5 amps

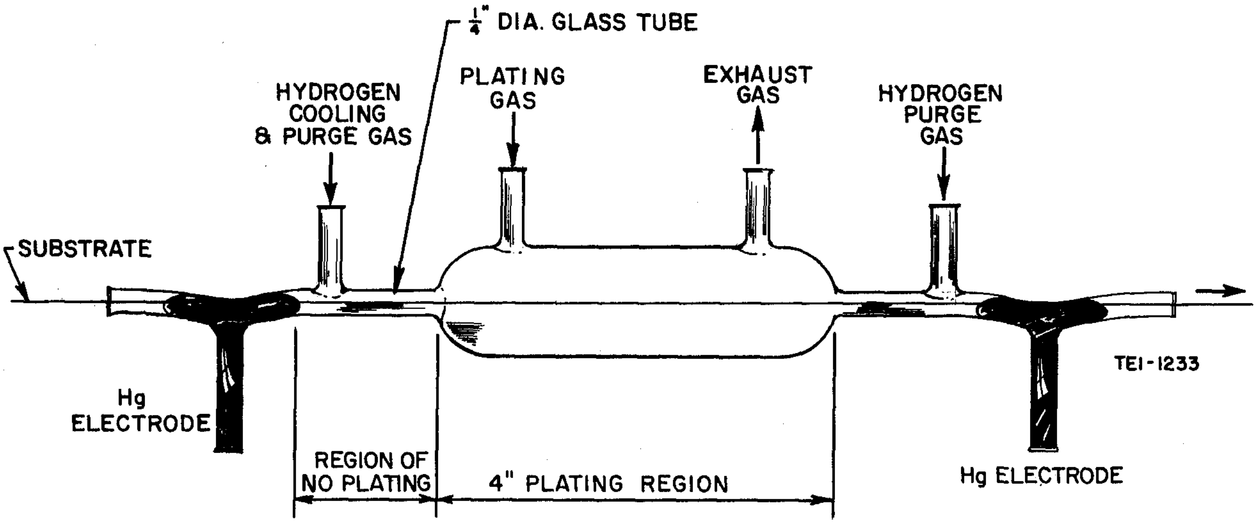


Fig. 1 Experimental Set-up for Substrate Cooling Experiments

would be many times the flow of plating gases (~2000 cc/min) normally used. Thus, dilution of the plating gases as well as hydrogen consumption would prohibit such an arrangment to be employed.

We also concluded that the mercury "T" electrodes, shown in Fig. 1, could not be used for TiB_2 and TiC without great difficulty, at least in the first-stage plating chambers. Because of possible reactions between the plating gases and mercury, and because the plating chamber would have to be heated to about 475°C to prevent condensation of $TiCl_3$, the mercury electrode must be isolated by a purge gas to prevent unwanted reactions with the plating gases. It must also be separated from the plating chamber to prevent excessive vaporization of the mercury. Thus, overheating of the substrate in this region would severely limit the size of fiber that could be made in a single chamber. The data presented above suggests that a deposit equivalent to an increase in current of only about 0.05 to 0.1 amps could be produced in a single chamber.

Producing filament requires good operability and high production rates, two factors which ultimately were evaluated by operating experience. However, it is important to consider these factors in the plating chamber design so that fatal design decisions are avoided. These would include those that would severely hamper restringing of the substrate, cause excessive arcing between substrate and the electrodes, or cause excessive downtime due to misapplication of glass and other fragile construction materials. Previous experience with the preparation of TiB_2 and TiC fibers on a batch basis revealed that deposition rates are quite low for these two systems (1). Usually several minutes deposition time was required to produce 4- to 5-mil diameter fibers. Emphasis was placed on incorporating design features which would increase production rates. Particular interest was focused on reducing the thermal gradient between electrodes to an absolute minimum so that as much of the substrate as possible would be at or near the deposition temperature.

In summary, the following factors were considered in the design of the CVP reactor for resistively heated substrates:

1. The reactor must be heated to about 450° to 500°C to prevent condensation of $TiCl_3$ and low-volatility reaction products on the walls of the deposition chamber

2. The distance between the electrode and the point where deposition begins must be held to a minimum (less than about 1/8 in.) to avoid overheating of the substrate in this region

3. There must be unobstructable visibility of the filament so that its temperature can be monitored over its entire length

4. The electrode material must have low volatility at operating temperatures and either be chemically resistant to the plating gases or separated from the plating gases

5. The reactor should be capable of satisfactory operation for substantial periods of time because it will be used for production as well as process development

6. Design features which will increase production rates should be emphasized.

B. PLATING CHAMBER DEVELOPMENT

The requirements outlined above led to the development of the plating chamber concept shown in Fig. 2. A cross-flow type chamber (i. e., the flow of plating gases perpendicular to the axis of the substrate) is externally heated and equipped with internally cooled standpipe electrodes which make contact with the substrate through the liquid metal meniscus on top of the electrode. The meniscus is shielded from the plating gases by a flow of purge gas emerging at high velocity from the annular space surrounding the electrode. Excessive heating of the liquid metal is prevented by the high flow of purge gas or by internal water cooling, if necessary. The plating gases enter at the bottom of the chamber and are distributed evenly along the length of the substrate by a close packing of glass microspheres. The substrate enters and discharges from the chamber through mercury seals which are sufficiently removed from the chamber so that heat will not cause vaporization of the mercury. Purge gas is introduced at each of the seals to prevent plating gases from either condensing on the seal or reacting with the mercury. The lower plenum of the chamber is heated by electrical tapes to a temperature above 200° to 250°C to prevent condensation of the reactants. The upper plenum is heated to 450° to 500°C with suitably insulated, custom-made, form-fitting heater panels. The chamber is constructed of stainless steel while the electrode shields and mercury seals are of glass. The substrate is made visible by a Vycor window installed on the front face of the chamber. This is offset from the hot chamber to prevent overheating of the O-ring seal in the window.

A prototype (Mark I) of this plating chamber concept was built and tested. Attempts to use Cerrolow 117 (a low melting (47°C) alloy with a low vapor pressure at 500°C) as the electrical contact were unsuccessful in that the material oxidized rapidly above 100°C during handling. Water-cooled mercury was used successfully as the electrical contact after attempts to cool the mercury with helium gas failed. This plating chamber was used for the preparation of boron and TiB_2 filament to identify its problems under actual plating conditions. No problems were encountered with the heating of the chamber or with maintaining the mercury temperature at 60°C or lower. However, the temperature profile along a 1-mil tungsten substrate was very poor. A hot spot, perhaps 1/8 to 1/2 in. long, depending on filament speed, occurred adjacent to the entrance

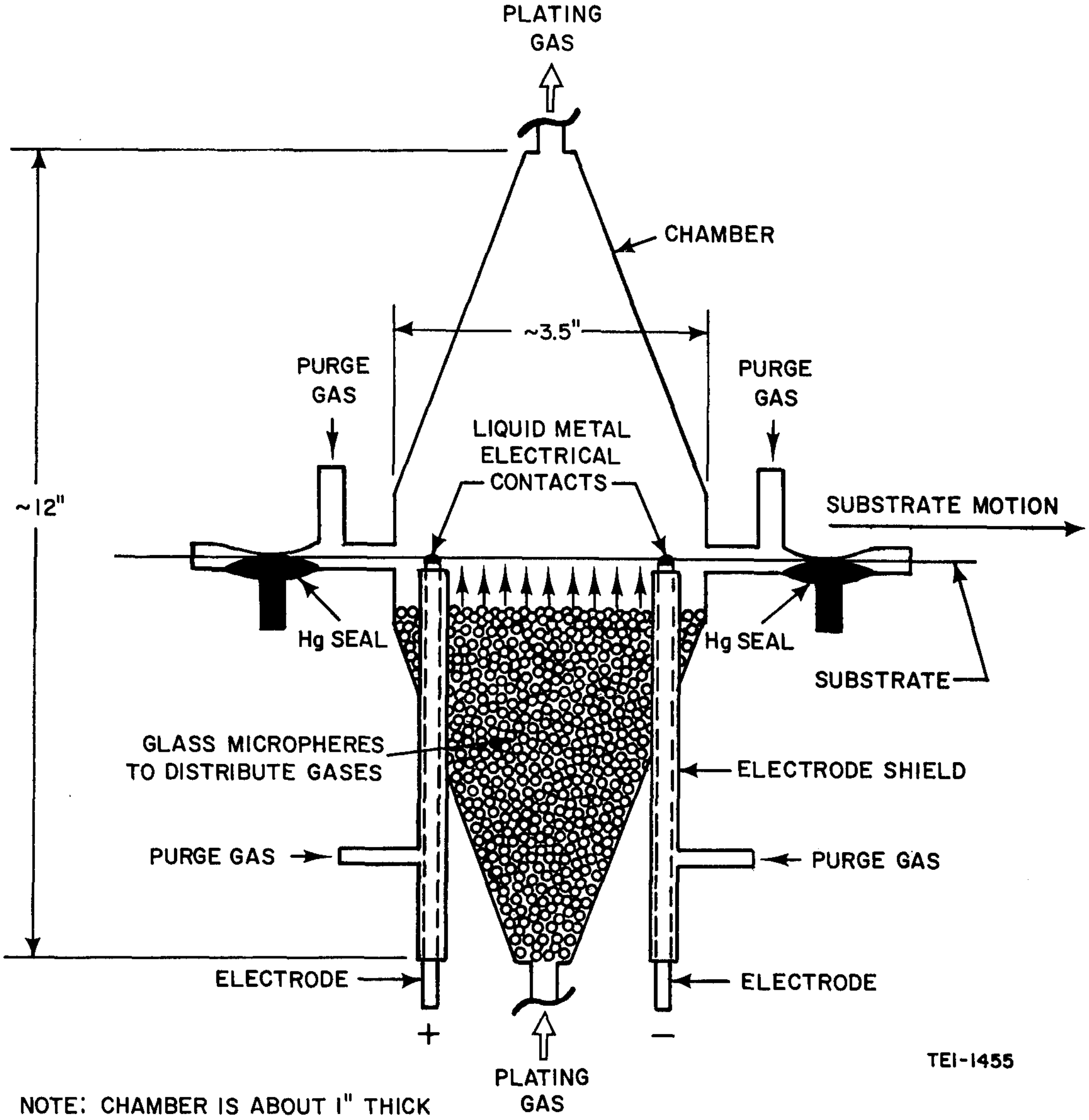


Fig. 2 Salient Features of Cross-Flow Plating Chamber with Standpipe Electrodes

electrode after which the temperature decreased gradually over the rest of the heated substrate. When the hot spot temperature was maintained at 1100°C, it was 50°to 100°C higher than the hotter end of the gradient while the gradient itself was 100° to 200°C. Thus, the temperature varied 150° to 300°C along the length of the heated substrate.

Another program at TEI demonstrated that, below some critical gas flow, the gases leaving a heated wire in a cross-flow chamber recirculated around the wire. We believed that the recirculation should be avoided because the large quantities of $TiCl_3$ produced and the decomposition products of hydrocarbons could adversely affect the deposition process. We also believed that better experimental repeatability could be realized if the heated wire were exposed to a streamlined flow over the gas-flow range of interest.

To study the gas-flow patterns within the plating compartment, a plastic model of the chamber was built. Cigarette smoke, diluted with air and helium, was used to reveal the flow patterns. These tests showed that severe recirculation occurred around the electrodes when the substrate was hot and that gas surrounding the heated filament also swirled and circulated across it. In addition, it was demonstrated that the lower plenum should be filled with spheres 1/16 in. or less in diameter rather than the 1/4 in. diameter spheres originally used.

The Mark I plating chamber was then modified by narrowing the exhaust plenum from 1 to 1/8 in. to produce a chimney effect above the substrate. Also, the electrodes were isolated from the reaction zone by thin baffle plates containing 1/8 in. holes to allow travel of the substrate wire through the plating chamber. The volume surrounding the electrodes was purged with inert gas to prevent seepage of plating gases into this region. Smoke tests in a plastic model (Fig. 3) of the modified chamber showed that the flow was streamlined over the flow range of interest (500 to 3000 cc/min) when the substrate was heated.

From experiments run on the modified Mark I chamber, information was obtained to design the plating chamber shown in Fig. 4. This unit, Mark II, is very similar to the modified Mark I model, except that minor refinements of the basic design were incorporated. The mercury electrodes are isolated from the plating region except for a 1/8 in. diameter hole through which the substrate passes. Purge gas is introduced to the electrode holes at the mercury seals and at the bottom of the glass electrode insulator. By regulating the valve at the top of the electrode insulator, a slight pressure, positive with respect to the plating region, is maintained so that there is a small flow of purge gas into the plating region. This prevents plating gases from entering the electrode region and reacting with the mercury.

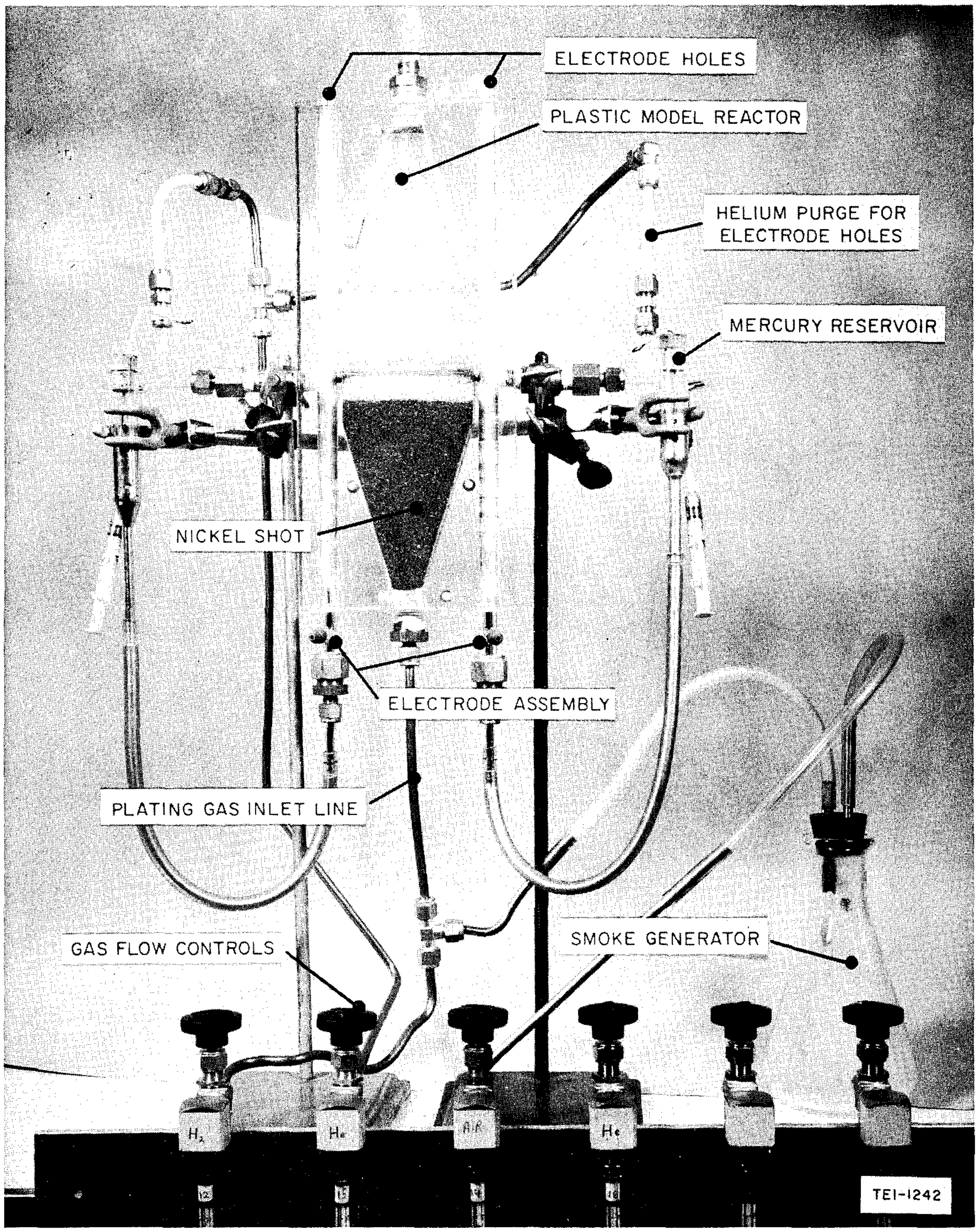


Fig. 3 Apparatus for Studying Gas-Flow Patterns in Modified Mark I Reactor

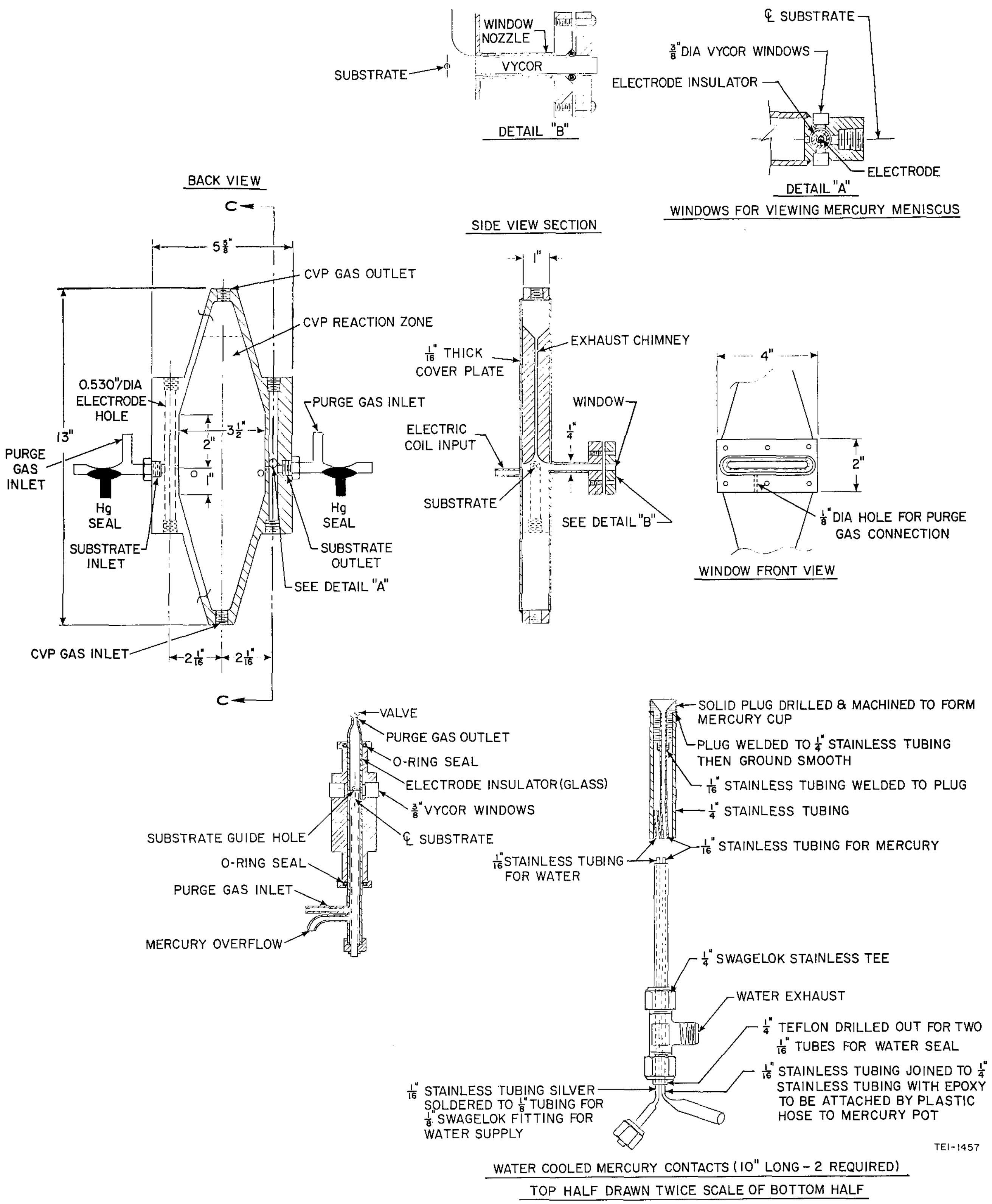


Fig. 4 Mark II Reactor Design

The electrode insulator is composed of two pieces of glass tubing which meet at the substrate centerline. A notch in the top tube serves as a guide for the substrate and keeps the substrate in contact with the mercury meniscus. This area is not visible from the large window in the plating region so 3/8 in. diameter Vycor windows are provided in the chamber wall adjacent to the mercury meniscus, thereby permitting observation of the Hg meniscus and substrate contact.

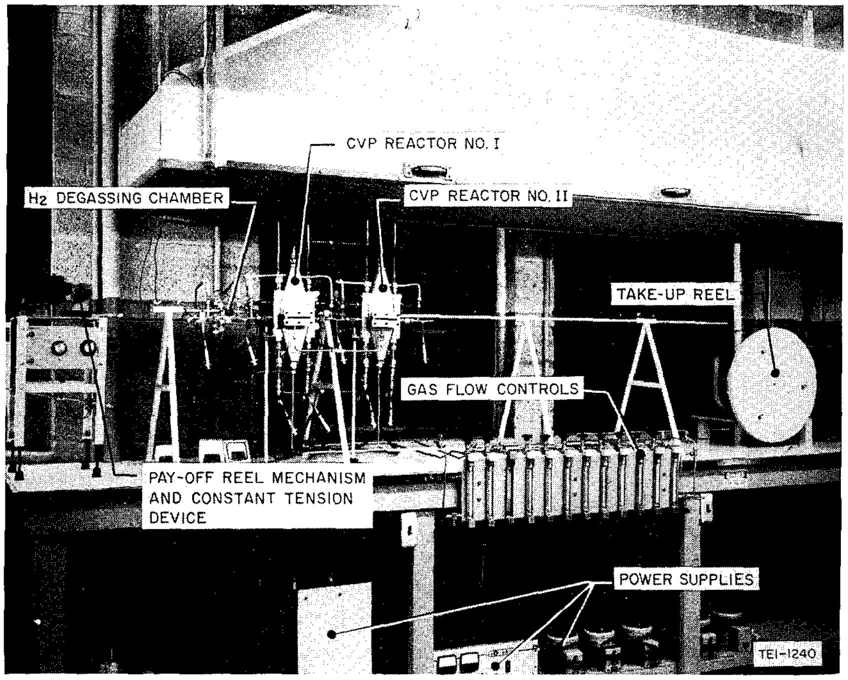
The window in the front face of the chamber was improved as shown in Detail B. A Vycor plate with parallel and polished edges is mounted in the window nozzle and sealed by an O-ring. The inside edge of the Vycor plate is adjusted so that it is flush with the inside face of the chamber. This configuration has less effect on the flow pattern of the plating gases than the Mark I window nozzle which was open. Each of the Vycor plates was calibrated for temperature correction which varied from 40° to 70°C. The filament temperatures reported for the cross-flow units contain this correction.

Electrical thru-connectors are provided in the back of the chamber about 1/4 in. below the centerline of the substrate. These supply power to heating elements located beneath the substrate. The purpose of the heating elements is to raise the temperature of the cooler end of the substrate and thus lessen the temperature gradient along the substrate.

The lower part of the chamber is heated to about 200°C by commercial heater tape that is covered by 1-1/2 in. thick insulation. The region of the chamber above the substrate is heated to 450° to 475°C by special heater panels composed of resistance heating wire and Sauereisen No. 31 molded to conform to the configuration of the chamber. The upper region is also covered with 1-1/2 in. thick insulation. Thermocouples are attached to the upper and lower regions to permit the necessary temperature control of the chamber.

C. PROCESS DEVELOPMENT UNITS

Two process development CVP units of identical design were constructed (Fig. 5). Provision was made for one substrate off-gassing chamber and two plating chambers (as shown). Each unit was equipped with a variable-speed, constant-tension, pay-off and take-up mechanism which transported the substrate through the chambers. The gases passed through rotameters into mixing chambers prior to their entry into the plating chamber. Liquids such as $TiCl_4$ were passed through a flash vaporizer before entering the mixing chamber. The flash vaporizers, mixers, and gas lines leading to the plating chambers were wrapped with resistance-type heating wire and were heated to 200°C to vaporize and prevent condensation of the $TiCl_4$. Three power supplies per unit were used to provide current to one hydrogen treating chamber and two CVP chambers in each unit.



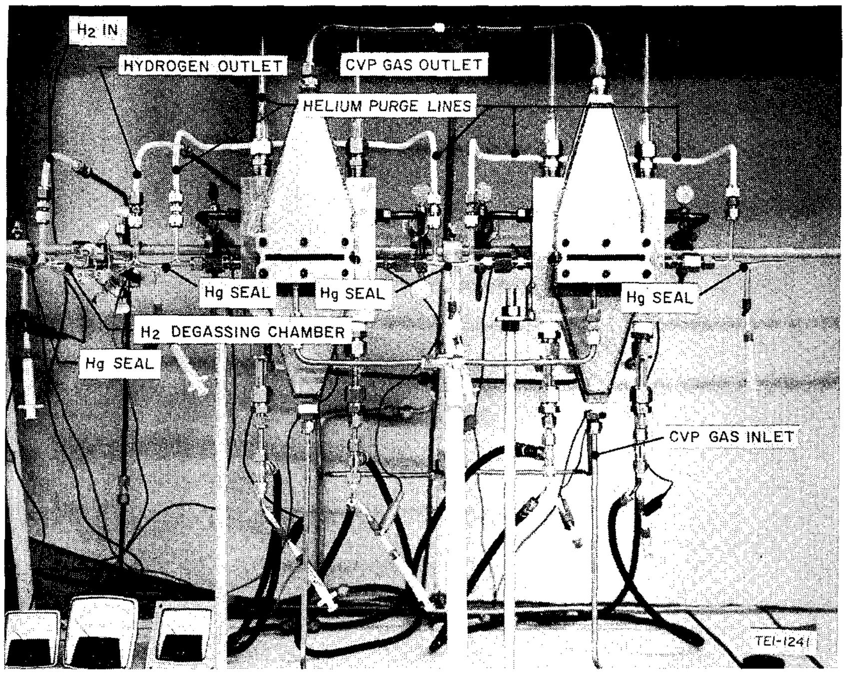


Fig. 5 Chemical Vapor Plating Units
Note: The reactors are shown without heaters and insulation

D. OPERABILITY OF CVP UNITS

Several problems were encountered during the initial experiments conducted in the cross-flow chambers for the preparation of TiB_2 filament. The first problem was the formation of a hot spot on the incoming substrate just inside the CVP region. Several factors were found which influence the intensity of the hot spot. Higher BCl_3 concentrations in the CVP gas mixture increased the hot spot intensity, while the use of argon in place of helium as the diluent gas resulted in virtually no hot spot formation. The use of larger diameter substrates also diminished its intensity.

The second problem was that of a large temperature gradient on the substrate. Although the hot spot was diminished, a temperature gradient of approximately 300°C occurred along the substrate, and to help alleviate this problem, experiments with a heating element beneath the substrate were conducted.

The heating elements are 1/8 in. diameter coils of 10-mil diameter tantalum wire on boron nitride cores with variable coil pitch to vary the linear heat generation along the substrate.

When plating on a 1-mil tungsten substrate, the use of the heating element reduced the gradient from 300° down to 150° or 100°C depending on the plating rate. This was when the incoming substrate temperature (adjacent to the inlet electrode) was set at 1100°C. The reduction in the temperature gradient did not improve the deposition rate substantially. These findings suggest that the deposition rate of TiB_2 from BCl_3-$TiCl_4$-H_2 mixtures decreases very rapidly below 1100°C and is insignificant at 950°C for the tested residence times of the substrate in the reactor.

The major cause of filament breakage in operating the cross-flow chambers was related to the exhaust gas system. To prevent air pollution, the exhaust gases are scrubbed prior to their release to the atmosphere by reacting them with water and limestone in a scrubbing tower. The exhaust lines leading into the scrubber frequently became plugged, resulting in a pressure build-up inside the plating chambers. This, in turn, caused the Hg seals to blow and the substrate to burn out. In addition, the loss of the seals released the pressure in the electrode areas of the chambers which permitted the CVP gases to contaminate these areas by hydrolyzing and coating the electrodes and windows with oxides.

The above problem was overcome by installation of water-cooled traps in each exhaust line to condense the $TiCl_4$ and prevent its buildup in low points in the exhaust lines (where it eventually hydrolyzed). A water aspirator was also added to the scrubbing system which places the exhaust system under a slight negative pressure and keeps the CVP gases flowing through the chambers with considerably less fluctuation of both flow and pressure.

Other causes of filament breakage were malfunctions of the let-off and take-up reels. The constant tension device on the let-off reel occasionally jerked the substrate, causing it to break. The take-up reel mechanism induced vibration into the substrate. If the vibration was excessive, arcing occurred at one or more of the electrodes and frequently resulted in filament breakage.

Damping was used to reduce the vibration of the filament. The gear ratios and the take-up reel mechanism were changed to permit the drive motor to run at a higher speed, thereby eliminating much of the jerking experienced earlier.

In later experiments the mercury-filled electrodes in the Mark II models were replaced with solid electrodes made from 1/4 in. diameter, stainless steel rods. These electrodes worked successfully when a hydrogen atmosphere was kept around the electrode-substrate contact in both TiB_2 and TiC filament preparation. In argon atmospheres, some arcing took place at the contacts. This phenomenon is not fully understood, but is possibly related to small air leaks around windows near the electrical contacts.

The successful use of solid electrical contacts in preparation of filament which has good electrical conductivity (as do TiB_2 and TiC) is an important contribution toward future CVP chamber designs: their use in heated CVP chambers would greatly simplify the design.

E. FILAMENT PREPARATION IN CROSS-FLOW PLATING CHAMBERS

TiB_2 Filament: Several aspects of the TiB_2 deposition process were studied in the cross-flow chambers. These included variables such as substrate type and size, gas composition, and temperature conditions. Deposits were made from CVP gas mixtures containing H_2, BCl_3, $TiCl_4$, and He or Ar.

All of the experiments were run on 2.0-mil diameter Ta wire or on 0.5- or 1.0-mil diameter W wire. The hot spot and temperature gradient problems described earlier were more severe when the smaller diameter substrates were used. Therefore, it was decided shortly after experiments began on TiB_2 preparation to use 2-mil diameter Ta wire as the substrate in future experiments. The temperature range of 1150° to 1175°C was found to produce the highest TiB_2 deposition rate without formation of weak deposits of high crystallinity. If the incoming Ta substrate temperature was maintained at 1175°C, a 150°C temperature gradient occurred. Under these conditions a final diameter of 3.5 mils was obtained when the two chambers were used with a substrate speed of 6 in. /min and a $BCl_3/TiCl_4$ mole ratio of 5:1. At a mole ratio of 2:1, the maximum fiber diameter obtained was 3. 1 mils.

At $BCl_3/TiCl_4$ ratios below 2:1, the deposition rate was extremely low, while at ratios above 2:1, although the deposition rates increased, the deposits tend to be rich in boron with considerable loss in strength. Thus it appears desirable to use the highest $BCl_3/TiCl_4$ ratio which will deposit stoichiometric TiB_2. Indications are that this ratio is near 2:1 $BCl_3/TiCl_4$. Argon was found to be more desirable than helium as a diluent because higher deposition rates occur with argon, which also eliminates the hot spot problem. The reason for this has not been recognized at this time.

Photomicrographs of cross sections of the TiB_2 filament prepared in the cross-flow chambers always show that the deposit consists of several distinct layers (see Fig. 6). In polishing the specimens, it was noted that the hardness of the layers is different. Because the composition of the layers is different this, in turn, may be related to the temperature gradient along the length of the heated substrate. Two layers are known to deposit in each of the two chambers.

None of the filament produced was of good quality. Some of the filament was smooth and optically reflective, but the surface perfection achieved with the batch fibers in reference (1) was not obtained. In general, the tensile strength of the filament was quite low (<75, 000 psi). The cause of this was not well known but there are at least three possibilities which were believed to contribute to the low quality:

1. The crystallite size was large compared to that of the higher quality TiB_2 reported in reference (1). However, the same deposition temperature, gas composition, and gas velocity reported in reference (1) to prepare higher quality TiB_2 fibers were also used here.

2. Due to the short residence time at temperatures in the continuous plating unit (< 1 min compared to about 15 min in the batch experiments (reference 1)), diffusion into the core or reaction with the core was not as great in the continuous filament. This suggested that preforming of the substrate, longer residence times at temperature (lower filament speeds or longer chambers), and post-heat treatment of the filament should be evaluated as means of promoting more interaction between the substrate and deposit.

3. The layering of the deposits may have had a weakening effect on the overall filament. Reduction of the temperature gradient may be an answer to this problem.

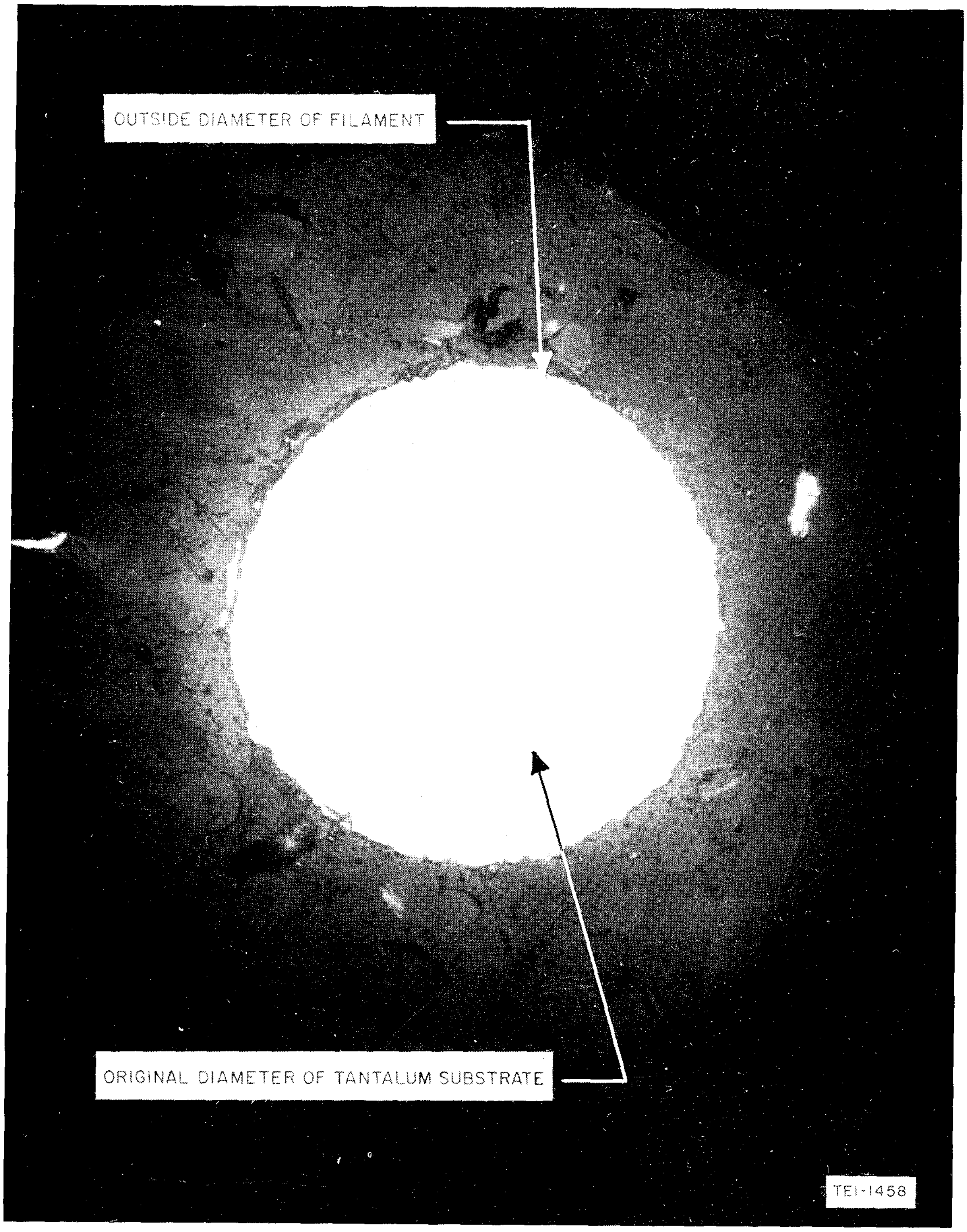


Fig. 6 Photomicrograph of Typical Two Reactor TiB_2 Filament

TiC Filament: A few experiments were run in the cross-flow reactors on TiC filament preparation using CVP gas mixtures containing H_2, $TiCl_4$, n-C_4H_{10}, and He or Ar. Substrate materials included 1.0- and 1.5-mil diameter W and 2.0-mil diameter Ta wire.

To deposit TiC, it was necessary to heat the incoming substrate to 1300 to 1350° C. A 200° C temperature drop occurred in each reactor across the CVP region of the substrate. Under these temperature conditions, with either a 2:1 or 1:1 $TiCl_4$/n-C_4H_{10} ratio, and using a 2-mil diameter substrate at 6 in./min, a final filament diameter of approximately 4 mils was obtained when two CVP reactors were employed. The use of the tungsten substrates resulted in final filament diameters of 3.0 to 3.5 mils. The 1:1 $TiCl_4$/n-C_4H_{10} ratio resulted in smoother deposits than the 2:1 ratio.

Photomicrographs of cross-sectional areas of the TiC filament (Fig. 7) show formation of a poorly defined layer in each reactor which is not as pronounced as in the TiB_2 deposition. It appears that, after a sizable quantity of TiC deposition occurs, possibly a thin layer of graphite deposits on the substrate as it passes through the cooler temperature region. There is also considerable porosity in the deposit.

None of the TiC deposits produced showed good adherence to the substrate. X-ray examination of the filament failed to detect carbides of Ta or W, which indicates little or no substrate conversion had occurred. Work on other projects within the Company has shown a strong relationship between increased tensile strengths and the amount of substrate conversion. It is generally believed that a lack of conversion results in poor bonding between the deposit and substrate. Many of the problems associated with the TiC filament preparation in the cross-flow reactors were the same as those discussed under TiB_2 filament preparation.

F. OTHER METHODS OF SUBSTRATE HEATING

The temperature gradient problem, although it could be ameliorated in some degree by the various techniques discussed, could not be sufficiently eliminated while using resistively heated substrates. Success of rf substrate heating in other programs in this laboratory led us to examine this technique. We recommended to the NASA Project Manager and the NASA Headquarters Representative that we make a feasibility test using rf heating. This test indicated a good probability of success and it was mutually agreed to convert our plating units to this process. This conversion and the results are presented in Section IV. Meanwhile, during the obtaining of suitable rf generators and building of the plating units, work was carried out on a batch unit for making parameter studies to assist in the subsequent continuous preparation of TiB_2 and TiC. The batch work is described in the following Section III.

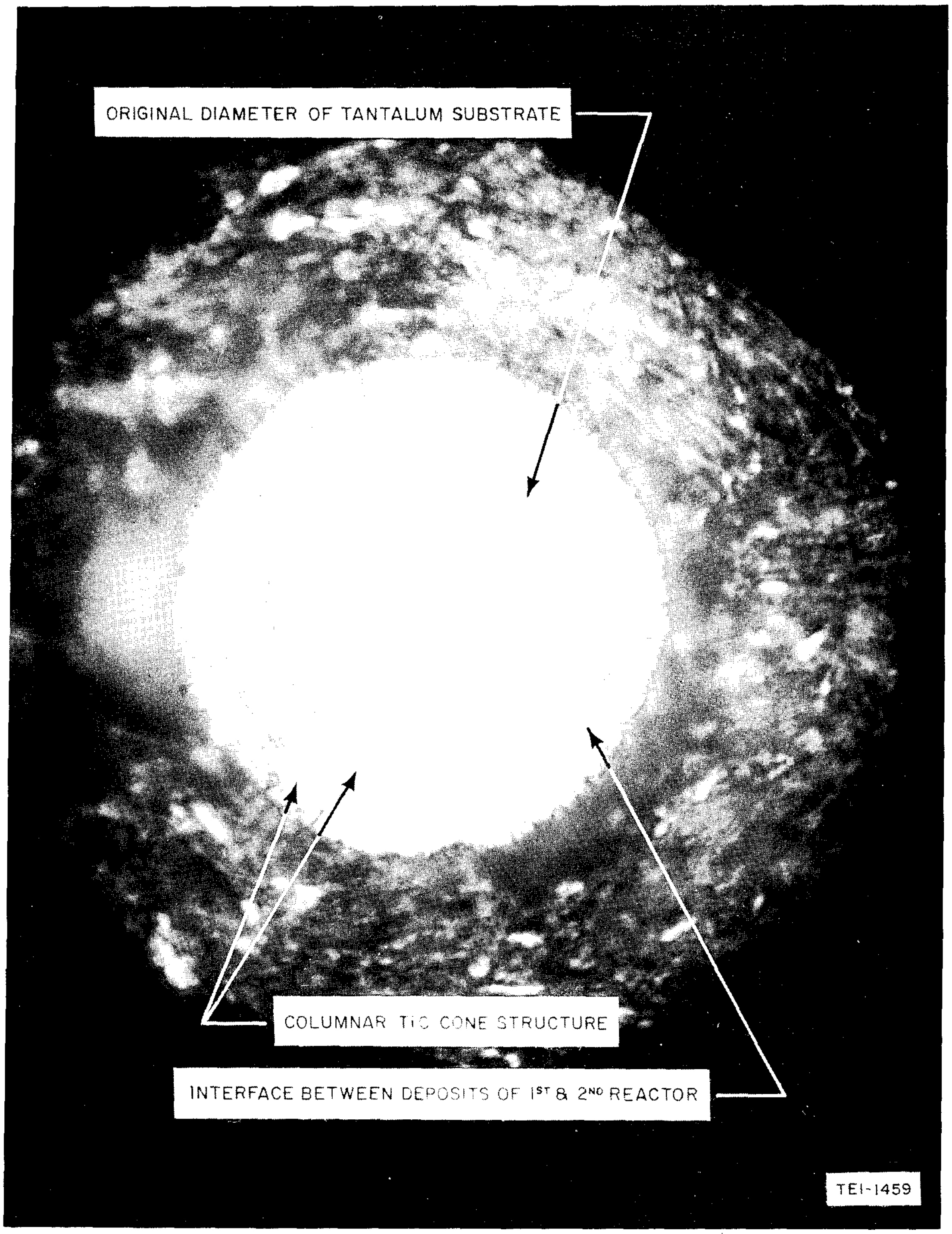


Fig. 7 Photomicrograph of Typical Two Reactor TiC Filament

III. BATCH PLATING OPERATIONS

The primary purpose of the batch experiments was to determine effective conditions to be used for continuous preparation of TiB_2 and TiC filament. This plating unit consisted of a horizontal, parallel-flow reactor and an outgassing chamber. The reactor was 1-in. OD and had a 12 in. space between electrodes; it was enclosed in an oven constructed from asbestos insulation over a metal frame. The front of the oven contained a Vycor window through which fiber temperatures were monitored with an optical pyrometer.

Strip heaters were used to heat the oven and the electrodes were made from 1/4-in. diameter stainless steel rods flattened and polished to give effective electrical contact with the substrate. Plating gases passed through rotometers and were mixed prior to entering the deposition chamber.

A. TiB_2 BATCH OPERATIONS

About fifty TiB_2 fibers were prepared in the apparatus. The CVP gas flows were varied over a wide range and it was found that high strength TiB_2 fibers (100 to 300 kpsi) could be prepared, even though the $BCl_3/TiCl_4$ ratio was varied widely. Deposition rates were higher at larger $BCl_3/TiCl_4$ ratios, but when the latter exceeded a value of 3, the fibers were found to contain excess boron and were weak. The amount of hydrogen in the CVP gas mixture was found to be extremely critical. Strong fibers could not be prepared unless the hydrogen content of the CVP gas mixture was in the range of 75 to 100 percent of the calculated stoichiometric amount of hydrogen needed for the complete reduction of the $TiCl_4$ and BCl_3.

The argon gas flow was maintained at approximately 6 times that of the total CVP gas flow. Several strong TiB_2 fibers were prepared at 1275°C on 0.5 mil electrolytically etched tungsten using a total gas flow of 1085 cc/min and a $TiCl_4$ gas flow of 20 cc/min. The gas flow ratios of the remaining gases were as follows:

$$\frac{BCl_3}{TiCl_4} = 2.5; \quad \frac{H_2}{TiCl_4} = 4.5; \quad \frac{Ar}{TiCl_4} = 46.2$$

Plating time for a 4 mil diameter TiB_2 fiber was about 1.5 min. It was necessary to maintain oven temperature at a minimum of 485°C in order to take accurate temperature readings during the entire time in which the fiber was prepared. The results of the experiments in which fibers of sufficient size and quality to be handled are summarized in Table III.

Table III

BATCH EXPERIMENT DATA

					Gas Ratios				
Run No.	Substrate	Temp. °C	Total Gas Flow cc/min	$TiCl_4$ Gas Flow cc/min	$\frac{BCl_3}{TiCl_4}$	$\frac{H_2}{TiCl_4}$	$\frac{Ar}{TiCl_4}$	Final Diameter mils	Tensile Strength psi
B-2	1 mil W	1020	250	10	2	3.5	18.5	3.7	51,000
B-3	1 mil W	1160	250	10	2	3.5	18.5	3.4	48,000-141,000
B-4	1 mil W	-	250	10	2	3.5	18.5	4.2	31,000-54,000
B-6	1 mil W	1190	250	10	2	3.5	18.5	4.6	Too weak to test
B-7	1 mil W	1020-1060	265	10	3.5	3.5	18.5	4.2	Too weak to test
B-8	1 mil W	1170	250	10	2	3.5	18.5	5.1	1,200-10,600
B-10	1 mil W	1045	250	10	2	3.5	18.5	5.4-6.2	Too weak to test
B-11	1 mil W	1245	250	10	2	3.5	18.5	4.6	11,900-38,300
B-13	1 mil W	1220	1090	25	2	3.5	37.0	5.2	17,500-59,300
B-14	1.5 mil W	1195	1090	25	2	3.5	37.0	4.6	8,100-13,400
B-15	0.5 mil W	1245	1090	25	2	3.5	37.0	5.2	10,170-47,500
B-16	0.5 mil W	1245	1090	25	2	3.5	37.0	5.4	2,000-39,300
B-17	0.5 mil W	1295	1090	25	2	3.5	37.0	3.4	30,200-81,400
B-18	0.5 mil W	1320	1090	25	2	3.5	37.0	crystalline	Too weak to test
B-19	0.5 mil W	-	1085	20	2.5	4.5	46.2	3.8	650-930
B-24	0.5 mil W	-	1085	20	2.5	4.5	46.2	2.7	250,500
B-25	0.5 mil W	1295	1085	20	2.5	4.5	46.2	4.2	94,300-123,200
B-26a	0.5 mil W	1295	1085	20	2.5	4.5	46.2	4.3	202,500-212,500
B-26b	0.5 mil W	1295	1085	20	2.5	4.5	46.2	2.3	172,000-340,000
B-26c	0.5 mil W	1295	1085	20	2.5	4.5	46.2	2.6	130,000-281,000
B-32	0.5 mil W	1245	1085	20	2.5	4.5	46.2	3.7	98,800
B-33	0.5 mil W	1245	1085	20	2.5	4.5	46.2	2.9	22,600-54,700
B-36	0.5 mil W	1220	1085	20	2.5	4.5	46.2	3.9	208,000
B-37	0.5 mil W	1220	1085	20	2.5	4.5	46.2	5.1	85,800-137,500
B-39	0.5 mil W	1220	1095	25	2	3.8	37.0	3.8	141,000
B-40	0.5 mil W	1220	1095	25	2	3.8	37.0	2.2	162,500-262,500
B-41	0.5 mil W	1220	1095	25	2	3.8	37.0	4.4	40,700-75,300
B-42	0.5 mil W	1220	1095	25	2	3.8	37.0	2.6	69,000-137,800
B-43	0.5 mil W	1220	1095	25	2	3.8	37.0	3.9	18,000-79,200
B-44	0.5 mil W	1220	1110	30	1.7	3.5	30.8	4.2	96,800
B-45	0.5 mil W	1220	1110	30	1.7	3.5	30.8	4.2	64,200-128,000
B-46	0.5 mil W	1220	1135	20	2.5	7.0	46.2	4.0	30,800
B-47	0.5 mil W	1220	1135	20	2.5	7.0	46.2	4.1	1,510-41,200
B-48	0.5 mil W	1220	1100	20	2.5	5.2	46.2	3.1	104,000-162,000
B-49	0.5 mil W	1220	1100	20	2.5	5.2	46.2	3.9	33,200
B-50	0.5 mil W	1220	1100	20	2.5	5.2	46.2	4.3	104,000-205,000

Note: The temperatures reported contain a +20°C sight glass correction.

X-ray analyses were run on twenty-three of the fibers in the as prepared condition. TiB_2 or W, and TiB_2 were found in all of the fibers tested.

Chemical analysis for titanium were run on twelve of the fibers, but no correlation was found between titanium content and tensile strength. The titanium content varied from 65.9 to 75.6 wt percent, compared to 68.9 wt percent Ti for stoichiometric TiB_2.

B. TiC BATCH OPERATIONS

In the experiments on TiC preparation in the batch reactor, gas mixtures containing $TiCl_4$, n-C_4H_{10}, H_2, and Ar were employed. When the oven temperature was maintained below 450°C, a dark brown deposit appeared on the wall which does not occur during TiB_2 fiber preparation. This deposit was not identified, but is believed to have formed from the vapor phase decomposition of n-C_4H_{10} and reaction with $TiCl_3$. The deposit was extremely difficult to remove and required the use of a boiling H_2SO_4 and $(NH_4)_2SO_4$ mixture for cleaning the deposition chamber.

In further experiments, C_2H_5Br was substituted for n-C_4H_{10} as the carbon precursor and some reduction in deposits was noted so that even at 460°C there was less with C_2H_5Br than with n-C_4H_{10} at 450°C. Nevertheless, the obscuration was so severe that it was believed that prolonged continuous operation was not feasible. This problem, coupled with the continuing difficulty of obtaining homogeneous TiC deposits in a controlled manner, led to the decision that TiC preparation by co-plating from $TiCl_4$ and a carbon precursor be halted.

C. TiC PREPARATION FROM CH_3TiCl_3

Literature surveys were made to determine if there were an organotitanium compound available which could be used as a single precursor for TiC. Such a compound must have a strong bond between the titanium and carbon atoms, so that upon heating, the compound would decompose to TiC. A compound, methyl titanium trichloride, was found which melts at 29°C and has an extrapolated boiling point of 120°C. Seventy grams of the material was prepared for us by Regis Chemical Co.

A new batch apparatus was constructed for experiments with this compound. (Fig. 8). The deposition chamber was equipped with stopcocks so that air could be evacuated prior to the addition of the CH_3TiCl_3 and its carrier gas. A condenser into which the compound was sublimed prior to the CVP experiment is attached to one arm of the deposition chamber.

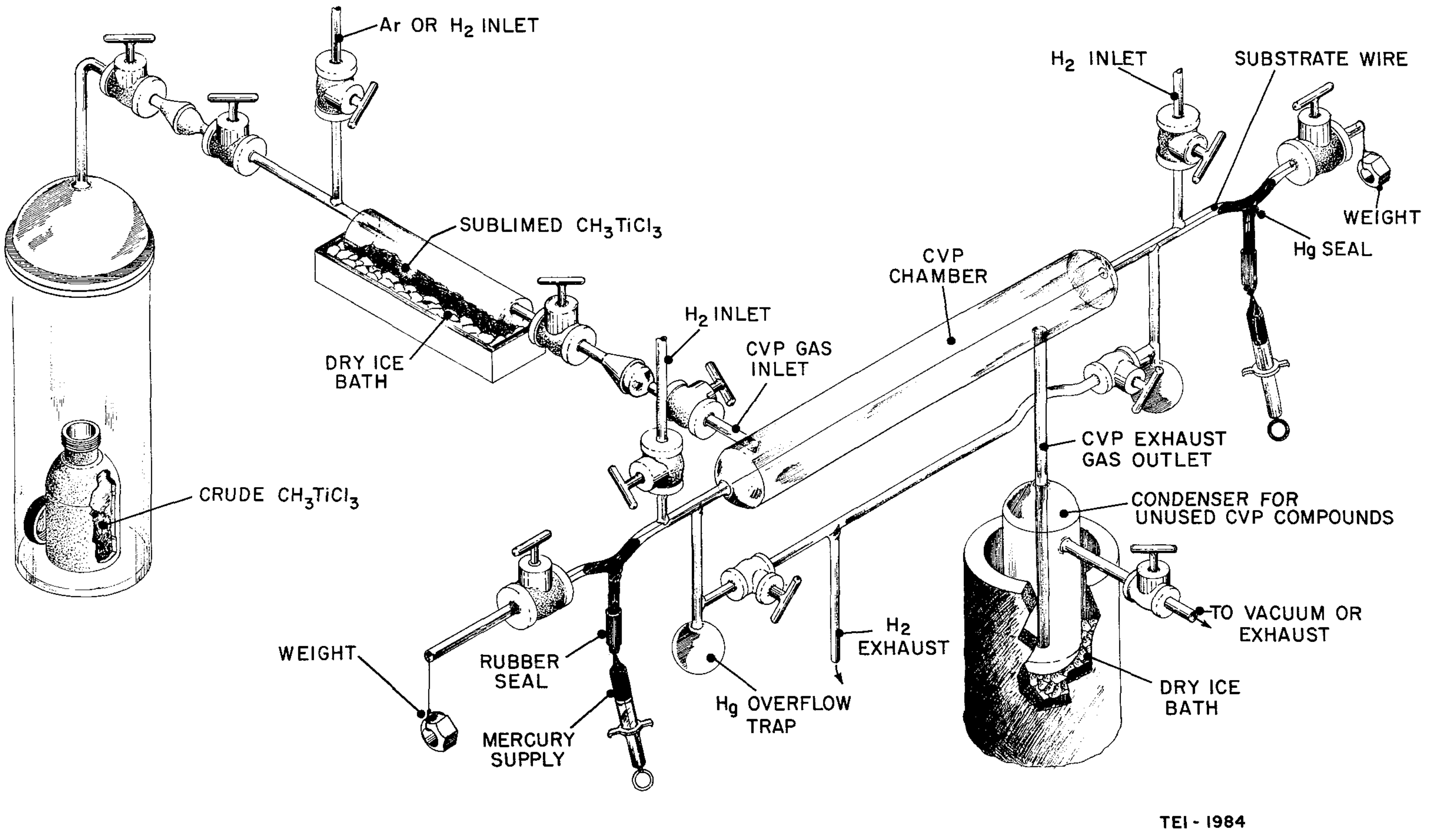


Fig. 8 Schematic of Apparatus for Preparation of TiC from CH_3TiCl_3

Initial experiments with this compound yielded a crystalline deposit of TiC. The deposit was prepared by passing a gaseous mixture of the compound with C_2H_5Br over a 1 mil tungsten wire heated to 1100°C. These results were promising since we had not prepared TiC in any form previously by CVP techniques below 1225°C. In later experiments where mixtures of H_2 and CH_3TiCl_3 gases were passed over 1 mil W substrates heated to 1000-1050°C, fibers up to 2.3 mils diameter were obtained. Tensile strengths varied from 77,000 psi on a 2.3 mil fiber to 243,000 psi on fibers in the size range of 1.4 to 2.0 mils. Figure 9 shows a polished cross-section of one of the TiC fibers. The deposit appears to be monolayered and of extremely small crystallite size. The chief drawbacks of using CH_3TiCl_3 as a TiC precursor are that it forms deposits in the reactor and that it is a difficult material to handle due to its room temperature instability and its rapid reaction with moisture.

Part of the problem of depositing a homogeneous TiC may be related to findings of E. Rudy et al. (12) on the TiC phase system. The compound previously thought to be stoichiometric TiC is actually TiC_{1-x} with a composition range from about 32 to 49 atomic per cent C, and contains a variable number of lattice vacancies depending upon the exact composition of the compound. Due to the variable number of vacancies and also to our CVP gas mixture containing carbon precursors which can decompose readily at our TiC deposition temperature to form free carbon, it may be extremely difficult to coplate a compound of a specific TiC or TiC_{1-x} composition.

After consultation with the NASA Project Manager, work on TiC was stopped and work was undertaken on ZrB_2 fiber preparation.

D. ZrB_2 BATCH STUDIES

Several exploratory experiments were run on ZrB_2 fiber preparation in the batch reactor. Zr metal turnings were heated to 335°C in a Vycor reactor and measured flow rates of chlorine gas were passed over the metal. Reaction appeared to be complete to $ZrCl_4$, and no free chlorine could be detected by very sensitive KI paper. Some difficulty was experienced in preventing condensation of $ZrCl_4$ in the transfer lines to the plating gas mixer and to the deposition chamber, so that the final CVP gas was quite deficient in $ZrCl_4$. A total of nine experiments was run, but no satisfactory fibers were produced. After a discussion with the NASA project manager, it was decided to withdraw manpower from the ZrB_2 batch experiments in order that as much TiB_2 filament as possible could be prepared before the end of the project.

Fig. 9 Photomicrograph of Cross-Section of TiC Prepared from CH_3TiCl_3

IV. CHEMICAL VAPOR PLATING UNITS UTILIZING RADIOFREQUENCY-HEATED SUBSTRATES

After serious problems were encountered using resistance-heated substrates for TiB_2 filament preparation, attempts were made to use radiofrequency (rf) heated substrates for this purpose. Initial attempts to deposit TiB_2 in this manner looked promising in that uniform temperature zones on a continuous substrate up to 18 in. long were obtained during the deposition. The tensile strength of the prepared filament was comparable to that of the strongest filament prepared on resistance-heated continuous substrates. At this point a decision was made to begin work on the preparation of continuous TiB_2 filament utilizing rf-heated substrates.

A. DESIGN CONSIDERATIONS

Some of the design criteria of an rf-heated substrate reactor are similar to those of resistance-heated substrate reactors. The formation of titanium compounds of low volatility requires the reactor to be heated. Accurate substrate temperature measurement is again of prime importance, as is good operability, since the reactor will be used for continuous filament production.

New design criteria include the use of some means of reactor heating other than resistance-type heaters, since coupling with the rf current would occur. Larger reactors are possible since the temperature gradient problem should be minimized. Mercury-filled glass tees are permissible as seals provided that adequate hydrogen or inert gas flows are used to prevent vaporization of the mercury. Proper rf shielding must be incorporated into the design for protection of the operator and to prevent emission of high intensity radio signals. Certain modifications of auxiliary equipment in the unit may be necessary to prevent interference with their operation by rf currents.

B. REACTOR DEVELOPMENT

The design considerations outlined above led to the development of the reactor shown in Fig. 10. The reactor was of the split-flow type and was mounted horizontally in the CVP unit. The deposition chambers were designed for 4 feet of actual plating lengths and were constructed of 1-in. diameter Vycor tubing. In the split flow reactor, plating gases enter from each end of the chamber and exhaust at a single center outlet. Mercury-filled glass tees seal each end of the chamber from the atmosphere, and the mercury is protected from the CVP gases by a small stream of H_2 or Ar gas which later mixes with the CVP gases. The power supply for each unit is a 120 megacycle-1.2 KW generator purchased from the Radio Frequency Corporation. The

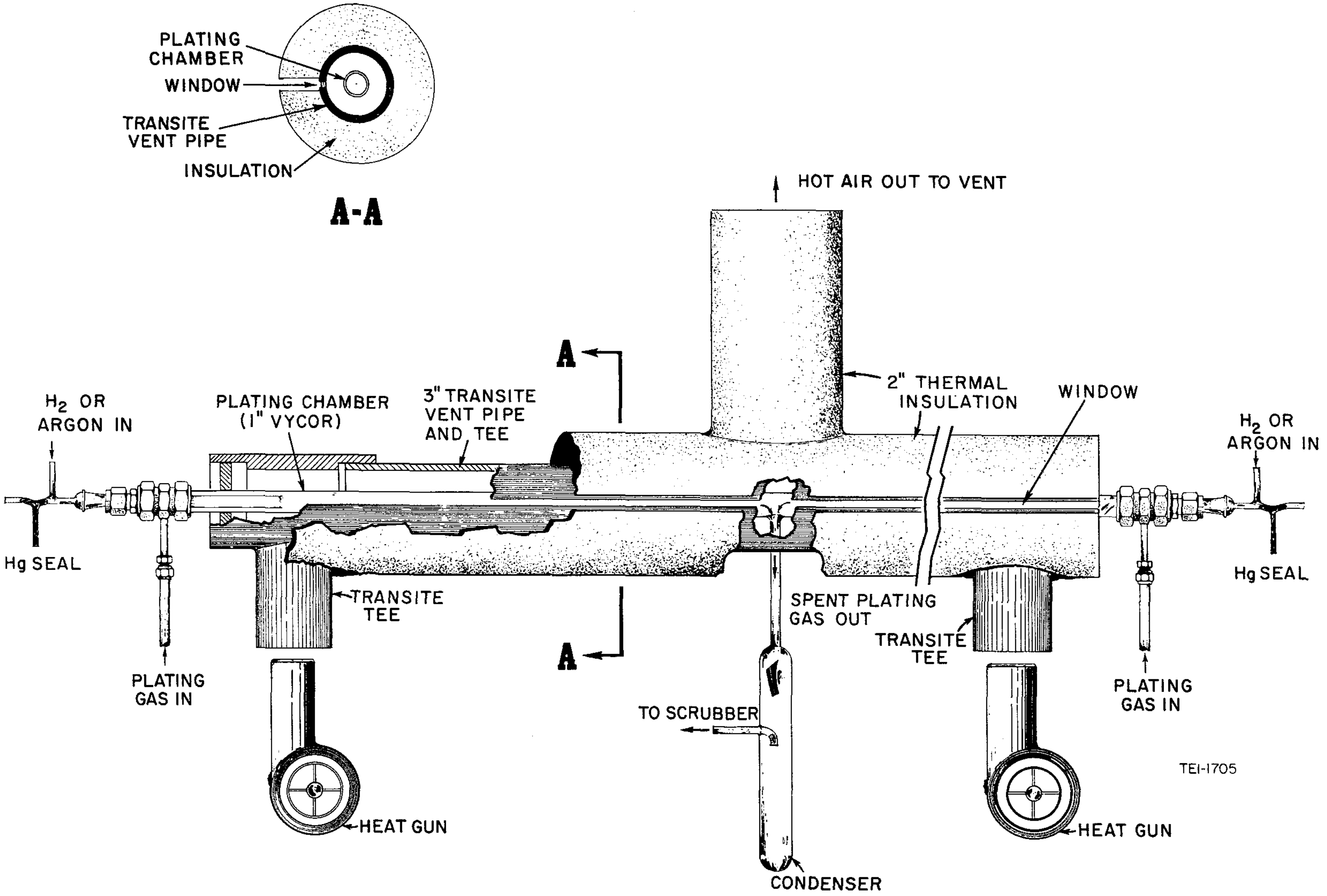


Fig. 10 Schematic of CVP Unit for Radiofrequency-Heated Substrates

electrical current is transferred to the substrate by an antenna made from two 1-in. wide copper strips 25 to 30 in. long. The strips are located on opposite sides of the deposition chamber and are bent to fit the curvature of the chamber's outer wall. Each strip is connected to an electrode of the rf power supply by another copper strip. The CVP region of the deposition chamber is surrounded by an oven made from transite pipe fittings and asbestos insulation. Temperatures of 450 to 500°C are maintained inside the oven by air entering each end of the oven from heat guns.

C. PROCESS DEVELOPMENT

Two process development CVP units of similar design were constructed as shown in Fig. 11. As in the cross-flow CVP units, each unit was equipped with a pay-off and a take-up mechanism for transporting of the substrate through the reactors. The CVP units were connected to the same rotameters, gas mixers, and vaporizors used with the cross-flow reactors. Each unit contained a power supply to provide current to a hydrogen treating (or tungsten substrate out-gassing) chamber.

In order to protect the operator from rf currents and to prevent strong radio signal emission, a wooden framework covered inside and outside with copper screen was built around each CVP unit (Fig. 12). The screens are completely separated and the outer screen is grounded with a 2-inch wide copper strip. The doors to the unit were equipped with bronze weather stripping and latches to serve as "radio frequency gaskets" to assure adequate rf electrical contact and shielding around the door edges. Later, electrical enclosure filters were added to all electrical lines entering each CVP unit and additional shielding was erected behind the units to further reduce the radio signal emission. Federal Communications Commission regulations (13) limit the radio signal intensity to 10 μ volts/meter at a distance of 1 mile. After the final shielding was installed, the radio signal intensity from the rf generators was measured in four directions (90° apart) at a distance of 1 mile and was found to have a maximum value of 3 μ volts/meter.

D. OPERABILITY OF CVP UNITS

The first major problem in operating the rf-heated substrate reactors was arrangement of the various physical components of the CVP unit so that a satisfactorily uniform heating of the substrate and fiber could be achieved. Although there is some knowledge of the heating of wires with rf power, the use of this concept to give a desired temperature profile and to permit CVP of continuous filament is believed to have been applied for the first time anywhere by the TEI laboratories. Thus the initial experiments required considerable trial and error before a length of substrate could be heated for several minutes with rf power.

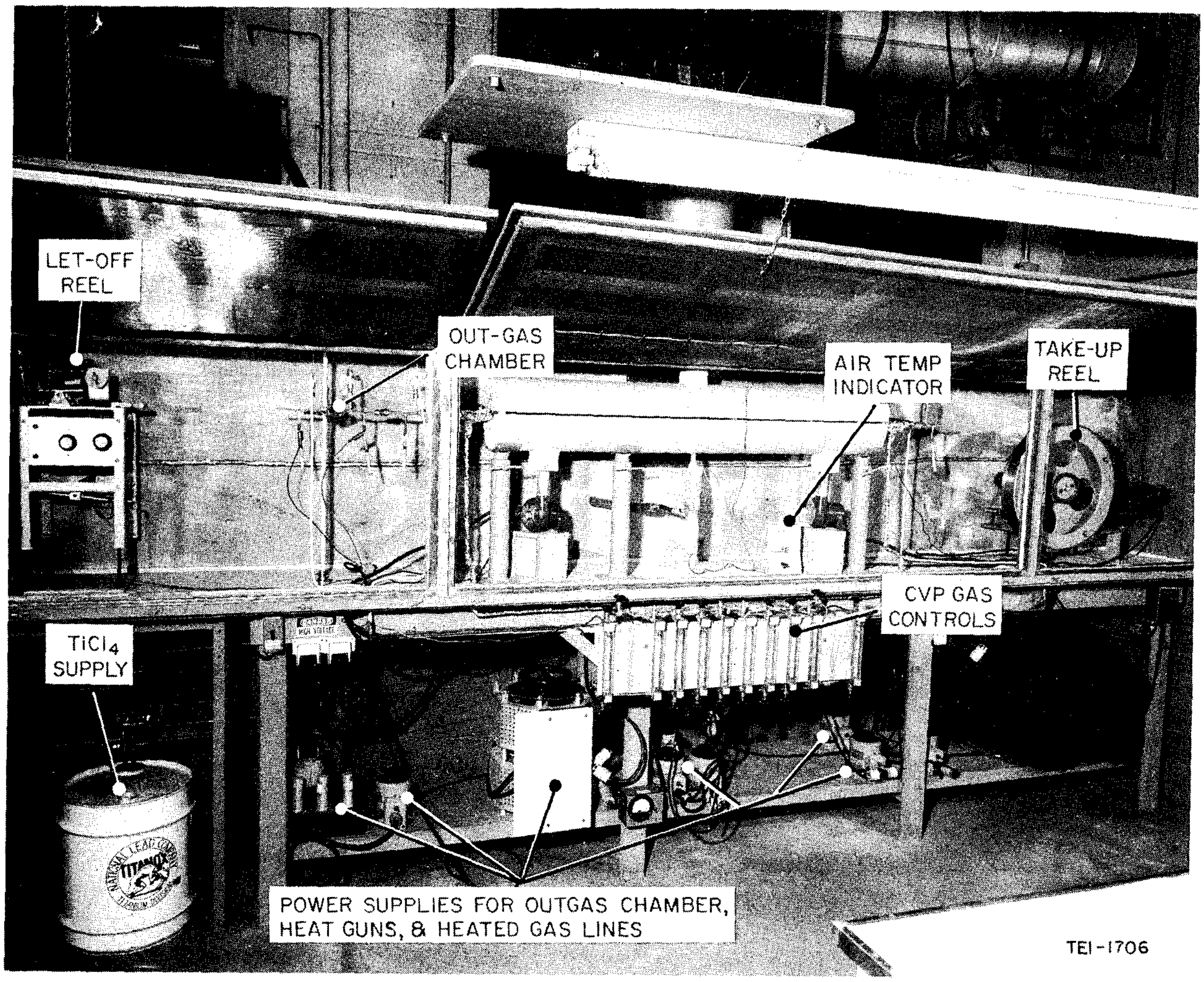


Fig. 11 Radiofrequency-Heated Substrate CVP Apparatus

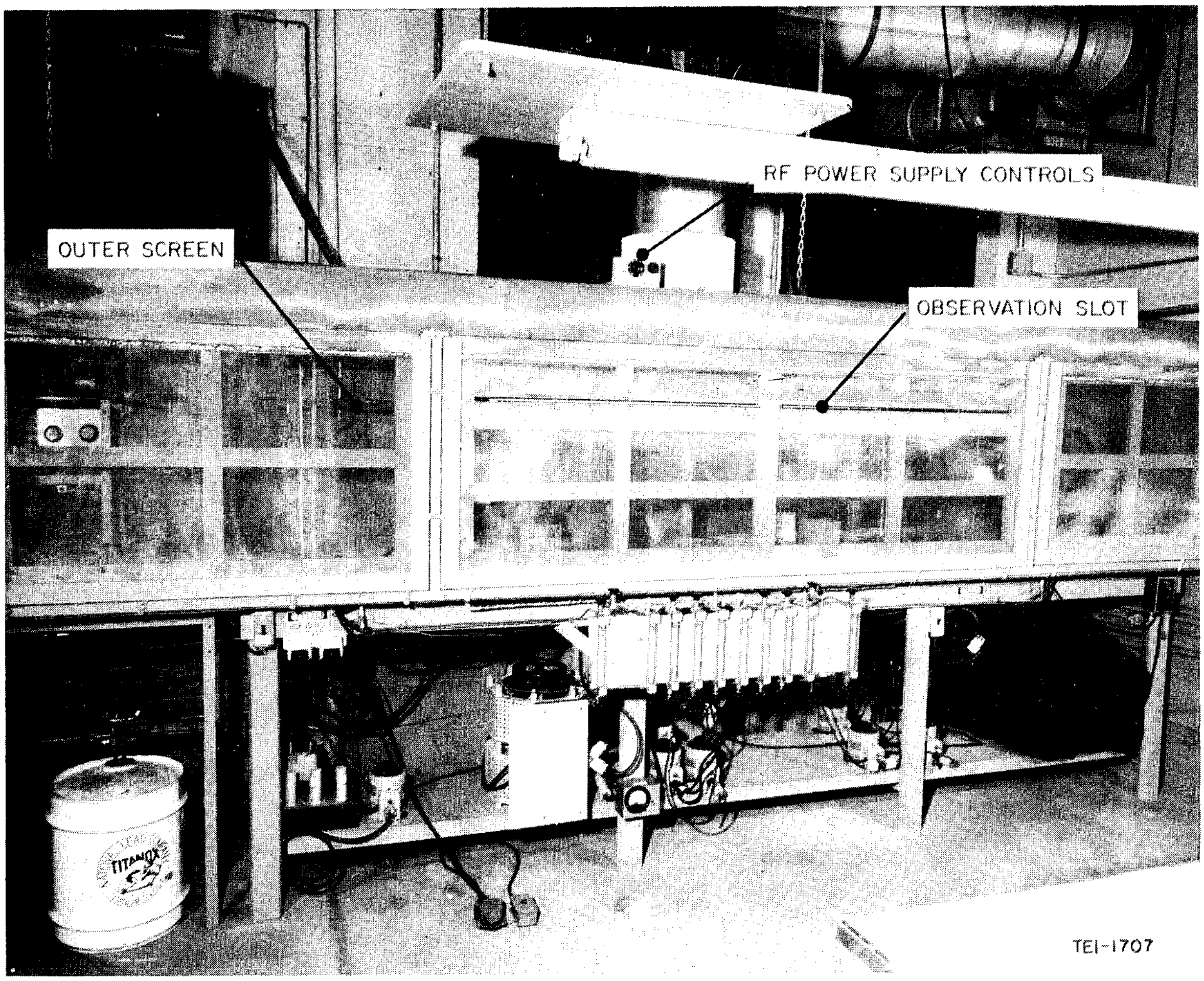


Fig. 12 Radiofrequency Shielding for CVP Apparatus

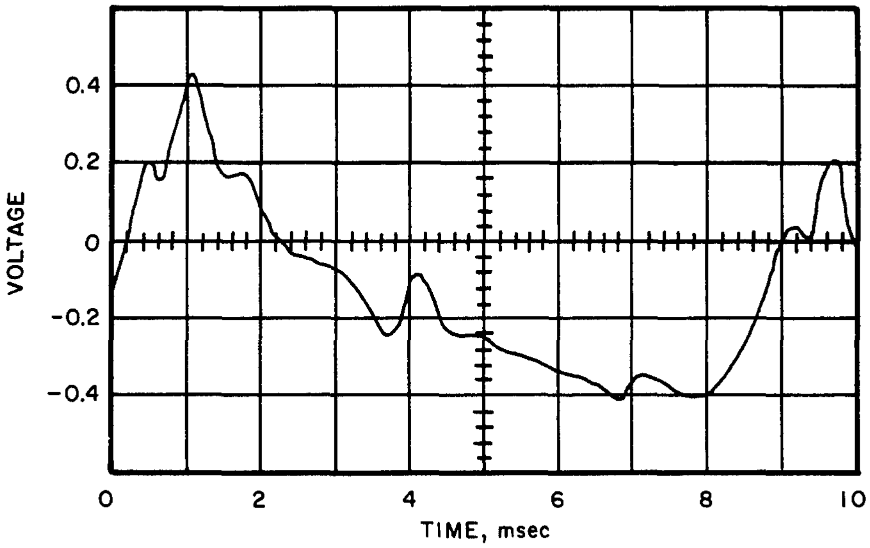
One of the initial problems was severe vibration of the substrate when it was heated. The vibration occurred with a frequency of 120 cycles per second and was caused by the generator power supply ripple. This was substantially eliminated by inserting two 2-microfarad capacitor filters in the circuit. Figure 13 shows oscillograph tracings of the radiated signal before and after the filters were inserted.

A second problem resulted from the installation of the rf shielding around the CVP equipment. This upset the previous tuning arrangement and difficulties were encountered in obtaining a uniform heat zone over the full length of substrate inside the CVP region of the deposition chamber. The new pattern consisted of two or three separate heat zones each about 6 in. long. This problem was corrected substantially by shortening the antenna from 32 in. to 27 in. and positioning more of the antenna on the right side of the chamber than on the left side. This arrangement caused the substrate to overheat initially on its exit side of the CVP region of the reactor during an experiment, but after the deposition began, and the power to the substrate was increased, the heat zone spread out nearly uniformly to lengths up to 36 in.

Another problem which occurred after the rf shielding was installed was heating of the filament on the take-up spool. This was corrected by connecting a 2-in. wide copper strip between the take-up spool frame and the mercury seal of the deposition chamber nearest the take-up spool.

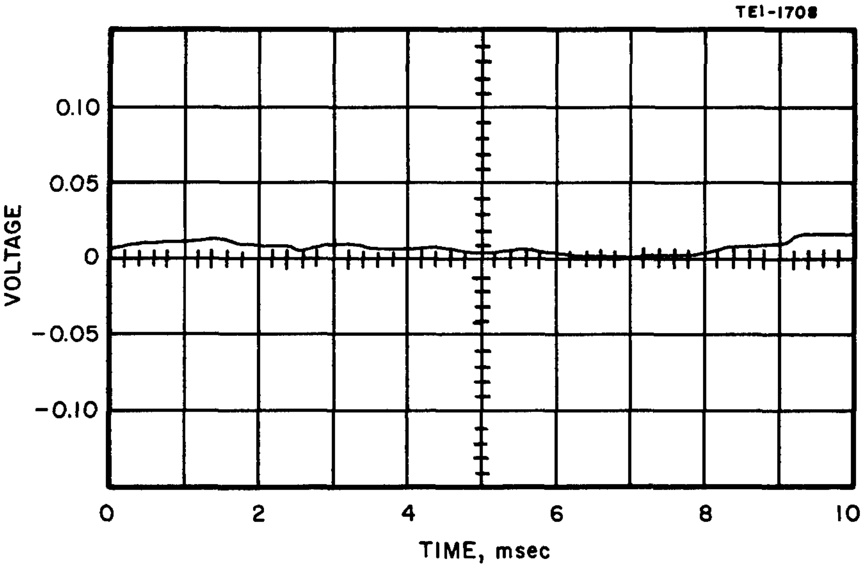
Accurate filament temperature measurement was a major problem when using the rf-heated substrate reactors since $TiCl_3$ flakes or crystals condensed in varying amounts throughout the deposition chamber in areas heated to 450 to 500° C. When a deposition chamber was heated above 500° C, a brown deposit occurred on the wall which was believed to be $TiCl_2$. Three methods of temperature measurement were considered. One was the use of standard temperature lamps behind the deposition chamber at several points. This idea was attempted but it was difficult to focus on the standard filament because of interference caused by imperfections in the Vycor reactor walls.

The second idea was to resistively heat the substrate wire with a certain dc voltage and amperage to a known temperature before and/or after a given experiment. This idea works for very thin fibers or deposits but normally the deposit was so heavy that temperatures to be corrected could not be read with the optical pyrometer. The third idea was to use a two color pyrometer. This instrument measures the ratio of energy at two wave lengths, and unless the deposit attenuates one wave length more than another, the ratio remains the same. A two-color pyrometer was demonstrated with partial success, but the instrument was not in our hands long enough for a



GENERATOR OUTPUT AS RECEIVED
PLATE VOLTAGE, 1700

PLATE AMPS, 0.06
WATTAGE, 102



GENERATOR OUTPUT WITH TWO 2 μf CONDENSERS
PLATE VOLTAGE, 3000

PLATE AMPS, 0.085
WATTAGE, 255

Fig. 13 Removal of Ripple from Radiofrequency Generator Output complete evaluation. It appeared necessary to eliminate all outside light to obtain a good reading. This would have meant modification of the front of the rf shield box and possibly some changes in the screening to prevent light interference.

Optical pyrometer readings were resorted to and were taken in the cleanest areas of the deposition chamber and showed temperatures of 1050 to 1125°C. When these areas were calibrated, the correction to be applied amounted to approximately + 135°C, which indicates our true substrate temperature to be in the range of 1185 to 1260°C.

E. INITIAL PREPARATION OF TiB_2 FILAMENT

During the initial experiments on filament preparation in an rf-heated substrate reactor, the chamber walls were not heated in order to keep the equipment as simple as possible during the tuning operations on the equipment. Both boron and pyrolytic graphite were prepared successfully on rf-heated substrates in the heated reactor. Pyrolytic graphite filament, which has electrical properties somewhat similar to those of TiB_2 and TiC filament, was prepared from CVP gas mixtures containing n-C_4H_{10} and BCl_3 at substrate speeds up to 12 in./min. and at substrate temperatures of 1100 to 1200°C. Plating zones up to 32 in. long were obtained on the substrate. Tensile strength values of the pyrolytic graphite filament ran as high as 127 kpsi which is 20 percent higher than previous values obtained on pyrolytic graphite prepared at TEI. It was concluded from these experiments that materials with high electrical conductivity could be prepared on rf-heated substrates, and the CVP units were then equipped with heated reactors for the purpose of preparing TiB_2 filament. Another important finding was that direct current could be passed through the substrate in addition to the rf current to produce an extended plating zone beyond that which could be obtained with the rf antenna alone. The electrical efficiency was also higher with the combination of currents than with rf power alone. For example a total power output of 420 watts from the rf generator was required to heat about 30 in. of 0.5 mil W wire to 1000°C while a combination of 210 watts rf power and 130 watts dc power heated 36 in. of the same wire to 1000°C. The limitation of this heating method is the maximum dc power that can be used without overheating the incoming substrate. Thus, where deposits of higher resistance are prepared, a greater portion of dc power can be used in the combined power source heating method.

In the initial experiments on TiB_2 filament preparation, the CVP gas flows which were used to prepare the strongest TiB_2 fibers in the batch reactor were employed in the rf-heated substrate reactors. A total gas flow of

1085 cc/min was brought into each end of the split-flow reactor. The gas flow ratios of the various gases based on the $TiCl_4$ gas flow of 20 cc/min were as follows:

$$\frac{BCl_3}{TiCl_4} = 2.5; \quad \frac{H_2}{TiCl_4} = 4.5; \quad \frac{Ar}{TiCl_4} = 46.2$$

The argon flow includes 25 cc/min brought into the reactor near the tees to protect the mercury seals from the CVP gases. Problems were encountered immediately when the substrate was heated. Overheating of the substrate occurred where its left side made initial contact with the CVP gases and it was necessary to lower the argon content of the mixture to reduce the substrate temperature at this point. This also reduced the length of the plating zone and resulted in reduced diameters of the prepared TiB_2 filament. Hydrogen was substituted for argon to protect the Hg seals and this resulted in less overheating of the substrate in these areas. The total flow of hydrogen was readjusted in order to minimize the overheating of the incoming substrate and still produce strong filament at a reasonable deposition rate. It was also necessary to change the $BCl_3/TiCl_4$ ratio from that which was used in the batch reactor. Before strong TiB_2 fiber could be produced, this ratio was lowered from 2.5 to 1.25. This change resulted in the preparation of filament which was bright in appearance and which generally had tensile strengths in excess of 100 kpsi but the deposition rate was about one half of that obtained in the batch reactor. Further information on CVP gas ratios is covered in the Appendix, section 8, CVP Gas Ratios.

The buildup of chamber deposits was more serious than in the batch reactor. This was due mainly to the length of time that the reactor was in operation in a given experiment. Higher $TiCl_4$ flows also resulted in thicker chamber deposits. The amount of rf power required to maintain a given temperature on the substrate had to be increased gradually during a run, and it is believed that the additional power requirement was caused by coupling of the rf current to the chamber deposits. After several hours of filament preparation in a reactor, the section of the deposit in contact with the reactor wall gradually changed to a mirror-like deposit believed to be titanium metal, and which would couple readily to rf currents. At the beginning of a TiB_2 preparation run in a clean deposition chamber, the rf power requirements were approximately 0.3 KW. After two hours the power requirements were about 0.8 KW. Over a period of several runs the power requirements would exceed the rf generator output and it became necessary to clean the deposition chamber. Pieces of broken filament left in the deposition chamber from previous runs also coupled to the rf current and often affected the location of the heated substrate zone. The loosely adhering chamber deposits and broken fibers could be removed from the deposition chamber in a few minutes by removing the ends of the chamber and pulling a gun brush through it. When the tightly adhering deposits used so much of the rf current that the substrate could not be heated to the required plating temperature, it was necessary to shut down the reactor and clean the deposition chamber in a dilute hydrocloric acid solution.

Since adequate temperature measurement could not be made, and the rf power requirements varied during a run, the only criterion which could be used to judge the quality of the prepared filament was its appearance as it left the deposition chamber. It was necessary to adjust the temperature of the substrate in a given run by setting the rf power at the point where the filament with the most reflective appearance was prepared. The degree of reflectiveness of the filament is usually a good indication of its strength.

The CVP gas flow rates or ratios at which most of the TiB_2 filament was prepared were as follows:

	Substrate Entrance Side of Reactor	Substrate Exit Side of Reactor
Total Gas Flow	410 cc/min	670 cc/min
$TiCl_4$ Gas Flow	20 cc/min	20 cc/min
$\frac{BCl_3}{TiCl_4}$ Ratio	1.25	1.25
$\frac{H_2}{TiCl_4}$ Ratio	5.0	5.0
$\frac{Ar}{TiCl_4}$ Ratio	13.2	26.3

(20 percent of the hydrogen was used to protect Hg filled tees and was combined with CVP gas mixture inside of deposition chamber).

A total of 3095 ft of TiB_2 filament prepared up to this point was shipped to TRW Systems, Redondo Beach, California. A summary of the properties of the filament and some of its preparation data are given in Table IV.

X-ray analyses were run on samples from approximately one half of the runs and each test showed the presence of TiB_2 or TiB_2 and W. As was shown in Table IV, only seven samples were analysed for titanium content. These results averaged higher in titanium content than the batch preparation samples, and no further samples were run when there appeared to be no correlation between titanium content and filament quality. The B/Ti ratio of the samples, based on the average titanium content, varied from 1.26 to 1.76.

F. SUPPLEMENTAL PREPARATION OF TiB_2 FILAMENT

Under an extension of the "Improved Ablative Materials" contract, a supplemental program was initiated which called for preparation of 12,000 ft of TiB_2

Table IV

CONTINUOUS TiB_2 FILAMENT PREPARATION DATA

Run No.		Gas Flows and Ratios					Filament		Tensile Strength	Deposit Density	Filament Length	Titanium Content
		Total	$TiCl_4$	$\frac{BCl_3}{TiCl_4}$	$\frac{H_2}{TiCl_4}$	$\frac{Ar}{TiCl_4}$	Speed in./min.	Diameter	kpsi	g/cc	ft.	Wt.%
JH-12	Exit	1082.5	20	1.25	4.38	46.8	12	2.4	142-229	4.38	30	Not run
	Ent.	1082.5	20	1.25	4.38	46.8			(205 Avg)			
JH-21	Exit	1245	20	1.25	5.0	55	12	2.5	73.2-308	4.25	200	69.5-74.2
	Ent.	274	20	1.35	5.35	6			(143 Avg)			(71.9 Avg)
JH-23	Exit	1110	33	0.82	3.03	28.8	12.5	2.7	194-208	4.28	100	73.4-80.1
	Ent.	660	20	1.25	5.3	25.5			(206 Avg)			(76.7 Avg)
JH-24	Exit	1110	33	0.82	3.03	28.8	12.5	3.8	167-170	4.38	55	76.8-79.0
	Ent.	660	20	1.25	5.3	25.5			(168 Avg)			(77.9 Avg)
JH-27	Exit	1110	33	0.76	3.3	28.8	12	2.6	100	4.44	180	74.2-80.2
	Ent.	655	20	1.25	5.0	25.5			(1 test)			(76.4 Avg)
JH-29	Exit	1095	20	1.25	5	47.5	12	3.1	80.5	3.77	100	70.6-72.1
	Ent.	655	20	1.25	5	25.5			(1 test)			(71.5 Avg)
JH-30	Exit	1095	20	1.25	5	47.5	12	3.2	105-141	4.18	30	71.2-72.9
	Ent.	655	20	1.25	5	25.5			(123 Avg)			(72.1 Avg)
JH-31	Exit	1095	20	1.25	5	47.5	12	2.3	81.7-198.0	4.40	100	73.8-78.0
	Ent.	655	20	1.25	5	25.5			(134 Avg)			(75.9 Avg)
JH-34	Exit	1095	20	1.25	5	47.5	12	1.9	17.0-168	4.53	100	Not run
	Ent.	655	20	1.25	5	25.5			(86 Avg)			
JH-36	Exit	670	20	1.25	5	26.3	12	2.0	40-159	4.04	110	Not run
	Ent.	410	20	1.25	5	13.2			(92 Avg)			
JH-39	Exit	670	20	1.25	5	26.3	12	2.2	126-166	4.34	40	Not run
	Ent.	410	20	1.25	5	13.2			(140 Avg)			
JH-40	Exit	670	20	1.25	5	26.3	20	2.3	92-104	4.08	100	Not run
	Ent.	410	20	1.25	5	13.2			(98 Avg)			
JH-41	Exit	670	20	1.25	5	26.3	20	1.7	51-159	4.54	75	Not run
	Ent.	410	20	1.25	5	13.2			(117 Avg)			
JH-42	Exit	670	20	1.25	5	26.3	20	2.4	96-126	4.42	100	Not run
	Ent.	410	20	1.25	5	13.2			(111 Avg)			
JH-43	Exit	670	20	1.25	5	26.3	20	2.3	86-129	4.72	115	Not run
	Ent.	410	20	1.25	5	13.2			(104 Avg)			
JH-44	Exit	670	20	1.25	5	26.3	20	2.5	39-117	4.23	185	Not run
	Ent.	410	20	1.25	5	13.2			(78 Avg)			
JH-45	Exit	670	20	1.25	5	26.3	20	2.1	100-170	4.44	135	Not run
	Ent.	410	20	1.25	5	13.2			(143 Avg)			
JH-46	Exit	670	20	1.25	5	26.3	20	2.3	118-161	4.61	75	Not run
	Ent.	410	20	1.25	5	13.2			(140 Avg)			
JH-47	Exit	670	20	1.25	5	26.3	20	1.6-2.5	72-117	5.15	90	Not run
	Ent.	410	20	1.25	5	13.2			(102 Avg)			
JH-48	Exit	670	20	1.25	5	26.3	20	2.3	39-124	4.57	30	Not run
	Ent.	410	20	1.25	5	13.2			(87 Avg)			
JH-49	Exit	670	20	1.25	5	26.3	20	2.0-3.0	58-139	4.06	60	Not run
	Ent.	410	20	1.25	5	13.2			(99 Avg)			
JH-50	Exit	670	20	1.25	5	26.3	20	2.6	105-174	4.38	60	Not run
	Ent.	410	20	1.25	5	13.2			(142 Avg)			
JH-51	Exit	670	20	1.25	5	26.3	20	2.8	49-169	4.53	175	Not run
	Ent.	410	20	1.25	5	13.2			(116 Avg)			
JH-52	Exit	670	20	1.25	5	26.3	20	2.7	93-119	4.41	90	Not run
	Ent.	410	20	1.25	5	13.2			(106 Avg)			
JH-53	Exit	670	20	1.25	5	26.3	20	3.2	29-91	4.48	50	Not run
	Ent.	410	20	1.25	5	13.2			(56 Avg)			
JH-54	Exit	670	20	1.25	5	26.3	20	2.8	74-131	4.33	170	Not run
	Ent.	410	20	1.25	5	13.2			(108 Avg)			
JH-55	Exit	670	20	1.25	5	26.3	20	2.4	48-80	4.09	105	Not run
	Ent.	410	20	1.25	5	13.2			(64 Avg)			
JH-56	Exit	670	20	1.25	5	26.3	20	2.4	126-198	4.34	355	Not run
	Ent.	410	20	1.25	5	13.2			(155 Avg)			
JH-57	Exit	670	20	1.25	5	26.3	20	2.1	86-121	4.46	80	Not run
	Ent.	410	20	1.25	5	13.2			(103 Avg)			

filament. The CVP equipment used in the previous work was reassembled in a new location and everything was done to duplicate the previous construction conditions as closely as possible to minimize problems of retuning the rf heating system.

Considerable difficulty was experienced, however, in retuning the equipment to obtain a satisfactory heat profile. This was eventually accomplished by placing electrical stubs on each end of the plating chamber and grounding them to the interior wall of the rf shield, and by reversing the direction of travel of the tungsten substrate through the chamber. Other problems which were corrected included a high HCl content of the BCl_3 gas supply and excess draft on the exhaust line. The excess draft caused air to leak in around the chamber seals thus contaminating the TiB_2 deposit. Except in a few initial experiments where as-drawn tungsten substrates were used, all of the TiB_2 filament was prepared on electro-etched tungsten substrate.

The CVP gas flow rates or ratios at which most of the TiB_2 filament was prepared were as follows:

	Substrate Entrance Side of Reactor	Substrate Exit Side of Reactor
Total Gas Flow	670 cc/min	920 cc/min
$TiCl_4$ Gas Flow	20 cc/min	20 cc/min
$\frac{BCl_3}{TiCl_4}$ Ratio	1.25	1.25
$\frac{H_2}{TiCl_4}$ Ratio	5.0	5.0
$\frac{Ar}{TiCl_4}$ Ratio	26.3	38.7

Occasionally it was necessary to vary the argon flow in either side of the reactor in order to maintain the proper temperature profile on the substrate. Larger volumes of argon were used here than in the previous work because it was found that a more uniform substrate temperature profile resulted in the present setup. The usual causes for the profile to change were pieces of broken filament left in the deposition chamber or accumulation of titanium compound deposits in various parts of the chamber.

Attempts were made to measure the filament temperature with the use of a 2-color pyrometer. It was found that the rf current interfered with the electronics of the pyrometer whenever the pyrometer was close enough to the CVP unit for a temperature measurement.

A further attempt was then made to measure the filament temperature with an ordinary optical pyrometer. This was done by placing a clean deposition chamber into the CVP unit and taking a filament temperature reading before Ti compound deposits clouded the chamber. The Vycor window was also removed from the oven to eliminate another source of correction for the reading. Using this method, an uncorrected temperature reading of 1150°C was obtained. The ordinary correction for the chamber glass is about 10°C resulting in a corrected reading of 1160°C.

The operability of the CVP unit was improved considerably during this phase of the contract. After the CVP unit became operable, average TiB_2 filament preparation exceeded 400 ft/day with a number of runs in excess of 600 ft/day. In the initial work this average was approximately 150 ft/day. The biggest factors leading to the improvement were cleaner deposition chambers and the better defined plating zone of the filament.

The oven temperature was maintained near 500°C in most of the runs and Ti compound deposit buildup was very slow. At temperatures of 450 to 475°C the buildup was much faster. There were virtually no filament breaks due to chamber deposits falling on the filament.

The addition of the electrical grounding stubs to the deposition chamber gave the filament a well-defined plating zone. This prevented overheating of the filament in areas outside of the stubs particularly at the start-up of a run.

Most of the filament breaks which did occur were due to the preparation of weak filament at the beginning of a run. Occasionally a break was caused by a piece of broken filament left in the chamber which caused local overheating of the new filament.

The combination of the cleaner deposition chamber and the more uniform heat zone of the substrate is believed responsible for the higher tensile strength and the better appearance of the TiB_2 filament produced during this period.

A total of 12, 100 ft of TiB_2 filament prepared under the supplemental filament preparation phase of the contract was shipped to TRW Systems, Redondo Beach, California for future experiments. A description of the filament and its preparation is given in Table V. Filament speed was 20 in. /min in all runs.

Only a limited number of titanium analyses and density determinations were run on filament produced in the supplemental phase of the program. Since tensile strength is the one measurable property which best describes the overall quality of the filament, considerable emphasis was placed on the

Table V

SUPPLEMENTAL TiB_2 FILAMENT PREPARATION DATA

		Gas Flows and Ratios						Tensile Strength kpsi		
Run No.		Total	$TiCl_4$	$\frac{BCl_3}{TiCl_4}$	$\frac{H_2}{TiCl_4}$	$\frac{Ar}{TiCl_4}$	Filament Diameter mils	Range	Average	Filament Length ft
TB-5	Exit	920	20	1.25	5.0	38.7	2.9	18-230	117	580
	Ent.	920	20	1.25	5.0	38.7				
TB-6	Exit	920	20	1.25	5.0	38.7	1.9	65-190	142	75
	Ent.	920	20	1.25	5.0	38.7				
TB-7	Exit	920	20	1.25	5.0	38.7	1.8	143-307	206	95
	Ent.	920	20	1.25	5.0	38.7				
TB-8	Exit	920	20	1.25	5.0	38.7	2.5	100-400	274	450
	Ent.	920	20	1.25	5.0	38.7				
TB-9	Exit	920	20	1.25	5.0	38.7	2.9	155-378	293	500
	Ent.	670	20	1.25	5.0	26.3				
TB-10	Exit	920	20	1.25	5.0	38.7	2.7	32-163	107	55
	Ent.	670	20	1.25	5.0	26.3				
TB-11	Exit	920	20	1.25	5.0	38.7	2.5	158-370	255	150
	Ent.	670	20	1.25	5.0	26.3				
TB-12	Exit	920	20	1.25	5.0	38.7	2.0	95-290	208	405
	Ent.	670	20	1.25	5.0	26.3				
TB-13	Exit	920	20	1.25	5.0	38.7	2.0	280-358	312	185
	Ent.	670	20	1.25	5.0	26.3				
TB-14	Exit	920	20	1.25	5.0	38.7	1.9	136-383	233	215
	Ent.	670	20	1.25	5.0	26.3				
TB-15	Exit	920	20	1.25	5.0	38.7	1.9	115-350	215	215
	Ent.	670	20	1.25	5.0	26.3				
TB-16	Exit	920	20	1.25	5.0	38.7	2.6	95-240	186	55
	Ent.	670	20	1.25	5.0	26.3				
TB-17	Exit	920	20	1.25	5.0	38.7	2.7	200-348	293	685
	Ent.	670	20	1.25	5.0	26.3				
TB-18	Exit	920	20	1.25	5.0	38.7	2.6	71-252	151	120
	Ent.	670	20	1.25	5.0	26.3				
TB-19	Exit	920	20	1.25	5.0	38.7	3.1	126-351	220	120
	Ent.	670	20	1.25	5.0	26.3				
TB-20	Exit	920	20	1.25	5.0	38.7	3.2	11-212	88	200
	Ent.	670	20	1.25	5.0	26.3				
TB-21	Exit	920	20	1.25	5.0	38.7	2.4	41-301	132	105
	Ent.	670	20	1.25	5.0	26.3				
TB-22	Exit	920	20	1.25	5.0	38.7	3.0	20-231	122	40
	Ent.	670	20	1.25	5.0	26.3				
TB-23	Exit	920	20	1.25	5.0	38.7	3.5	31-236	117	325
	Ent.	670	20	1.25	5.0	26.3				
TB-24	Exit	920	20	1.25	5.0	38.7	3.0	40-191	121	115
	Ent.	670	20	1.25	5.0	26.3				
TB-25	Exit	920	20	1.25	5.0	38.7	2.8	15-221	108	220
	Ent.	670	20	1.25	5.0	26.3				
TB-27	Exit	920	20	1.25	5.0	38.7	3.0	90-360	232	430
	Ent.	670	20	1.25	5.0	26.3				
TB-28	Exit	920	20	1.25	5.0	38.7	2.8	97-292	220	155
	Ent.	670	20	1.25	5.0	26.3				
TB-29	Exit	920	20	1.25	5.0	38.7	2.6	140-359	248	350
	Ent.	670	20	1.25	5.0	26.3				

Table V (Cont'd)

TB-31	Exit	920	20	1.25	5.0	38.7	2.8	59-141	96	140
	Ent.	670	20	1.25	5.0	26.3				
TB-32	Exit	920	20	1.25	5.0	38.7	2.1	21-260	146	315
	Ent.	670	20	1.25	5.0	26.3				
TB-33	Exit	920	20	1.25	5.0	38.7	3.0	48-251	96	355
	Ent.	670	20	1.25	5.0	26.3				
TB-34	Exit	920	20	1.25	5.0	38.7	2.1	20-278	158	400
	Ent.	670	20	1.25	5.0	26.3				
TB-35	Exit	920	20	1.25	5.0	38.7	2.5	110-502	315	615
	Ent.	670	20	1.25	5.0	26.3				
TB-36	Exit	920	20	1.25	5.0	38.7	2.3	220-272	240	250
	Ent.	670	20	1.25	5.0	26.3				
TB-37	Exit	920	20	1.25	5.0	38.7	2.1	140-301	215	595
	Ent.	670	20	1.25	5.0	26.3				
TB-38	Exit	920	20	1.25	5.0	38.7	2.0	71-381	255	615
	Ent.	670	20	1.25	5.0	26.3				
TB-39	Exit	920	20	1.25	5.0	38.7	2.4	130-241	201	265
	Ent.	670	20	1.25	5.0	26.3				
TB-40	Exit	920	20	1.25	5.0	38.7	2.5	179-259	208	625
	Ent.	670	20	1.25	5.0	26.3				
TB-41	Exit	920	20	1.25	5.0	38.7	2.5	79-431	287	175
	Ent.	670	20	1.25	5.0	26.3				
TB-42	Exit	920	20	1.25	5.0	38.7	2.6	79-319	186	400
	Ent.	670	20	1.25	5.0	26.3				
TB-43	Exit	920	20	1.25	5.0	38.7	1.7	35-285	157	85
	Ent.	670	20	1.25	5.0	26.3				
TB-45	Exit	920	20	1.25	5.0	38.7	2.3	180-261	232	225
	Ent.	670	20	1.25	5.0	26.3				
TB-46	Exit	920	20	1.25	5.0	38.7	2.1	120-335	260	150
	Ent.	670	20	1.25	5.0	26.3				
TB-47	Exit	920	20	1.25	5.0	38.7	2.6	72-325	181	115
	Ent.	670	20	1.25	5.0	26.3				
TB-48	Exit	920	20	1.25	5.0	38.7	2.6	148-331	229	535
	Ent.	670	20	1.25	5.0	26.3				
TB-49	Exit	920	20	1.25	5.0	38.7	2.6	28-208	127	395
	Ent.	670	20	1.25	5.0	26.3				

determination of a good average tensile strength for each batch of filament. Other data which were obtained are included in section IV(H) Fiber Properties, Supplemental TiB_2 Filament Preparation.

Experiments were run to determine the effect of substrate transit speed vs. TiB_2 filament final diameter. The results are tabulated below:

Substrate Rate of Transit (in/min)	Final Diameter of Filament (mils)
7.5	3.8
12.5	3.3
18	2.8
21	2.5

G. FIBER PROPERTIES (INITIAL TiB_2 FILAMENT PREPARATION)

In addition to the fiber strength and density reported in the previous section, some determinations were made of modulus, hardness and cross sectional and surface appearance. Elastic modulus measurements were made on three samples of continuous TiB_2 filament. The method involved determination of the buckling load of a long slender column (the fiber) as described in the appendix. The results are tabulated below:

Sample	Property Data from Table IV		Diameter Mils	Elastic Modulus Million psi
	Average Tensile Strength kpsi	Average Deposit Density g/cm^3		
JH-24	168	4.38	3.5	61.4
			3.6	53.3
JH-27	100	4.44	2.65	116.0
			2.65	57.5
JH-30	123	4.18	2.55	45.7
			3.35	71.5

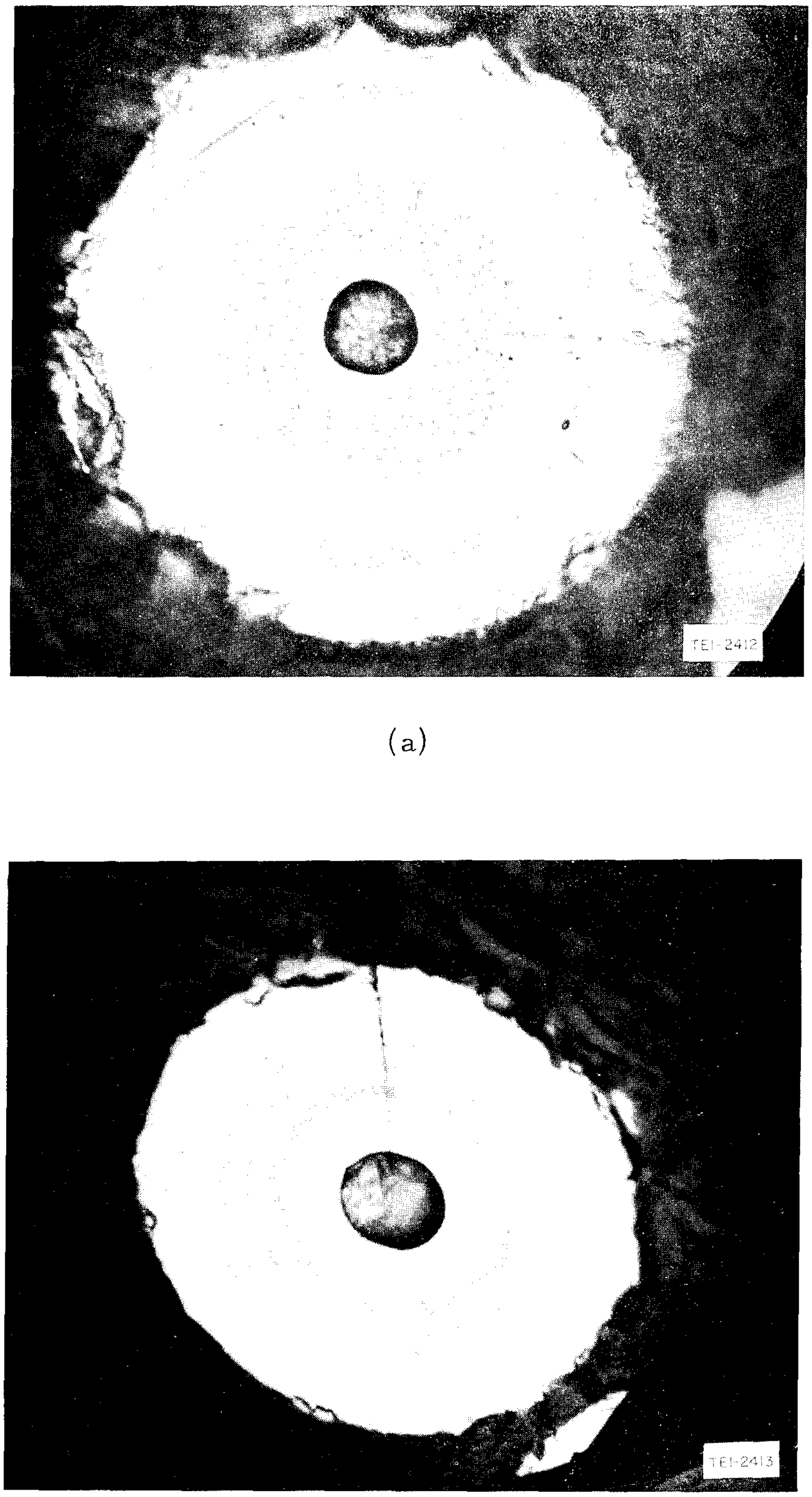
These values are generally somewhat lower than the range of 75 to 84 million obtained on batch prepared fibers reported for the previous program (1). However, the value of 116 million for one sample of run JH-27 appears to be a valid value. This sample was rerun seven times with the same result. The diameters were checked repeatedly and the fiber was deliberately broken off to permit measurement as a shorter length. The same average value of 116 million was obtained. One possible reason for the high value may be indicated by the cross sectional examination discussed below.

The polished cross section of fibers JH-24 and JH-30 are shown in Fig. 14. Both fibers show ring structure. The shiny rings are presumably better material than the dark or mottled material, and as will be shown later, the shiny areas are appreciably harder. The alternate rings of hard and somewhat softer material undoubtedly have an effect on the stiffness. It was anticipated that the extremely high modulus of the fiber JH-27 sample might have resulted from less ring structure, and a very short sample was available for polishing. This material was so hard that it was difficult to polish but examination under the microscope indicated fewer rings. In a final polishing operation preparatory to taking a picture, the material broke out of the polishing mount. Because of time limitation, no additional section of fiber could be polished. However, a sketch of the nearly polished JH-27 was made and is shown in Fig. 15. It appears that there was a substantially larger area of homogeneous material than observed for JH-24 and JH-30 and this suggests that the stiffness of a completely uniform TiB_2 deposit might indeed be quite high.

The hardness of the material in JH-24 and JH-30 was measured on a Tukon micro hardness tester. These results were obtained for us at the Texaco Research Center, Beacon, New York. Figure 16 shows the cross sections used in the hardness test. JH-24 is the same polished cross section seen in Fig. 14, but lighted by oblique illumination which reveals an uneven surface caused by "relief polishing". The central plane region, P, had a Knoop hardness number (50-gram load) of 2600 kg/mm^2, while the high torus region, T, had a number of 4250.

In Fig. 16, JH-30A is the same cross section as shown in Fig. 14, but with the hardness test indentations. The two large marks, indicated by arrows, were made with 50-gram loads but these were too large for this type of sample. All other scars were made with 25-gram loads. JH-30B is a repolished face of JH-30A, and additional indentations were made. The length of each scar was measured three times and averaged. The hardness tabulated below corresponds to the numbered indentations. From these, it appears that the light bands are significantly harder than the dark bands.

Scar No.	Photo	Knoop Hardness No., Kg/mm^2 25-gram load
1	JH-30A	4800
2		2140



(a)

(b)

Fig. 14 Photomicrographs of Cross-Sections of TiB_2 Fibers

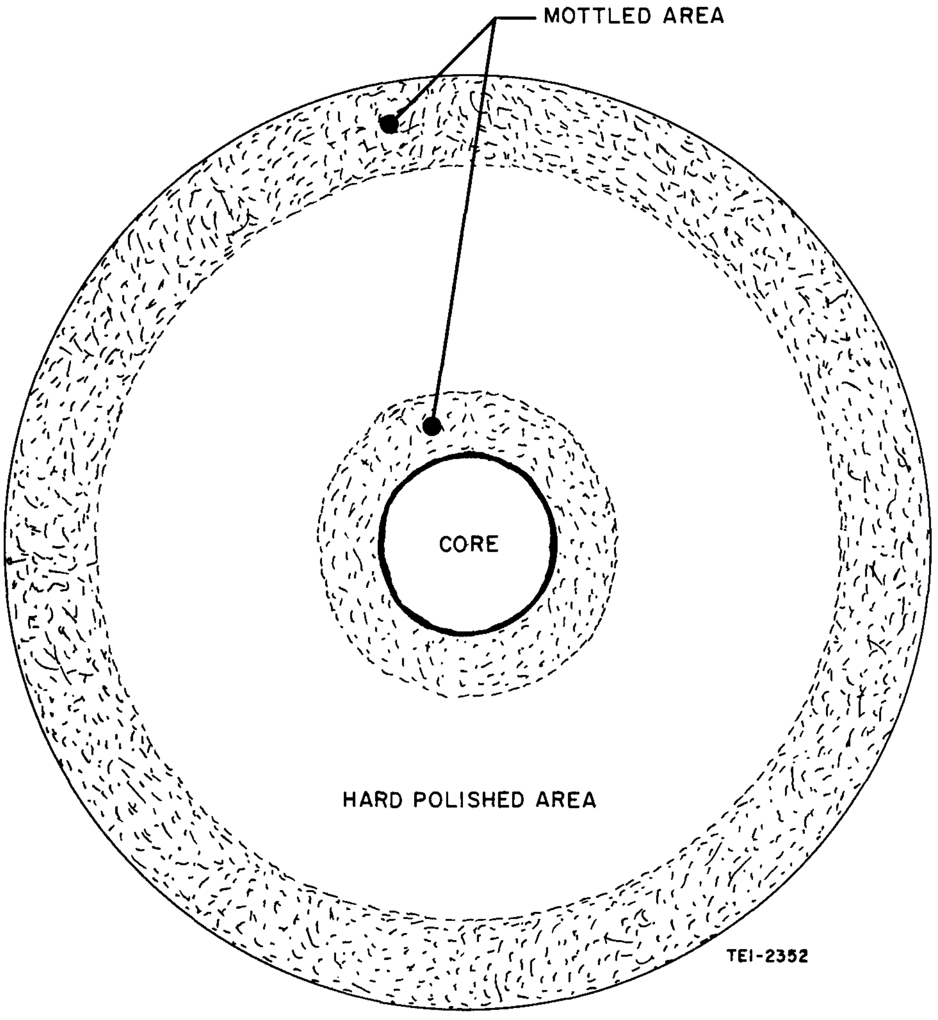
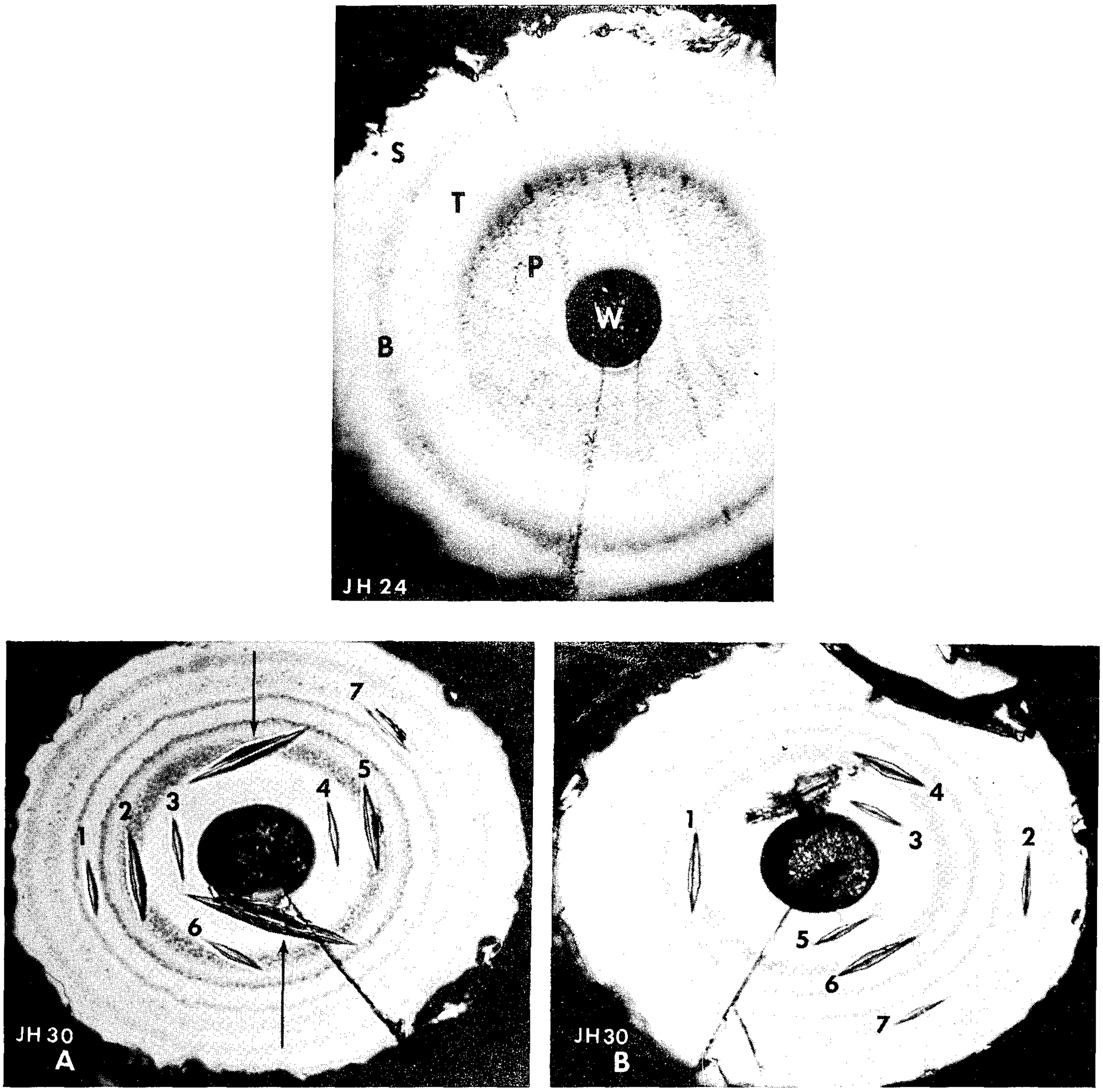


Fig. 15 Sketch of Semi-Polished Cross Section of TiB_2 Fiber JH-27



TEI-1981

Fig. 16 Photomicrographs of Cross-Sections of TiB_2 Fibers Used in Microhardness Testing

3		4310
4		4060
5		2355
6		3440
7		Spalled out
1	JH-30B	2390
2		3700
3		4390
4		2265
5		3530
6		2040
7		4070

Figure 17 shows the relatively smooth surface appearance of two samples which are typical of the produced filament.

H. FIBER PROPERTIES (SUPPLEMENTAL TiB_2 FILAMENT PREPARATION)

Density determinations were made on pieces of filament taken from run Nos. TB-9 and TB-35. The respective density values of the deposited material were 4.43 and 4.46 g/cm^3 which are close to the theoretical density value of 4.50 g/cm^3. X-ray analysis of a few samples showed TiB_2 and W to be present.

Samples from run Nos. TB-9 and TB-13 were analyzed colorimetrically for titanium and boron content. The analysis showed the samples to have B/Ti ratios of 1.93 and 1.96 respectively compared to 2.0 for stoichiometric TiB_2.

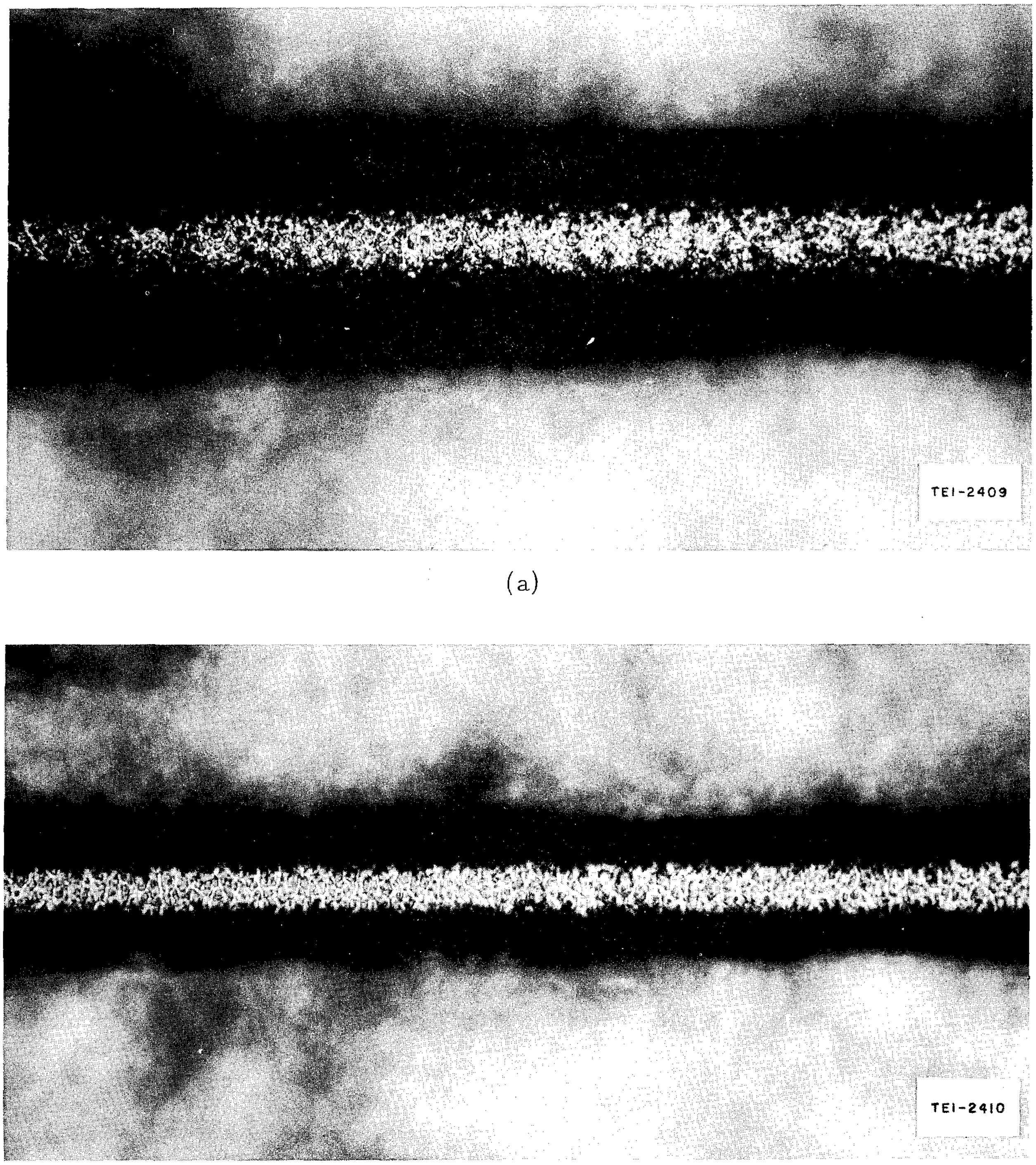
Elastic modulus measurements were made with both tensile and compression type experiments on TiB_2 filament from run No. TB-9. Both types of tests showed average values of about 71×10^6 psi.

The average tensile strength distribution of TiB_2 filament prepared in the supplemental phase of the contract is shown below:

Average Tensile Strength Distribution

$$\left(\frac{\text{no. feet in each range} \times 100}{12,100} \right)$$

Range	%
Below 100 kpsi	5.7
100-125 kpsi	11.0



(a)

(b)

Fig. 17 Photomicrographs of the Surface of TiB_2 Fibers

125-150 kpsi	7.4
150-175 kpsi	5.0
175-200 kpsi	4.8
200-225 kpsi	15.3
225-250 kpsi	21.7
250-275 kpsi	11.2
275-300 kpsi	11.3
over 300 kpsi	6.6
	100.0

The above figures show that approximately two thirds of the material has average tensile strengths in excess of 200 kpsi.

A highly etched cross-section of fiber TB-8 is shown in Figure 18. Although the axis of the fiber was not perpendicular to the face of the mount, this photograph is used to point out the absence of rings in the TiB_2 filament possessing relatively high tensile strength.

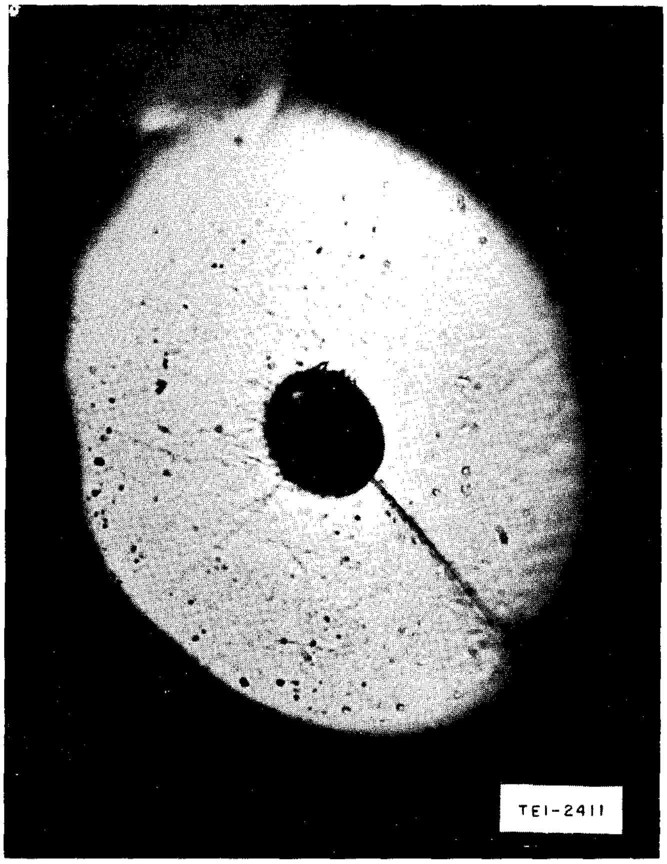


Fig. 18 Photomicrograph of Cross-Section of TiB_2 Fiber Prepared in Supplemental TiB_2 Filament Preparation Program

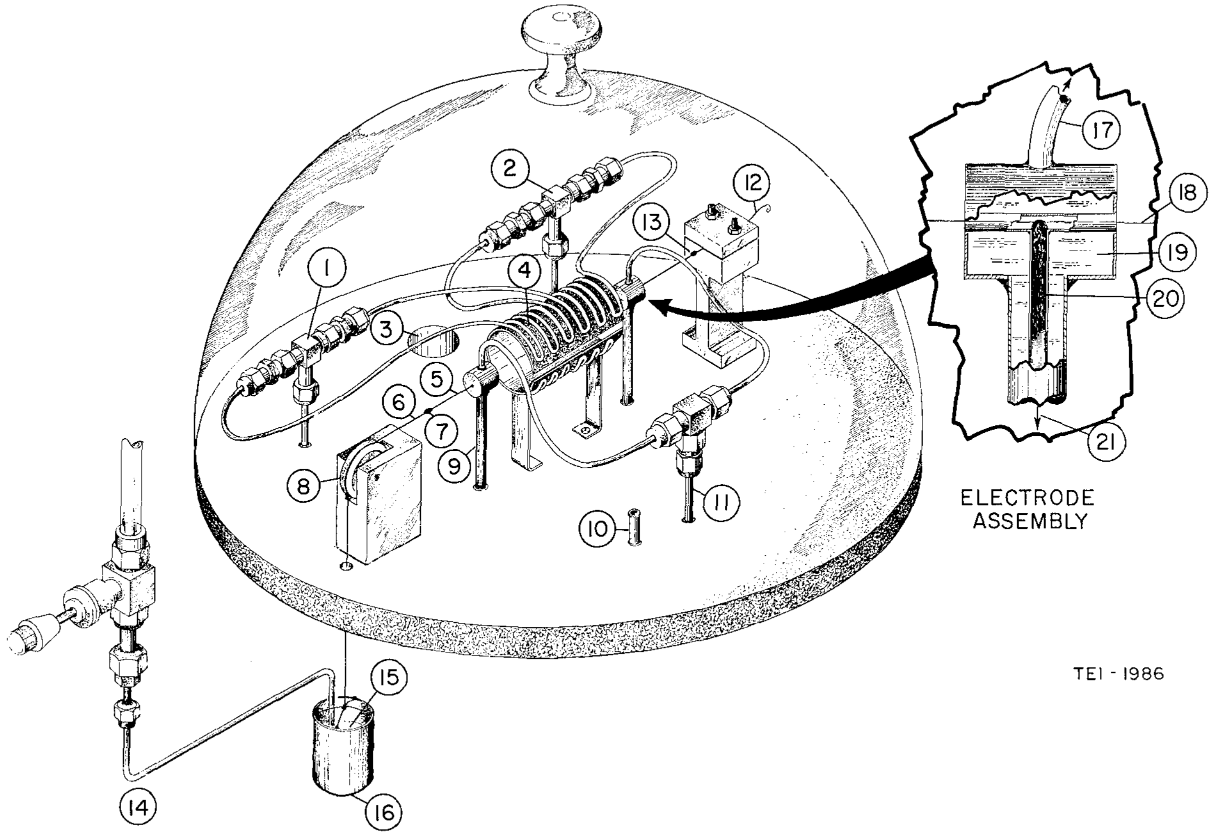
V. HIGH TEMPERATURE STRENGTH DETERMINATION OF TiB_2 FIBERS

In work done in the previous contract (1) tests were run on TiB_2 fibers which resulted in considerable weakening and spalling of the deposit when the fibers were heated to temperatures of 2000°C and above in either inert gas or in corrosive atmospheres. It was decided to further investigate this phenomenon by running high temperature tests on TiB_2 fibers prepared in this program.

In preliminary experiments several samples of TiB_2 filament which had been prepared in the cross-flow reactors were heated to temperatures up to 1800°C for periods up to 2 hours in argon atmospheres. The apparatus used for the experiments was similar to that shown in Fig. 1. Considerable cracking and spalling of the fibers occurred during the tests. X-rays taken of the samples before and after the tests showed varying degrees of core interaction with the deposit. Before heating, x-ray analysis of the samples showed the presence of TiB_2, Ta, and TaB_2. (The TiB_2 was deposited on 2 mil Ta substrates.) After the tests, x-ray analyses showed TiB_2, Ta, and TaB, and in one sample a new phase was found which was tentatively thought to be $TaTiB_2$.

An apparatus was then designed and constructed for use in the high temperature tensile testing of fibers prepared in this program (Fig. 19). The chief components of the apparatus are a bell jar, a water-cooled electrode assembly, a heat shield, and a mechanical vacuum pump. Fibers are heated resistively in the apparatus to temperatures in excess of 2000°C in argon atmospheres. Temperature measurement is made with an optical pyrometer by observing the sample through a slit in the heat shield. The electrodes contain mercury for making electrical contact with the fiber and are located on each side of the heat shield. One end of the fiber to be tested is glued to a short nichrome wire which is fastened rigidly to a support inside the bell jar. The other end of the fiber is glued to a wire supported by a pulley from which the wire extends loosely through the base of the apparatus. A container to which mercury is added during a test is hung on the end of the wire below the base. The bell jar seals the parts above the base from the atmosphere. Prior to a test, air is pumped from the bell jar which is later purged with argon during the fiber test. The high temperature strength of the fiber is calculated from the weight of mercury needed to break a fiber during the test.

Several pyrolytic graphite and TiB_2 fibers were tested in the apparatus at room temperature before any high temperature tensile tests were run. The results of these tests were in the same general range as those obtained in



1. WATER INLET
2. WATER OUTLET
3. TO VACUUM
4. HEAT SHIELD
5. TEST FIBER
6. STAINLESS STEEL WIRE
7. GLUED JOINT
8. NYLON PULLEY
9. ELECTRODE
10. ARGON INLET
11. WATER OUTLET
12. SUPPORT WIRE
13. GLUED JOINT
14. MERCURY SUPPLY
15. MERCURY
16. BUCKET FOR MERCURY WEIGHT
17. WATER OUTLET
18. TEST FIBER
19. COOLING WATER
20. MERCURY CONTACT
21. TO MERCURY RESERVOIR

Fig. 19 Schematic of High Temperature Testing Apparatus standard tensile tests. In another experiment a pyrolytic graphite fiber was heated to 2500°C in the apparatus to determine how well the various components of the apparatus would behave during high temperature tests. No overheating of any of the components occurred and good electrical contact was maintained for several minutes.

Three selected TiB_2 fibers were then tested in the apparatus at 800, 1200, 1600, and 2000°C. Table VI shows the results of these tests as well as room temperature data obtained from standard tensile tests. In the 800°C tests the fibers did not break when the mercury container was completely filled. Thus the figures given are minimum values.

Table VI shows little or no weakening of the TiB_2 fibers at 800°C, but considerable loss of strength has occurred at 1200°C and 1600°C. Three possible explanations are offered for the rapid strength loss above 800°C. One is that the core, which is believed to be mainly unreacted substrate metal, interacts with the contiguous deposit at high temperature to locally change the stoichiometry of the TiB_2 deposit and possibly produce voids or cracks in the deposit. Since the boron atom is extremely mobile at high temperature, considerable interaction of core and deposit should occur in a matter of minutes. A second explanation is derived from the fact that most of the polished TiB_2 cross-sections show considerable layering of the deposit. Microhardness tests show the dark layers to be much softer than the light layers indicating a difference in chemical composition of the layers or the presence of porosity in the dark layers. Upon heating, cracking may occur from stresses set up by porosity or by voids resulting from layer interaction. The third explanation is derived from the fact that chemical analysis of the fibers, before testing, generally show a high titanium content. If free titanium was present at temperature where melting could occur, this would result in considerable fiber strength loss. However, this does not account for strength loss in the temperature region of 1200-1600°C.

Figure 20 shows a cross-section of a TiB_2 fiber after the fiber was heated to 1800°C for 45 minutes. Much spalling has occurred in the outer layers, while the core and innermost deposit layer are relatively unchanged. This indicates that the outer regions of the deposit have been seriously weakened by the heating process. The exact reason for this phenomena may be related to one or more of the above explanations.

High temperature data were also obtained on TiB_2 filament prepared in the supplemental phase of the program. Since these fibers were known to have a much higher room temperature tensile strength than those previously tested, the apparatus was equipped with a larger mercury container so that higher strengths could be measured, particularly at the lower test tempera-

Table VI

TENSILE STRENGTH DATA FOR TiB_2 FIBERS

Fiber No.	R. T. Tensile Strength kpsi	800°C Tensile Strength kpsi	1200°C Tensile Strength kpsi	1600°C Tensile Strength kpsi	2000°C Tensile Strength kpsi
JH-24	167-170 (168 Avg)	> 75	40	12.9	< 3
JH-30	105-141 (123 Avg)	>100	65	15.3	4.7
JH-54	74-131 (108 Avg)	>100	67	20.0	9.3

Fig. 20 Photomicrograph of Cross-Section of TiB_2 Fiber Heated to 1800°C for 45 Minutes

tures. A test was run in this series at 1000°C instead of 800°C in order to further pin down the temperature at which the fiber strength begins to drop rapidly. The data are shown below:

Fiber No.	Room Temp. T. S. (kpsi)	1000°C T. S. (kpsi)	1200°C T. S. (kpsi)	1600°C T. S. (kpsi)	2000°C T. S. (kpsi)
TB-9	155-378 (293 avg)	247	87	19.5	5.2

Although this filament retained its tensile strength through 1000°C, the tests run at 1600 and 2000°C show the tensile strength to be in the same range at these temperatures as the filament prepared in the initial phase of the contract. Apparently the room temperature tensile strength is retained up to a temperature near the filament preparation temperature, but loses strength rapidly with increasing temperatures above this point.

VI. CONCLUSIONS

A. Filament of nominal TiB_2 and TiC composition can be prepared on resistively-heated 2-mil diameter tantalum substrates in heated cross-flow reactors. The low strength of the resulting filament is believed to be directly related to a substrate temperature gradient problem which is associated with the preparation of deposits of good electrical conductivity on resistively-heated substrates. The temperature gradient problem can be reduced but not eliminated by the use of heated coils in the reactor below the cool end of the substrate and by the use of substrates with relatively large diameters.

B. The "hot spot" problem, which refers to the severe over-heating of a resistively-heated substrate as it enters the CVP region of the cross-flow reactor, can be eliminated by the combination of the use of larger diameter substrates and the use of argon instead of helium as the diluent gas in the CVP gas mixture.

C. TiB_2, TiC and other transition metal borides and carbides are metallic-like conductors in contrast to B, SiC, and B_4C which are semiconductors. The latter because of their high resistivity, compared to the substrate, are amenable to preparation by resistance heating since the conductivity of the fiber is only slightly altered during the deposition. The metallic-like deposits increase the fiber conductivity roughly in proportion to the cross section of the growing fiber. This leads directly to the temperature gradient problem.

D. Stainless steel electrical contacts can be used in place of mercury contacts in CVP reactors where the prepared filament has relatively high electrical conductivity such as TiB_2 and TiC.

E. High strength continuous TiB_2 filament can be prepared successfully on radiofrequency-heated substrates. The TiB_2 filament diameter, under otherwise constant conditions, is a function of substrate speed. The diameter averages 2.6 mils when prepared on 0.5 mil W substrate at a speed of 20 in./min where split-flow reactors are used, and substrate temperatures of 1160 to 1200°C are maintained over a uniform temperature zone of 32 inches long by radio frequency heating.

F. From the evaluation of data obtained on TiB_2 filament prepared under this contract, it appears possible to prepare TiB_2 continuous filament with average tensile strengths in the range of 200 to 300 kpsi with individual values in excess of 500 kpsi, elastic moduli in excess of 70×10^6 psi, a density of approximately 4.5 g/cc and a Knoop hardness (25 gram load) up to 4800 kg/mm^2.

G. The tensile strength of the TiB_2 filament drops off rapidly above 1000°C. This may be caused by reaction of the core with the deposit at high temperature or be related to the ringed structure which occurs in much of the TiB_2 filament.

H. Much of the continuous TiB_2 filament has ring structure which is believed to affect the filament tensile strength. Little or no ring structure was found in a sample of TiB_2 filament which had an average tensile strength of 274 kpsi.

I. Titanium carbide filament is extremely difficult to prepare by coplating from $TiCl_4$ and carbon precursors. Reaction products formed by the reduction and/or decomposition of the above compounds prevent continuous operation of reactors because of severe obscuration of the reactor wall. It is also difficult to obtain homogeneous TiC deposits in a controlled manner.

J. Titanium carbide filament (1.4 to 2.0 mils diameter) with tensile strengths up to 243,000 kpsi can be prepared on 1 mil diameter tungsten substrates from the decomposition of CH_3TiCl_3 at 1000 to 1100°C. This plating compound is very unstable which might make it difficult to adapt its use to continuous TiC filament preparation.

K. A combination of rf current and direct current can be used to heat substrate wires in CVP reactors. The combination gives greater heating efficiency and longer heated substrates than when rf power alone is used, and a substrate temperature gradient does not occur as when dc power alone is used.

VII. RECOMMENDED FUTURE WORK

The fibers prepared in this program will be composited elsewhere by a NASA contractor and tested for effectiveness as an ablation reinforcement. No further fiber preparation is contemplated at this time. However, if additional work is to be done with TiB_2 filaments, the following aspects should be considered.

1. Deposits on plating chamber walls. The deposit of $TiCl_3$ on the reactor walls, together with the disproportionation to $TiCl_2$ add to the difficulty in operation. Although the deposits were substantially decreased in the supplemental program of fiber preparation they still tend to obscure the fiber and make temperature measurement difficult. Periodically, material falls on the fiber, and this sometimes results in fiber failure. This latter problem can possibly be overcome by using a vertical plating chamber of suitable design. Any dislodged wall deposits would then not fall on the fiber. Wall deposits can probably be reduced by vacuum operation. This would increase the $TiCl_3$ volatility and permit lower wall temperatures with lowered probability of $TiCl_2$ formation. The feasibility of TiB_2 preparation under vacuum would have to be demonstrated and the equipment design using radiofrequency heating would be more complex.

2. Temperature measurement. The temperature measurement of the filament is made difficult by the wall deposits as discussed above. However, various schemes for providing clear windows can be devised and the use of a two-color pyrometer suitably protected by screening against rf interference may give major improvement even under current conditions.

3. Substrate weakness during startup. When the filament is broken during operation, the restringing of the substrate was not especially difficult. However, during the first 2-5 minutes after startup the substrate is rendered very weak and the filament is apt to break until it has built up to proper size. If operation can be continued for more than about 5 minutes, the operation becomes satisfactory. The tension on the substrate and therefore failure could be substantially reduced by utilizing a vertical plating chamber.

4. Fiber ring structure. Fiber quality can be improved by reduction in the ring structure. Any operational improvement which will give a more uniform deposit should be valuable. Improved control of gas composition, gas flow dynamics, temperature, substrate transport tension and speed, and radiofrequency power should be sought.

VIII. APPENDIX

1. Calibration of Equipment

The equipment used in connection with process control or data acquisition, including rotameters, optical pyrometers, take-up reels, and a diameter measuring device, was calibrated. The rotameters were calibrated by various methods, depending upon the chemical reactivity of the gas or liquid. Helium, argon, hydrogen, and n-butane were passed through a soap solution into a calibrated glass tube where flows were determined by timing the movement of gas bubbles through the tube. The $TiCl_4$ flow was measured as a liquid by passing it from a pressurized reservoir through the rotameter into a buret under a cover of argon. Flows of BCl_3 were measured by passing the gas through the rotameter into water to form H_3BO_3 and HCl. The boron content of each sample was determined and calculated as BCl_3. The use of Freon 12 as a substitute for BCl_3 in calibration by the gas bubble method was also utilized. The two methods were found to give comparable flow data results.

2. Gas Analysis

Analyses for $TiCl_4$, H_2 and BCl_3 were furnished by the respective vendors and are shown below:

$TiCl_4$ from National Lead Company

Iron	< .0009%	Nickel	< .0004%
Vanadium	< .0002%	Lead	< .0002%
Silicon	< .004%	Chromium	.00005%
Tin	.02%	Copper	< .00005%
Aluminum	.003%	Magnesium	< .00006%
Antimony	< .001%	Manganese	< .00002%

H_2 from The Matheson Company

Oxygen	< .0001%
Nitrogen	< .0005%
Methane	< .00002%
Dew Point	Better than -85°F

BCl_3 from American Potash and Chemical Co.

Boron Trichloride	$>$ 99.90%	Phosgene	$<$ .085%
Chlorine	$<$ .01%	Silicon	$<$ .0005%

On long time standing, HCl tends to build up in the BCl_3 supply cylinder, presumably by reaction with moisture trapped in B_2O_3 scale on the container walls. The HCl content was found by the TEI analytical section to be 0.7%. This was reduced and kept low by periodic bleeding off the vapor from above the liquefied BCl_3 in the cylinder. The n-C_4H_{10} was C. P. grade (99.0% min. purity) and was purchased from The Matheson Co. The argon was high purity grade (99.996% min. purity) and the helium was C. P. grade (99.997% min. purity). Both of these gases were obtained from Air Products and Chemicals Inc. Further precautions were taken to be sure the argon contained no moisture by passing the stream to the plating chamber over titanium metal turnings maintained at 900°C.

3. Chemical Analysis for Titanium and Boron

Initially, the titanium diboride fibers were analyzed quantitatively for titanium by the following procedure. First, the fibers were weighed on a Cahn Microbalance, and their lengths were measured. They were then placed in covered teflon beakers and dissolved in a hot solution composed of concentrated nitric acid and one milliliter of concentrated hydrofluoric acid. The solutions were cooled, five milliliters of concentrated sulphuric acid were added and the solutions were reheated without covers to remove the fluoride ion and water. When the volumes of liquid were reduced, the samples were transferred to Erlenmeyer flasks and covered with still heads (condensers) for refluxing. They were heated until fumes of sulphur trioxide evolved for a few minutes. The samples were cooled and placed in volumetric flasks. Two milliliters of hydrogen peroxide, which forms a yellow colored complex ion with titanium, were added to each flask, and they were then filled with distilled water and mixed well. The absorbance of each sample was then measured on a Bausch and Lomb Colorimeter or a Beckman DU Spectrophotometer (constant sensitivity) at 410 millimicrons against water as a blank. The absorbances of the samples were compared to those obtained on standard titanium solutions prepared from Bureau of Standards TiO_2.

It was thought possible to improve the speed and accuracy of the titanium analyses by using atomic absorption flame spectrometer techniques. However, it was found that the fluoride would interfere and it had to be completely expelled from the HF-HNO_3 solution and this was difficult and time consuming. It was discovered that the fibers could be satisfactorily dissolved in 30% H_2O_2 solution, but unfortunately the peroxide also interfered with the atomic absorption method. The final procedure employed solution by peroxide, followed by suitable water dilution and measuring the titanium content colorimetrically. Standard solutions of slightly lower Ti content and containing about the amount of boron as the fibers were used as reference blanks on the DU spectrophotometer. The precision was limited by the absorbance measurement and was found to be within 0. 1 ppm in the working solution. The titanium content was corrected for the substrate content so that the reported result represents the titanium percentage in the TiB_2 deposit. When both titanium and boron were determined in a fiber, boron was analyzed in another aliquot of the sample solution by a titrimetric method. High purity boric acid was used as a standard for the analysis.

4. Tensile Strength Determinations

The tensile strengths of fibers produced in this program were determined on a Model TM-L Instron tensile tester. The samples were 1 in. gage length and were tested at a cross head speed of 0. 05 in. per minute. The diameter of each sample was determined from measurements made on an optical comparator.

5. Density Determinations

The TiB_2 densities were determined from the volume and mass of a given length of fiber. The sample was weighed to an accuracy of ±0. 00002 gm and its diameter and length were measured to ±0. 000635 cm and ±0. 01 cm respectively. The densities were corrected for the mass of the core which was computed from its length, diameter, and density, using the original substrate material values of diameter, specimen length, and the density.

6. X-ray Diffraction

X-ray diffraction were run on a Norelco X-ray unit using the standard Debye-Scherrer method. Copper K_α radiation was used with a nickel filter at 35 KW and 20 ma. Samples were run in a 57. 3 mm diameter camera and were exposed for three hours. Samples of special interest were powdered and exposures were made for six hours. Identification of the diffraction spectra was made primarily from ASTM diffraction data cards.

7. Elastic Modulus Determination

The elastic modulus of fibers was determined by two methods. The first was based on the critical buckling load of a long slender column (the fiber). A short piece (~ 1/2 in.) of fiber was placed vertically in a small cone-shaped recess in a platen mounted on one of the heads of an Instron testing machine. The sample was held in place by a gel. A vertical compression force was then applied to the free end of the fiber by a matching platen with a cone-shaped recess. The cone-shaped recesses simply kept the sample aligned axially with the load. The cross-head speed was set at 0.05 in. per minute and the chart speed at 2 in. per minute. The critical buckling load was noted as the maximum load at which the load deflection curve deviated from a straight line. The elastic modulus was then computed from the formula

$$E = \frac{64\ PL^2}{\pi^3 D^4\, 453.6}$$

where E is the elastic modulus in psi, P is the critical buckling in grams, L is the length of the fiber in inches, and D is the diameter of the fiber in inches. The diameter D was measured on an optical comparator and was averaged from several determinations.

The second method was based on the change of force required to produce a given change in length per unit length of a fiber under tension. A fiber of 10 in. gage length was pulled in a standard tensile test using a Model TM-L Instron tensile tester. The slope of the line obtained on the chart was used to calculate the elastic modulus according to the following formula:

$$E = \frac{\dfrac{\Delta F}{\Delta L/_{L}}}{A}$$

where E is the elastic modulus in psi, ΔF is the force required to produce a given change in length ΔL per unit length L, and A is the cross-sectional area of the fiber.

8. CVP Gas Ratios

The correct CVP gas ratio requirements for the preparation of high strength TiB_2 filament were found to vary with each style of reactor used in the program. Apparently several factors influence these requirements and include substrate temperature and temperature gradients, mass flow rates of the gases, and the gas flow patterns inside the reactors.

It was noted in the batch reactor work that a slightly different CVP gas ratio altered the maximum substrate temperature at which small crystallite TiB_2 could be prepared. This temperature varied from 1220 to 1295°C. While the H_2 content of the CVP gas mixture was extremely critical in the batch reactor, it was varied over wide ranges in the rf-heated substrate reactors without formation of poor quality TiB_2 filament. However, part of the H_2 was brought into the rf reactor through the tees in order to protect the Hg seals rather than in the CVP gas mixture, and this may have resulted in a CVP gas mixture of variable composition along the entire length of heated substrate. This may also account for the fact that deposition rates in the rf reactors were always lower than those obtained in the batch reactor for a given length of heated substrate since the H_2 entering from the tees may have shielded several inches of substrate from the CVP gases. Another factor which may have resulted in lower deposition rates in the rf reactors was the limitation on maximum CVP gas flows which was needed to prevent excessive formation of titanium compounds on the reactor wall. Sufficient depletion of the gas constituents may have occurred to limit the TiB_2 deposition rate.

In the cross-flow reactors, the CVP gas flow patterns were completely different from the batch and rf reactors. This was due to the flow of gases from beneath the substrate instead of parallel to it and also due to the presence of the substrate temperature gradient. Thus it appears necessary to determine the correct CVP gas ratios for each style of CVP reactor.

9. Temperature Data in Previous Work

In the work of the previous contract (1) our maximum temperature for TiB_2 fiber preparation was set at 1100°C uncorrected. The readings were low since they were taken through a glass shield and a thick-walled pyrex reactor. Also no correction was made for 1 1/2 in. of atmosphere in the reactor which contained some Ti compound particles. The combined glass correction was measured as + 65°C, but no good estimate can be made of the atmosphere correction. These correctional factors show that our true deposition temperature was some value in excess of 1165°C. Thus the actual deposition temperature was undoubtedly in the corrected temperature range (1160 to 1200°C) used throughout the present program.

IX. REFERENCES

1. Gordon H. Miller and George C. Robinson, Jr., "Investigation of Fiber Systems for Ablative Materials," Final Report, Contract NAS3-4196, NASA CR-54722, 1965
2. Handbook of Chemistry and Physics, 44th Edition
3. Encyclopedia of Chemical Technology, Vol. 14, Edited by R.E. Kirk and D.F. Othmer, Interscience Encyclopedia Inc., N. Y. 1955
4. D. J. Cameron and R. A. J. Shelton, "The Vapor Phase Deposition of Boron on Titanium by the Reaction Between Gaseous Boron Trichloride and Titanium Metal," AEEW-R424, 1965
5. Lawrence L. Quill, The Chemistry and Metallurgy of Miscellaneous Materials, First Edition, McGraw-Hill Book Company, N. Y., 1950, p 221
6. General Electric Product Data Sheet 1300-C, 1962
7. G. V. Samsonov, High Temperature Materials No. 2, Properties Index, Plenum Press, N. Y., 1964
8. P. T. B. Shaffer, High Temperature Materials No. 1, Materials Index, Plenum Press, N. Y., 1964
9. G.V. Samsonov, Refractory Transition Metal Compounds, Academic Press, N. Y., 1964, pp 172-177
10. I. R. King, F. E. Wawner, Jr., G. R. Taylor, Jr., and C. P. Talley, "Preparation and Characterization of Single Crystal Boron," Boron II, Preparation, Properties and Applications, Edited by Gerhart K. Gaule, Plenum Press, N. Y., 1965, p 45
11. Encyclopedia of Chemical Technology, Vol. 13, Edited by R. E. Kirk and D. F. Othmer, Interscience Encyclopedia, Inc., N. Y., 1955
12. E. Rudy, D. P. Harmon, and C. E. Brukl, Ternary Phase Equilibria in Transition Metal-Boron-Carbon-Silicon Systems, AFML-TR-65-2, Part I, Vol. II, 1965
13. Federal Communications Commission, Rules and Regulations. Vol. II, Part 18, Paragraph 102, Section D, 1966

DISTRIBUTION LIST FOR FINAL REPORT, NASA CR-72016

"Improved Ablative Materials"

CONTRACT NAS3-7948

Texaco Experiment Incorporated
Richmond, Virginia 23234

National Aeronautics and Space Administration (1)
Lewis Research Center
21000 Brookpark Road
Cleveland, Ohio 44135
Attention: Contracting Officer, MS 500-313

National Aeronautics and Space Administration (8)
Lewis Research Center
21000 Brookpark Road
Cleveland, Ohio 44135
Attention: Liquid Rocket Technology Branch,
MS 500-209

National Aeronautics and Space Administration (1)
Lewis Research Center
21000 Brookpark Road
Cleveland, Ohio 44135
Attention: Technical Report Control Office, MS 5-5

National Aeronautics and Space Administration (1)
Lewis Research Center
21000 Brookpark Road
Cleveland, Ohio 44135
Attention: Technology Utilization Office, MS 3-16

National Aeronautics and Space Administration (2)
Lewis Research Center
21000 Brookpark Road
Cleveland, Ohio 44135
Attention: AFSC Liaison Office, MS 4-1

National Aeronautics and Space Administration (2)
Lewis Research Center
21000 Brookpark Road
Cleveland, Ohio 44135
Attention: Library

National Aeronautics and Space Administration (1)
Lewis Research Center
21000 Brookpark Road
Cleveland, Ohio 44135
Attention: D. L. Nored, MS 500-209

National Aeronautics and Space Administration (1)
Lewis Research Center
21000 Brookpark Road
Cleveland, Ohio 44135
Attention: Office of Reliability & Quality Assurance,
MS 500-203

National Aeronautics and Space Administration (1)
Lewis Research Center
21000 Brookpark Road
Cleveland, Ohio 44135
Attention: J. Kennard

National Aeronautics and Space Administration (1)
Lewis Research Center
21000 Brookpark Road
Cleveland, Ohio 44135
Attention: E. W. Conrad, MS 100-1

National Aeronautics and Space Administration (1)
Lewis Research Center
21000 Brookpark Road
Cleveland, Ohio 44135
Attention: Mr. Robert Signorelli, MS 106-1

National Aeronautics and Space Administration (2)
Washington, D. C. 20546
Attention: Code RPX

National Aeronautics and Space Administration (2)
Washington, D. C. 20546
Attention: Code RPL

Scientific and Technical Information Facility (6)
P. O. Box 33
College Park, Maryland 20740
Attention: NASA Representative
Code CRT

National Aeronautics and Space Administration (1)
Ames Research Center
Moffett Field, California 94035
Attention: Library

National Aeronautics and Space Administration (1)
Flight Research Center
P. O. Box 273
Edwards, California 93523
Attention: Library

National Aeronautics and Space Administration (1)
Goddard Space Flight Center
Greenbelt, Maryland 20771
Attention: Library

National Aeronautics and Space Administration (1)
John F. Kennedy Space Center
Cocoa Beach, Florida 32931
Attention: Library

National Aeronautics and Space Administration (1)
Langley Research Center
Langley Station
Hampton, Virginia 23365
Attention: Library

National Aeronautics and Space Administration (1)
Manned Spacecraft Center
Houston, Texas 77001
Attention: Library

National Aeronautics and Space Administration (1)
George C. Marshall Space Flight Center
Huntsville, Alabama 35812
Attention: Library

National Aeronautics and Space Administration (1)
George C. Marshall Space Flight Center
Huntsville, Alabama 35812
Attention: Keith Chandler, R-P&VE-PA

Jet Propulsion Laboratory (1)
4800 Oak Grove Drive
Pasadena, California 91103
Attention: Library

Office of the Director of Defense Research (1)
& Engineering
Washington, D. C. 20301
Attention: Dr. H. W. Schulz, Office of Asst. Dir.
(Chem. Technology)

Defense Documentation Center (1)
Cameron Station
Alexandria, Virginia 22314

RTD (RTNP) (1)
Bolling Air Force Base
Washington, D. C. 20332

Arnold Engineering Development Center (1)
Air Force Systems Command
Tullahoma, Tennessee 37389
Attention: AEOIM

Advanced Research Projects Agency (1)
Washington, D. C. 20525
Attention: D. E. Mock

Aeronautical Systems Division (1)
Air Force Systems Command
Wright-Patterson Air Force Base
Dayton, Ohio 45433
Attention: D. L. Schmidt, Code ASRCNC-2

Air Force Missile Test Center (1)
Patrick Air Force Base, Florida
Attention: L. J. Ullian

Air Force Systems Command (1)
Andrews Air Force Base
Washington, D. C. 20332

Air Force Rocket Propulsion Laboratory (RPR) (1)
Edwards, California 93523

Air Force Rocket Propulsion Laboratory (RPM) (1)
Edwards, California 93523

Air Force FTC (FTAT-2) (1)
Edwards Air Force Base, California 93523
Attention: Col. J. M. Silk

Air Force Office of Scientific Research
Washington, D. C. 20333
Attention: SREP, Dr. J. F. Masi

Office of Research Analyses (OAR) (1)
Holloman Air Force Base, New Mexico 88330
Attention: RRRT

U. S. Air Force (1)
Washington, D. C. 20325
Attention: Col. C. K. Stambaugh
Code AFRST

Commanding Officer (1)
U. S. Army Research Office (Durham)
Box CM, Duke Station
Durham, North Carolina 27706

U. S. Army Missile Command (1)
Redstone Scientific Information Center
Redstone Arsenal, Alabama 35808
Attention: Chief, Document Section

Bureau of Naval Weapons (1)
Department of the Navy 20390
Washington, D. C.
Attention: J. Kay, Code RTMS-41

Commander (1)
U. S. Naval Missile Center
Point Mugu, California 93041
Attention: Technical Library

Commander (1)
U. S. Naval Ordnance Test Station
China Lake, California 93557
Attention : Code 45

Commander (1)
U. S. Naval Ordnance Test Station
China Lake, California 93557
Attention: W. F. Thorm, Code 4562

Commanding Officer (1)
Office of Naval Research
1030 East Green Street
Pasadena, California 91101

Director (1)
U. S. Naval Research Laboratory
Washington, D. C. 20390
Attention: H. W. Carhart
Code 6180

Picatinny Arsenal (1)
Dover, New Jersey 08701
Attention: I. Forsten, Chief
Liquid Propulsion Laboratory

U. S. Atomic Energy Commission (1)
Technical Information Services
Box 62
Oak Ridge, Tennessee 37830
Attention: A. P. Huber, Code ORGDP
Box P

Air Force Aero Propulsion Laboratory (1)
Research & Technology Division
Air Force Systems Command
United States Air Force
Wright-Patterson AFB, Ohio 45433
Attention: APRP (C. M. Donaldson)

Aerojet-General Corporation (1)
P. O. Box 296
Azusa, California 91703
Attention: Librarian

Aerojet-General Corporation (1)
11711 South Woodruff Avenue
Downey, California 90241
Attention: F. M. West, Chief Librarian

Aerojet-General Corporation (1)
P. O. Box 1947
Sacramento, California 95809
Attention: Technical Library 2484-2015A

Aeronutronic Division of (1)
Philco Corporation
Ford Road
Newport Beach, California 92600
Attention: Technical Information Department

Aeroprojects, Incorporated (1)
310 East Rosedale Avenue
West Chester, Pennsylvania 19380
Attention: C. D. McKinney

Aerospace Corporation (1)
P. O. Box 95085
Los Angeles, California 90045
Attention: Library-Documents

Arthur D. Little, Inc. (1)
Acorn Park
Cambridge, Massachusetts 02140
Attention: A. C. Tobey

Astropower, Incorporated (1)
Subs. of Douglas Aircraft Company
2968 Randolph Avenue
Costa Mesa, California 92626
Attention: Dr. George Moc
Director, Research

Astrosystems, Incorporated (1)
1275 Bloomfield Avenue
Caldwell Township, New Jersey 07006
Attention: A. Mendenhall

ARO, Incorporated (1)
Arnold Engineering Development Center
Arnold AF Station, Tennessee 37389
Attention: Dr. B. H. Goethert
Chief Scientist

Atlantic Research Corporation (1)
Shirley Highway & Edsall Road
Alexandria, Virginia 22314
Attention: Security Office for Library

Battelle Memorial Institute (1)
505 King Avenue
Columbus, Ohio 43201
Attention: Report Library, Room 6A

Beech Aircraft Corporation (1)
Boulder Facility
Box 631
Boulder, Colorado 80302
Attention: J. H. Rodgers

Bell Aerosystems, Inc. (1)
Box 1
Buffalo, New York 14205
Attention: T. Reinhardt

Bendix Systems Division (1)
Bendix Corporation
Ann Arbor, Michigan 48103
Attention: John M. Bureger

The Boeing Company (1)
Aero Space Division
P. O. Box 3707
Seattle, Washington 98124
Attention: Ruth E. Peerenboom (1190)

Chemical Propulsion Information Agency (1)
Applied Physics Laboratory
8621 Georgia Avenue
Silver Spring, Maryland 20910

Chrysler Corporation (1)
Missile Division
Warren, Michigan 01608
Attention: John Gates

Chrysler Corporation (1)
Space Division
New Orleans, Louisiana 70150
Attention: Librarian

Curtiss-Wright Corporation (1)
Wright Aeronautical Division
Woodridge, New Jersey 07075
Attention: G. Kelley

University of Denver (1)
Denver Research Institute
P. O. Box 10127
Denver, Colorado 80210
Attention: Security Office

McDonnell Douglas Aircraft Co. (1)
Santa Monica Division
3000 Ocean Park Boulevard
Santa Monica, California 90405
Attention: J. L. Waisman

Fairchild Stratos Corporation (1)
Aircraft Missiles Division
Hagerstown, Maryland 21740
Attention: J. S. Kerr

General Dynamics/Astronautics (1)
P. O. Box 1128
San Diego, California 92112
Attention: Library & Information Services (128-00)

General Electric Company (1)
Re-Entry Systems Department
P. O. Box 8555
Philadelphia, Pennsylvania 19101
Attention: F. E. Schultz

General Electric Company (1)
Flight Propulsion Lab. Department
Cincinnati, Ohio 45215
Attention: D. Suichu

Grumman Aircraft Engineering Corporation (1)
Bethpage, Long Island,
New York 11102
Attention: Joseph Gavin

Hercules Powder Company (1)
Allegheny Ballistics Laboratory
P. O. Box 210
Cumberland, Maryland 21501
Attention: Library

IIT Research Institute (1)
Technology Center
Chicago, Illinois 60616
Attention: C. K. Hersh, Chemistry Division

Kidde Aero-Space Division (1)
Walter Kidde & Company, Inc.
675 Main Street
Belleville, New Jersey 07109
Attention: R. J. Hanville,
Director of Research Engineering

Lockheed Missiles & Space Company (1)
P. O. Box 504
Sunnyvale, California 94088
Attention: Technical Information Center

Lockheed-California Company (1)
10445 Glen Oaks Boulevard
Pacoima, California 91331
Attention: G. D. Brewer

Lockheed Propulsion Company (1)
P. O. Box 111
Redlands, California 92374
Attention: Miss Belle Berlad, Librarian

Lockheed Missiles & Space Company (1)
Propulsion Engineering Division (D. 55-11)
1111 Lockheed Way
Sunnyvale, California 94087

Marquardt Corporation (1)
16555 Saticoy Street
Box 2013, South Annex
Van Nuys, California 91404
Attention, Librarian

Martin-Marietta Corporation (1)
Martin Division
Baltimore, Maryland 21203
Attention: John Calathes (3214)

McDonnell Douglas Aircraft Co. (1)
P. O. Box 6101
Lambert Field, Missouri 63145
Attention: R. A. Herzmark

North American Rockwell Corporation (1)
Space & Information Systems Division
12214 Lakewood Boulevard
Downey, California 90242
Attention: Technical Information Center,
D/096-722 (AJ01)

Northrop Space Laboratories (1)
1001 East Broadway
Hawthorne, California 90250
Attention: Dr. William Howard

Purdue University (1)
Lafayette, Indiana 47907
Attention: Technical Librarian

Radio Corporation of America (1)
Astro-Electronics Division
Defense Electronic Products
Princeton, New Jersey 08540
Attention: S. Fairweather

Republic Aviation Corporation (1)
Farmingdale, Long Island,
New York 11738
Attention: Dr. William O'Donnell

Rocket Research Corporation (1)
520 South Portland Street
Seattle, Washington 98108

Rocketdyne Division (1)
of North American Rockwell Corporation
6633 Canoga Avenue
Canoga Park, California 91304
Attention: Library, Department 596-306

Rohm and Haas Company (1)
Redstone Arsenal Research Division
Huntsville, Alabama 35808
Attention: Librarian

Space-General Corporation (1)
777 Flower Street
Glendale, California 91201
Attention: C. E. Roth

Stanford Research Institute (1)
333 Ravenswood Avenue
Menlo Park, California 94025
Attention: Thor Smith

General Technologies Corporation (1)
708 North West Street
Alexandria, Virginia 22310
Attention: H. M. Childers

Thiokol Chemical Corporation (1)
Alpha Division
Huntsville Plant
Huntsville, Alabama 35800
Attention: Technical Director

Thiokol Chemical Corporation (1)
Reaction Motors Division
Denville, New Jersey 07834
Attention: Librarian

Thiokol Chemical Corporation (1)
Redstone Division
Huntsville, Alabama 35805
Attention: John Goodloe

TRW Systems, Incorporated (1)
1 Space Park
Redondo Beach, California 90200
Attention: G. W. Elverum

TRW Systems, Incorporated (1)
1 Space Park
Redondo Beach, California 90200
Attention: STL Technical Library
Document Acquisitions

TRW Systems, Incorporated (1)
1 Space Park
Redondo Beach, California 90200
Attention: Dr. Eugene Burns

TRW, Incorporated (1)
23555 Euclid Avenue
Cleveland, Ohio 44117
Attention: P. T. Angell

United Aircraft Corporation (1)
Corporation Library
400 Main Street
East Hartford, Connecticut 06118
Attention: Dr. David Rix

United Aircraft Corporation (1)
Pratt & Whitney Division
Florida Research & Development Center
P. O. Box 2691
West Palm Beach, Florida 33402
Attention: Library

United Aircraft Corporation (1)
United Technology Center
P. O. Box 358
Sunnyvale, California 94088
Attention: Librarian

Vought Astronautics (1)
Box 5907
Dallas, Texas 75222
Attention: Warren C. Trent

Aerotherm Corporation (1)
460 California Avenue
Palo Alto, California 94306
Attention: Mr. Roald Rindal