1.0

1.1

1.25   1.4   1.6

4.5
5.0
5.6

2.8   2.5

3.2   2.2

3.6

4.0   2.0

1.8

MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU

LEVEL II ②

AFML-TR-79-4219

ADA085153

INVESTIGATION OF CNTD SILICON NITRIDE ON COMPLEX SHAPES

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February 6, 1980

TECHNICAL REPORT AFML-TR-79-4219

Interim Report for Period 1 July 1978 – 1 July 1979

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CNTD Si_3N_4
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The project reported on herein represents an attempt to extend the technique of CVD to the efficient, economical, one step coating of complex shapes. A limitation in state of the art CVD processing is that planar of axisymmetric shapes are required if coatings having uniform thickness and consistent properties are desired. It was therefore proposed to design, build and test a deposition chamber in which a complex shape such as a turbine blade or vane could be reproducibly and evenly coated on all surfaces in one operation. (over)

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The present report describes the rationale for the chamber design, experiments leading to the demonstration of its capabilities, and the characterization of the resulting Si_3N_4 coatings which were deposited on RBSN turbine vanes. A complete description of the chamber and ancillary equipment is given.

FOREWORD

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

SUMMARY

The present program encompasses the design and construction of a unique chemical vapor deposition (CVD) chamber for the deposition of Si_3N_4 onto complex substrate shapes. Included is an analysis of chamber design parameters and their effects on Reynolds number calculations to characterize fluid dynamic conditions during deposition. Experiments which demonstrate the effects of increased Reynolds number are described. Finally, deposition experiments within the new chamber and the results thereof are outlined; RBSN vanes were given a coating of Si_3N_4 to demonstrate the capabilities of the chamber. These experiments are described in detail.

The program spanned a one year period. The initial eight months were devoted to the design and construction of the chamber. During this period, deposition experiments were carried out in conventional, once-through chambers. Gas velocities were greatly increased over those normally used in CVD (100 to 1000 times normal) in order to explore these effects as soon as possible in the program. The final months were devoted to the establishment of deposition conditions within the circular, turbulent flow chamber.

A unique chamber was designed and built to take advantage of high velocity, high Reynolds number, centrifugal flow of reactant gases to deposit a relatively uniform Si_3N_4 layer on four RBSN turbine vanes in a single deposition run. Deposition runs using this chamber produced vanes on which all surfaces were coated, thereby demonstrating the potential of this type of chamber for cost effective, one step deposition.

The objective of this program has only partially been reached. Microstructural studies of cross sections of coated vanes indicated varying thicknesses of deposit, but reasonably uniform grain size and hardness.

SECTION I

INTRODUCTION

Chemical Vapor Deposition (CVD) techniques have not found industrial application to complex shapes because of the formation of stable boundary layers around the substrate. These boundary layers cause thickness variations and inhomogeneous microstructure and properties. On the other hand, application of a pure, dense layer of Si_3N_4 to a high temperature structural ceramic part could provide significant advantages in performance, e.g. higher strength and greater erosion and oxidation resistance.

The program discussed herein has as its major goal the design and demonstration of a CVD reactor which would permit deposition of a uniform Si_3N_4 layer onto a complex substrate such as a turbine vane or blade. Secondary objectives were to characterize the deposited Si_3N_4 and to gain experience in the operation of the chamber in order to optimize its design.

The design rationale was based on developing true turbulent flow conditions over the entire sample surface within the deposition chamber. It is recognized that the boundary layer which is present in all non-turbulent deposition promotes inhomogeneity of deposit thickness, chemistry, and properties. Thus, elimination of the boundary layer should permit attainment of the program goals.

The primary objective of this program was to design, construct, and demonstrate feasibility for a deposition chamber which would take advantage of fluid dynamic turbulence to chemically vapor deposit a uniform layer of Si_3N_4 on a complex shape such as a turbine vane or blade. Secondary objectives included an evaluation of the quality of the deposit and investigation of its characteristics as related to deposition parameters.

Important ancillary studies were performed to evaluate the effects of

1

deposition from high velocity gas streams. It is reasonable to expect morphology and other coating properties to change as gas stream velocities increase from the 10 to 100 cm/min range to the 50,000 to 100,000 cm/min range where turbulence exists (depending on temperature).

SECTION II

BACKGROUND

1. CLASSICAL CVD

Structural ceramics such as SiC and Si_3N_4 have been actively investigated over the past few years because of their potential for replacing high cost and temperature limited metallic alloys in advanced heat engines, as well as for other military and civilian applications. Physical property exploration and development has proceeded. However, it is apparent that the currently available bulk processed ceramic materials (sintered, reaction bonded, hot pressed) have limitations. These limitations result from either inherent low density, or from property degrading densification additives. Additionally, hot pressing suffers from limitations in size and complexity of the shape which can be produced, and requires expensive diamond machining.

In contrast, Chemical Vapor Deposition (CVD) techniques can produce net-shape materials of greater purity and density without the need for binders to achieve consolidation. Coupled with these advantages, Chemetal has developed a proprietary version of CVD called Controlled Nucleation Thermochemical Deposition (CNTD)[1] which results in an extremely fine-grained, equiaxed microstructure in deposited materials such as SiC[2]. Work is proceeding on a parallel program to develop a CNTD technique for Si_3N_4[3]. The CNTD grain structure results in increased mechanical strength and erosion resistance. The technique for CNTD Si_3N_4 was not sufficiently developed at the outset of the subject contract to use it in the present program. However, it will be seen that the present reactor-chamber design and techniques lend themselves well to any normal CVD/CNTD type reaction. Reference 2 describes conditions and parameters leading to the deposition

of CNTD SiC. There are no factors which will prevent the a priori use of the high velocity centrifugal flow chamber to make CNTD SiC.

Only in a limited number of applications have CVD systems made the transition from laboratory scale reactions to commercial usefulness. These applications, such as deposition of silicon in the electronics industry, have not required deposition of a material on a complex shape. In most commercial applications, flat planar surfaces are used, low temperatures (500 to 1000°C) and relatively slow reactant gas velocities (100 to 1000 cm/min STP) prevail. These conditions may be described by Reynolds numbers, N_{Re}, in the order of 10 to 100 (laminar flow). Under such conditions, a distinct boundary layer surrounds the part, becomes well established, and may be quite thick. This boundary layer will control the deposition rate by restricting the availability of fresh reactants at the surface of the deposit and/or by restricting the removal of reaction products.

2. THE BOUNDARY LAYER PROBLEM

Van den Brekel[4,5] described the conditions which prevail during deposition under laminar flow conditions, deriving a quantity which he called the "CVD number." The magnitude of the CVD number (here denoted {CVD}) is an indication as to which is the controlling deposition process. When the diffusion of reactants through the boundary layer is the rate limiting condition, then {CVD}>>1. When surface reactions control the process, then {CVD}<<1. The condition of {CVD}≈1 corresponds to the transition from diffusion controlled to surface reaction controlled growth of the deposit. Physically, the CVD number represents a ratio between the resistances experienced by the diffusive flux and the mass transfer flux at the surface of the deposit, (i.e. the surface kinetics term). Figure 1 graphically displays these relations using a plot of the log of the growth rate, G, vs reciprocal

4
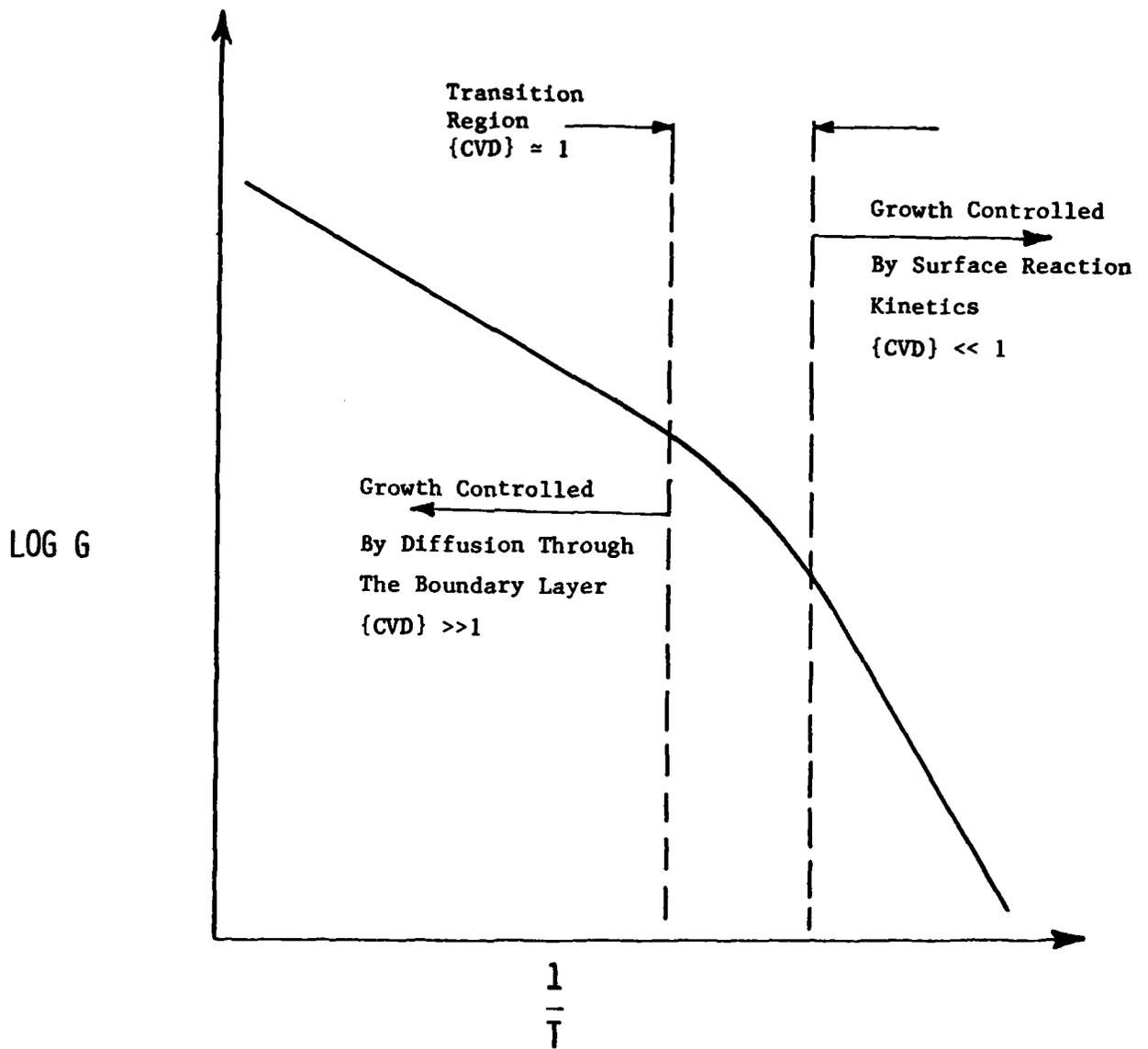
FIGURE 1   PLOT OF LOG {GROWTH RATE} VS $\frac{1}{T}$ SHOWING "CVD NUMBER" [4,5]
REGIONS WITHIN THE LAMINAR FLOW REGIME.

temperature. The two regions described by the extreme values of von den Brekel's "CVD number" are indicated as regions of different slope in Figure 1.

Van den Brekel's analysis shows that the limitation of conventional CVD lies in its dependence on the boundary layer phenomenon. In attempting to develop a cost effective deposition technique for a structural material which must be present in thicknesses of the order of 0.25 mm to 2.5 mm (0.01 in to 0.100 in), one must devise a way to avoid at least the diffusion limited regime but yet remain in the upper temperature region (refer to Figure 1) which occurs for Si_3N_4 at temperatures of approximately $1350^\circ C$ or higher. Unfortunately, the deposition rate has just begun to approach a reasonably large value at those temperatures, reaching ≈ 0.25 mm (0.010 in) per hour or more. Another practical problem in the Si_3N_4 system, which is aggrevated at lower temperatures, is the tendency to form intermediate compounds in the gas phase which leads to homogenous nucleation in the gas phase and the undesirable deposition of solid particles on the substrate. For this reason, when depositing Si_3N_4, it is desired to keep the reactant gases separated as long as possible, combining them ideally in the immediate vicinity of the substrate.

CHEMETAL'S practical experience with this problem on previous and con-current programs over a period of approximately two years has pointed up the need for a radical departure from classical laminar flow type deposi-tion chambers, where the gas is passed slowly by the part in order to maxi-mize the amount of reactant used during this one and only pass. Prior experience in coating gun barrels with tungsten and various alloys using higher velocity gas streams (~1000 cm/min compared to ~100 cm/min, at STP)

6

indicated that deposit uniformity was improved and greater lengths of coating were achieved at the expense of a lower deposition rate. Low velocity, single pass vertical or horizontal chambers permit temperature gradients and thick stable boundary layers to exist which produce variations in deposited thickness, deposit morphology, and microstructural and physical properties as a function of radial and axial location. Radial variations may be minimized by reducing the size of the chamber, but this eliminates multiple part processing, as well as limiting the adaptability of the chamber to different size/shape components.

The goal of the present effort was to develop a process capable of depositing a uniformly thick layer of Si_3N_4 on all surfaces of a complex part (such as a turbine blade or vane). The deposit should have uniform properties and microstructure at all locations. The key point here was the beneficial effect of high velocity of the gas stream. If the reactant gases could be accelerated into the turbulent flow regime (Reynolds number, $N_{Re} \geq 2000$) or at least the upper laminar velocity regime (say, $N_{Re} \geq 1000$), the major influence of the boundary layer surrounding the substrate might be minimized or eliminated. This would, in turn, permit deposition of Si_3N_4 at all points on the substrate from a reactant gas stream of essentially constant composition and temperature, thus making surface kinetics the controlling factor in the quality and rate of deposition.

3.   TURBULENT FLOW

At this point having defined the goal and approach to be taken in achieving the goal, certain practical, engineering questions become apparent. The first problem is to predict what velocity will be required, choosing reasonable temperatures, chamber dimensions and reactants to achieve hydrodynamic turbulence. The problem of achieving desired velocities is simplified by the device of using a nonreactive diluent or carrier gas. An excellent candidate is nitrogen. Since the chamber pressure compatible with exhaust equipment

7

in use is between 50 and 100 Torr and the temperature of the gas stream will be typically 500 to 700°C as a result of preheating, one may calculate the velocity necessary to achieve a Reynolds number of ≈2000 for a stream of pure nitrogen using:

$$N_{Re} = \frac{DV\rho}{\mu} = \frac{DV}{\nu} \tag{1}$$

Where: D = Effective diameter of the chamber through which the nitrogen is flowing. For circumferential flow, an effective toroid containing the circulating gases may be defined.

V = Velocity of the gas stream at the temperature and pressure of interest.

μ = Viscosity of the gas stream at the temperature and pressure of interest.

ρ = Density of the gas stream at the temperature and pressure of interest.

μ/ρ = ν, Kinematic viscosity.

Choosing values for D, μ, ρ (or ν) as follows for nitrogen:

P = 90 Torr

T = 700°C

ΔP = (Pressure of interest -1) atm

ΔT = (Temperature of interest -0°C)

D = 0.875 in = 2.22 cm

μ (T = 973°K, P = 90 Torr)   = $175 \times 10^{-6} + (4.55 \times 10^{-7})\Delta T + (2.28 \times 10^{-7})\,\Delta P$
= 493×10^{-6} poise
ρ (T = 973°K, P = 90 Torr)   = 41.5×10^{-6} gm/cm^3

The expression for μ is taken from American Institute of Physics Handbook [9]. The velocity necessary to achieve the transition from laminar to turbulent flow is calculated to be:

V = 24,000 cm/min, STP, pure nitrogen.

These conditions were calculated for a single pass, verticle flow, cylindrical chamber in which a bend bar type sample could be placed to verify the effects of achieving high N_{Re} in preliminary experiments. An example of the calculation of N_{Re} actually achieved in the centrifugal chamber is given in the Experimental Results section and in the Appendix. Results of preliminary experiments in the single pass, cylindrical chamber are also given.

An important conclusion arising from such calculations is that the volume of carrier gas will be so large that it will be uneconomical to pass over a substrate once and then exhaust it. Further, a large amount of thermal energy contained in the gas would be wasted, and a large, expensive exhaust heat exchanger would be required. If one considers recycling the exhaust gases from a single pass chamber, the thermal energy losses would still be troublesome and the formation of gas phase particulate intermediates becomes a problem. The removal from the gas stream of such particulates during recycling would result in problems of control of the gas stream composition. These factors result in the consideration of a circular chamber into which high velocity gases enter tangentially at the periphery and then circle the chamber many times before being exhausted. The details of such a chamber will be described in the Experimental section.

A detailed calculation of N_{Re} for the centrifugal flow chamber is given in the Appendix. The effect of acceleration through the entrance ports is taken into account, even though the velocity (and N_{Re}) decays rapidly after the gasses enter the chamber.

9

SECTION III

EXPERIMENTAL PROCEDURE

This section describes equipment and deposition conditions used in experiments on high velocity deposition of Si_3N_4. The centrifugal flow chamber designed, built, and tested during the program is described. In addition exploratory experiments are described which were performed in typical once through CVD chambers but at much higher velocities than normal.

1. EQUIPMENT

The centrifugal chamber is shown in sectional views in Figures 2, 3, and 4. Figures 5 through 12 show the chamber in various stages of assembly. In Figure 5 the details of the substrate rotation mechanism are shown. The large graphite table rotates in either direction as do the small graphite substrate holders. These rotational combinations are shown schematically in Figure 13. Figure 6 shows the rotating graphite table on which the (independently) rotating graphite substrate holders are mounted. The combined effect of the rotating table with rotating individual part holders is to produce a planetary motion of the substrates being coated. Two small (1/15 hp) electric motors mounted below the deposition chamber drive the table and the substrate holders independently (through a planetary gear system). Thus, both rotational speed and direction of rotation of table and holders are independently controlled. Rotational speeds are variable from 0 to 80 rpm for both table and holders.

Figure 7 depicts one way of mounting a graphite prototype turbine blade shape (see Figure 15, page 34) on the substrate holder. The "blade" in this case is vertical, and the "base" is affixed to the horizontal surface of the substrate holder and is parallel to the holder. RBSN vanes were

10

High Volume
$N_2 + SiCl_4$
in

$N_2 + H_2$
$+ NH_3$
in

Cooling Water Out

Cooling Water In

Cooling Water Out

Cooling Water In
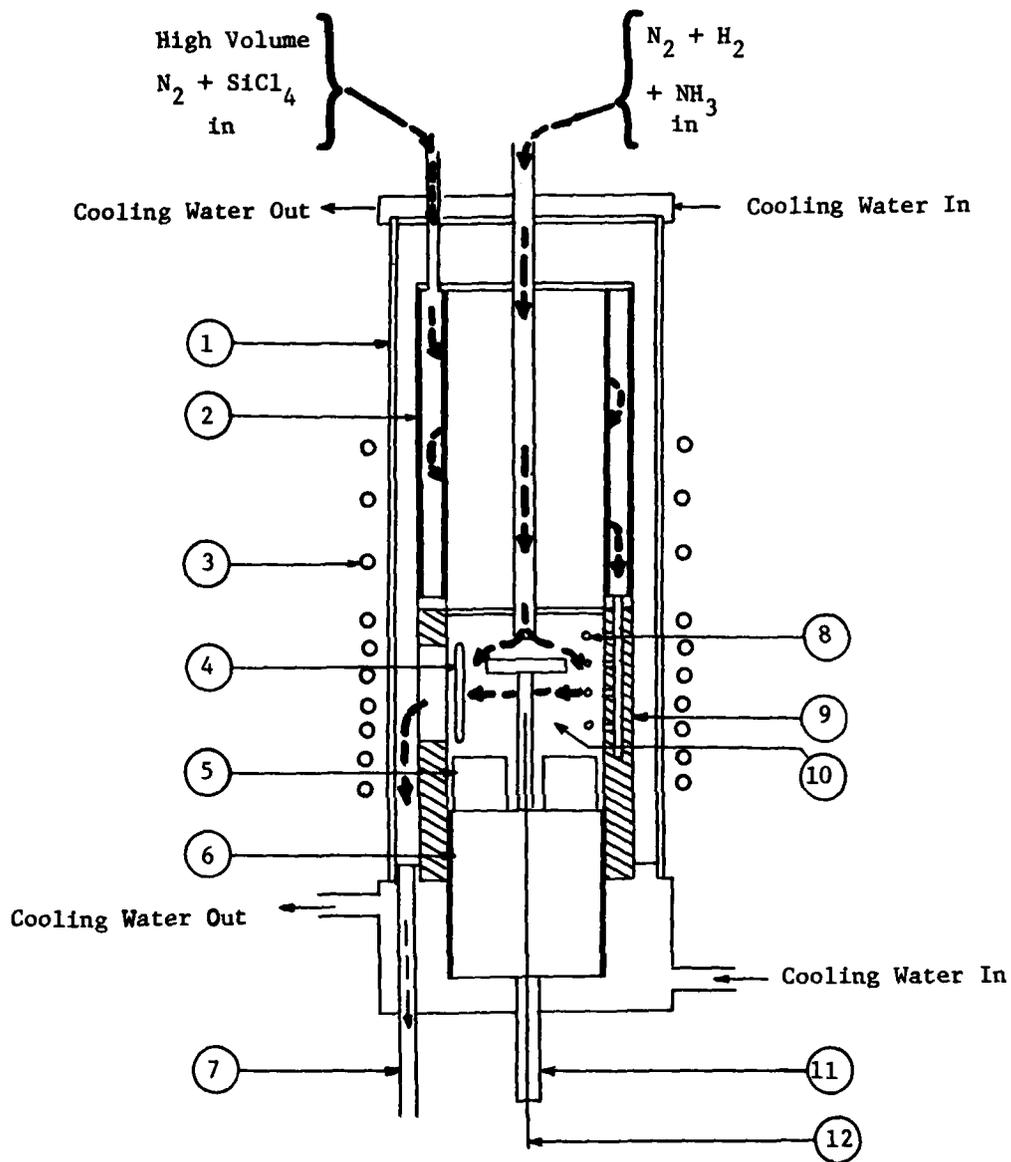
1. Quartz Chamber
2. N_2 Heat Exchanger, HLM Graphite
3. Induction Coil
4. Exhaust Port
5. Rotating Part Holder, HLM Graphite
6. Rotating Table, HLM Graphite

7. Gas Exhaust
8. Injection Port
9. Susceptor, HLM Graphite
10. Reaction Chamber
11. Drive Shaft
12. Pt/Pt-13Rh (Type R)
      Thermocouple

FIGURE 2: VERTICAL SECTION ASSEMBLY, CENTRIFUGAL
DEPOSITION CHAMBER.

11

.062 DIA. GAS HOLES TANGENTIAL TO WALL

.25 X 3.5 EXHAUST SLOTS TO .56 DIA. HOLES

60°

15° TYP.

DRL. .0625 THRU. 59 PLCS.
C.B. .187 DIA & PLUG

INJECTION PORTS

15° TYP.

3.375 RAD

15° TYP

MATERIAL: GRAPHITE, HLM

.56 DIA THRU
28 PLCS
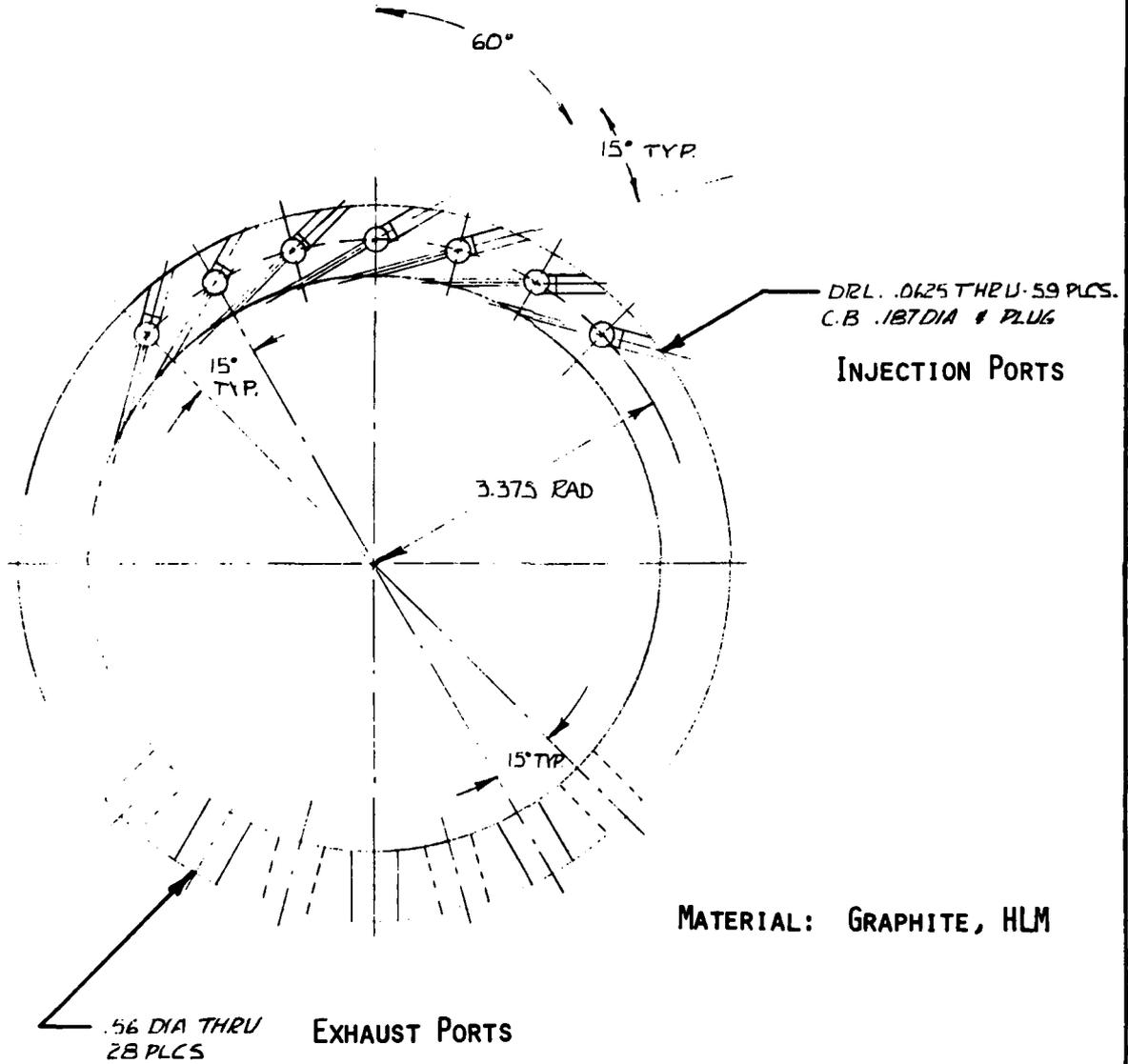
EXHAUST PORTS

SECTION - A - A

FIGURE 3: HORIZONTAL SECTION OF DEPOSITION CHAMBER SHOWING
INJECTION AND EXHAUST PORTS.

12

Hot Gases Injected

Spent Gases Out

OFF SET EACH ROW .50

MATERIAL: GRAPHITE

7.48 DIA

5.980 DIA

10.00

5.00

.50

.25

1.50

.10 TYP.

2.0

DRL .25 DIA. 5.0 DEEP 7 PL'S. C.B. .50 DIA. .50 DEEP
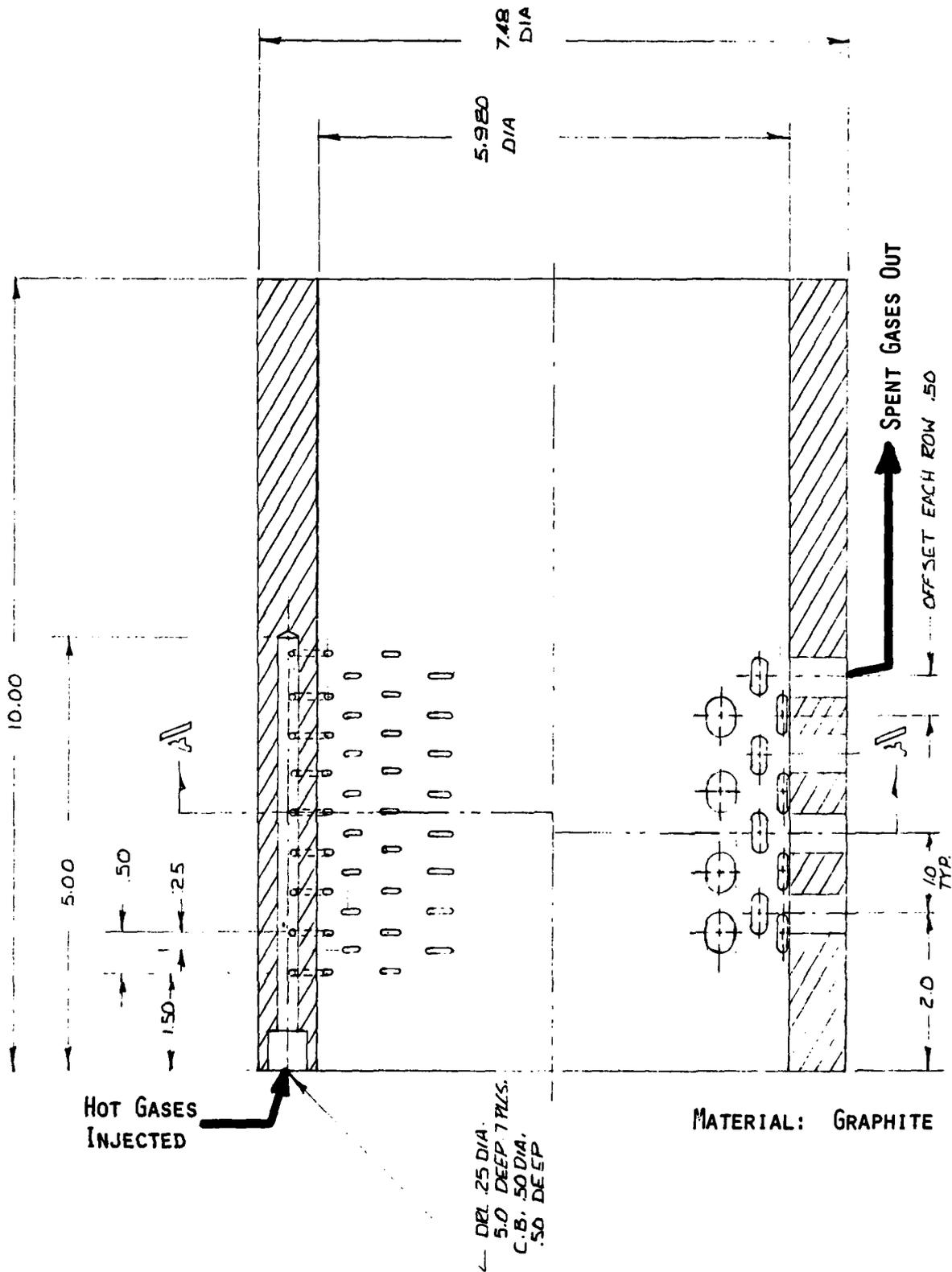
FIGURE 4: VERTICAL SECTION OF DEPOSITION CHAMBER

13
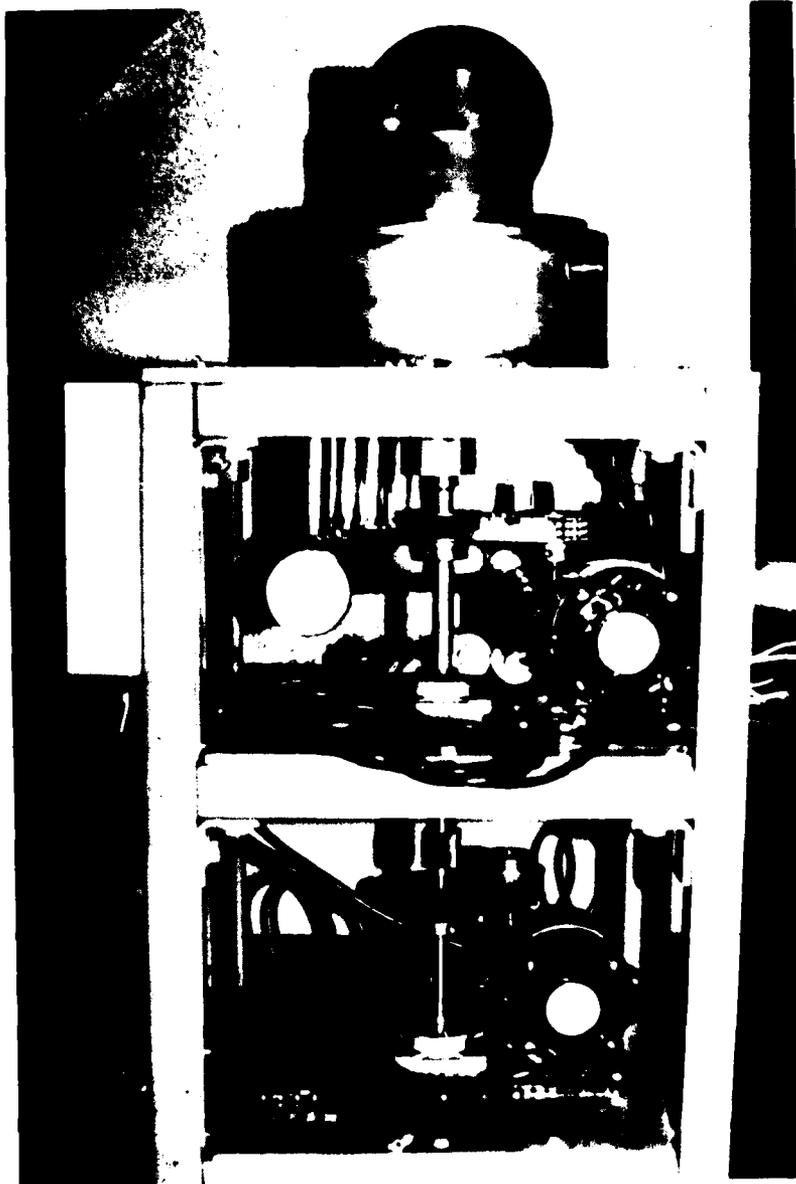
FIGURE 5: DRIVE SHAFT MOTORS AND CONCENTRIC SHAFT ASSEMBLY. THE EXHAUST GAS MANIFOLD CAN BE SEEN ON THE UPPER TIER.
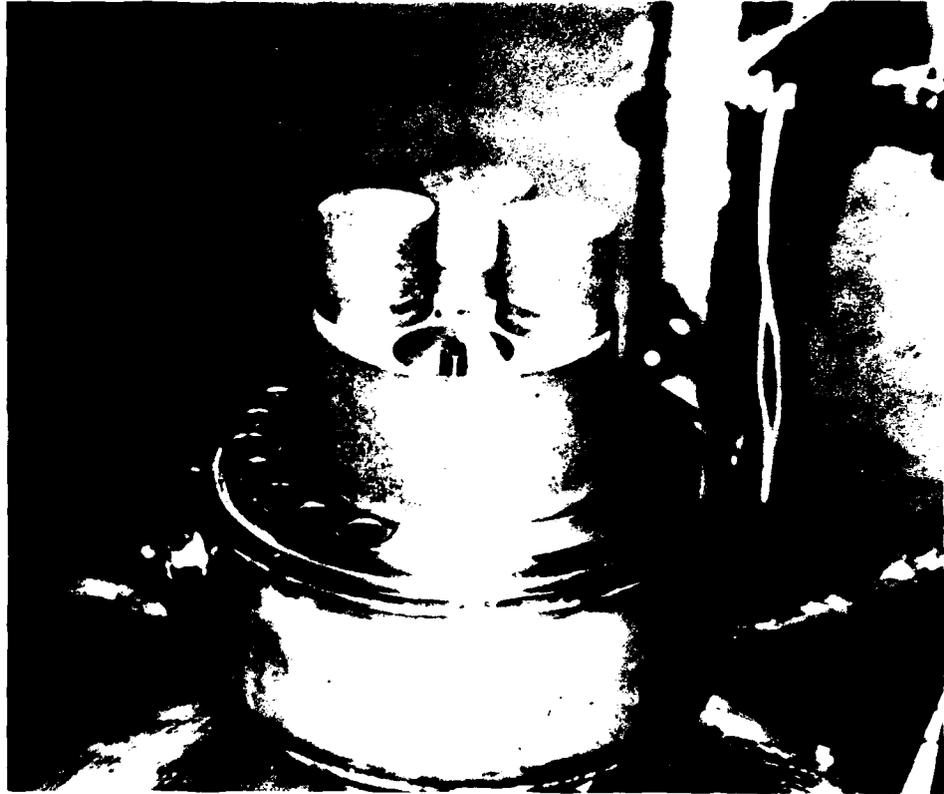
FIGURE 6:   ROTATION TUBE, ROTATING PART HOLDERS AND
             EXHAUST GAS HEADERS TO THE LEFT. ONE OF THE
             PART HOLDERS IS REMOVED TO SHOW THE DRIVE
             SHAFT FOR EACH INDIVIDUAL PART.

15

FIGURE 7:   THREE GRAPHITE SUBSTRATES SIMULATING TURBINE
             BLADES POSITIONED IN IHE PART HOLDER.

16
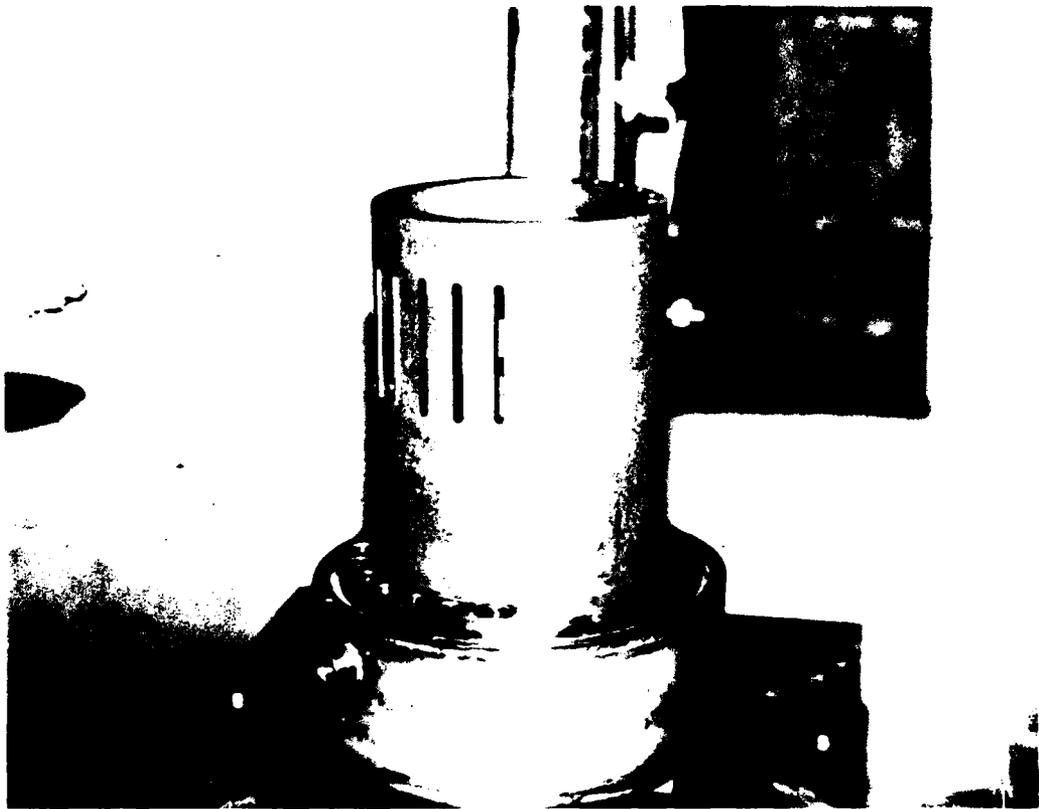
FIGURE 8:   REACTION CHAMBER IN POSITION AROUND THE PARTS.
NOTE THE VERTICAL EXHAUST SLOTS.

17

FIGURE 9:   OVERHEAD VIEW OF THE REACTION CHAMBER.   THE
           NITROGEN INLET ORIFICES AND SUPPLY HOLES CAN
           BE SEEN ON THE RIGHT.

18
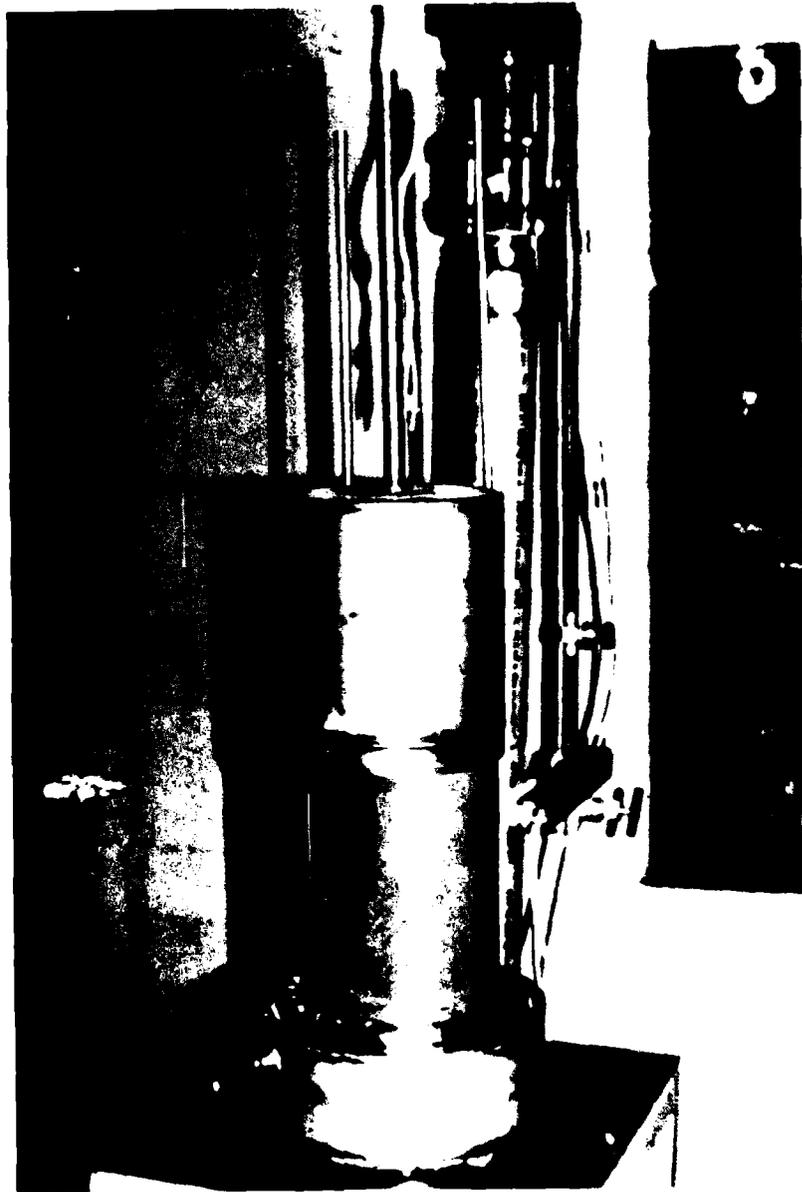
FIGURE 10:   NITROGEN HEAT EXCHANGER CHAMBER POSITIONED
ABOVE THE REACTION CHAMBER.

19
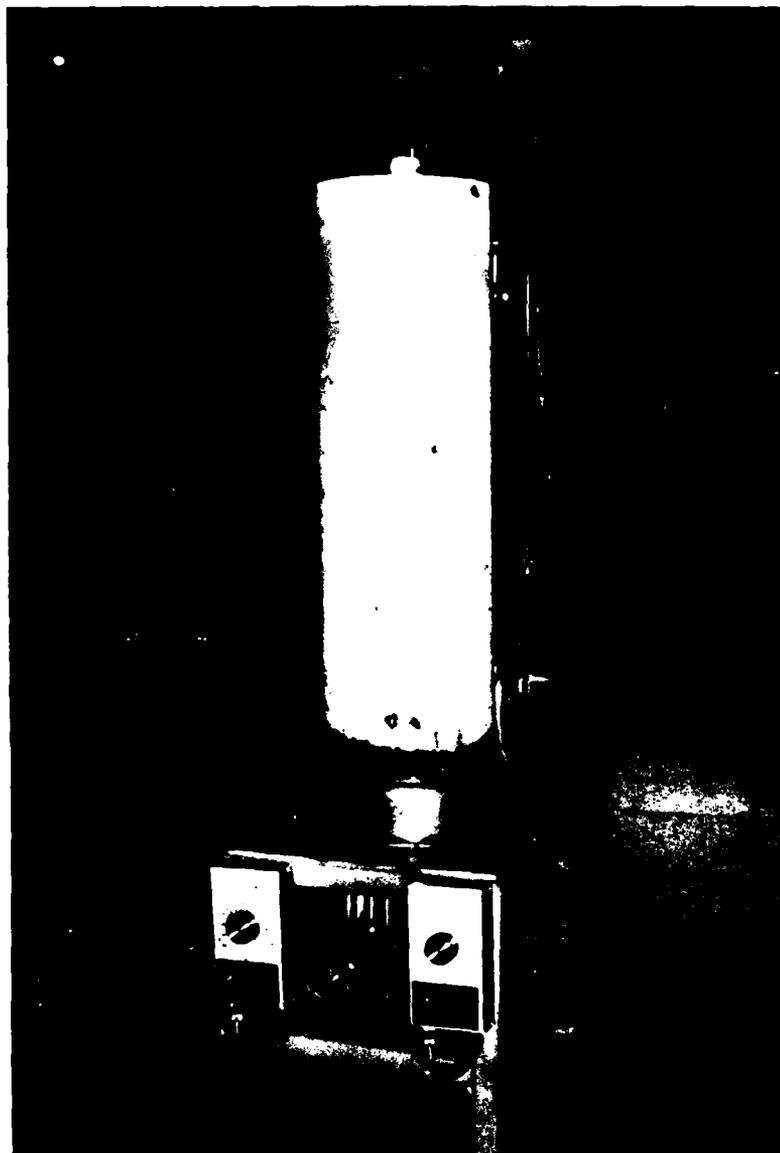
FIGURE 11:   QUARTZ CHAMBER AND WATER COOLED TOP FLANGE
SURROUNDING THE REACTION CHAMBER.
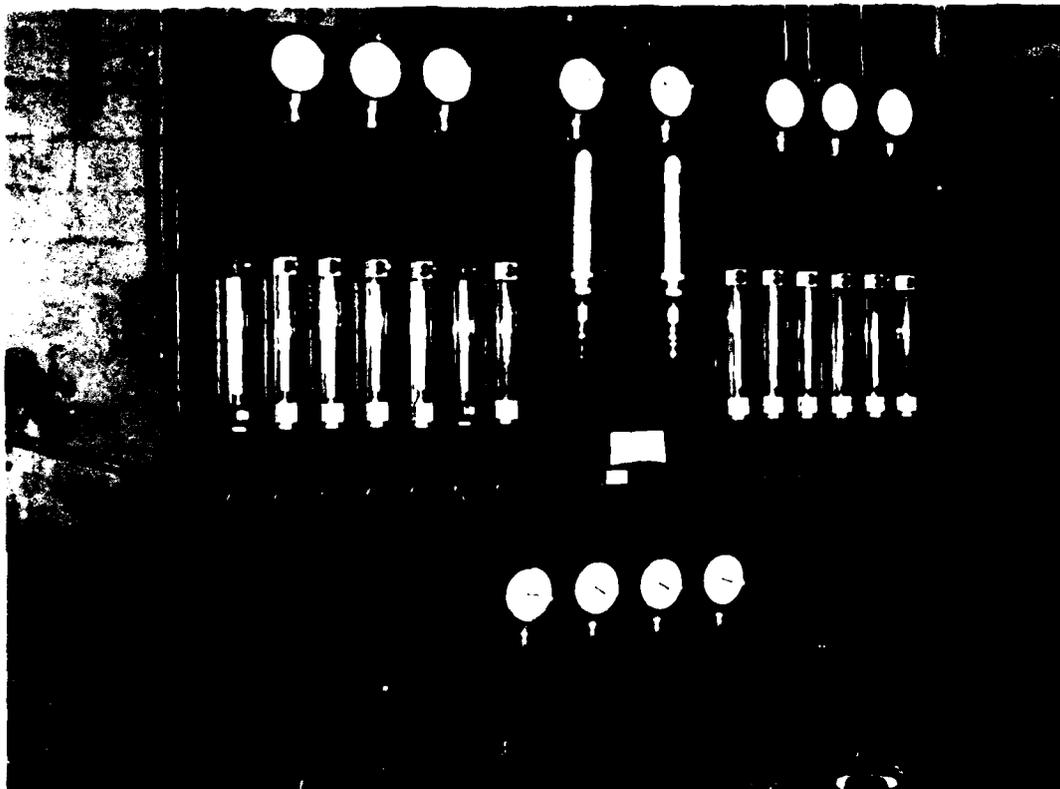
FIGURE 12   CONTROL PANEL EQUIPPED WITH INDIVIDUAL GAS
            FLOW MONITORS, PRESSURE AND TEMPERATURE
            INDICATORS.

21

Graphite Substrate Holders--Can Be Rotated In Both Directions

Graphite Table Can Be Rotated In Both Directions

Gas Exhaust

Gas Inlet

Graphite Furnace Chamber
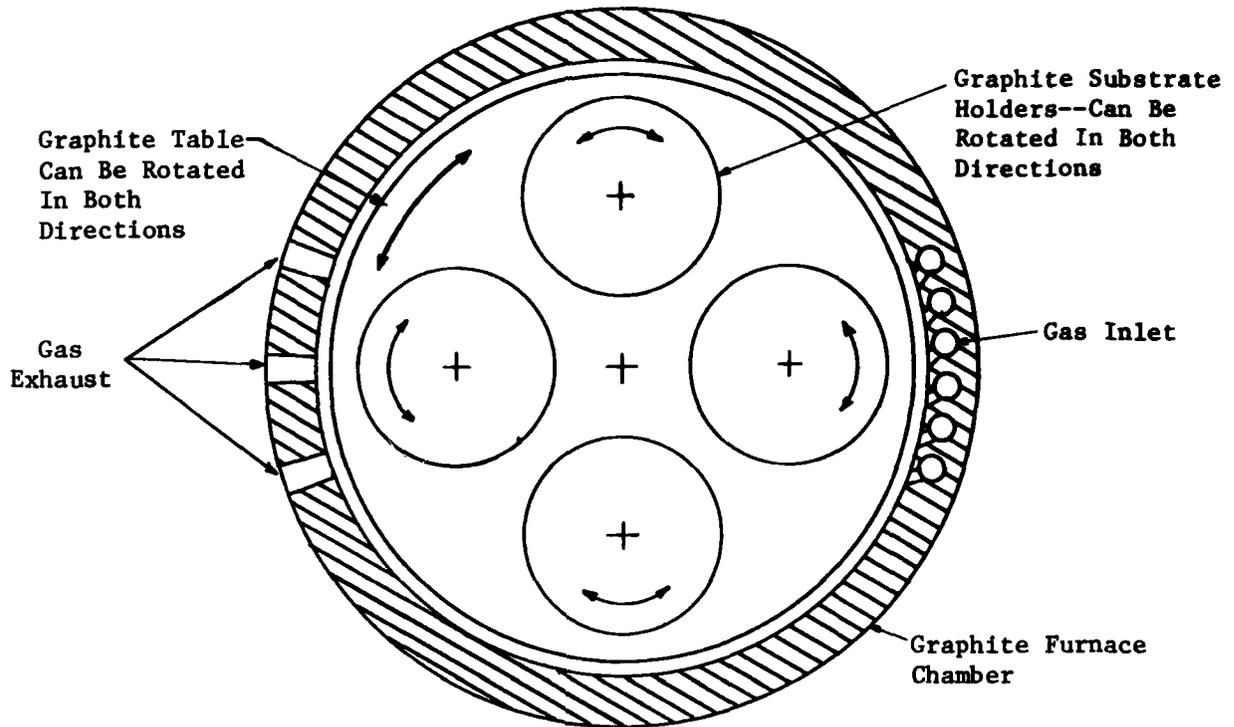
Table and substrate holder speeds continuously variable from 0 to 80 rpm.

A speed of approximately 20 rpm was chosen for both table and holders.

See text for additional details.

FIGURE 13   SUBSTRATE AND TABLE ROTATION CAPABILITIES.

22

obtained* and mounted as shown in Figure 15, by holding in a graphite

fixture attached to the trailing edge of the airfoil. Another view of

the blade indicating the attachment location is given in Figure 20, p. 41.

Figures 8 through 12 show the remainder of the components in various

stages of assembly. The completely assembled system is shown in Figure

11 and the flow control board in Figure 12. A 30 kw/10,000 cps motor-

generator power supply was used.

Two once-through, vertical flow chambers (OTVC) were used for the

preliminary experiments to determine the effects on deposition of high

velocity gases. A schematic drawing representative of both chambers is

shown in Figure 14. The difference between them was the chamber diameter

as noted in the figure. It was anticipated that mechanical and fluid dy-

namics problems would be identified in this relatively simple facility,

and that these could be solved or avoided in the centrifugal flow cham-

ber. No attempts were made to optimize coating parameters. Standard

graphite bend bars 2.5 mm x 5 mm x 7.6 mm (0.10 in x 0.20 in x 3 in) were

used, mounted with their long axes vertical as shown in the schematic

(Figure 14). A substrate rotation table was available as part of this

chamber, but its use did not seem to affect, either favorably or adversely,

the coatings obtained. The gases used were identical to those to be used

in the centrifugal flow chamber runs.

The same flow control panel (Figure 12) was used for both the OTVC

and the centrifugal chamber experiments. Rotameters** were calibrated for

---

*RBSN vanes were kindly supplied by Messrs. D. Richerson and K. Styhr
of Garrett AiResearch Corp.

**Lab Crest, subsidiary of Fisher and Porter, Scientific Glass Co.,
Commerce, CA 90022.

23

Chromel/Alumel
(Type K) Thermocouple

(copper tubing)

$SiCl_4 + N_2$

$NH_3 + H_2 + N_2$

(copper tubing)

Chamber Pressure,
To Manometer

A: 2" DIA or
0.875" DIA

To Pumping System

Pt/Pt-13Rh (Type R)
Thermocouple
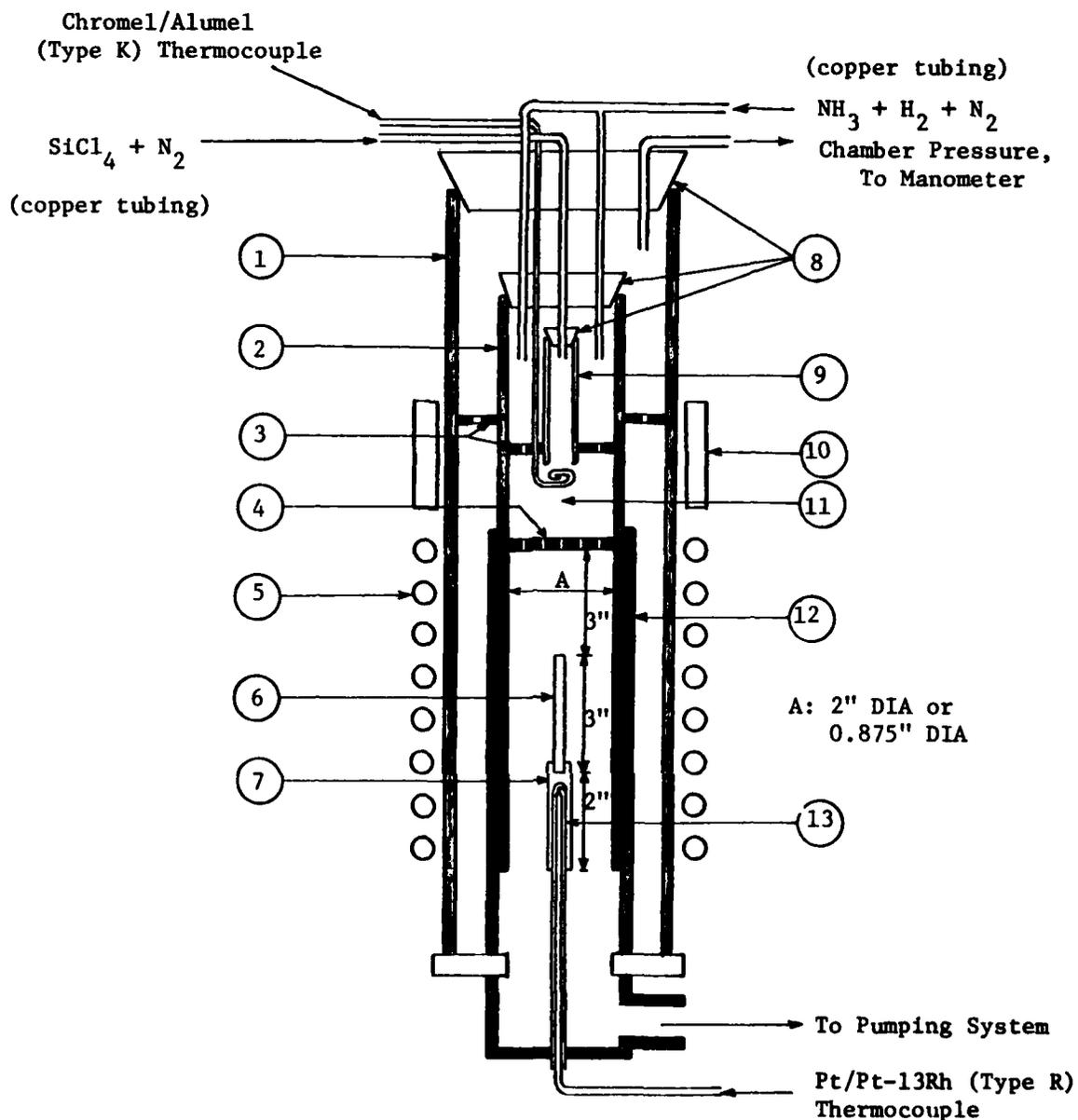
1. Quartz Chamber
2. Quartz Injector
3. Spacers, HLM Graphite
4. Diffuser Disc, HLM Graphite
5. Induction Coil (14 turns x 10" long)
6. HLM Graphite Substrate Bar (0.1" x 0.2" x 3" long)

7. HLM Graphite Substrate Holder
8. Rubber Corks
9. Quartz Tube
10. Clamshell Heater
11. Mixing Chamber
12. HLM Graphite Furnace
13. Al_2O_3 Thermocouple Sheath

FIGURE 14: SCHEMATIC SHOWING DESIGN OF ONCE-THROUGH VERTICAL
REACTORS (TWO DIFFERENT FURNACE DIAMETERS)

24

metering the various gases by passing known flows of each gas through them over the flow range of interest and plotting calibration curves. Multiple lines were used for the large quantities of nitrogen required. A Hastings electronic flow meter was built into the system for verifying the rotameters when desired without removal from the panel. Chromel-alumel thermocouples were used to check gas preheat temperatures, and Pt-Pt-Rh thermocouples were used to control substrate temperatures in both OTVC and centrifugal chambers. In the OTVC, the substrate thermo-couple was located in the base of the sample holder as shown in Figure 14, whereas in the centrifugal chamber it was placed along the center-line of the chamber within the tube through which the $H_2/H_2/NH_2$ mixture flowed onto the splash plate (Figure 2). They were installed to be approximately at the midpoint of the vanes or other substrates being coated.

Materials of construction for the centrifugal chamber were a cause for some concern initially due to the large volume of hot gases to be used. Stainless steel was used for the exhaust plenum, and type 304 stainless steel was used for the exhaust heat exchanger. Readily avail-able graphite and aluminum silicate felts were used for thermal insulation.

2. CONDITIONS

The flow parameters used initially were based on the experience gained in previous development work which extended over approximately a year prior to the start of the present effort. The increased velocity experiments in the OTVC were begun using the range of conditions which had yielded the best deposited Si_3N_4. See Table 1 (p. 26).

TABLE 1

Deposition Parameters At Start Of OTVC Experiments (2.22 cm D.)

Furnace Temperature:	$1400°$ to $1500°C$
Chamber Pressure:	30 to 50 Torr
$SiCl_4$ Flow:	50 to 100 cm^3/min
NH_3 Flow:	300 to 400 cm^3/min
Nitrogen Flow:	3000 to 25,000 cm^3/min
Hydrogen Flow:	4000 to 10,000 cm^3/min
Total Gas Flow:	7000 cm^3/min to 31,000 cm^3/min

TABLE 2

Deposition Parameters In Larger OTVC (5.1 cm D.)

$SiCl_4$ and NH_3 Flows:	1000 and 4000 cm^3/min, respectively
Total Nitrogen and Argon Flow:	25,000 cm^3/min
Hydrogen Flow:	800 cm^3/min
Total Flow:	26,300 cm^3/min
Chamber Pressure:	70 Torr
Gas Temperature:	Approximately $1000°C$
Active Gas Partial Pressure:	1.33 Torr

26

The flows from Table 1 through a 2.22 cm (7/8 in) diameter furnace resulted in gas velocities of approximately 84,000 cm/min to 373,000 cm/min at the substrate after correction for the effect of reduced pressure and increased temperature. These velocities in turn correspond to Reynolds numbers, N_{Re}, of approximately 175 to 700 respectively.

The conditions in the scaled-up OTVC, 5.1 cm (2 in) diameter are given in Table 2 (p. 27). The substrates deposited in this chamber were 0.63 mm x 25.4 mm x 102 mm (0.25 in x 1.00 in x 4 in) rectangular bars. The conditions stated correspond to a gas velocity of approximately 65,800 cm/min at the substrate position.

Reynolds number calculations predicted that with the limitations of the gas handling equipment available at the beginning of the program, velocities could be reached in the OTVC corresponding to Reynolds numbers of the order of 600 to 800. This constitutes an increase of approximately a factor of ten over Reynolds numbers for "normal" CVD of 10 to 100. Such an increase was anticipated to be important in reducing boundary layer effects on the deposited material.

It should be pointed out that the calculation of N_{Re} depends strongly on the values chosen for density, ρ, viscosity, μ or kinematic viscosity, ν. All of these properties depend more or less strongly on temperature and pressure. Pressure is determined fairly well by manometers which determine the pressure drop between the inlet side of the system and the exhaust side. Accurate temperature measurement is another matter. Referring to figure 14, it can be seen that the gas stream thermocouple is located at the point of mixing of the two reactant gases, however, it is reasonable to expect that the actual temperature (thus density, viscosity, and Reynolds number) will continue to change as it approaches the substrate which is typically 500 degrees higher. In the OTVC this may not be a significant source of error, but in the centrifugal flow chamber where the

residence time of a given volume of gas should be longer, this error should be more significant.

Conditions were produced in the centrifugal flow chamber analogous to those described above by maintaining approximately the same active gas partial pressure. This was accomplished by summing the $SiCl_4$ and NH_3 flows, dividing by the total flow, and multiplying by the chamber pressure. It was obvious throughout this program that similar deposits (hardness, surface morphology, microstructure, etc.) of Si_3N_4 were obtained by maintaining an active gas partial pressure between 1 and 2 Torr and increasing or decreasing the total gas flows to achieve arbitrary velocities and Reynolds number conditions. A wide range of $SiCl_4$:NH_3 ratios was acceptable within the 1-2 Torr limitation on active gas partial pressure. It was assumed that the thermo dynamic and fluid dynamic conditions optimized in the once through chambers would translate to the centrifugal flow chamber. The conditions selected for the centrifugal flow chamber are given in Table 3 (p. 29). Assuming that the effective diameter of the chamber is defined by the cross sectional area of an annulus through which the high velocity gases pass while circling the chamber, an effective diameter of 8.0 cm (5.1 cm x 10.2 cm) is determined and the Reynolds number describing conditions within the centrifugal chamber is calculated to be approximately 400. This calculation assumes only nitrogen gas and neglects the effects of the entrance ports on the velocity of incoming gases. Refer to the appendix for a calculation which includes this effect as well as a more complete treatment of gas mixture viscosities. The more precise calculation gives N_{Re} between 1854 ($1000^o C$) and 2482 ($1400^o C$).

3. RESULTS

Results of experiments in the OTVC and the centrifugal chamber will be presented separately.

28

TABLE 3

Deposition Parameters For Centrifugal Flow Chamber (CFC)

NH3 and $SiCl_4$ Flows:	700 and 400 cm^3/min, respectively
Total Nitrogen Flow:	25,000 cm^3/min
Hydrogen Flow:	20,600 cm^3/min
Argon Flow To Carry The $SiCl_4$:	650 cm^3/min
Total Gas Flow:	47,350 cm^3/min
Active Gas Partial Pressure:	Approximately 2.0 Torr
Chamber Pressure:	85 Torr
Gas Temperature:	1000^oC

3.1 ONCE THROUGH VERTICAL CHAMBERS (OTVC)

Approximately 80 deposition experiments were carried out in the
OTVC. The emphasis was on determining the parameters which would result
in an acceptable material for deposition in the centrifugal flow chamber.
This program was not directed toward material optimization. Of the experi-
ments carried out in OTVC, approximately 75 were in the small (2.22 cm)
diameter furnace using 2.5 mm x 5.0 mm x 76 mm (0.1 in x 0.2 in x 3 in)
HLM* graphite bend bar substrates. The other five experiments were in the
larger (5.1 cm) diameter furnace using 6.0 mm x 25.4 mm x 10.2 mm (0.25 in
x 1.0 in x 4 in) HLM graphite bar substrates.

The first twenty experiments in the small (2.2 cm) chamber were
conducted to determine the deposition parameters which would give an ac-
ceptable Si_3N_4 deposit so that later experiments could investigate the
effects of gas velocity. The criteria for an acceptable deposit were a
Vickers hardness (500 gm load) of 2500-3000 Kg/mm^2 and a reasonably fine
grained structure having an average grain size of 50μ or smaller. These
criteria were quickly met, and elevated velocity experiments were begun.

It was determined in the first few high velocity experiments that it
was necessary to preheat reactant gases adequately to prevent formation
of lower temperature intermediates. Failure to do this resulted in non-
cohesive, weak deposits. These experiments also showed that as volume
rates of flow increased, large amounts of heat must be removed to prevent
damage to plastic components in the exhaust lines downstream from the
chamber. Accordingly, a water cooled heat exchanger was built and added
to the exhaust line. This modification permitted gas velocities to be
increased to the values given above [pages 26 (Tables 1 and 2) and 27].

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*Great Lakes Carbon Corp., New York, New York

The most encouraging result of the OTVC experiments was the observation that the uniformity of thickness of deposit along the length of the substrate was greatly improved as gas velocity increased by a factor of 10. Low velocity gases usually resulted in wedge shaped deposits, thicker at the top of the substrate where the boundary layer presumably was not as thick or well formed as it was farther down the substrate.

Deposition rates decreased about 50% in the high velocity experiments, for instance, rates of 0.13 mm to 0.26 mm (0.005 in to 0.010 in) per hour at higher (10x) velocities. Interestingly, the improvement in thickness uniformity was observed after a factor of 10 increase in velocity (N_{Re} ~ 600 in the small chamber) which is well below that necessary for turbulent flow.

The uniformity of the deposition was maintained in experiments conducted in the larger (5.1 cm) chamber using the 10.2 cm graphite substrate. Typically, the 0.1 mm (0.004 in) thick deposit varied less than 0.025 mm (0.001 in) from one end to the other end of the 7.6 cm (3 in) long bend bar. The same thickness variation was observed for the 10.2 cm (4 in) long substrate. These results correspond to a thickness variation of less than 25% of the maximum thickness compared to thickness variations of 50 to 75% in low velocity deposition.

Results of the characterization of deposits formed in the OTVC experiments are as follows. The surface morphology was generally blocky, pyramidal, and crystalline, having an average size of approximately 50μ. Most of the deposits possessed a broken, columnar habit and were translucent to transparent; no attempts were made to optimize the latter property.

Three as-fabricated RBSN bars* having approximate dimensions of 0.25 mm x 0.5 mm x 5.1 mm (0.1 in x 0.2 in x 2 in) were coated in the high velocity OTVC experiments with encouraging results in that adhesion of the coating was very good as observed on a fracture surface by scanning electron microscopy (SEM). X-ray diffraction revealed standard, single phase α - Si_3N_4 structures. No extraneous crystal structures were observed. Breaking strengths were not computed for these bars because the RBSN bars had previously been rejected for internal defects. Evaluation of adhesion was the principal object of these experiments.

Hardnesses of the coated RBSN bars were observed to vary somewhat from 2500 to 3000 Kg/mm^2, HV$_{500}$, and fracture toughnesses were generally between 4.0 and 6.0 MPa$\sqrt{m}$. Some effort was made early in the program to improve flexure strength from values of 103 to 138 MPa$\sqrt{m}$ (15,000 to 20,000 psi) in four point bending. These efforts were somewhat successful in that strengths of 172 to 207 MPa (25,000 to 30,000 psi) in four point bending were achieved by the time experiments in the centrifugal chamber were to begin.

3.2 CENTRIFUGAL FLOW CHAMBER

Prior to coating substrates in the centrifugal flow chamber (CFC), preliminary experiments were conducted to insure that the gas supply system, the plumbing and the other supporting equipment were operating correctly. Both cold and elevated temperature runs were made with nitrogen only. No problems were encountered until attempts were made to heat the deposition chamber to 1300 to 1400°C, the desired deposition temperature. It was found that the rotating table transmitted excessive heat

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*Supplied by Garrett AiResearch Corp.

downward to the gearing and drive mechanisms. Additional thermal insulation solved the problem at least so that a two hour run could be made with gas flows between 45,000 and 50,000 cm^3/min STP and a specimen/deposition chamber temperature of 1400°C.

The first two experiments in the CFC were conducted using a graphite blade prototype substrate as detailed in Figure 15. Two hour experiments were made at a chamber temperature of 1410 to 1415°C and a total pressure of 85 Torr. The graphite "blades" were partially covered with crystalline Si_3N_4 and some loose, incoherent, possibly amorphous material. Adjustments were made prior to the third CFC experiment in the thermal insulation of the deposition chamber and in the sample positioning within the chamber with respect to the inlet ports. Additionally, the method of injection of the reactant gases was reversed. Previously, $SiCl_4$ carried by argon had been injected down the centerline of the deposition chamber with $NH_3/H_2/N_2$ injected through the wall of the chamber. This order was reversed with NH_3/H_2 injected down the centerline and $SiCl_4$/argon/N_2 through the wall. These changes resulted in a totally crystalline deposit in the third run. The deposit was nonuniform in the sense that the vertical "blade" of the prototype was well coated, but very little material had been deposited on the "blade" platform.

The fourth run was made after the "blade" substrates were raised 2.54 cm (1 in) with respect to the gas inlet holes. The temperature, pressure, gas flows and time (two hours) remained the same. NH_3 was injected down the centerline and $SiCl_4$ through the chamber wall. This adjustment resulted in a Si_3N_4 coating over both horizontal and vertical surfaces, indicating that positioning problems were relieved sufficiently

33

1.5 in.

1.5 in.

0.25 in.

0.25 in.

2.0 in.
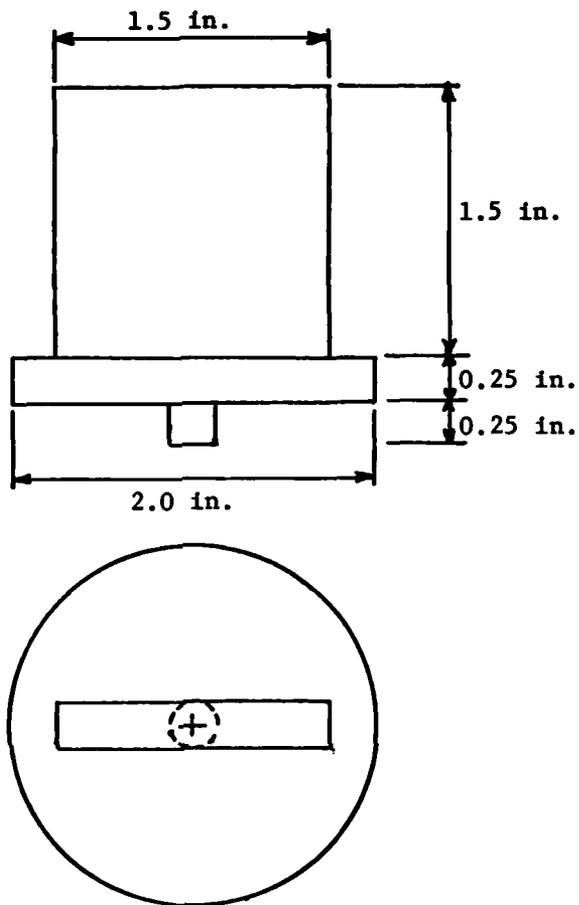
Material: HLM Graphite

FIGURE 15:   GRAPHITE PROTOTYPE TURBINE BLADE SUBSTRATE.
THIS SUBSTRATE WAS USED DURING EARLY RUNS
(#1, 2, 3, 4, 5) IN THE CENTRIFUGAL FLOW REACTOR.

34

that RBSN vane coating experiments could begin.

Rejected RBSN turbine vanes produced on a Garrett funded program had been received from Garrett AiResearch Corp., Pheonix, Arizona and Torrance, California*. One such vane was included in the fifth run. Unfortunately, a malfunction in the exhaust system (not related to the centrifugal flow chamber or its components) caused flow fluctuations and increased the total pressure resulting in a very nonuniform whisker growth on the substrates. Variations in surface morphology and color of the deposits was observed. The latter are indications of nonhomogeneity in the gas stream. However, coverage of the RBSN vane was complete. No other characterization was done on these parts due to the questionable pressure conditions existing during the run.

Four RBSN vanes were coated in the sixth run. In addition to the four vanes, two RBSN bend bars which were furnished with the vanes (and fabricated concurrently with them) were coated in this run. The temperature in the chamber was 1405 to 1415°C, and the gas inlet temperature (prior to entering the chamber) was 850 to 900°C during the two hour run. Chamber pressure was constant at 85 Torr, and gas flows and ratios were as described previously. Visual results were very encouraging in that all surfaces of the vanes and bars were coated with a layer of Si_3N_4 having a surface morphology of 25 to 50µm grain size. Some nonuniformity of grain size was noted on the airfoil and at re-entrant corners and angles where a generally finer structure (< 25µm) was seen. Mounting technique and orientation of these substrates may be seen in Figure 16 (shown prior to removing them from the sample mounts). One vane from this run was furnished to the AFML

*Supplied through the courtesy of Messrs. D. Richarson and K. Styhr.
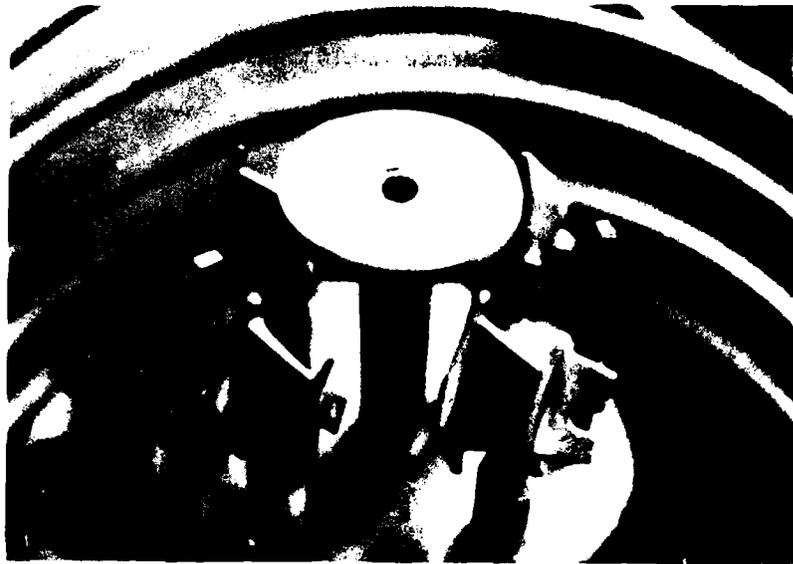
FIGURE 16:   RBSN VANES AND BEND BARS MOUNTED WITHIN CENTRI-
FUGAL FLOW REACTOR AFTER DEPOSITION RUN #6.

36

project monitor for evaluation by sectioning and microscopy--both visual

and SEM. Results of SEM investigations at AFML indicated generally ex-

cellent bonding to the RBSN substrate and verified that coverage was com-

plete, but also characterized some variation in coating thickness over

the surfaces. Generally, corners and re-entrant angles had the least

material, and edges received the thickest coating. Airfoil and shroud

surfaces received intermediate amounts.

These results were verified by in-house characterization of another

vane from the same deposition run. This vane, whose Garrett identifica-

tion number is 3102471-2 (serial number 562) is shown in various views in

Figure 17a, b, and c after slicing for ceramographic evaluation. The

reassembled vane is shown in a; a section through the airfoil parallel

to the shrouds is shown in b; and two pieces obtained by sectioning through

one of the original half sections perpendicular to a shroud are shown in

c. All slicing was done on a Buehler Isomet saw using a diamond blade.

The cross sections so obtained were then polished for thickness and hard-

ness measurements. Subsequent to thickness and hardness characterization,

pieces were broken from various locations in the sections for SEM investi-

gations of bond quality and fracture surface appearance.

Figures 18 and 19 show sketches of the two principle cross sections

which provided thickness and hardness uniformity data along with the

thickness and hardness data which were obtained at various locations. The

location from which a fracture specimen was taken is shown. Scanning

electron micrographs from those locations are shown in Figures 21 thru 28.

In addition to the vane sent to the project monitor from run number 6,

another coated vane was submitted to the project monitor from run number 7.
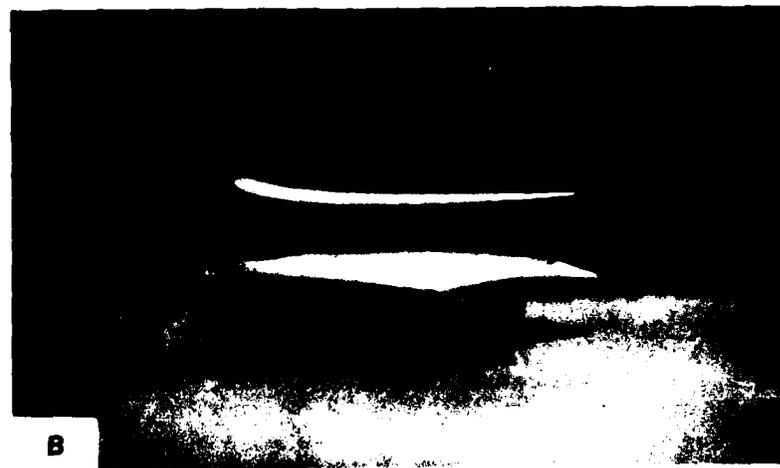
FIGURE 17: RBSN VANE (GARRETT #3202471-2, SERIAL #562) SECTIONED AFTER Si_3N_4 DEPOSITION IN RUN #6.

38
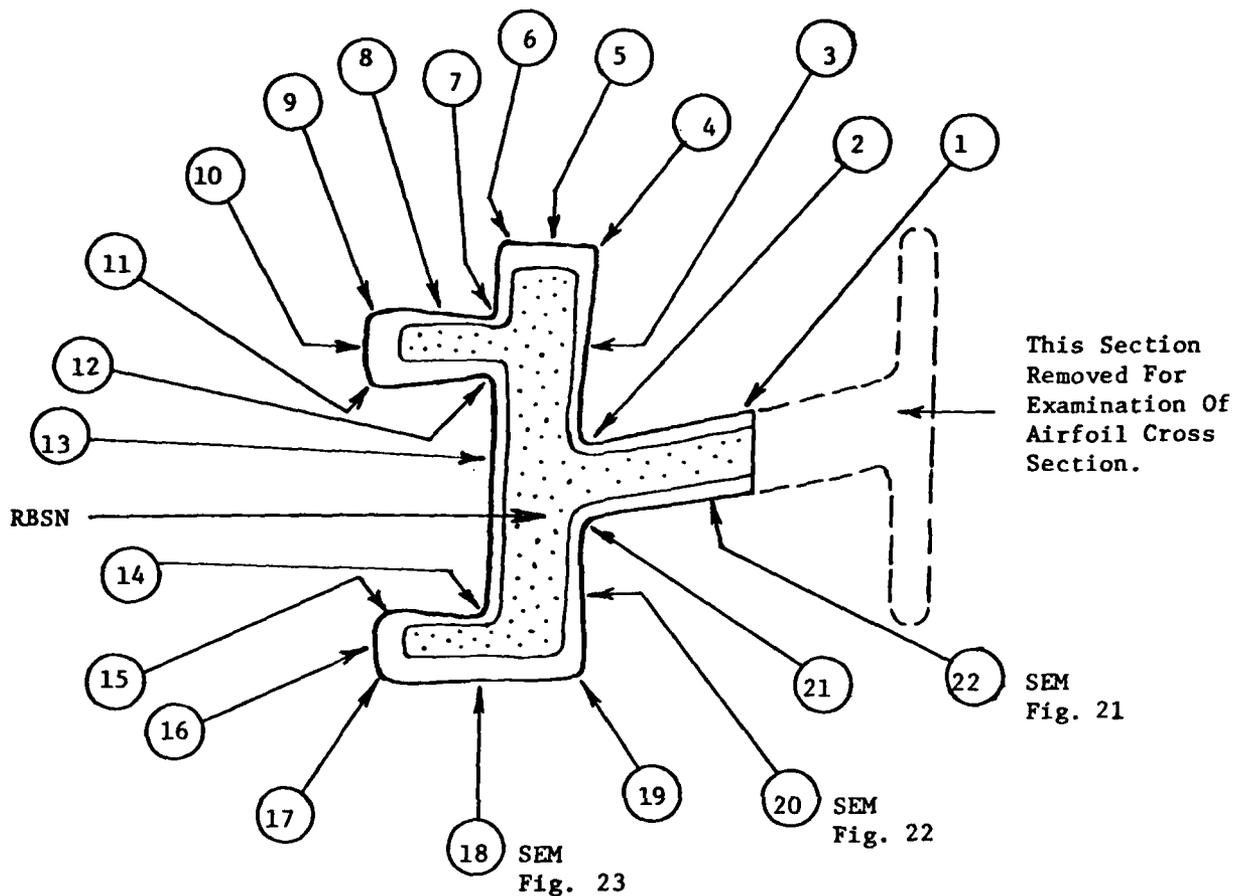
Location	Thickness (Microns)	Hardness/ Load	Location	Thickness (Microns)	Hardness/ Load
1	24.5	$3580/HV_{100}$	12	43.7	$3330/HV_{200}$
2	3.8	too thin	13	49.5	$3260/HV_{200}$
3	24.5	$2870/HV_{200}$	14	17.5	too thin
4	92.6	$3030/HV_{500}$	15	93.5	$2635/HV_{500}$
5	73.5	$2800/HV_{500} (K_c=5.0\ MPa\sqrt{m})$	16	87.2	$2830/HV_{500}$
6	111.6	$2525/HV_{500}$	17	228.0	$2785/HV_{500}$
7	57.2	$3660/HV_{200}$	18	128.8	$2635/HV_{500}$
8	91.2	$3060/HV_{200}$	19	218.0	$2610/HV_{500}$
9	180.0	$3000/HV_{200}$	20	47.5	$2890/HV_{500}$
10	161.7	$2090/HV_{500}$	21	18.9	$3480/HV_{100}$
11	245.2	$2930/HV_{500} (K_c=3.9\ MPa\sqrt{m})$	22	53.0	$2725/HV_{500}$

FIGURE 18: RBSN VANE ROOT SECTIONED FOR EVALUATION. HARDNESS VALUES AT VARIOUS LOCATIONS ARE SHOWN.
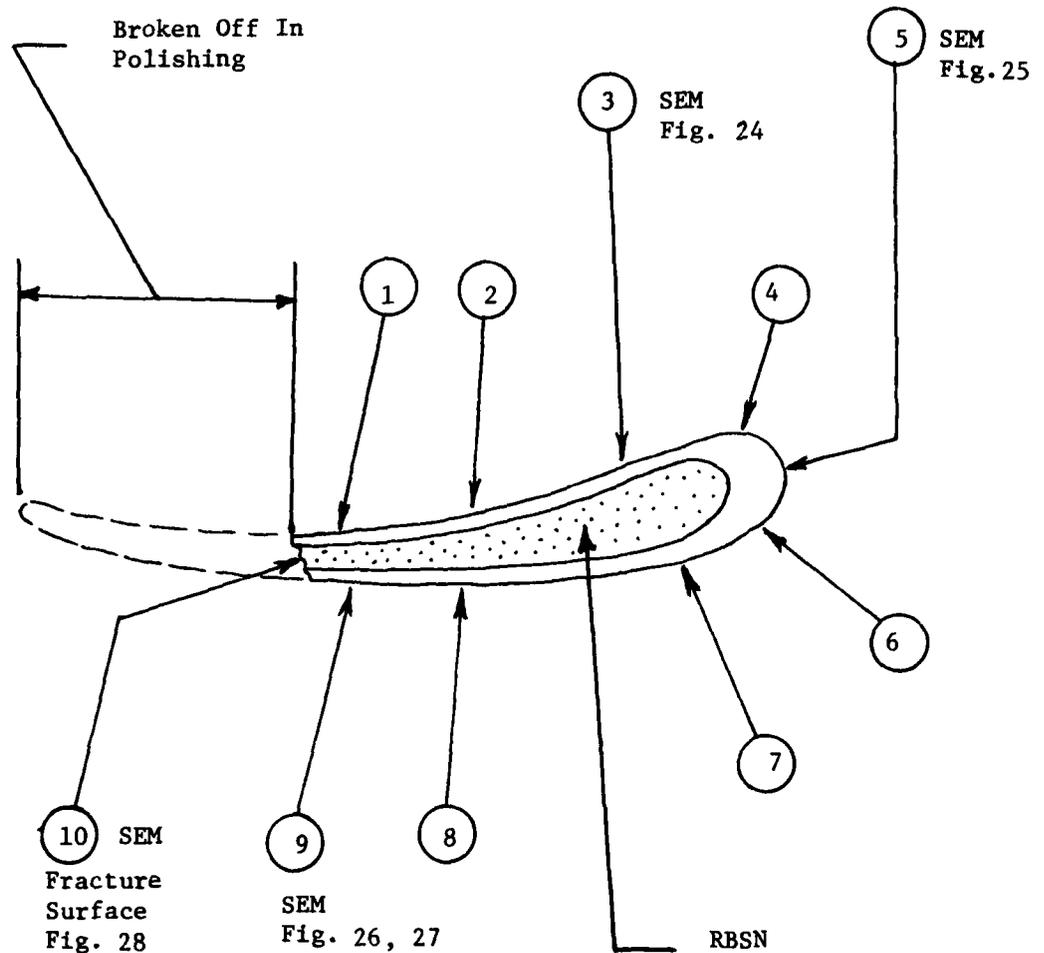
Location	Thickness (Microns)	Hardness/ Load	Location	Thickness (Microns)	Hardness/ Load
1	27.6	too thin	6	57.1	$2460/HV_{500}$
2	20.8	too thin	7	23.7	too thin
3	20.0	too thin	8	31.5	too thin
4	34.0	$3450/HV_{200}$	9	39.6	too thin
5	81.6	$2525/HV_{500}$			

FIGURE 19: RBSN VANE AIRFOIL SECTIONED FOR EVALUATION.
HARDNESS VALUES AT VARIOUS LOCATIONS ARE SHOWN.

FIGURE 20: SI_3N_4 COATED RBSN VANE. LOCATION OF THE AIRFOIL
WHERE VANE WAS HELD DURING COATING IS SHOWN BY
ARROW.

41
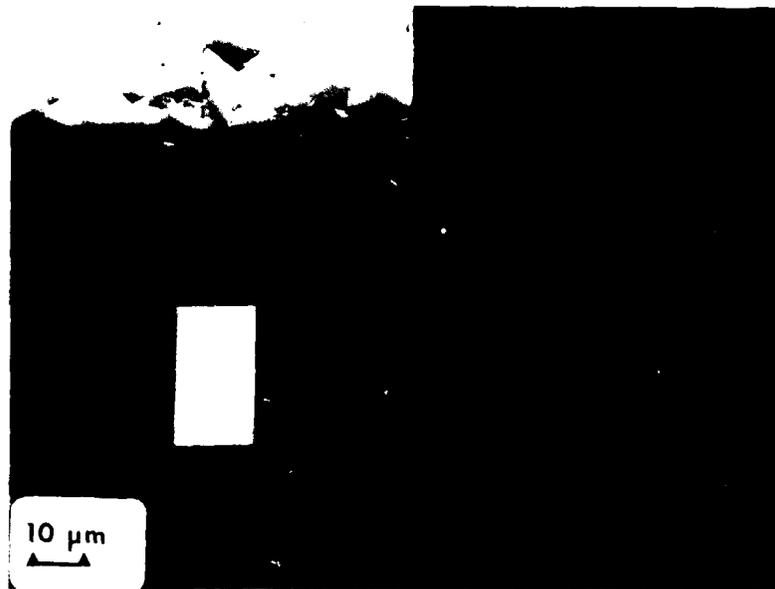
FIGURE 21:   VERTICAL SECTION THROUGH THE AIRFOIL SHOWING
               ETCHED MICROSTRUCTURE AT POINT 22 OF FIGURE 18.
               THE HIGHLIGHTED RECTANGULAR AREA ON THE LEFT IS
               MAGNIFIED 5 TIMES ON THE RIGHT (ETCHANT: 50% HF).

42

FIGURE 22: VERTICAL SECTION THROUGH THE BOTTOM SHROUD
SHOWING ETCHED MICROSTRUCTURE AT POINT 20 OF
FIGURE 18. THE HIGHLIGHTED RECTANGULAR AREA ON
THE LEFT IS MAGNIFIED 5 TIMES ON THE RIGHT
(ETCHANT: 50% HF).

43

FIGURE 23: VERTICAL SECTION THROUGH THE BOTTOM SHROUD AT THE POINT 18 OF FIG. 18, WHERE TWO SEGMENTS OF THE MOLD FOR THE RBSN WERE JOINED. THE HIGHLIGHTED REC-TANGULAR AREA ON THE LEFT IS MAGNIFIED 5 TIMES ON THE RIGHT (ETCHANT: 50% HF).
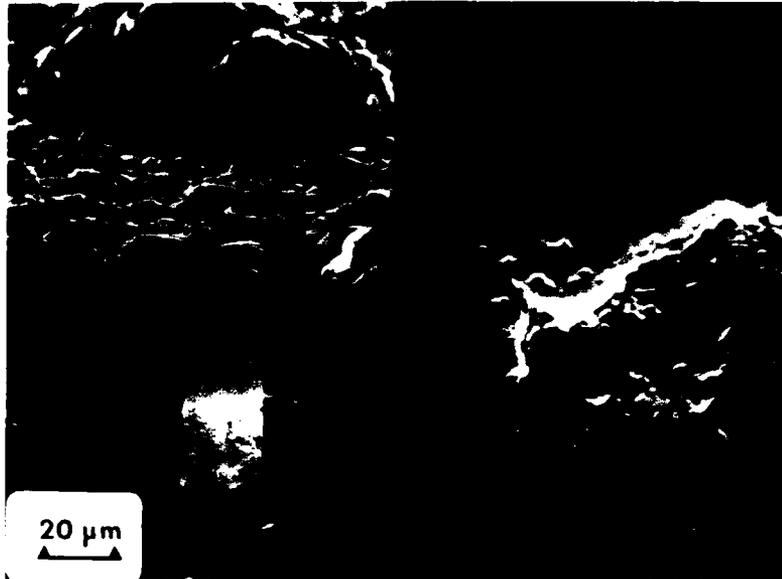
FIGURE 24:   HORIZONTAL SECTION THROUGH THE AIRFOIL SHOWING
              ETCHED MICROSTRUCTURE AT POINT 3 OF FIG.19.   THE
              HIGHLIGHTED RECTANGULAR AREA ON THE LEFT IS
              MAGNIFIED 5 TIMES ON THE RIGHT (ETCHANT: 50% HF).

45
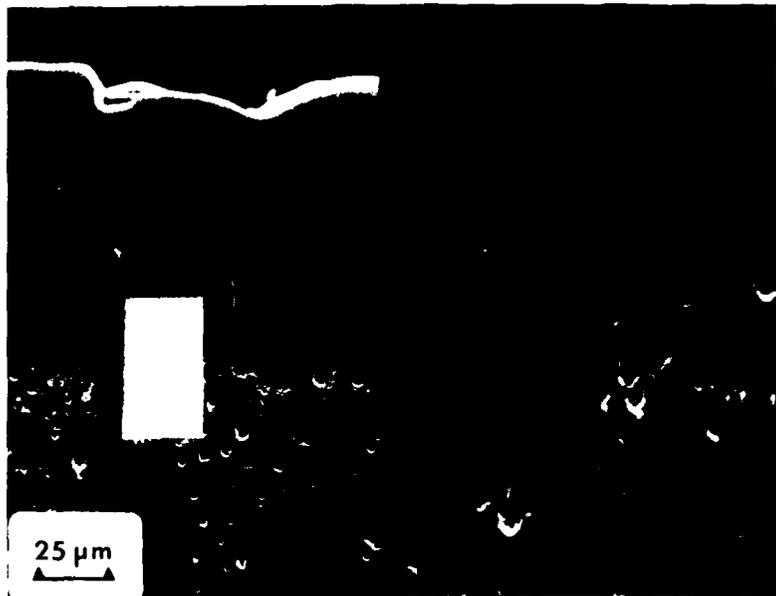
FIGURE 25:   HORIZONTAL SECTION THROUGH THE AIRFOIL SHOWING
ETCHED MICROSTRUCTURE AT POINT 5 OF FIG. 19.   THE
HIGHLIGHTED RECTANGULAR AREA ON THE LEFT IS MAGNI-
FIED 5 TIMES ON THE RIGHT (ETCHANT: 50% HF).

FIGURE 26: HORIZONTAL SECTION THROUGH THE AIRFOIL SHOWING
ETCHED MICROSTRUCTURE AT POINT 9 OF FIG.19.
(ETCHANT: 50% HF).

25 µm
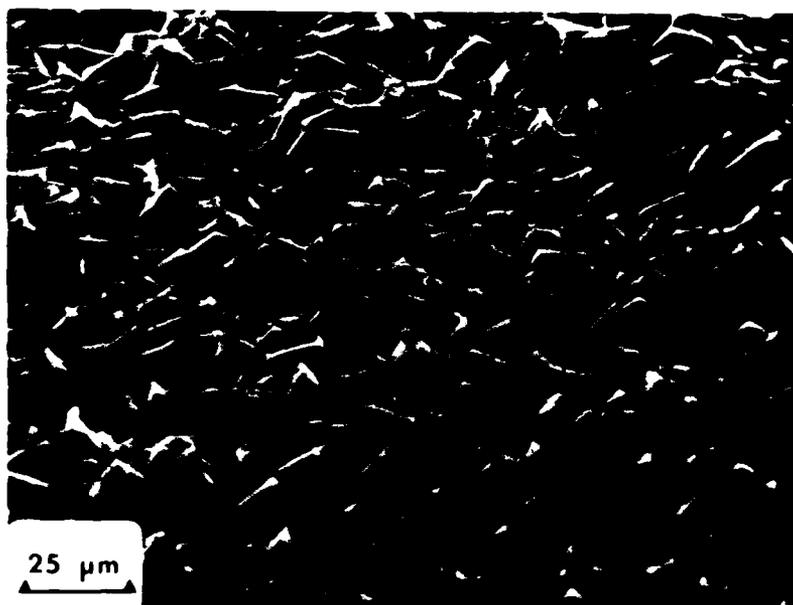
FIGURE 27: CRYSTAL MORPHOLOGY OF THE CVD Si_3N_4 DEPOSIT ON THE RBSN VANE AT POINT 9 OF FIG. 19.

5 μm
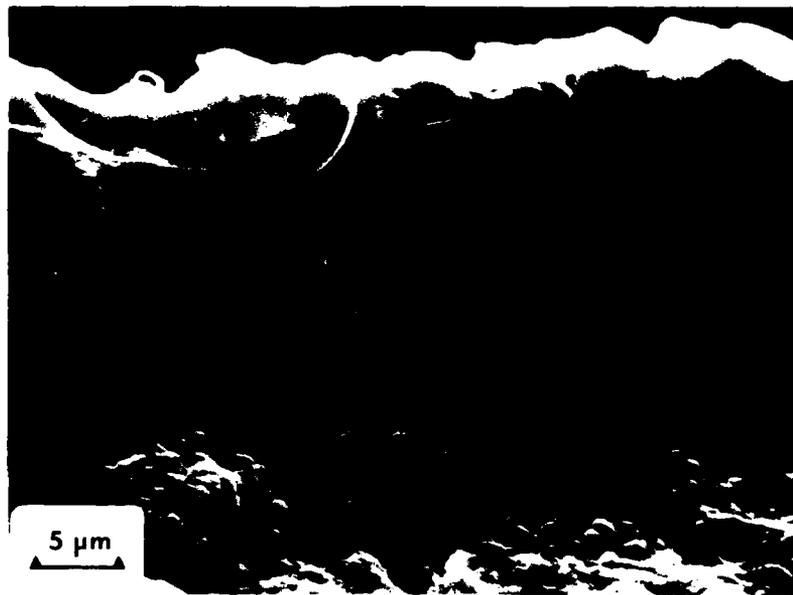
FIGURE 28:   FRACTOGRAPH OF THE EXIT EDGE OF THE AIRFOIL
SHOWING THE NATURE OF THE CVD Si_3N_4 DEPOSIT
AT POINT 10 OF FIG. 19.

A second coated vane from run number 7 was sent to Garrett AiResearch Corp., Pheonix (Mr. D. Richarson), for evaluation.

Two RBSN bars which were included in run number 6 were coated uniformly with a crystalline Si_3N_4 deposit having a surface morphology of angular crystal facets corresponding to a crystallite size of 25 to 50µ. Adherence was again very good by microscopic inspection of a fractured cross section.

SECTION IV

DISCUSSION OF RESULTS

The classical approach to CVD technology is characterized by attempts to "live with" the boundary layer phenomenon and the limitations it imposes on deposition rate, complexity of substrate shape, and number of substrates processed in one run. With very few exceptions (see, e.g. references 6, 7) reference to high laminar or turbulent conditions is notably absent from the CVD literature. Although there are no phenomenological expressions available for deposition rate having the Reynolds number as a parameter, it was clear that the desired general goal was attained. An extremely complex part was coated on all exposed surfaces with CVD Si_3N_4 although not uniformly in terms of thickness. The hardness data obtained on the coated vane (see Figures 18 and 19) cross sections was between 2500 and approximately 3000. Values higher than 3000 were obtained with loads less than 500 gm which were used on the thinner sections. This effect is common with hard materials and can be caused by underestimating the dimensions of small microhardness indents. An additional problem may contribute to higher hardness measurements, to wit, a contribution from elastic relaxation which may be negligible for a 500 gm indent might not be negligible for a 100 gm indent. The observed hardness values are typical of those reported in the literature, as well as those observed in previous efforts at Chemetal. In evaluating whether the Si_3N_4 deposited on the RBSN vanes is "normal" material, it is interesting to note the following. A previously deposited (by Chemetal) sample of Si_3N_4 having a hardness of 2850 (HV_{500}) exhibited resistance to sand blast type erosion that was 2 to 3 times better than RBSN (Norton NC 350) against 50μ Al_2O_3 grit and 5 to 6

51

times better than RBSN against 50μ SiO_2 sand grit. These results were obtained in a Chemetal sponsored testing program and were reported in detail elsewhere [8].

An observation of deposition on a complex surface has thus been made and is taken as circumstantial evidence that the boundary layer which forms during most CVD operations (characterized by a Reynolds number, $N_{Re} \simeq 10$ to 100) has been reduced by raising the velocity by a factor of $\simeq 100$. The Reynolds number for the conditions evolved in the present study has also been raised, probably to a value between 300 and 500. Problems were encountered in defining the conditions which exist within the deposition chamber and more importantly, at the substrate, e.g. the pressure, velocity, and temperature of the gas stream during and after injection. As a result, the Reynolds numbers calculated herein must be considered approximations, especially for the centrifugal chamber. Sources of error lie in neglecting the acceleration of the gases through the "nozzles" in the centrifugal chamber and their deceleration as they approach the substrate.

Thickness nonuniformity suggests that the boundary layer has not been eliminated. This is indicated by a Reynolds number $\simeq 400$ even though this is probably a lower bound on the value. The true Reynolds number probably lies between this value and the value calculated in the Appendix taking into account acceleration through the entrance ports.

The existence of the same type of boundary layer is suggested by the thickness nonuniformity as shown in Figures 18 and 19. The thickness build up on edges of sections is consistent with the existence of a boundary layer. The morphology of the deposit surface, however, is more uniform in appearance than would be the case if a well developed stable boundary layer

52

existed for the period of the two hour run. In the latter case, the morphology would be rough with large crystal facets protruding and possibly spiky, branched growth as well. In any event it is clear that conditions in the centrifugal flow chamber have drastically altered the boundary layer typically surrounding a substrate during CVD.

A major problem in depositing Si_3N_4 from the gas phase is that the silicon bearing gases which may be used can react at lower temperatures with NH_3 to form solid intermediates. Thus, it is necessary to keep the reactant gases separated until they both have reached the approximate substrate temperature. Prior experience has shown that a safe temperature at which to form Si_3N_4 using $SiCl_4$ and NH_3 is $1100^\circ C$ if reasonable reaction rates and crystalline material are desired (see below). The reaction under those conditions is:

$$3 \ SiCl_4 \ (g) + 4NH_3 \ (g) \xrightarrow{T>1100^\circ C} Si_3N_4 \ (s) + 12 \ HCl \ (g)$$

$$(2)$$
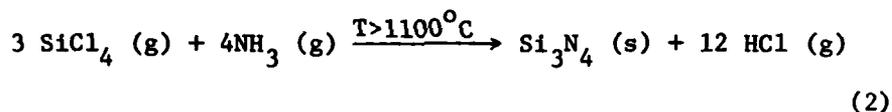
A concurrent program [3] was being carried out during the course of the present studies. Its goal was to explore the process parameters of reaction (2) and other Si_3N_4 forming reactions including alloying additions in a search for techniques which would effect grain refinement in a CVD type deposit. Drawing on the results of that work and prior experience on in-house programs, the reactant gas temperature was raised as close to $1100^\circ C$ as possible before combining them within the deposition chamber. The deposition chamber (and the substrates) were held at $1400^\circ C$.

Using these conditions, the formation of intermediate, low temperature compounds was prevented during the time the substrates were exposed to the reactant gases and Si_3N_4 deposited.

The resultant deposition rate, as obtained on RBSN vanes in runs 6 and 7, varied from approximately 0.013 mm (0.0005 in) per hour to 0.13 mm (0.005 in) per hour. This variation of thickness of deposit indicates that some masking of certain locations on the vane was occurring during deposition. The expected average deposition rate should have been in the range of 0.08 to 0.13 mm (0.003 to 0.005 in) per hour for "normal" velocities and gas flows under the given pressure and temperature conditions. The areas of least deposition (refer to Figures 18 and 19) are those at which shrouds join the airfoil or surfaces change direction, e.g. positions 2, 7, 12, 14, 21 in Figure 18. This situation might be corrected by considering more carefully the mounting of a given shape with respect to gas flow and the relationship between the rotational modes of the substrate and gas flow direction.

Experience gained during this project has highlighted certain shortcomings in the design of the CFC. The available evidence indicates that the present deposition chamber is too inefficient to produce turbulent flow throughout the chamber. These inefficiencies contribute directly to masking effects, as mentioned above, which would hopefully be negligible if true turbulence were achieved. Specific suggestions for improving the efficiency, and thereby the coating uniformity of the CFC are given in Section V below.

SECTION V

CONCLUSIONS AND RECOMMENDATIONS

The work described in this report definitely has shown that the
CVD process for depositing onto complex shapes can be significantly
improved by the use of a relatively high velocity gas flow. Deposition
experiments conducted in both the once-through and centrifugal flow
chambers have produced deposits on complex substrates with much more
uniform properties and thicknesses than have ever been possible with
conventional CVD processes.

The ease with which deposition conditions were translated from
experiments with the once-through chamber into appropriate conditions
for the centrifugal flow chamber demonstrates that the new turbulent
flow CVD process will probably present no unusual scale-up problems.
This conclusion is important since the basic design of the CFC has
several advantages over the once-through design in a large scale opera-
tion. Multiple pass rotation of the reactant gases is at the same time
an internal "recycling" and an effective technique for the promotion of
uniform reactive gas concentrations throughout the chamber.

Although the experiments which were performed in the CFC have demon-
strated that a relatively high flow rate will aid in the deposition of
uniform coatings, they have also demonstrated that the velocities so
far achieved have not been high enough. Coatings have been deposited
much more uniformly than could be expected from conventional CVD pro-
cesses yet still insufficiently uniform for most potential applications.
Since the velocity of pumping gases upon entering the CFC seems quite
sufficient to produce turbulent flow, the apparently insufficient velo-
city near the specimens indicates an inefficient chamber design causing

55

ineffective transfer of momentum from the pumping gases to the recircu-
lating gases.

Several design deficiencies are evident in the present CFC design.
These deficiencies should be eliminated and an improved CFC tested. Any
improved design should incorporate the following improvements over the
present CFC.

1.   Eliminate "short circuit" flow paths.

Recirculating gas flow was impeded by other than toroidal flow paths
present in the existing design. These should be eliminated by lowering
the roof of the chamber, raising the bottom of the chamber, and adding
a suitable center baffle. The chamber will thereby be changed into a
true annulus rather than a cylinder.

2.   Increase the through-put and exhaust volume flows.

The present design has not been able to provide a sufficient amount of
pumping power to maintain the necessary velocity of recirculating gases
within the chamber. To solve this problem, the external exhaust mani-
fold should be aerodynamically cleaned and enlarged, and a new high
volume vacuum pump will be installed.

3.   Improve momentum transfer from pumping gas.

Probably the most important proposed design change is the pumping gas
injector ports. The present design allows very little contact between
the recirculating gases and the input pumping gas, an ineffective trans-
fer of pumping momentum to the recirculating gases. These injection
ports should be redesigned to better approach the configuration of a
true jet pump and thereby increase pumping efficiency (see Figures 29
and 30).

56

Figure labels:

Exhaust Port

Reactive Gas Port

High Pressure N_2 Injection (With Or Without Reactive Gas)

Flow

Substrate Pedestal
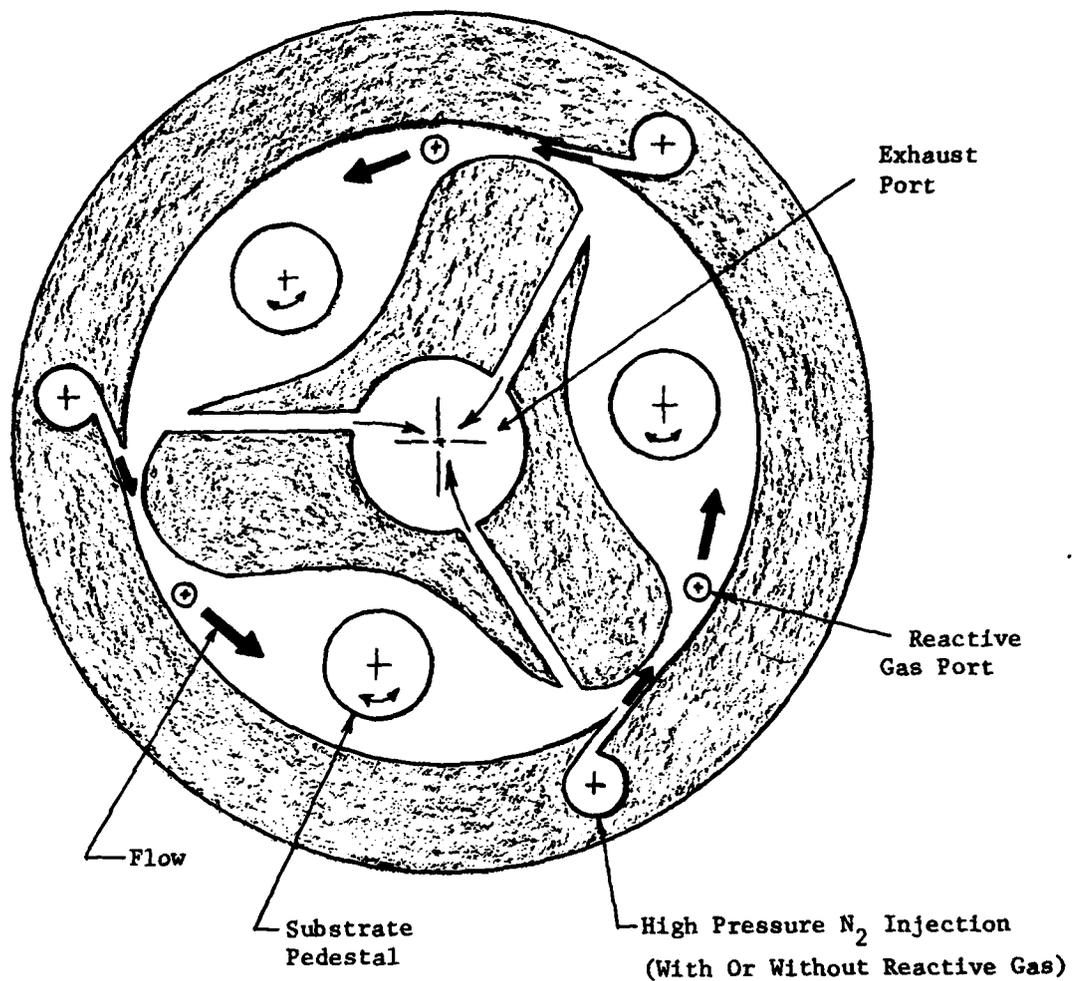
NOTE: ALL CHAMBER COMPONENTS (INCLUDING PEDESTALS) ARE GRAPHITE.

FIGURE 29: HORIZONTAL SECTION, POSSIBLE REDESIGN OF CENTRIFUGAL FLOW DEPOSITION CHAMBER.

FLOW

FLOW

Substrate
Pedestal

Substrate

Exhaust

Exhaust

High Pressure N_2 Injection
(With Or Without Reactive Gas)

Chamber
Center Line
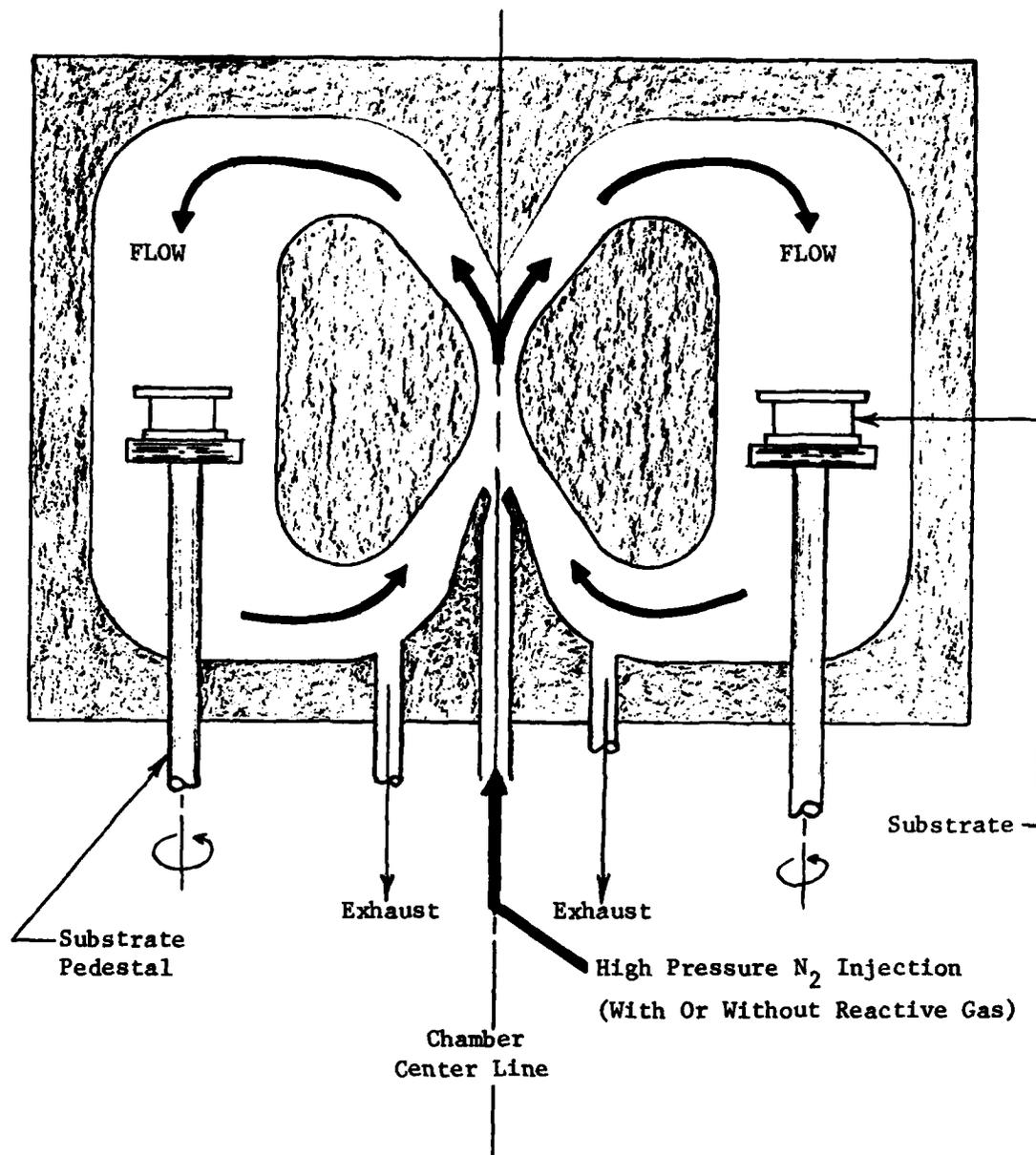
NOTE: ALL CHAMBER COMPONENTS (INCLUDING PEDESTALS)
ARE GRAPHITE.

FIGURE 30: VERTICAL SECTION, POSSIBLE REDESIGN OF CENTRIFUGAL
FLOW DEPOSITION CHAMBER.

4. Improve axial symmetry.

Again, in order to achieve more efficient transfer of momentum between injection gas and recirculating gas, and to achieve uniform conditions around the annulus, injection ports and exhaust ports should be arranged in an axially symmetric pattern. This change will allow the elimination of planetary rotation of turbine vanes around the annular chamber. Greater flexibility will thereby be possible in the placement of reactant feed ports which will in turn allow for better mixing of reactant gases.

5. Instrument the chamber for accurate gas velocity measurements (Pitot tube).

6. Because no optimization of thermodynamic deposition conditions was attempted, the following effects should be investigated in the redesign chamber.

    a. The influence of partial pressure of reactant species on yield per pass.

    b. The heat transfer and momentum relationships in tangential flow vectors.

    c. Total flow (reactant plus diluent) and its effect on recirculation and uniformity.

    d. The effect on preheat requirements of additional diluent gas flow.

    e. The effect of total pressure on recirculation.

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APPENDIX

Calculation of N_{Re} In Centrifugal Flow Chamber

The various approximations used in previous sections of this report served to indicate trends in N_{Re} due to gross changes in processing conditions. It is worthwhile, however, after having established the utility of the centrifugal flow chamber, to calculate N_{Re} for conditions existing within the chamber making as few approximations as possible. It will be seen below that the approximate calculations were conservative and that the actual N_{Re} present in the chamber is probably in the high laminar regime, i.e. $N_{Re} \geq 1000$. This result is consistent with the type of deposit obtained on the RBSN vanes. It was observed that thickness variations persisted, but the gross variations in surface morphology (including grain size) which are present when $N_{Re} < 100$ were not observed.

The following is a calculation of N_{Re} for the gas mixture <u>as it enters the centrifugal chamber</u> through the entrance ports, which are effectively nozzles. An expression for viscosity of gas mixtures is used which takes account of interactions among the various component gases. Finally, a set of values for N_{Re} is calculated assuming different temperatures in order to show the effect of uncertainty in temperature measurement. Reynolds number values near the substrates are expected to be lower because the gas stream decelerates on entering the chamber and the temperature increases. Both of these effects act to depress the Reynolds number. This depressant effect increases as the substrate position is farther away from the entrance ports. Chamber redesign is suggested which will permit measurement of velocities and pressures at sample locations and calculations of N_{Re} at these locations.

61

The deposition conditions in the centrifugal flow chamber were as follows (refer to Section III, Conditions, and Table 3).

Total Pressure:	85 Torr (0.11 atm)
Temperature	$1000^{\circ}C$, $1400^{\circ}C$
Total Gas Flow Rate:	47,350 cm^3/min
Gas Composition:	N_2 = 25,000 ml/min
	H_2 = 20,600 ml/min
	Ar = 700 ml/min
	NH_3 = 650 ml/min
	$SiCl_4$ = 400 ml/min

The gases, entering the annular graphite jacket through the vertical holes in the wall, exited through the 59 holes, the total area of cross section of which was 0.317 cm^2.

For the calculation of the kinematic viscosity of the gas mixture, the presence of the active gases ($SiCl_4$ and NH_3) was neglected. Values for $SiCl_4$ were not available. In addition, the fractions of these two gases are extremely small in the overall gas composition. Individual values of the absolute viscosities of N_2, H_2 and Ar were calculated using the equations given below[9].

$$N_2: \quad \mu = 175 \times 10^{-6} + (4.55 \times 10^{-7} \text{ poise/}^{\circ}C) \cdot \Delta T$$
$$+ 2.28 \times 10^{-7} \text{ poise/atm}) \cdot \Delta P, \text{ poise}$$

$$H_2: \quad \mu = 0.882 \times 10^{-6} + (2.0 \times 10^{-7} \text{ poise/}^{\circ}C) \cdot \Delta T$$
$$+ 0.14 \times 10^{-7} \text{ poise/atm}) \cdot \Delta P, \text{ poise}$$

$$Ar: \quad \mu = 222.5 \times 10^{-6} + (6.37 \times 10^{-7} \text{ poise/}^{\circ}C) \cdot \Delta T$$
$$+ (3.0 \times 10^{-7} \text{ poise/atm}) \cdot \Delta P, \text{ poise}$$

From the values of the absolute viscosity of these gases, the viscosity of the gas mixture was obtained by using Wilke's equation [10]:

$$\mu_m = \sum_{i=1}^{n} \frac{\mu_i}{1 + \frac{1}{x_i} \sum_{\substack{j=1 \\ j \neq i}}^{j=n} x_i \, \phi_{ij}}$$

where

$$\phi_{ij} = \frac{\left[1 + \left(\frac{\mu_i}{\mu_j}\right)^{\frac{1}{2}} \left(\frac{M_j}{M_i}\right)^{\frac{1}{4}} \right]^2}{\frac{4}{\sqrt{2}} \left[1 + \left(\frac{M_i}{M_j}\right) \right]^{\frac{1}{2}}}$$

where μ_i = absolute viscosity of the ith component

where x_i = mol fraction of the ith component

where M_i = molecular weight of the ith component

The density of the gas mixture was corrected for the chamber pressure and temperature and used with absolute viscosities calculated as above to obtain the kinematic viscosity of the gas mixture, given by $\nu = \mu/\rho$ stokes. The following table summarizes the results of these calculations.

Gas Composition	Temperature $^{\circ}$C	μ, x 10^{-6} poise	ρ, x 10^{-6} g/cm^3	ν stokes	v m/sec	N_{Re}
N$_2$	1000	630	30	21	16	2861
	1400	803	23	35	21	2256
H$_2$	1000	200	2.15	93	16	615
	1400	364	1.64	222	21	339

63

Calculations (continued)

Gas Composition	Temperature °C	μ, x 10^{-6} poise	ρ, x 10^{-6} g/cm^3	ν stokes	v m/sec	N_{Re}
Ar	1000	859	43	20	16	2860
	1400	1100	33	34	21	2245
N_2:H_2:Ar 53:42:5	1000	459	19.0	24.2	16	2482
	1400	616	14.46	42.6	21	1854

These calculations indicate that the gas mixture used in the centrifugal flow chamber achieved turbulence at the point of entry into the reaction chamber at 1000°C, and was close to turbulent flow at the higher temperature. The results also show that pure N_2 and Ar are nearly as effective individually as carrier gases from the fluid dynamic point of view. Finally, the importance of choosing or determining gas temperature pressure, and velocity is demonstrated.

Attempts to calculate the Reynolds number of the reactant gas stream at various points within the chamber are frustrated by the lack of velocity data and sufficiently precise temperature and pressure data.