Best Available Copy

FABRICATION OF BERYLLIUM OXIDE

RADOMES BY PYROLYTIC DEPOSITION

Final Engineering Report
Contract Now 64-0512-f

National Beryllia Corporation
Haskell, New Jersey

FABRICATION OF BERYLLIUM OXIDE
RADOMES BY PYROLYTIC DEPOSITION

Contract NOw 64-0512-f
Department of the Navy
Bureau of Naval Weapons
Washington 25, D. C.

Final Engineering Report
for the Period 28 May 1964 to 1 June 1965

Release to ASTIA without restriction. The Con-
tractor imposes no limitation or restriction upon
the distribution of this document by the Government
to both Government and non-Government recipients.

National Beryllia Corporation
Haskell, New Jersey

ABSTRACT

Beryllium oxide, because of such properties as low density, high melting point, and excellent thermal conductivity is highly regarded as a material for advanced radomes and electromagnetic windows. The program involved an investigation of three forms of beryllium oxide, monolithic beryllia ceramic, foam structures, and structures reinforced with beryllia fibers.

The pyrolytic method was investigated as a means of preparing dense beryllia and fibers of the oxide. Specifically, a chemical vapor deposition process involving a reaction between a halide of beryllium and water (hydro-pyrolytic reaction) and the pyrolysis of an organic adduct of beryllium were studied as means of preparing continuous deposits of beryllia. The vapor phase oxidation of beryllium metal was also investigated as a process for preparing beryllia fibers or whiskers.

The parameters of the dependent and independent variables such as substrate temperature, flow rate, vaporization temperatures, geometric factors, and source materials were studied for both the chemical vapor deposition and the vapor phase oxidation processes.

Deposits of limited thickness were prepared by the hydro-pyrolytic reactions involving oxygen donor systems such as either water or nitrogen dioxide. For either system, evidence points toward the fairly rapid attainment of equilibrium conditions

wherein the deposit of beryllia produced by the reactions is eroded by the volatile non-metallic oxides of the reactants or products of the reactions.

Preliminary results indicated that adherent, dense, and hard deposits of conceivably unlimited thickness could be prepared by the pyrolysis of a volatile organic adduct of beryllium.

Sporadic success was attained in growing beryllia fibers by the vapor phase oxidation of beryllium metal. It was found that the sensitivity of beryllium to free oxygen prevented the direct use of the element. Oxygen donors such as water were therefore also studied as source materials for the formation of beryllia fibers.

This contract is a continuation of the work performed under Contract NOw 63-0412c.

Prepared by: _____
Dr. W. A. Taebel

_____
G. Hoekstra

Approved by: _____
K. H. Styhr

FABRICATION OF BERYLLIUM OXIDE RADOMES
BY PYROLYTIC DEPOSITION

I. Introduction

1.1 Purpose of the Program

This program has been established to perform the following

tasks:

a) To design, construct, and modify when deemed necessary

experimental equipment for producing continuous deposits,

foam structures, and fibers or whiskers of beryllia.

b) To conduct research and development to permit deposition

of pyrolytic and filamentary forms of beryllia.

c) To prepare pyrolytic beryllia samples representative

of radome material.

d) To prepare composite structures consisting of fiber

reinforced foam over-laid with a coating of pyrolytic

beryllia.

1.2 Present Status

This report summarizes the work performed on the subject

Contract NOw 64-0512f during the period 28 May 1964 to 1 June

1965.

Task (a) given above has been essentially completed in

that equipment redesign and modification has been completed when-

ever experimental results dictated the necessity of change in

order to achieve the next higher plateau of success with respect

to continuous or fibrous deposits.

Extensive experiments have led to success on Task (b) in that laboratory techniques were established which permitted the preparation of reproducible coatings of pyrolytic berillia. However, additional experimentation is definitely required in order to finalize the engineering parameters involved in producing massive structures or coatings on extensive surfaces.

In general, vapor phase oxidation of beryllium metal was found to offer definite possibilities proveded adequate and precise control can be exercised for the oxidant.

In the relatively short period of study, only the principal parameters could be rather precisely defined and additional research is necessary to establish the relationships of those parameter to one another and to permit translation of laboratory findings into more advanced pilot equipment for monolithic deposits and large quantities of fibers.

Small samples consisting of sintered beryllia substrates coated with an adherent deposit of pyrolytic BeO measuring approximately .010 inches in thickness were prepared as part of Task (c). Work was initiated on preparing a second type of sample consisting of a foam substrate bearing a coating of pyrolytic beryllia. Samples of a third type which are similar to the second type except that a reinforced foam substrate is to be used, were not prepared because the supply of reinforcing beryllia fibers was inadequate. These samples should be forthcoming at a later date and thereby permit us to complete the assigned tasks.

II. Experimental

2.1 Materials

It has been the general practice of most investigators to use, as the source material, a halide of the metal whose oxide they are endeavoring to prepare by vapor phase reactions. This selection is prompted by the fact that many metal halides in the anhydrous condition exhibit appropriate vapor pressures at temperatures significantly below their dissociation or decomposition temperature. The chloride and bromide of beryllium are two such compounds.

The anhydrous chloride or bromide can be prepared conveniently by passing anhydrous hydrogen chloride or bromide respectively through a bed of beryllium metal chips maintained at a temperature of approximately 600°C. At this temperature the compounds vaporize and consequently fresh metal is constantly exposed to the action of the reactive gases. The anhydrous halides of beryllium are exceedingly hygroscopic and therefore must be handled in a moisture-free atmosphere. We circumvened this problem by preparing the respective halides in loco so that they could be conducted directly from the reaction vessel to the pyrolytic chamber.

Compounds other than the halides can be used to prepare pyrolytic oxides. In general such source compounds are organic adducts of the metal whose oxide is desired. Beryllium basic formate was chosen as a source material because it, like other formates, should decompose when heated to the proper temperature
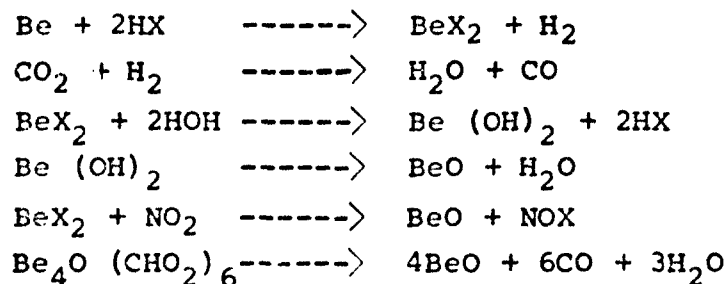
to yield pure beryllium oxide, thermally stable carbon monoxide, and water. The compound was prepared by dissolving the basic carbonate, which was obtained by treating a solution of beryllium nitrate with ammonium carbamate, in concentrated (88%) formic acid. A white granular product was prepared by pulverizing the cake obtained after evaporating the basic formate solution at approximately 110°C.

The water required to hydrolyze the beryllium halides in the hydro-pyrolytic reactions was prepared in loco by reducing carbon dioxide with hydrogen. Other sources of oxygen such as nitrogen dioxide were conveniently drawn from a cylinder of the gas.

Substrate material in general was sintered beryllia ceramics in the form of flat plates, crucibles, rods, cones, and tubes. Other substrate material consisted of alumina ceramics, graphite, and Vycor or Pyrex glass.

2.2 General Procedures

The apparatus used for producing continuous deposits of beryllium oxide was based on consideration of the following reactions where "X" is either the chloride or bromide ion:

$$Be + 2HX \longrightarrow BeX_2 + H_2$$
$$CO_2 + H_2 \longrightarrow H_2O + CO$$
$$BeX_2 + 2HOH \longrightarrow Be(OH)_2 + 2HX$$
$$Be(OH)_2 \longrightarrow BeO + H_2O$$
$$BeX_2 + NO_2 \longrightarrow BeO + NOX$$
$$Be_4O(CHO_2)_6 \longrightarrow 4BeO + 6CO + 3H_2O$$

The experimental system used for either the hydro- or the nitro- pyrolysis of the beryllium halides is shown schematically in Figure 1. High purity compressed gases were purchased from the Matheson Co. The cylinders of gases were connected to the pyrolysis or reaction chamber through a train consisting of a tower containing a drying agent such as Drierite, calibrated flow meters, needle valves, and a mixing chamber. Thus each gas could be monitored and regulated to yield any desired partial pressure in the reaction atmosphere. The oxidants were fed into the reaction chamber at either one of two entrances so that either con- or counter- current flow conditions could be achieved.

Molybdenum wire-wound electric heater, controlled by variable transformers and monitored by thermocouples and/or by optical pyrometers, were used to indirectly heat the beryllium converter or the substrate object to the specified temperatures. Thus, the heaters were not used as the actual walls of either item.

Substrate materials which were used consisted of beryllia or alumina in the form of cylinders, rods, discs, plates, and cones. The exit gases were conducted to a burn-off nozzle through a condenser partially filled with water and glass beads.

This system, then, permitted experiments to be performed under a variety of controlled conditions such as

1) either beryllium chloride or beryllium bromide at definite
   a) temperatures
   b) flow rates
   c) concentrations

2) oxidants in the form of water, carbon dioxide, or nitrogen dioxide at specified

    a) concentrations
    b) flow rates
    c) flow directions

3) substrates of alumina or beryllia to permit studies of the effect of

    a) temperature
    b) geometry
    c) material
    d) surface

The system used for the pyrolysis of the basic formate shown schematically in Figure 2. It will be noted that it considerably less complex than that used to study the beryllium lides. Since the compound can be volatilized and decomposed thermal means, there is no need for the auxiliary and reactive ses and their associated entrance and exit ports.

The reaction chamber was connected to a vacuum pump through tower packed with glass wool. In general the tests were de at a pressure of 2 to 10 mm of mercury. In a few of the sts an argon carrier gas was used at atmospheric pressure. me tests were also made with a small constant flow of air rough the system. In the latter two cases, the gases were nitored and controlled by flow gauges and needle valves. These ses were introduced into the system through an orifice in close oximity to the generator so that blending of the gases occurred ior to their reaching the substrate. The substrate and nerator were heated indirectly by means of molybdenum wire-und heaters which were controlled by variable transformers and nitored by an optical pyrometer or thermocouples.

The generator consisted of a three-piece 304 stainless steel assembly consisting of a threaded well with a mating joint for accommodating a hood which could be locked firmly to the well by means of a threaded ring nut. A series of hoods were used, each of which was pierced with a definite and different sized opening. The generator was of sufficient size to hold approximately two grams of the pulverized basic formate. The system therefore was operated on an intermittent basis.

This system permitted experiments to be performed with beryllium basic formate as the source material under controlled and varied conditions involving such factors as

1) substrate materials, geometry, and position
2) vaporization temperatures
3) degradation temperatures
4) atmosphere

The system used for the investigations of the vapor phase oxidation of beryllium as a method of preparing beryllia whiskers is shown schematically in Figure 3. In addition, a horizontal molybdenum wound tube furnace was used in some of the experiments. The unit shown in Figure 3 consists of a container which can be evacuated and sealed from the atmosphere. This container houses the reaction chamber proper which consists of a molybdenum wire-wound heater surrounding a tube, the lower half of which transmits heat to the crucible containing beryllium metal, and the upper portion of which acts as a condenser for fibrous growth. These components were made from beryllia ceramics in order to assure that any oxide fibers that were produced were not those of any other metal. Temperatures were controlled and

and monitored as mentioned above.

Various atmospheres consisting of argon, argon-air, argon-water vapor, and other combinations were introduced into the system through a preheater after passing through a water vapor generator and were essentially directed to flow through the reactor-condenser tube. The oxidants and diluents were controlled and monitored by means of flow gauges and needle valves. Provisions were made so that the non-aqueous gases could be introduced without or with the addition of water vapor; the latter condition was achieved either by passing the gases through the free space above the water or by bubbling them through the liquid.

This system together with the horizontal tube furnace permitted studies to be made relative to such parameters as:

1) reaction temperature
2) atmospheres - oxidants and carrier gases, flow rate, concentrations, pressures
3) source material - purity, physical form

III. RESULTS AND DISCUSSION

3.1 Hydro-Pyrolytic Process

The experiments performed on this task were designed to develop techniques and acquire fundamental data and information which would define the problems associated with the hydro-pyrolytic method so that the ultimate objective of preparing radomes could be realized.

The range of the experimental parameters investigated in this task is given in Table I and a condensed description of the runs

which were made is given in Summary Sheet No. 1A: Hydro-pyrolysis of Beryllium Chloride-Experimental Objectives, Condisions, and Observations.

TABLE I

Range of Process Variables for Hydro-Pyrolysis of Beryllium Chloride

Temperature - °C	1050-1550
Flow Rates liters/min.	
HCL	0.01 - 0.1
CO_2	0.08 - 1.5
H_2	0.3 - 3.0
$BeCl_2$: H_2O ratio	1:1.5 - 1:125
Time - Hours	0.5 - 3.0

The work performed on prior contracts had shown that the hydro-pyrolysis of beryllium chloride to yield beryllium oxide involves a series of reaction which are thermodynamically favorable in the range of 1000 to 1500°C. The primary object then of the work performed during the reporting period was to define the parameters involved so that process optimization could be achieved.

As a guide in selecting significant experiments, the model which we used encompassed the following concepts:

1) pyrolytic beryllia is derived from a highly reactive beryllium hydroxide;

2) Since beryllium hydroxide is non-volatile at the operating temperature, it must be formed at or in very close proximi to the heated substrate;

3) the temperature of the chlorinator should be at least 50°C above the sublimation temperature of beryllium chloride in order to maintain a reactive beryllium metal surface;

4) the available moisture content of the reactant should be in excess in order to prevent the formation of complex oxy-chlorides;

5) the most important parameters include substrate temperature, reactant flow rates and concentrations, substrate-reactant delivery system relationships, and time.

Beryllium chloride is exceedingly sensitive to water and can be easily hydrolyzed to the non-volatile hydroxide. Premature formation of the hydroxide would limit the quantity of this compound which reaches the substrate to that which is mechanically transported by an inert carrier gas. The efficiency of the process would therefore be very low. In addition, the orderly deposition of the oxide on the molecular scale which is characteristic of the true pyrolytic process would not take place due to agglomeration of the discrete particles during their travel through distances which are orders of magnitude longer than their mean free path. It was found therefore that the reactant delivery system should lead the reactants or direct them to the substrate and in order to prevent clogging of the delivery lines, the line used for the beryllium chloride together with any inert carrier gas should be separate from the delivery line used for the carbon-dioxide-hydrogen mixture. An arrangement consisting of parallel delivery lines with the nozzle of the beryllium chloride line terminating closer to the substrate than that of the carbon dioxide line proved more effective than systems involving simple introduction, and hence diffuse conditions, of the reactants through ports terminating at the reactor wall; counter-current flow conditions involving either upward or downward movement of the separate

reactants respectively; or a system of concentric lines whereby the reactants could be fed to the substrate separately through either an inner or an outer tube. The major problem experienced with the latter arrangement was that clogging of the beryllium chloride delivery tube occurred due to back diffusion of the water regardless of whether this line were the inner or the outer member of the concentric system.

The flow rates of the reactants were found to be important with respect to texture of the deposit and its deposition rate. At the one extreme of reactant movement equivalent to that present during diffusion, the deposit was hard and glass-like but of insignificant thickness; at the opposite extreme of flow velocities of the order of 3000 cm/min, the deposit was powdery and non-adherent although of considerable initial thickness. This would indicate that meaningful growth rates of deposits exhibiting satisfactory properties could be achieved at low rather than at high flow rates. This was verified by experimentation and it was found that flow velocities of the order of 100 - 300 cm/min. were satisfactory.

The relative concentrations of the reactants or their ratios are important factors of the hydro-pyrolytic process. High concurrent concentrations of the components, $BeCl_2$ and H_2O yield a light, fluffy non-adherent deposit. Stoichiometric quantities of the reactants are not acceptable with respect to deposition rates but the coating exhibits satisfactory properties. Other conditions being equal, it was found that water must be present in excess -

its deleterious effect is discussed below - and that a dynamic

mol ratio of 1 $BeCl_2$ to 3 - 6 H_2O fairly well defines the satis-

factory operating conditions.

In the interest of clarification, three factors will be

discussed collectively. In general, for a given set of conditions,

the amount of deposit as determined by its weight or thickness is

proportional to the duration of the run. This proportionality

exists over a certain temperature and moisture range. At tempera-

tures of the order of 900°C, the deposit is porous and non-ceramic

in texture. Consequently, it can be removed from the substrate

merely by washing. In the temperature range of approximately 1000

to 1200°C, an adherent, dense deposit is obtained in thicknesses

depending upon the duration of the run. Above this temperature, one

obtains a dense compact deposit but its thickness remains at a

level of approximately 0.010 inches. Under the conditions which

were explored this limited thickness of the deposit is attributed

to an equilibrium reaction involving simultaneous deposition and

water vapor transport of the beryllia. At elevated temperatures,

the reaction between beryllium oxide and water vapor may actually

occur more rapidly than the deposition rate resulting in an actual

loss of material. This can be illustrated by the equation

$BeO + H_2O \rightleftharpoons Be(OH)_2$ being driven to the right at elevated

temperatures and evidence of this etching action of water vapor at

approximately 1400°C is presented in the photomicrograph of Figure 4.

These observations led us to investigate compounds other

its deleterious effect is discussed below - and that a dynamic

mol ratio of 1 $BeCl_2$ to 3 - 6 H_2O fairly well defines the satis-

factory operating conditions.

In the interest of clarification, three factors will be

discussed collectively. In general, for a given set of conditions,

the amount of deposit as determined by its weight or thickness is

proportional to the duration of the run. This proportionality

exists over a certain temperature and moisture range. At tempera-

tures of the order of 900°C, the deposit is porous and non-ceramic

in texture. Consequently, it can be removed from the substrate

merely by washing. In the temperature range of approximately 1000

to 1200°C, an adherent, dense deposit is obtained in thicknesses

depending upon the duration of the run. Above this temperature, one

obtains a dense compact deposit but its thickness remains at a

level of approximately 0.010 inches. Under the conditions which

were explored this limited thickness of the deposit is attributed

to an equilibrium reaction involving simultaneous deposition and

water vapor transport of the beryllia. At elevated temperatures,

the reaction between beryllium oxide and water vapor may actually

occur more rapidly than the deposition rate resulting in an actual

loss of material. This can be illustrated by the equation

$BeO + H_2O \rightleftharpoons Be(OH)_2$ being driven to the right at elevated

temperatures and evidence of this etching action of water vapor at

approximately 1400°C is presented in the photomicrograph of Figure 4

These observations led us to investigate compounds other

than water as the reactant for converting the beryllium halides
into beryllia. These studies are discussed in the section
below.

3.2 Nitro-Pyrolysis of Beryllium Halides

A number of substances other than water can be used to
provide the oxygen required to convert the beryllium halides
into beryllium oxide by thermal means. Nitrogen dioxide, NO_2
(actually a dimer) is such a compound. Various hypothetical
equations, all favorable thermodynamically, can be written for
the reactions between beryllium halides and this compound to
yield beryllium oxide at elevated temperatures. These reactions
have been identified therefore as "nitro-pyrolytic" to
differentiate them from those in which water constitutes the
source of the oxygen for the formation of beryllia.

Further consideration and calculations show that the over-
all "nitro" conversion of beryllium to beryllium oxide via the
bromide is thermodynamically more favorable than via the
chloride. Since a high purity hydrogen bromide is as readily
available as the high purity hydrogen chloride, a series of
experiments were performed which involved bromination of beryllium
metal by means of gaseous hydrogen bromide and exposing the sub-
limed beryllium bromide at elevated temperatures to an atmosphere
containing nitrogen dioxide. The system used in this series of
experiments is shown schematically in Figure 1; the range of
the experimental parameters which were investigated is given in
Table 2, and a tabulation of the pertinent conditions, objectives,

and observations is presented in Summary Sheet No. 1B Nitro-Pyrolysis of Beryllium Halides.

TABLE 2

Range of Process Variables for Nitro-Pyrolysis of Beryllium Bromide

Temperature - $^\circ$C   1000 - 1350
Flow Rates   liters/min.

HBr	0.01 - 0.04
NO_2	0.07 - 0.15
A	0.0 - 3.0
H_2	0.0 - 3.0
$BeBr_2$: NO_2 ratio	1:4 - 1.5:1
Time - hours	0.3 - 1.0

Hydrogen was used as the carrier gas in approximately one-half of the experiments and argon was used in the remainder. Experiments which did not involve hydrogen were of relatively short duration, primarily due to heater failure. Another problem experienced with the utilization of beryllium bromide as the source material was that of low yields of the compound as determined by the amount of beryllium consumed when hydrogen bromide gas was passed over the metal. The problem, however, was regarded as of secondary concern since it probably could have been solved by brominating at a higher temperature. This expedient, however, was not investigated since a few experiments indicated that other than a calculated thermodynamic advantage, beryllium bromide showed no decided superiority over beryllium chloride.

A few experiments were therefore conducted on the nitro-pyrolysis of beryllium chloride. The range of process para-

meters covered in the study is shown in Table 3.

TABLE 3

Range of Process Variables for Nitro-Pyrolysis of Beryllium Chloride

Temperature $^\circ$C	1250 - 1475
Flow Rates liters/min	
HCl	0.02 - 0.04
NO_2	0.10 - 0.15
H_2	3.0
$BeCl_2$: NO_2 ratio	1:4 - 1:2
Time - Hours	1

The above experiments together with those performed using beryllium bromide as the source material demonstrated that oxides other than water could be used to provide the oxygen for the conversion of beryllium halides to beryllium oxide and in this manner one could circumvent the devastating etching action and vapor transport of the beryllia deposit when water is one of the reactants.

It was also realized that modification of the heating system would be required if an inert gas such as argon were to be used instead of hydrogen in the nitro-pyrolysis system. This definitely would have been done were it not for the fact that concomitant with carrying out experiments on the nitro-pyrolysis of the halides, studies were made on using organic adducts of beryllium as the source material. Preliminary investigations appeared exceedingly promising and consequently the total effort was directed toward the use of such compounds in place of the halides. The experiments involving the basic formate are described in the next section.

3.3 Pyrolysis of Beryllium Basic Formate

The selection of beryllium basic formate as the source material was based on the knowledge that its decomposition products should not contaminate the beryllium oxide derived therefrom with carbonaceous material. Furthermore the reaction products should contain a minimum quantity of water of constant amount and since it would be diluted with other gaseous products the water vapor transport mechanism might be restricted to a very minor role.

A schematic of the apparatus used for the pyrolysis of the organic adduct of beryllium - beryllium basic formate - is shown in Figure 2.

A condensation of the experimental runs which were made is given in Summary Sheet No. 2, Pyrolysis of Beryllium Basic Formate and the range of the parameters investigated is given in Table 4.

TABLE 4

Range of Process Variables for Pyrolysis of Beryllium Basic Formate.

Sublimation Temperature $^{\circ}C$	165 - 330
Substrate Temperature $^{\circ}C$	400 - 1250
Time at Temperature - hrs.	0.25 - 3.0
Substrate Material--Ceramic BeO, Al_2O_3; glass;	
metal, graphite	
Substrate Shape--Flat plates, rods, tubes, cones	

A few preliminary experiments established the sublimation temperature of the basic formate as $175^{\circ}C$ at a pressure of approximately 5 mm. To allow for slight variation in pressure a temperature of $185^{\circ}C$ was normally regarded as the point at which an adequate sublimation rate occurred.

Most investigators have found that the preparation of

pyrolytic materials requires temperatures above 1000°C. Our

prior experience had demonstrated that the hydro- or nitro-

pyrolytic reaction yielded dense beryllia materials only at

temperatures above approximately 1100 °C. Our initial tempera-

ture range therefore for the pyrolysis of the basic formate

was equivalent to the values given above.

Experiments performed in this range showed that if pyrolysis

were to be achieved at temperatures of 1000 to 1250°C it would

be necessary to confine the vapor path of the basic formate

so that it would flow through a very narrow channel surrounding

the substrate. Progressive constriction of the flow channel

to essentially compress the vapors toward the substrate sur-

face was not instrumental with respect to the formation of an

adherent dense deposit of BeO.

It should also be mentioned that at the temperature range

mentioned above, the formation of a satisfactory deposit was

not promoted by changing either the shape of the substrate or

its distance from the orifice of the generator.

In the next series of experiments, the substrate temperature

was systematically decreased by appropriate increments and it was

found that initiation of adherent, dense, and hard deposits were

obtained at temperatures below 650°C. This of course applies only

to the parameters of the system being used and consequently does

not mean that if another system were used one would be restricted

to a substrate temperature of the order of 650°C. Conceivably higher temperatures could be used with success providing forced or pressurized flow conditions were used together with an extremely sharp temperature gradient.

Having established the working level for the temperature of the substrate the next series of experiments were directed toward securing basic information on the effect of vaporization rate, substrate geometry and composition, nozzle-substrate relationships, thermal decomposition range of the formate, effect of multiple deposits on adherence, and reproducibility of the operating characteristics of the system.

Observations made during the early runs pointed toward a definite tendency for the basic formate vapors to seek an escape route which would lead away from the hottest region of the substrate. A confining tubular substrate was therefore used in most of the experiments so that the effectiveness of modifying any one of the multiple variables involved could be followed.

Thermocouples placed at various locations along the axis of the substrate showed that the deposition of pyrolytic BeO from the formate occurred over a temperature range of 400 to 600°C. This is several hundred degrees below the temperature used in most pyrolytic reactions and hence a patent application has been filed on the low temperature process.

The low deposition temperature for the pyrolytic BeO prepared from the basic formate offers a distinct advantage

in that it significantly broadens the types of materials which
can be used as substrates. Substrate material other than
ceramic BeO or Al_2O_3 was used in some of the runs, the objectives
being to prepare deposits which could be used to positively
identify the material, to determine whether or not preferred
orientation was present, and possibly to improve the ceramographic
contrast between the base and the coating. Adherence to Vycor
glass was rather poor, conceivably because of the difference in
thermal expansion values of the two materials. Good adherence
was observed when soft glass, graphite and aluminum oxide were
used.

Initially, little success was realized in coating a plane
surface with a deposit of pyrolytic beryllia. In these investigations,
the substrate was mounted with a flat surface perpendicular to the
vapor stream. Almost without exception under this arrangement,
the major deposition occurred on the wall of the chamber and the
vapors appeared to be channeled around the substrate as if it
were an obstacle. Changing the temperature or substrate-orifice
distance did not solve the problem.

The effect of temperature uniformity was studied by using
a small beryllia crucible as a self contained heater-substrate
assembly. The crucible was wound with resistance wire so that
its flat bottom would serve as a substrate which was heated by
conduction rather than radiation from the walls of the reaction
chamber. The crucible was placed essentially in the center of
the throat of a beryllia tube leading from and maintained at

the temperature of the generator. Again, however, success was not attained.

Other experiments involving substrate geometry with respect to the edges and protrusions of a flat surface were not successful. A study of the deposition pattern using a series of wires which were suspended at various points in the vapor stream indicated that plane surfaces of a substrate would be coated if the substrate were oriented so that the surfaces were close to the orifice of the generator and parallel to the vapor stream, rather than at right angles to it. This observation was confirmed by successfully coating graphite plates placed on end in the cavity of the reaction chamber and slightly above the plane of the orifice of the generator.

Success in coating an object of any geometry ranging from rods, tubes, and flat or curved surfaces was attained by maintaining the temperature of the substrate in the range of 400 to 600°C and placing the substrate in the path of the vapors of the sublimed beryllium basic formate. Test samples measuring approximately one square inch in area were made by this process by coating ceramic BeO plates with pyrolytic beryllia.

3.4 Properties of Pyrolytic BeO

X-ray analysis of the material laid down on a substrate of Vycor showed that the deposit was BeO and that preferred orientation had not occurred.

The hardness of the pyrolytic deposit is compared with that of a sintered BeO substrate in Table 5.

TABLE 5

Microhardness of Pyrolytic and
Ceramic BeO
Knopp values - Kg/sq. mm, 100 gm load

Pyrolytic BeO	Ceramic BeO Substrate
1285	1290
1170	1460
1285	1100
1470	1320
1300	1150
Average 1300	1260

The microstructure of the deposit appears to be exceedingly fine grained. Polished surfaces do not reveal the presence of grain boundaries at a magnification of 600X. It should also be mentioned that the normal columnar structure observed in a number of pyrolytic materials is not evident in the deposit as prepared above. Thus it would appear that the coating is built from sub-micron sized particles which are fairly uniformily deposited on the substrate surface.

As mentioned above the adherence of pyrolytic BeO to ceramic beryllia is excellent as measured qualitatively by a scratch test or by heating a coated substrate rapidly to 1700°C. The latter test promotes epitaxial grain growth at the deposit-substrate junction showing the presence of an initial strong bond.

3.5 Beryllia Fibers

A number of methods have been used to prepare fibers of certain metal oxides. These include vapor transport, thermal degradation of an appropriate volatile oxygen containing compounds, and oxidation of the metal.

A review of prior experience indicated that the vapor phase oxidation of beryllium metal offered a likely method of preparing beryllia fibers.

A schematic of the fiber growing apparatus used in a number of experiments is shown in Figure 3. In addition, a standard high temperature tube furnace was available and was used to broaden the opportunities for exploration of the process.

These units permitted us to conduct a number of parametric studies embracing the ranges shown in Table 5.

TABLE 6

Range of Process Variables for Vapor Phase Oxidation of Beryllium

Temperature - $^{\circ}C$ 1300-1650
Time at temperature - hrs   0.2-64
Carrier Gas - type-reducing $(3H_2-IN_2)$-Pure H_2
Flow Rate   1/min   2-7
Flow Velocity cm/min.   75-600

A tabulation of the pertinent data of the experimental runs is presented in Summary Sheet No. 3 Beryllia Fibers - Experimental Objectives, Conditions, and Observations.

The fundamental objective of these experiments was to define the conditions under which BeO fibers could be grown from the metal at meaningful rates.

The principal factors involved in the studies were concerned with the nature of the furnace atmosphere and its effect on fiber growth.

Preliminary trials in which the beryllium metal contained in BeO boats was placed in the hot zone of an aluminum oxide

muffle were not promising in that gross oxidation of the metal
occurred prior even to melting. This oxidation is attributed
to the fact that the alumina was significantly reduced by the
hydrogen atmosphere to yield an excessive amount of the oxidant,
namely, water. If a high concentration of water were present,
the beryllium metal would be oxidized in all likelihood before
it could vaporize.

A fairly dense graphite tube was used in place of the
aluminum oxide muffle and two successful runs in which fibers
of BeO were produced seemed to indicate that the analysis of
the problem was correct and that the problem had been solved.
Thereafter, however, disappointingly small yields of fibers
occurred and the major deterrent to growth appeared to be
premature oxidation of the metal. Inspection of the graphite
tube after a few more runs revealed that it had a small crack
near the hot zone and consequently moisture from the reaction
between hydrogen and the furnace ceramic materials could enter
the reaction chamber and oxidize the metal. This series of
experiments demonstrated that the composition of the atmosphere
of the reaction chamber was probably the most important para-
meter of the vapor phase oxidation process if fibers were to
be produced.

A 300 series stainless steel tube was then substituted
for the graphite tube. Although this replacement placed restrictions
on the upper level of the temperature which could be used, the
operating range for the stainless material was sufficiently
above the melting point of beryllium metal and permit a series

of meaningful experiments. The fiber growth pattern experienced above with the graphite tube was duplicated with the stainless reaction chamber in that the quantity of fibers decreased with each successive run. Examination of the tube revealed that gross grain growth had occurred as evidenced by rupture of the grain boundaries. In all probability furnace moisture migrated through the pores of the metal tube and oxidized the beryllium. In passing it should be mentioned that the stainless material was that designated as 310. Other series of course might not exhibit this almost catastrophic grain growth in a hydrogen atmosphere at temperatures above $1300^\circ C$.

The final series of experiments were runs in which a reducing agent such as carbon was either blended directly with the metal or spread as a blanket in order to conceivably prevent the pre-oxidation of beryllium. This technique, however, did not depress the oxidation of the metal sufficiently to prevent oxidation prior to volatilization and consequently the growth of fibers did not occur.

In conclusion, the vapor phase oxidation of beryllium was found to be a reaction capable of yielding well-formed fibers of beryllia under exact but as yet not completely defined conditions. These conditions involve a delicate and sharp maximum for the concentration or availability of an oxidant. This is quite apparent by referring to Figure 5. This shows two boats, both supposedly, but obviously, not exposed with their initial contents to similar conditions since

in one the growth of fibers is evident without oxidation of the
parent metal whereas in the other or upper boat, the initial
granular metal has been completely oxidized to a white powder
without fibers being formed.

IV. CONCLUSIONS AND RECOMMENDATIONS

An analysis of the results obtained during the period covered
by the contract have led to the following conclusions:

1) The hydro-pyrolysis of beryllium halides at the present time
is limited to the preparation of deposits of the order of 25 microns
in thickness due to the etching and vapor transport of beryllia by
water vapor.

2) Oxidants such as the oxides of nitrogen, and oxygen itself,
offer definite possibilities for the conversion of beryllium halides
into pyrolytic beryllia without deleterious side reactions such as
that experienced when water is used as the oxidant. Additional
experimentation is necessary in order to establish the parameters
of the process.

3) Pyrolytic deposits of dense, hard, and adherent beryllia
can be prepared by thermal decomposition of the volatile beryllium
basic formate at temperatures of 500°C and below.

4) The preparation of beryllia fibers via the vapor phase
oxidation of beryllium metal has been shown to be feasible.

We believe it in order to make the following recommendations
with respect to future programs involving pyrolytic beryllia
materials:

Additional studies are definitely needed in order to confirm the tentative conclusions and findings stated above with regard to the utilization of an organic adduct of beryllium as the source material for the preparation of beryllium oxide. Early confirmation is anticipated however and the program should then be directed towards establishing the parameters and degree of control which must be exercised in order to capitalize on a low temperature reaction.

The limited success experienced in growing beryllia fibers by the vapor phase oxidation of beryllium metal definitely indicates that the method is feasible. Experiments directed toward pinpointing the precise conditions under which filamentary growth rather than coatings occur should therefore be made at an early date.

We believe that such a program will be highly successful and permit the development of techniques which can be applied to the preparation of useable hardware such as radomes, microwave windows, re-entry structures and protective coatings for such devices.

THERMOCOUPLES

HCl
(HBr)

BERYLLIUM
CONVERTER

INLET
NOZZLE HEATER

INNER
SHELL

REACTOR
SHELL

$2 + H_2$
$2) (N_2)$

SUBSTRATE
HEATER

SUBSTRATE

PYROMETER
SIGHT
HOLES

PEDESTAL

MANOMETER &
RELEASE VALVE

$CO_2 + H_2$
$(NO_2) (N_2)$

EXIT THROAT HEATER

GAS EXIT

CONDENSER

WATER INLET
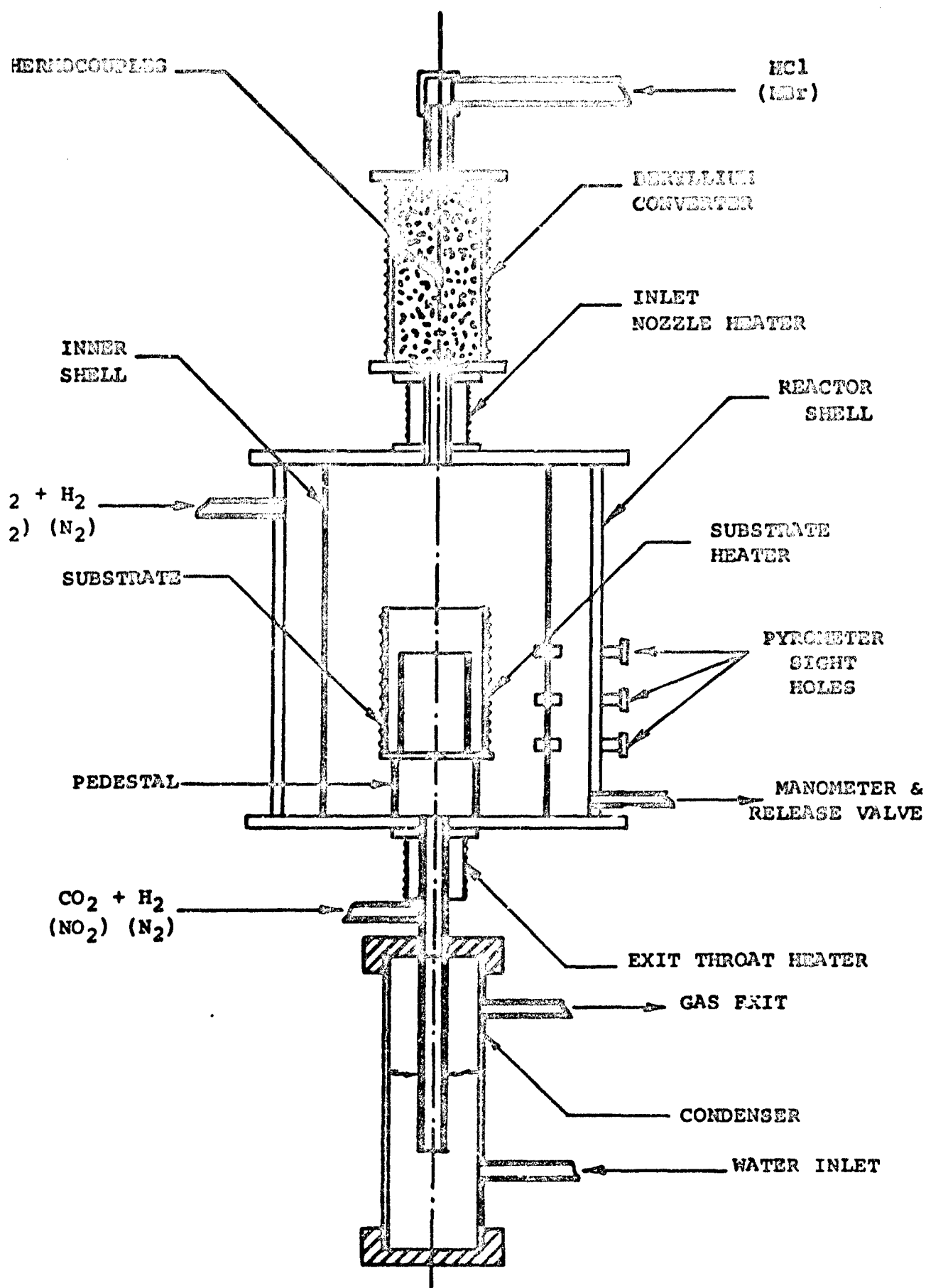
Figure 1 - ASSEMBLY DRAWING

INNER SHELL

REACTOR SHELL

VACUUM

SUBSTRATE

SUBSTRATE HEATER

PYROMETER SIGHT HOLES – THERMOCOUPLE PORTS

GENERATOR

MANOMETER

ARGON (AIR)

GENERATOR HEATER
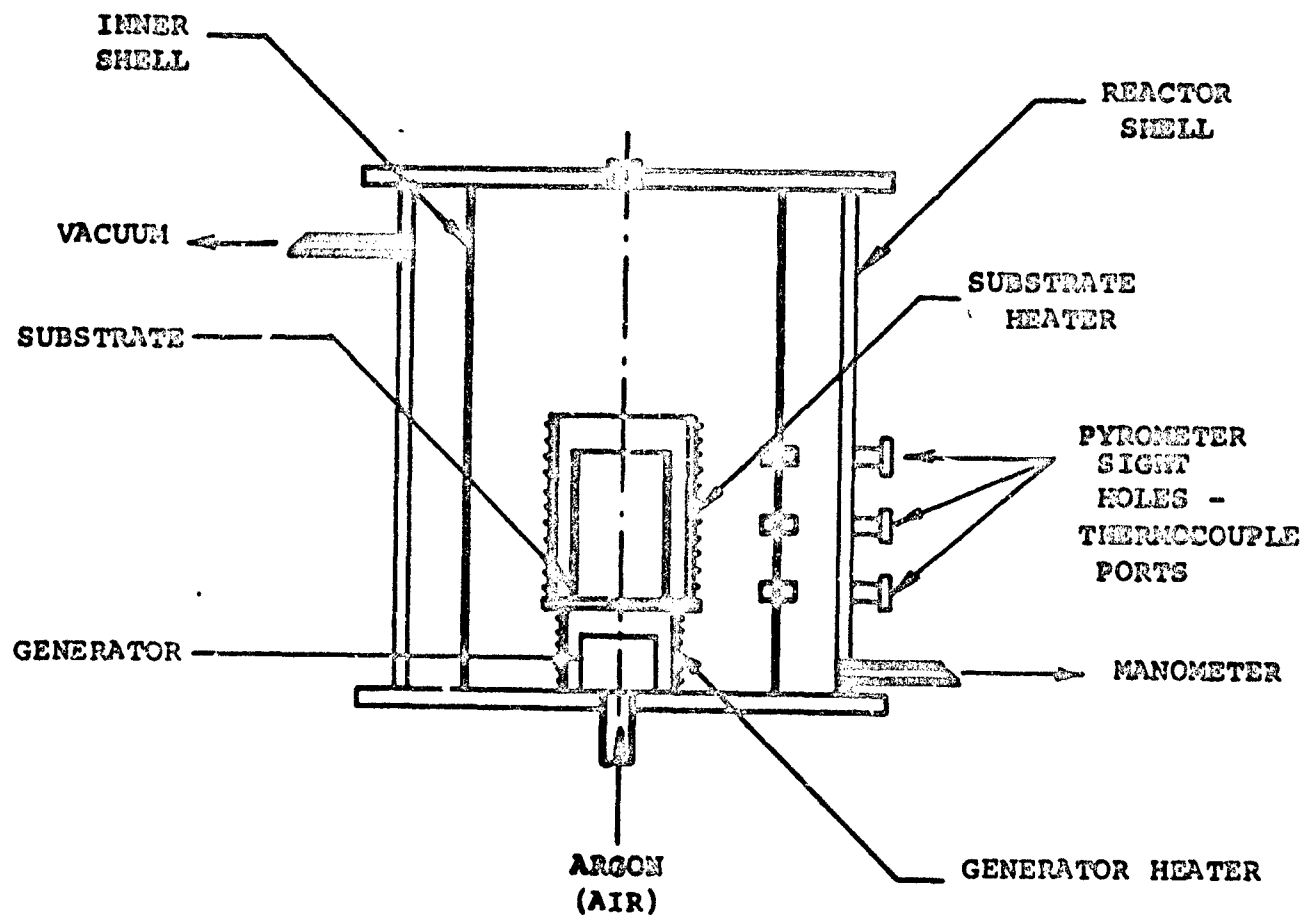
Figure 2 – ASSEMBLY DRAWING
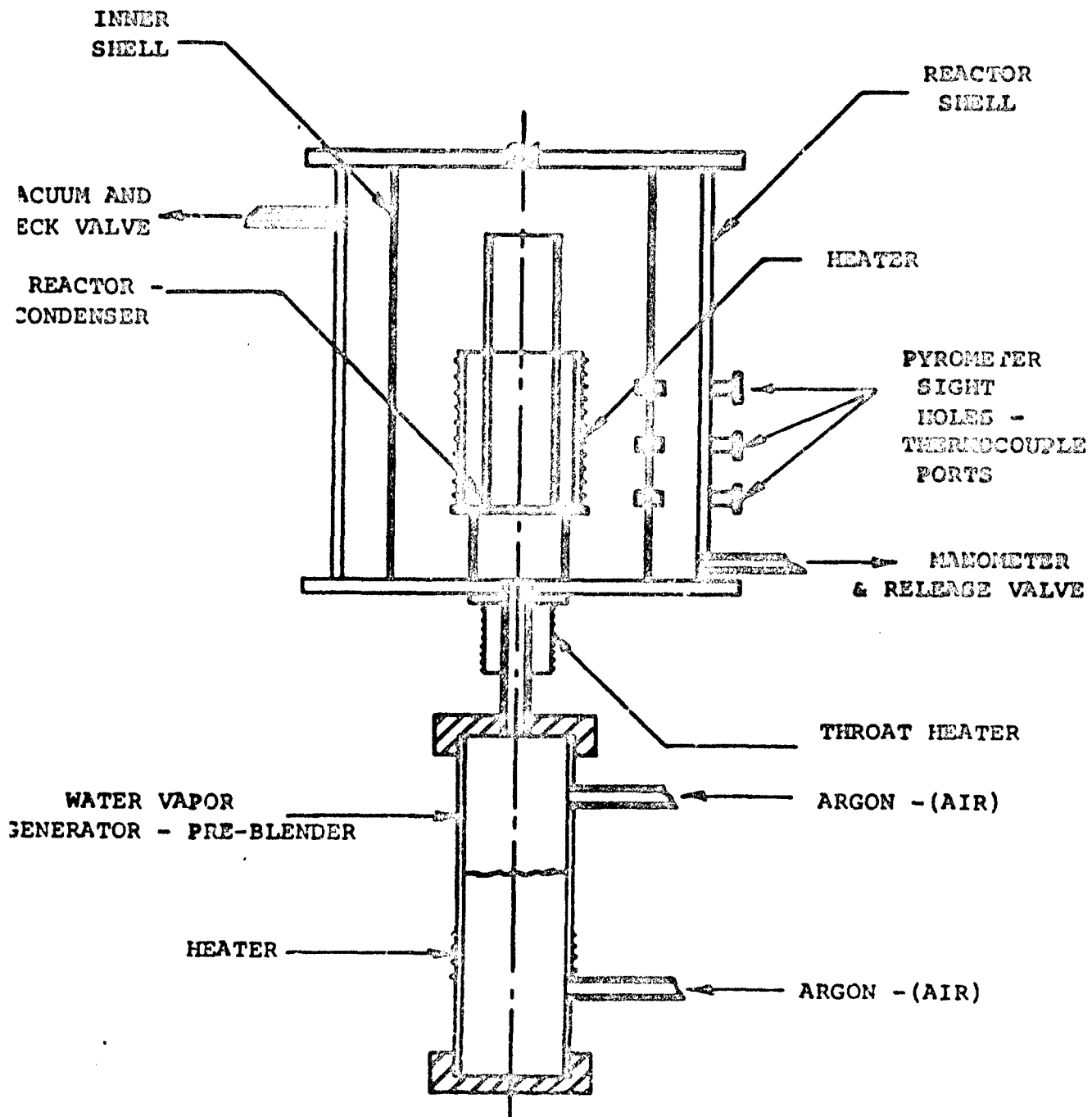
Figure 3 - ASSEMBLY DRAWING

INNER SHELL

REACTOR SHELL

VACUUM AND CHECK VALVE

REACTOR - CONDENSER

HEATER

PYROMETER SIGHT HOLES - THERMOCOUPLE PORTS

MANOMETER & RELEASE VALVE

THROAT HEATER

WATER VAPOR GENERATOR - PRE-BLENDER

ARGON - (AIR)

HEATER

ARGON - (AIR)
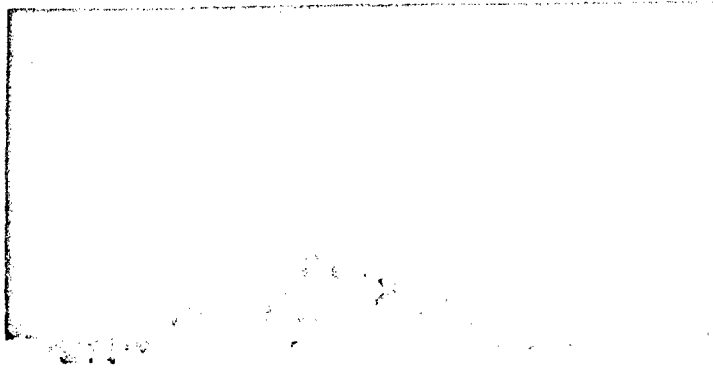
FIGURE 4. HYDRO VAPOR ETCHING OF BERYLLIA 133X
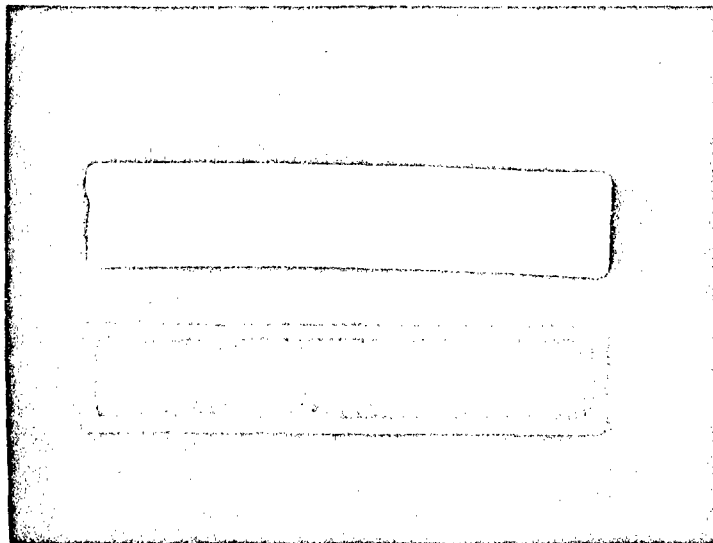
FIGURE 5. FIBROUS (A) AND NON-FIBROUS (B)
GROWTH OF BeO

PURPOSE	RUN NO.	SUBSTRATE	DEPOSITION TEMP. °C	FLOW RATE 1/min.			
				HCL	H_2	CO_2	H_2
ect of time at re	76	Outer wall of BeO crucible	1150	0.1	3	1.5	--
ect of blending close to substrates	77	BeO disc 45° to vapor stream	1060	0.04	3	0.08	--
ect of temp.	78	like 77	1550	0.04	3	0.08	--
ect of $BeCl_2$ conc.	79	like 77	1550	0.02	3	0.08	--
ect of preblending near substrate	80	like 77	1365	0.02	3	0.08	--
Run No. 80	81	see 77	--	0.02	2	1.0	1.0
	82			0.02	0.2	0.1	0.1
	83			0.02	0.2	0.1	0.1
	84			0.02	0.5	0.1	0.1
	85			0.02	1.5	0.1	0.1
Run No. 80	86	see 77	1350	0.01	2.0	0.1	0.1
Run No. 86 inc.	87	BeO disc	1350	0.02	2.0	0.1	0.1
f preblending atm.	88	Narrow strip	1410	0.02	2.5	0.1	0.5
f flow rate	89	Blind tube	1400	0.10	2.5	0.5	0.5
f flow pattern	90	Blind tube	1450	0.02	2.5	0.1	0.5
bove	91	From above	1410	0.1	2.5	0.5	0.5
f atm.	92	Blind tube	1415	0.02	2.5	0.5	0.5
f HCl conc.	93	From above	1450	0.01	2.5	0.5	0.5
f CO_2 conc.	94	From above	1440	0.01	2.5	1.0	0.5

A

DEPOSITION TEMP. °C	FLOW RATE l/min.				BERYLLIUM CONSUMED Gms.	TIME AT TEMP. MIN.	SUBSTRATE GAIN Gms.
	HCL	H_2	CO_2	H_2			
1150	0.1	3	1.5	--	4.0	150	0.1
1060	0.04	3	0.08	--	2.0	120	<0.005
1550	0.04	3	0.08	--	0.8	105	0.03
1550	0.02	3	0.08	--	1.1	165	0.015
1365	0.02	3	0.08	--	1.0	120	0.03
--	0.02	2	1.0	1.0	--	--	--
	0.02	0.2	0.1	0.1	--	--	--
	0.02	0.2	0.1	0.1	--	--	--
	0.02	0.5	0.1	0.1	--	--	--
	0.02	1.5	0.1	0.1	--	--	--
1350	0.01	2.0	0.1	0.1	1.0	115	<0.01
1350	0.02	2.0	0.1	0.1	0.4	25	<0.01
1410	0.02	2.5	0.1	0.5	0.3	35	--
1400	0.10	2.5	0.5	0.5	--	110	0.01
1450	0.02	2.5	0.1	0.5	--	60	0.4
1410	0.1	2.5	0.5	0.5	--	60	0.2
1415	0.02	2.5	0.5	0.5	--	60	0.1
1450	0.01	2.5	0.5	0.5	--	120	<0.02
1440	0.01	2.5	1.0	0.5	--	60	

BERYLLIUM CONSUMED Gms.	TILE AT TEMP. °C.	SUBSTRATE GAIN Gms.	REMARKS AND OBSERVATIONS
4.0	150	0.1	Deposit highly localized, fluffy
2.0	120	<0.005	No adherent deposit
0.8	105	0.03	Sl. deposit over entire substrate
1.1	165	0.015	$BeCl_2$ conc. too low, but deposit is very smooth
1.0	120	0.03	CO_2 flushes substrate first, deposit is soft.
--	--	--	Abortive runs - delivery tubes cleaned
--	--	--	
--	--	--	
--	--	--	
--	--	--	
1.0	115	<0.01	Soft deposit
0.4	25	<0.01	Soft deposit - Clogging
0.3	35	--	Non-adherent deposit - Recheck system $BeCl_2$ from bottom
--	110	0.01	Heavy loose deposit. CO_2 and $BeCl_2$ from bottom
--	60	0.4	$BeCl_2$ in from bottom, CO_2 in from top. Fluffy deposit, whisker growth.
--	60	0.2	Firm deposit on tip. No fibers
--	60	0.1	Heavier deposit on tip.
--	120	<0.02	Non-adherent deposit above hot zone
--	60		Non-adherent deposit

C

OBJECT - PURPOSE	RUN ID.	SUBSTRATE	DEPOSITION TEMP. °C	
Establish Parameters	1	BeO Disc	1275	0
Effect of Temp.	2	BeO Plate	1215	0
Effect of Atm.	3	BeO Plate	1350	0
Improve system	4	BeO Plate	--	0
Improve system	5	BeO Square	1000	0
Effect of Temp.	6	BeO Rectangle	1100	0
Effect of Atm.	7	From 6	1300	0
Locate deposition zone	8	BeO Plate	1300	0
Effect of beryllium	9	From 8	1400	0
				H
Effect of Halide	10	From above	1400	0
Effect of preblending atm.	11	BeO Plate	1250	0
Effect of temp.	12	From above	1475	0
Effect of flow pattern	13	Narrow strip	1420	0

A

POSITION TP. °C	FLOW RATE l/min				BERYLLIUM CONSUMED Gms.	TIME AT TEMP.-Min.	SUBSTRATE GAIN-Gms.	REMARKS
	HBr	A	NO_2	A				
1275	0.01	2.5	0.4	0.5	0.1	20	0.01	Sl. glass
1215	0.01	2.5	0.1	0.5	0.3	20	0.02	Hard cry:
1350	0.03	−	0.07	−	−	30	0.001	H_2 used i oxidation
−−	0.01	2.5	0.1	0.5	−	−	−	Heater sh
1000	0.01	2.5	0.1	0.5	−	30	−	No deposi
1100	0.04	1.0	0.13	0.5	0.4	15	0.005	Heater fa
1300	0.04	(2.5) H_2	0.13	(0.5) H_2	0.1	60	0.04	H_2 to rep
1300	0.04	(2.5)	0.13	(0.5)	−	60	0.001	No adhere
1400	0.04	(2.5)	0.13	(0.5)	−	60	0.001	High dilu reaction
	HCl	H_2	NO_2	H_2				
1400	0.04	2.5	0.13	0.5	0.6	60	0.005	HCl gas t deposit
1250	0.04	2.5	0.13	0.5	0.8	60	0.008	Counter-c
1475	0.02	2.5	0.13	0.5	0.8	60	0.01	Deposit l
1420	0.02	2.5	0.13	0.5	0.4	60	−	Non-adhel

B

EXPERIMENT CONSUMED Gms.	TIME AT TEMP., Min.	SUBSTRATE GAIN-Gms.	REMARKS AND OBSERVATIONS
5	0.1	20	0.01	Sl. glassy deposit noted
5	0.3	20	0.02	Hard crystalline coating
	-	30	0.001	H_2 used in place of A to prevent oxidation of heater
5	-	-	-	Heater shorted & failed
5	-	30	-	No deposit formed
5	0.4	15	0.005	Heater failed, no deposit
5)	0.1	60	0.04	H_2 to replace A. No firm deposit
.5)	-	60	0.001	No adherent deposit. H_2 in place of A
.5)	-	60	0.001	High dilution of HBr with H_2 prevents reaction
.5	0.6	60	0.005	HCl gas to replace HBr. Non-adherent deposit
.5	0.8	60	0.008	Counter-current flow. Sl. deposit
.5	0.8	60	0.01	Deposit like above
.5	0.4	60	-	Non-adherent deposit

C

JECT - PURPOSE	RUN NO.	SUBSTRATE	DEPOSITION TEMP. ^{o}C	GENERATOR TEMP. ^{o}C	TIME AT TEMP. - Hi
ish Parameters	1	BeO[1]	1150	185-200	0.75
ish Parameters	2	From 1	1050	185-200	1.0
ish Parameters	3	From 2	1200	195-210	0.5
ish Parameter	4	From 3	1100	175-185	0.1
ish Parameters	5	From 4	500	185-200	0.5
ish Parameters	6	From 5	750	185-200	0.9
ional flow	7	From 6	750	185-200	0.75
ional flow	8	From 7	750	170-185	1.0
ional flow	9	From 8	750	185-200	1.5
ate Geometry	10	Flat Plate	750	185-200	2.5
10	11	Flat Plate	800	185-300	2.0
tor design	12	Flat Plate	735	185-210	2.0
12	13	Flat Plate	750	185-210	1.0
tor design	14	Flat Plate	735	185-210	3.0
tor-Substrate onship	15	Flat surface	660	185-210	0.6
15	16-19	Flat surface	650	185-200	2.5

	DEPOSITION TEMP. ^{o}C	GENERATOR TEMP. ^{o}C	TIME AT TEMP. - Hrs.	GENERATOR CHARGE -Gms.	FORMATE USED -Gms.	SUBSTRATE GAIN -Gms.
	1150	185-200	0.75	0.9	0.8	0.00
	1050	185-200	1.0	1.3	--	0.00
	1200	195-210	0.5	1.0	0.95	-0.00
	1100	175-185	0.1	1.4	0.03	0.00
	500	185-200	0.5	0.75	0.5	0.00
	750	185-200	0.9	0.9	0.83	0.00
	750	185-200	0.75	0.6	0.4	0.00
	750	170-185	1.0	0.7	0.64	0.00
	750	185-200	1.5	0.98	0.9	>0.001
	750	185-200	2.5	0.91	0.85	>0.005
	800	185-300	2.0	2.0	1.8	0.00
	735	185-210	2.0	1.5	1.2	0.00
	750	185-210	1.0	1.9	1.0	0.00
	735	185-210	3.0	--	--	0.00
ce	660	185-210	0.6	1.1	1.0	0.00
ce	650	185-200	2.5	0.35	0.33	>0.005

43

NERATOR ARGE -Gms.	FORMATE USED -Gms.	SUBSTRATE GAIN -Gms.	REMARKS AND OBSERVATIONS a) all runs made with vacuum of 2-3 mm.
0.9	0.8	0.00	(1) Heating coil inserted in BeO tube. No deposition occurred
1.3	--	0.00	No visible deposit
1.0	0.95	-0.00	No deposit - substrate lost weight
1.4	0.03	0.00	Vapor collimator used - no deposit
0.75	0.5	0.00	No deposit
0.9	0.83	0.00	No visible deposit
0.6	0.4	0.00	Formate reacted with copper line
0.7	0.64	0.00	Stainless steel single orifice Generator - No deposit.
0.98	0.9	>0.001	Same as above - very sl. deposit
0.91	0.85	>0.005	Flat plate used in place of curved surface Definite evidence of deposit
2.0	1.8	0.00	No evidence of deposit
1.5	1.2	0.00	Baffle design to channel vapors No deposit
1.9	1.0	0.00	No deposit Formate questioned.
--	--	0.00	Aluminum shields
1.1	1.0	0.00	Sl. evidence of deposit
0.35	0.33	>0.005	Very sl. deposit

C

OBJECT - PURPOSE	RUN NO.	SUBSTRATE	DEPOSITION TEMP. °C	GENERATOR TEMP. °C	T TE
Study effect of deposition temperature	20	BeO tube 3.6"x.375"x.25"	525-575	180-190	
Verify substrate gain of run 20	21	Same as 20	525-575	190-210	
Study effect of deposition temperature	22	BeO tube as above	525-575	205-215	
Secure deposit for x-ray analysis	23	Vycor tube 90 x 9 x 7 cm	525-575	200-210	
Secure deposit for x-ray analysis	24	Soft glass plate 1"x 1"	est. 550	180-190	
Study deposition pattern	25	Al_2O_3 disc 1.5 OD x 0.06	500-520	180-190	
Study deposition pattern	26	BeO closed tube 4" x 0.3	est. 600	200-220	
Determine vaporization rate	27	BeO tube as in run 20	est. 600	185-225	
Improve ceramographic contrast. Study effect of substrate	28 A	Al_2O_3 tube 4"x.375" x .25"	est. 600	185-230	
Study nature of multiple deposits	28 B	as above	est. 600	185-225	
	C	as above	est. 600	185-215	
	D	as above	est. 600	185-225	
	E	as above	est. 600	185-215	
	F	as above	est. 600	185-225	
Improve ceramographic contrast	G	as above	est. 600	185-225	
Study effect of time at temperature	30	BeO tube as in run 20	590-610	185-225	
Study effect of sublimation temperature	31 A	Opposite end from above	480-490	155-165	
	B	from above	440-460	165-170	

A

RATOR °C	TIME AT TEMP. HRS.	GENERATOR CHARGE-GMS	FORMATE USED-GMS	SUBSTRATE GAIN-GMS	REMARKS & OBSERVA' a) all runs made with va
·190	1.0	2.3	1.2	0.074	Very hard dense deposit on s contact with generator.
·210	1.25	1.2	0.75	0.157	Dense hard deposit as above. that of run 20.
·215	3.0	1.1	0.74	0.137	Deposit similar to that note
·210	2.75	1.56	1.03	0.20	Deposit located approx. 1" a cracked & loosely bonded. X
-190	1.0	1.14	0.54	- -	Plate directly over and ± to of 009". No deposit over or adhering deposit away from c
-190	1.0	1.57	0.90	0.02	Deposition pattern as above. from hottest zone and decomp Deposit fairly adherent.
-220	0.17	2.01	0.98	- -	Abortive run. Substrate chi of substrate in down positic
-225	0.5	1.59	0.94	0.22	Heavy deposit extending up t used to press substrate agai
-230	0.5	1.2	0.8	0.17	Comments of run 27 apply.
-225	0.5	0.87	0.61	0.12	Deposit appears blended with Weight gain indicates depos:
-215	0.3	3.1	1.39	0.025	New lot of formate used. De
-225	0.5	1.9	0.89	0.02	Above formate used again.
-215	1.0	0.69	0.23	0.05	New lot of formate used. Lc
-225	2.0	0.36	0.12	0.00	Above formate used. '
-225	2.5	1.2	0.9	0.22	New lot of formate used. O Good sublimation. Weight g
-225	2.0	1.38	1.13	0.30	Firm, dense, hard, deposit 0.75" in substrate.
-165	1.0	1.1	0.05	- -	Sublimation rate exceedingl
-170	2.0	1.0	0.05	- -	Amount of sublimation very

FORMATE USED-GMS	SUBSTRATE GAIN-GMS	REMARKS & OBSERVATIONS e) all runs made with vacuum of 2-3 mm.
1.2	0.074	Very hard dense deposit on substrate at area of contact with generator.
0.75	0.157	Dense hard deposit as above. Weight gain twice that of run 20.
0.74	0.137	Deposit similar to that noted above.
1.03	0.20	Deposit located approx. 1" above generator. Appears cracked & loosely bonded. X-ray confirms BeO.
0.54	- -	Plate directly over and ⊥ to generator orifice at distance of 009". No deposit over orifice. Ring pattern of adhering deposit away from orifice.
0.90	0.02	Deposition pattern as above. Vapor tends to move away from hottest zone and decompose-deposit at cooler zones. Deposit fairly adherent.
0.98	- -	Abortive run. Substrate shifted during run. Closed end of substrate in down position.
0.94	0.22	Heavy deposit extending up tube for approx. 0.75". Yoke used to press substrate against generator.
0.8	0.17	Comments of run 27 apply.
0.61	0.12	Deposit appears blended with that of run 27. Weight gain indicates deposition occurred.
1.39	0.025	New lot of formate used. Decomposition without deposition.
0.89	0.02	Above formate used again. " " "
0.23	0.05	New lot of formate used. Low sublimation & deposition.
0.12	0.00	Above formate used. " " " "
0.9	0.22	New lot of formate used. Opposite end of substrate used. Good sublimation. Weight gain average.
1.13	0.30	Firm, dense, hard, deposit obtained extending up approx. 0.75" in substrate.
0.05	- -	Sublimation rate exceedingly low.
0.05	- -	Amount of sublimation very small.

C

NAME - PURPOSE	RUN NO.	SUBSTRATE	DEPOSITION TEMP. °C	SUBLIMATION TEMP. °C	TIME AT TEMP. HRS.	GR
above	32	from run 31	470-480	185-195	1.0	
above	33	from run 32	490-510	165-170	1.7	
waste system	34	BeO tube as in run 20	640-660	165-170	2.0	
above	35	from run 34	640-660	160-165	1.0	
rates sublimation & constancy thereof	36 A B	BeO tube 250 x 7 x 5 cm from above	640-660 640-660	170-175 165-170	1.0 1.0	
above ostructure study	37 A B	BeO tube as in run 36 from above	590-610 590-610	190-195 190-195	2.0 1.0	
waste system	38	BeO tube as in run 36	590-610	190-195	1.0	
above	39	BeO tube as in run 36	640-660	190-195	1.0	
above	40	from above	590-610	190-195	1.0	
ate test	41	from above	590-610	190-195	1.0	
ate test	42	BeO tube as in run 36	590-610	190-195	0.5	
ate test	43	from above	590-610	190-195	1.0	
ate test	44	from above	540-560	195-200	1.0	
ate test	45	BeO tube as in run 36	540-560	190-195	1.0	

A

DEPOSITION TEMP. °C	GENERATOR TEMP. °C	TIME AT TEMP. HRS.	GENERATOR (?)-CM?	FURNACE (?)-CM?	SUBSTRATE (?)-CM?	a) all
470-480	185-195	1.0	1.0	0.05	- -	Abortive consider couple.
490-510	165-170	1.7	1.0	0.05	- -	Comment
640-660	165-170	2.0	0.97	0.66	0.1	Thermoc formed.
640-660	160-165	1.0	0.31	0.03	0.00	Re-run run 34
640-660	170-175	1.0	1.5	0.4	0.025	New lot
640-660	165-170	1.0	1.1	0.09	0.00	New lot in run
590-610	190-195	2.0	1.49	0.75	0.12	Abortive
590-610	190-195	1.0	1.64	0.72	0.05	Slight parts; 1700°C.
590-610	190-195	1.0	1.4	0.6	0.12	Yoke use resting
640-660	190-195	1.0	1.49	0.06	0.004	New lot of seal
590-610	190-195	1.0	1.67	- -	0.04	Abortive
590-610	190-195	1.0	1.52	1.39	0.02	Formate
590-610	190-195	0.5	1.43	0.59	0.00	Formate
590-610	190-195	1.0	1.31	1.12	0.008	Formate
540-560	195-200	1.0	1.96	1.62	0.12	Firm, h
540-560	190-195	1.0	1.67	1.4	0.16	Firm, h

IN B	FORMATE (MODE-C 2)	SUBSTRATE (CATHODE)	REMARKS & OBSERVATIONS a) all runs made with vacuum of 2-3 μ.
	0.05	- -	Abortive run. Temperature of generator found to be considerably lower than that shown. Faulty thermocouple.
	0.05	- -	Comments above apply.
	0.66	0.1	Thermocouple inserted in base of generator. Deposit formed.
	0.03	0.00	Re-run to determine if material in generator from run 34 will sublime - essentially none did.
	0.4	0.025	New lot of formate, low sublimation
	0.09	0.00	New lot of formate is questionable since sublimation in run 36A exhausted material.
	0.75	0.12	Abortive run, substrate shifted during assembly.
	0.72	0.05	Slight deposit formed. Deposit sectioned into three parts; one as is, fire one at 1500°C, fire one at 1700°C. Still loss of vapors.
	0.6	0.12	Yoke used to press substrate against Teflon washer resting on generator top. Deposition normal.
	0.06	0.004	New lot of formate, sublimation poor. Refinement of sealing technique.
	- -	0.04	Abortive run - seal mechanism failed.
	1.39	0.02	Formate decomposes without subliming.
	0.59	0.00	Formate decomposes without subliming. Discard.
	1.12	0.008	Formate decomposes without subliming.
	1.62	0.12	Firm, hard deposit obtained.
	1.4	0.16	Firm, hard deposit obtained.

C

OBJECT - PURPOSE	RUN NO.	SUBSTRATE	DEPOSITION TEMP. °C	GENERATOR TEMP. °C	TIME AT TEMP. HRS.
Evaluate Formate No. 7	46	New BeO Tube	540-550	190-195	1.0
Evaluate Formate No. 9	47	New BeO Tube	540-550	190-195	1.0
Evaluate Formate Mix 7-8	48	New BeO Tube	540-550	145-150	1.0
Confirm Run 48 at 190"C	49	Tube 46	540-550	190-200	1.0
Re-evaluate Formate No. 9	50	Tube 48	540-550	180-185	1.0
Study effect of Deposition Temperature	51	Tube 50	640-650	170-175	0.5
Study effect of Deposition Temperature-Time	52	Tube 45	660-670	170-175	1.0
Evaluate reprocessed No. 1	53	Tube 47	640-650	190-195	1.0
Study Substrate Geometry	54	BeO Disc	540-550	190-200	0.5
Study Generator-Substrate Relationship	55	BeO Crucible	600+	200-220	0.5
Study Substrate Geometry	56	BeO Crucible	590-600	200-220	0.5
Study Substrate Geometry	57	BeO Crucible	590-600	200-220	0.5
Study Substrate Geometry	58	Disc 54	515-520	210-230	0.5
Study Substrate Geometry	59	Disc 54	515-520	210-230	0.5
Study Generator-Substrate Relationship	60	BeO Wafer	495-500	210-230	0.5
Study Generator-Substrate Relationship	61	BeO Crucible	590-600	165-170	0.5

A

AT HRS.	GENERATOR CHARGE-GMS	FORMATE USED-GMS	SUBSTRATE GAIN-GMS	REMARKS & OBSERVATIONS a) all runs made with vacuum of 2-3 mm.
)	1.59	1.36	0.14	Deposit approx. 4" above bottom Formate No. 7 approved. Mix with No. 8.
)	3.6	2.3	0.01	Reprocess Formate No. 9
)	2.97	2.48	0.30	Deposit approx. 4" above bottom. Generator shielded from substrate heater. Mixture appears satisfactory.
)	3.1	2.8	0.26	Firm deposit. Mixture approved
)	1.16	0.74	0.04	No visible deposit. Reprocess.
)	1.16	0.84	0.09	Relatively low yield - see 49.
)	1.38	1.03	0.01	Yield decreased by increased in temperature - see 51.
)	2.69	1.55	0.00	Formate cannot be reprocessed by vacuum baking.
)	1.29	1.1	0.00	Light, fluffy non-adherent deposit.
)	1.78	1.5	0.15	Good weight gain. Shows deposition in semi-sealed chamber.
)	1.39	1.2	0.13	Abortive run - substrate moved.
)	1.2	1.0	0.11	Inner periphery but not bottom of crucible was coated.
)	1.37	0.17	0.03	Disregard, temperature control poor.
)	1.36	1.13	0.10	Similar to Run 54.
)	1.15	1.0	0.12	BeO wafer suspended in BeO tube. No deposit on flat wafer.
)	1.5	1.3	0.00	Generator inverted - downward flow. No deposit - Blockage of generator.

OBJECT - PURPOSE	RUN NO.	SUBSTRATE	DEPOSITION TEMP. °C	GENERATOR TEMP. °C	TIME AT TEMP. HRS.
Study Generator-Substrate Relationship	62	BeO Wafer	585-590	190-200	0.5
Study Temperature of Substrate	63	BeO Crucible	475-480	190-200	1.75
Study Deposition Area	64	Suspended Wire	525-535	220-240	0.7
Determine Deposition Area	65	Suspended Wire	500-505	220-240	1.0
Determine Deposition Area	66	Multiple Wires	520-530	200-220	0.1
Determine Deposition Area	67	Wire Coil	520-530	220-240	0.3
Study Generator-Substrate Relationship	68	BeO Wafer	500-520	200-220	0.5
Study Generator-Substrate Relationship	69	Multiple Wafers	500-520	190-200	0.5
Study Deposition Pattern	70-74	Graphite Wafers	500-520	190-200	0.5 ea.

A

GENERATOR CHARGE-GMS	FORMATE USED-GMS	SUBSTRATE GAIN-GMS	REMARKS & OBSERVATIONS a) all runs made with vacuum of 2-3 mm.
1.22	1.0	0.08	Ref. No. 60. Generator-substrate closer together.
3.73	3.37	0.03	Crucible heater used so that bottom serves as substrate. No deposit.
1.4	1.2	+	Wire coated with firm deposit.
1.2	1.0	+	Ref. No. 64. Wire moved 0.125 in. to center. Wire coated with firm deposit.
1.0	0.8	+	Ref. No. 64. Radial arrangement of wires. All coated.
- -	- -	+	Inner area of coil coated.
1.3	1.1	0.04	Wafer coated - Standing position.
1.5	1.3	0.11	Wafers coated on stream side.
1-1.5	0.9-1.3	0.06-0.1	Pyrolytic BeO build-up for each run.

OBJECT - PURPOSE	RUN NO.	TEMP. °C	CHARGE-GM	TIME-HR.	ATM.*	FLOW RATE
Effect of Temperature	A	1350	- -	0.5	$3H_2 - N_2$	2 l/min
Effect of Temperature	B	1550	- -	0.5	$3H_2 - N_2$	2 l/min
Prevent premature Oxidation	1	1570	0.47	0.5	$3H_2 - N_2$	2 l/min
Effect of Temperature	2	1650	0.38	0.5	$3H_2 - N_2$	2 l/min
Effect of Time	3	1650	0.49	16	$3H_2 - N_2$	2 l/min
Effect of Time to Temperature	4	1630	0.44	0.5	$3H_2 - N_2$	2 l/min
Repeat of No. 4	5	1620	0.42	0.5	$3H_2 - N_2$	2 l/min
Effect of Container	6	1640	- -	0.6	$3H_2 - N_2$	2 l/min
Container Study	7	1640	None	64	$3H_2 - N_2$	2 l/min
Effect of Container	8	1640	0.36	0.6	$3H_2 - N_2$	2 l/min
Effect of Atmosphere	9	1600	0.31	2	$3H_2$ N_2	2 l/min
Study Fiber Growth in Non-ceramic Muffle	10	1340	0.3	1.5	H_2	2.4 l/min
Repeat 10 - Effect of Temperature	11	1300	0.42	1.5	H_2	2.4 l/min
Repeat 10 - Effect of Reducible Oxide	12	1300	0.37	1.5	H_2	2.4 l/min
Repeat 10 - Compact Be into Disc	13	1320	0.53	1.5	H_2	2.4 l/min

A

ERS - EXPERIMENTAL OBJECTIVES, CONDITIONS AND OBSERVATIONS

IM.*	FLOW RATE	FLOW VELOCITY	WT. GAIN GM.	REMARKS
- N_2	2 1/min	100 cm/min	- -	Pronounced oxidation of metal powder. Muffle - Porous aluminum oxide tube.
- N_2	2 1/min	100 cm/min	- -	Pronounced oxidation of metal powder. Reaction chamber as above.
- N_2	2 1/min	400 cm/min	0.49	Light fiber growth present. Very slight surface oxidation, Graphite reaction chamber.
- N_2	2 1/min	400 cm/min	- -	Substantial fiber growth.
- N_2	2 1/min	400 cm/min	- -	Very few fibers present. Metal not excessively oxidized.
- N_2	? 1/min	400 cm/min	0.42	Boat & contents pushed directly into hot zone in place of three stages as above. Very few fibers present. Reddish colored material noted.
- N_2	2 1/min	400 cm/min	0.31	Graphite boat used. Technique & observations as above.
- N_2	2 1/min	400 cm/min	- -	Trace of fibers only. Metal darkened.
- N_2	2 1/min	400 cm/min	0.54	Weight loss of BeO boat indicates slow loss of material due to vapor transport.
- N_2	2 1/min	400 cm/min	0.53	Molybdenum boat used. No fibers.
- N_2	2 1/min	400 cm/min	0.3	Hydrogen used. Very few fibers.
	2.4 1/min	600 cm/min	- -	310 stainless steel to be used. Small amount of wool formed.
	2.4 1/min	600 cm/min	- -	Be melted, small amount of wool. Compare with No. 23.
	2.4 1/min	600 cm/min	- -	Be melted, fibers like above.
	2.4 1/min	600 cm/min	- -	Small fiber growth from surface of disc.

OBJECT - PURPOSE	RUN NO.	TEMP. °C	CHARGE-GM	TIME-HR.	ATM.*	FLOW RATE
Study Effect of Flow Rate and Dew Point, Al_2O_3 Muffle	14	1475	0.39	0.5	$3H_2$- N_2	4.0 l/min
Study Effect of Temperature and Dew Point	15	1635	0.44	2.0	$3H_2$- N_2	2.0 l/min
Vary Temperature of No. 15	16	1525	0.27	1.5	$3H_2$- N_2	2.0 l/min
Add Graphite to Prevent Excessive Oxidation of Be	17	1530	0.33	0.5	$3H_2$- N_2	2.0 l/min
Vary Temperature of No. 15	18	1330	0.45	1.0	$3H_2$- N_2	2.0 l/min
Study Effect of Atmosphere	19	1500	0.4	0.8	H_2	1.5 l/min
Repeat No. 19	20	1450	0.36	1.2	H_2	2.0 l/min
Study Fiber Growth using Molybdenum Boat	21	1575	1.0	0.2	$3H_2$- N_2	2.0 l/min
Study Effect of Flow Rate	22	1650	0.5	0.5	$3H_2$- N_2	7.0 l/min
Compare with No. 11	23	1300	0.7	0.5	$3H_2$- N_2	2.0 l/min
Use Compact of Be	24	1650	0.25	0.5	$3H_2$- N_2	2.0 l/min
Use Compact of Be Effect of Time	25	1650	0.5	16.0	$3H_2$- N_2	2.0 l/min

* $3H_2$- N_2 indicates cracked ammonia.

	FLOW RATE	FLOW VELOCITY	WT. GAIN GI.	REMARKS
!	4.0 1/min	200 cm/min	- -	Be completely oxidized at dew point of 13°F.
!	2.0 1/min	100 cm/min	- -	Be completely oxidized at dew point of 12°F.
?	2.0 1/min	100 cm/min	- -	Same as prior run.
?	2.0 1/min	100 cm/min	- -	Graphite did not prevent oxidation of Be. Dew point - 18°F.
?	2.0 1/min	100 cm/min	- -	Be completely oxidized. Dew point 18°F.
	1.5 1/min	75 cm/min	Slight growth	Most of Be oxidized. Whisker growth present. Dew point 9°F.
	2.0 1/min	100 cm/min	- -	Be completely oxidized. Dew point 9°F.
2	2.0 1/min	100 cm/min	- -	Some alloying between Be and Mo.
2	7.0 1/min	350 cm/min	- -	Be completely oxidized. Dew point 20°F.
2	2.0 1/min	100 cm/min	- -	Be completely oxidized. Dew point 18°F. Compare with No. 11.
2	2.0 1/min	100 cm/min	Slight growth	Some fiber growth as observed in No. 13. Dew point 20°F.
2	2.0 1/min	100 cm/min	Slight growth	Fibers equal to No. 24. Most of Be oxidized.

OBJECT - PURPOSE	RUN NO.	TEMPERATURE °C	CHARGE Gr.	TII H:
Establish Parameters	26	1365	Be 1.3	0.
Establish Parameter	27	1500	Be 1.0	0.
Effect of time	28	1500	Be 1.3	7.
Effect of TiO$_2$	29	1500	Be 0.9	2.
Effect of Time	30	1500	Be 1.3	3.
Effect of oxidant	31	1425	Be 1.5	1.
Effect of oxidant	32	1500	Be 1.5	3.
Effect of oxidant	33	1525	Be 1.3	2.
Repeat run 33	34	1500	Be 1.4	3.
Preheat Atm.	35	1350	Be 0.7	2
Effect of Temp.	36	1550	Be 1.0	2
Effect of Atm.	37	1500	Be 0.9	2
Effect of Atm.	38	1500	Be 1.1	2
Effect of Charge	39	1500	Be 2.5	2
Effect of Charge	40	1500	Be 1.0	2

A

CHARGE Gm.	TIME Hr.	ATM.	FLOW RATE 1/min	FLOW VELOCITY Cm/min	WT.GAIN Gm.	REMARKS
Be 1.3	0.75	H_2	2	100	-	Be-TiO₂ blen melt
Be 1.0	0.3	H_2	2	100	-	Be-TiO₂ blend formed. Be d
Be 1.3	7.0	H_2	2	100	-	Fiberous gro blend 10:1 u
Be 0.8	2.0	H_2	2	100	-	No whiskers
Be 1.3	3.0	H_2	2	100	-	Very light g
Be 1.5	1.0	H_2	2	100	-	Be-TiO₂ blen growth. Pre-
Be 1.5	3.0	H_2	2	100	-	Be-TiO₂ blen
Be 1.3	2.5	H_2	2	100	-	Be-TiO₂ blen growth.
Be 1.4	3.5	H_2	2	100	-	As above
Be 0.7	2	$3H_2$-N_2	2	100	-	Be-TiO₂ blen of Be.
Be 1.0	2	$3H_2$-N_2	2	100	-	Be-TiO₂ blen growth.
Be 0.9	2	N_2	2	100	.	As above
Be 1.1	2	H_2 dried	2	100	-	As above
Be 2.5	2	H_2 dried	2	100	-	As above
Be 1.0	2	H_2 dried	2	100	-	TiO₂ layer ov growth. Pre-

	FLOW RATE l/min	FLOW VELOCITY Cm/min	WT.GAIN Gm.	REMARKS
	2	100	-	Be-TiO_2 blend 12:1 used. Be did not melt
	2	100	-	Be-TiO_2blend 10:1 used. Few whiskers formed. Be did not melt
	2	100	-	Fiberous growth. Be melted. Be-TiO_2 blend 10:1 used
	2	100	-	No whiskers
	2	100	-	Very light growth
	2	100	-	Be-TiO_2 blend 10:1.2 used. Very small growth. Pre-oxidation.
	2	100	-	Be-TiO_2 blend as above. Pre-oxidation
	2	100	-	Be-TiO_2 blend as above. Fine fiber growth.
	2	100	-	As above
	2	100	-	Be-TiO_2 blend 1:0.5 used. Preoxidation of Be.
	2	100	-	Be-TiO_2 blend 10:1.2 used. Very slight growth.
	2	100	-	As above
·ied	2	100	-	As above
·ied	2	100	-	As above
·ied	2	100	-	TiO_2 layer over Be metal. Very slight growth. Pre-oxidation of Be.

C