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Formation of Alumina Coatings on Beryllia
By a Vapor Deposition Process

G.R.VanHouten
J.F.White
J.M. Botje

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A VAPOR DEPOSITION PROCESS**

G. R. VanHouten
J. F. White
J. M. Botje

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ABSTRACT

This report describes the theoretical and experimental work performed in developing a manufacturing process for cladding BeO and BeO base tubes with α - alumina (corundum). The process employs the formation of alumina from the vapors of aluminum chloride according to the reaction

Suitable process gas compositions and process temperatures for depositing approximately 0.001 inch of dense α - alumina per hour were determined. It was further established that:

1. The production of water vapor by reacting H_2 and CO_2 is the critical rate determining step in the process.
2. Carbon monoxide depresses the rate of alumina deposition.
3. High hydrogen concentrations promote the formation of water vapor by reduction of carbon dioxide.
4. Depending on the process gas composition and operating variables different crystal forms of alumina can be obtained. The recommended operating procedure produces α - alumina having a density of 4.00 gms/cm³.
5. The use of graphite or carbon components of the apparatus causes the formation of carbon monoxide which suppresses the rate of alumina deposition but this effect can be reduced by adding excess H_2 and coating the graphite parts with Al_2O_3 .

A pilot run is described during which the bores of approximately 700 tubes were coated with α Al_2O_3 to a thickness of 0.0006 inch.

TABLE OF CONTENTS

	Page
1.0 Introduction	7
1.1 Reasons for Coating of BeO	7
1.2 Reasons for Selecting Al ₂ O ₃	7
1.3 Disadvantages of Al ₂ O ₃	7
1.4 Scope of Present Work	8
2.0 Background Information and Vapor Deposition	8
2.1 Definition of Terms	8
2.2 History of Vapor Deposition	8
3.0 Theoretical Developments	10
3.1 Thermo-Chemistry	10
3.2 Kinetics	10
3.3 Gas Properties	14
3.4 Heat Transfer	15
3.5 Thermal Stress Analysis	23
3.5.1 Coating Stresses for High Temperature Deposition	28
3.5.2 Thermal Stresses Due to Nonuniform Temperature	28
3.5.3 Stress Relaxation and Residual Stress	28
4.0 Experimental Studies	28
4.1 Factorial Experiment (Series A)	29
4.2 Flow Rate Experiment (Series B)	42
4.3 Surface Temperature Experiment (Series C)	42
4.4 General Discussion of Experimental Results	44
4.5 Summary of Conclusions for Series A, B, and C	45
5.0 Pilot Production Studies	45
6.0 Conclusions	51
References	52
Appendix A	54
Appendix B	61
Appendix C	72

LIST OF ILLUSTRATIONS

	Page
Fig. 3.1 - Free Energy of Reaction vs Temperature	11
Fig. 3.2 - Equilibrium Constant vs Temperature	12
Fig. 3.3 - Variation of Feed Gas Physical Properties With Changes in Initial Composition	16
Fig. 3.4 - Model for Heat Transfer Analysis	18
Fig. 3.5 - Radial ΔT Through Tube Wall vs Distance at Various Flow Rates for a "Typical" Gas Composition	19
Fig. 3.6 - Radial ΔT Through Tube Wall vs Distance at Various Flow Rates for a Very High Conductivity Gas	20
Fig. 3.7 - Required Radiant Wall Temperature for Uniform (Exterior) Sample Temperature for Typical Gas	21
Fig. 3.8 - Required Radiant Wall Temperature for Uniform (Exterior) Sample Temperature for Very High Conductivity Gas	22
Fig. 3.9 - Temperature of Gas Inside Tube vs Distance Through Tube at Various Flow Rates for a "Typical" Gas Composition	24
Fig. 3.10 - Temperature of Gas Inside Tube vs Distance Through Tube at Various Flow Rates for a Very High Conductivity Gas	25
Fig. 3.11 - Temperature of Gas Outside Tube vs Distance Through Tube at Various Flow Rates for a "Typical" Gas Composition	26
Fig. 3.12 - Required Power Input for Uniform (Exterior) Sample Temperature for a "Typical" Gas	27
Fig. 4.1 - Apparatus	30
Fig. 4.2 - Vapor Deposition Flow Diagram	31
Fig. 4.3 - Averaged Effects of Controlled Variables on Al_2O_3 Deposition Rate . .	39
Fig. 4.4 - Crystalline Forms of Al_2O_3	41
Fig. 4.5 - Effect of Al_2Cl_6 Concentration on the Deposition Rate of Al_2O_3	43
Fig. 5.1 - Coating Thickness as a Function of Run to Run Control	48
Fig. 5.2 - Longitudinal Profile by Transverse Sections of Thin Al_2O_3 Coatings . .	49
Fig. 5.3 - Defective Coating Area	50
A1 - Vapor Pressure of $AlCl_3$ as a Function of Temperature	59
B1 - Diffusivity of Hydrogen as a Function of Gas Temperature and Composition .	67
B2 - Diffusivity of Carbon Dioxide as a Function of Gas Temperature and Composition	68
B3 - Diffusivity of Alumina Chloride as a Function of Gas Temperature and Composition	69
B4 - Viscosity of Process Gas as a Function of Composition and Temperature . .	70
B5 - Prandtl Number and Thermal Conductivity as a Function of Gas Composition and Temperature	71
C1 - Flow Diagram of Production Process	73
C2 - Rig for Al_2O_3 Vapor Deposition on Bore of Tubes	75

LIST OF TABLES

	Page
Table 4.1 - Selected Levels for Process Control Variables (Series A)	32
Table 4.2 - Combinations and Results of Factorial Experiment	33
Table 4.3 - Optimum Operating Conditions	38
Table 4.4 - Analysis of Experimental Data - Test Series A	40
Table 4.5 - Experimental Design and Results for Experiment C	42
Table 5.1 - Results of Runs to Produce Thin Al_2O_3 Coatings	47
Table A1 - Method of Selecting Multiplying Factors	55
Table A2 - Calculation of Free Energies and Equilibrium Constants for the Reaction $2\text{AlCl}_3 + 3\text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{Al}_2\text{O}_3 + 3\text{CO} + 6\text{HCl}$ As a Function of Temperature	56
Table A3 - Equilibrium AlCl_3 Vapor Pressure for Different Feed Gas Compositions and Temperatures	60
Table B1 - Initial or Feed Gas Compositions	66
Table C1 - Coating Time Schedule	76

1.0 INTRODUCTION

The present report will present the technology developed in the ANP Program on coating beryllium oxide (BeO) fuel elements with thin coatings of α - alumina (Al_2O_3). The discussion will be limited to presenting the methods and processes developed to meet the needs of the ANP program at the time the development work was done. Consequently values for the process variables have been determined which produce in a consistent manner the desired product, but the methods employed do not necessarily represent a final set of optimal values from both the points of view of economy and technique. The authors are of the opinion that the present work represents a well founded starting point for further development of alumina coatings should the need arise in the future.

1.1 Reasons for Coating of BeO

It is sufficient for the purpose of this report to mention that beryllium (Be) has excellent neutron moderating properties, i. e., low absorption cross section in the thermal energy range and a low atomic weight, which make this element a good choice for a moderator or reflector material. In addition, the ability of beryllium to form stable oxides which have a low vapor pressure and good mechanical strength up to temperatures as high as 2600° F, makes it an attractive choice as a material for high temperature reactor fuel carrier or moderator elements for a direct air cycle reactor. A detailed discussion of the above points may be found in Reference 1.

In the presence of water vapor, however, beryllium oxide has a tendency to hydrolyze, according to the chemical reaction

The above reaction has been identified previously (cf. References 2 and 3) and a detailed discussion is presented in Ref. 1, Vol. 1, pp 93-112.

The coating of BeO is required to prevent the above mentioned hydrolysis or water vapor corrosion. In addition to this primary advantage, when coated BeO is used as a fuel carrier there are some secondary advantages such as a decrease in activity level due to a decrease in fission fragment release, either by recoil or diffusion. This subject is adequately covered in Ref. 1, Vol. 2, pp 33-81.

Also a decrease in surface roughness of the heat transfer surfaces can be obtained by using the coatings. This results in an improvement in cycle performance by reducing parasitic pressure losses.

1.2 Reasons for Selecting Al_2O_3

The selection of alumina as a coating material was based on the fact that alumina forms a dense and strong phase which is not susceptible to hydrolysis. In addition to this the nuclear cross section for absorption is small so that the poisoning effect is small. Also the material does not present an activation problem.

In the design area the introduction of alumina coatings presents an acceptable weight penalty and the thermal conductivity of the alumina is sufficiently high so that it does not result in unacceptable design penalties in the aero-thermodynamic design area.

1.3 Disadvantages of Al_2O_3

The most outstanding disadvantage to the use of alumina as a coating for beryllia results from the incompatibility of the thermal expansion of these materials. This incompatibility results in thermal stresses even if the fuel elements are at a uniform temperature. The temperature variations within the fuel element due to the internal heat flows tend to further aggravate this problem. In serious cases the difference in thermal expansion may result in cracking or spalling of the coating.

In relation to this thermal expansion problem, it must be appreciated that a lower value of the thermal conductivity of the coating will result in a larger temperature drop through the coating which in turn tends to add to the thermal stress problem.

1.4 Scope of Present Work

The program conducted at GE-ANPD was directed primarily toward developing on a short time basis a process which would yield in a reproducible manner a coating of dense α -alumina. Primary emphasis was placed on developing this process for application to relatively small batches of tubes, in which case the economy of the process was not an overriding factor. It is the opinion of the authors, however, that the present process can be successfully applied without major modification to large scale production.

The following aspects of the problem were investigated in detail and will be discussed in the subject report: Thermo Chemistry, Reaction Kinetics, Gas Properties, Heat Transfer, and Stress Analysis.

The theoretical and experimental work will be discussed where applicable, in that order. In line with the above remarks it should be pointed out that the effects of adding inert carrier gases to the process gas and also that the effects of operating the process at reduced pressure, i.e., less than atmospheric, were not investigated. It is thought that these two devices may result in a superior process, particularly in case of large scale operations, but as mentioned previously, these aspects were not considered pertinent to the problem as posed at the time.

2.0 BACKGROUND INFORMATION ON VAPOR DEPOSITION

2.1 Definition of Terms

Vapor Plating - Electroplating is a term normally restricted to the deposition of a coating which is expected to adhere to a base layer, as opposed to electrowinning (as in extractive metallurgy) or electroforming (as for wave guides), where the presence of a base layer is only incidental and usually temporary. Accordingly, the term, vapor plating, will be used to describe a vapor deposition operation where the end objective is a coated surface.

Vapor Pyrolysis - Pyrolysis is defined as chemical decomposition by the action of heat. While some inorganic coatings may be formed by vapor decomposition, the deposition of alumina by reaction of vapor phase halide with oxygen or an oxygen compound is actually a displacement reaction. Use of the term vapor pyrolysis will be restricted to those cases where it is technically correct.

2.2 History of Vapor Deposition

Mellor⁴ refers to the pioneering efforts of the following: Berzelius (circa 1824)⁵, Serullas (circa 1831)⁶, Beketoff (circa 1859)⁷, Friedel and Ladenburg (circa 1869)⁸, Berthelot (circa 1878)⁹, Seubert and Schmidt (circa 1892)¹⁰, Vigoroux et al (circa 1896 - 1907)¹¹, and Parravano and Mazetti (circa 1923)¹².

Chemical Abstracts for 1907 lists at least seven papers on the reaction of volatile metal halides by a single author (Vigoroux)¹³.

Berzelius⁵ found that when silicon tetrachloride vapor struck heated potassium, potassium chloride and metallic silicon were formed. Seubert and Schmidt¹⁰ found that silicon tetrachloride vapor reacted with hot (dull red) magnesium to form magnesium silicide and silicon. Vigoroux formed iron, chromium, cobalt and nickel silicides in a similar fashion. Mond and coworkers¹⁴ and Berthelot⁹ discovered the existence of volatile metal carbonyls. Each of these carbonyls yields a bright metallic mirror on decomposition. In 1890, Mond

et al reported, "... and when the tube through which the gas passes is heated, a mirror of metallic nickel is produced."

By 1910, metallic mirror films formed by the pyrolysis of metal carbonyls included nickel, iron, chromium, cobalt, molybdenum, tungsten, ruthenium and the other platinum group metals and probably copper. Rhenium films were formed later in a similar manner.

Wöhler¹⁵ in 1827 noted that anhydrous aluminum chloride fumed in moist air, and smelled of hydrogen chloride. Berthelot in 1878 stated that when aluminum chloride vapor was heated with oxygen to red heat, chlorine was displaced, either due to the formation of an oxychloride or to the balanced reaction

Mellor (in 1926) accepted these concepts, stating that since the heat of formation of Al_2O_3 was 391.6 kcal and that of Al_2Cl_6 was 301.8 kcals, the latter reaction was thermodynamically feasible.

Powell et al¹⁶ have included a selective literature review in their book, and also in their original report¹⁷ and in a subsequent publication¹⁸. All of these describe the evolution of various vapor deposition techniques.

During the late 1940's experiments were conducted at Battelle Memorial Institute (BMI) on the vapor deposition of ceramics, including the direct reaction of volatilized metallic compounds with oxygen. It was found that the reaction rates were difficult to control and oxygen donors were substituted for oxygen. Water vapor was found to react quite rapidly with the volatile halides and consequently carbon dioxide and hydrogen were substituted for the water vapor. The rate of formation of water vapor from the latter reaction can readily be controlled by manipulating the temperature level.

It could thus be considered as established that inorganic coatings can be formed by the reaction or decomposition of the appropriate vapor at or near the surface to be coated. The coatings formed in this manner may combine many of the advantages associated with electrodeposited coatings with some advantages unique to vapor deposition. It is, for instance, possible to apply the coating at or near the intended operating temperature of the substrate or at least with the substrate being at that temperature. This procedure can result in a noticeable reduction in the tendency toward spalling. Many coatings are highly stressed in the as-deposited condition (cf. Ref. 19); furthermore, if the effects of the mismatches in the values of the coefficients of thermal expansion are additive the stress at the operating temperature may cause strains beyond the elastic limit of the coating or the substrate (cf. Ref. 20, 21, and 22).

Vapor-plated coatings may also exhibit better continuity and freedom from intercommunicating porosity than the usual electro-deposits of equivalent thickness; moreover, the thickness of the coating can be readily varied and coatings may be applied to irregular shapes and machined or ground surfaces.

It was consequently decided to investigate the application of vapor plating alumina onto a beryllia substrate. Preliminary experiments at the General Engineering Laboratory of the General Electric Company at Schenectady, New York had yielded promising results. Initial attempts at GE-ANPD to reproduce these results also yielded good coatings, but in general the reproducibility was poor.

It was attempted to learn as much as was practicable about the reaction while improving the reproducibility of the process and reducing the time required to apply the coating.

3.0 THEORETICAL DEVELOPMENTS

3.1 Thermo-Chemistry

Powell et al¹⁶ describe a procedure for the vapor plating of surfaces with alumina. The procedure employs a mixture of aluminum chloride, carbon dioxide and hydrogen gases. It is intuitively obvious and it has been experimentally verified that selection of the proper operating temperature, pressure and gas composition will drive the reaction

to the right. However, little is found in the literature concerning this reaction. Accordingly, as a first step, it was decided to derive data on the thermochemical behavior of this reaction as a function of temperature using known free energies of formation of the various reagents and reaction products employing the data given in Reference 23. The procedure followed is described in detail in Appendix A.

The results of the calculations are presented in Figures 3.1 and 3.2. It is apparent from the figures that thermodynamics of the reaction are favorable over the entire temperature range of interest. It is also apparent both from intuition and from the examples presented in the Appendix A that the final equilibrium concentrations of any of the reagents or reaction products can be controlled at any desired level by proper choice of initial concentrations of the reagents provided the reaction proceeds at a reasonable rate under the given set of operating conditions.

It is now reasonable to proceed with an analysis of the probable kinetics of the reaction as a function of temperature because the thermodynamic aspects of the reaction appear favorable over a very wide temperature range.

It should be understood, however, that different reagents might be used as a source of Al^{+++} and O^{--} , if the kinetics of the present reaction cause unsurmountable process scale-up problems. Other vapor plating reactions which also yield Al_2O_3 as a product can be evaluated in a fashion similar to that presented in Appendix A.

Exit gas compositions were calculated starting from a number of different feed gas compositions for a range of temperatures. The results are presented in Appendix A, Table A3. It is apparent upon inspection of these results that the equilibrium reaction tends to move to the right until the partial pressure of one of the reagents decreases to less than 3.5 mm Hg.

It is possible to maintain a relatively high equilibrium concentration of AlCl_3 by supplying a low CO_2 or H_2 pressure in the feed gas. This may be required if the reaction is a surface reaction, where the rate is dependent on the number of AlCl_3 particles striking the surface per unit time. The desirability of low CO_2 or H_2 pressures will be further evaluated in the discussion of the kinetics of the reaction. It may also be observed that an addition of CO to the feed gas inhibits the trend of the reaction to the right.

All of the results presented in Table A3 apply for a total system pressure of one (1) atmosphere. While total system pressure is important thermodynamically it is much more important kinetically and will be discussed in that part of the study.

3.2 Kinetics

Literature searches conducted in connection with the present work have not resulted in finding specific information on the reaction mechanism of the alumina vapor plating process. Therefore, the relative importance of each of several possible mechanisms as a

function of temperature, pressure, gas composition, etc., was, at first, primarily a matter of conjecture. Such conjecture, however, is extremely valuable in establishing or in reviewing an experimental program to assure that the proper experiments are selected to provide the necessary answers over the entire range of process operating conditions.

Presently the probable importance and effects of the water-gas reaction will be reviewed. It is known that even at room temperatures and below, water vapor will spontaneously and rapidly react with anhydrous aluminum chloride to form hydrated, mixed aluminum-oxychlorides. Providing the ambient temperature is sufficiently high alumina is formed rather than the oxychloride. Therefore, the over-all reaction $2\text{AlCl}_3 + 3\text{CO}_2 + 3\text{H}_2 \rightarrow \text{Al}_2\text{O}_3 + 3\text{CO} + 6\text{HCl}$ may well proceed as a sequence of reactions in which the formation of water vapor is a key step.

In a recent experimental study Graven and Long²⁴ point out the fact that the reaction $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{H}_2\text{O} + \text{CO}$ is not surface catalyzed. Obviously, however, if the surface is hotter than the main gas stream, the gas will react faster at or near the hot surface than in the colder areas. The authors cite five references to show that above 500°C the reaction reaches equilibrium in seconds or less.

Graven and Long developed the following empirical equations to describe the over-all forward and reverse reaction rates as functions of temperature. The equations represent the data very well over the temperature range studied (0°C to 900°C).

Forward:

$$\frac{d [\text{H}_2\text{O}]}{dt} = \frac{9.5 \times 10^{10} \exp (-57000/RT) [\text{H}_2]^{1/2} [\text{CO}_2]}{1 + 3.6 \times 10^3 [\text{CO}]}$$

Reverse:

$$\frac{d [\text{CO}_2]}{dt} = \frac{5.0 \times 10^{12} \exp (-67300/RT) [\text{CO}]^{1/2} [\text{H}_2\text{O}]}{(1 + 1.2 \times 10^4 [\text{H}_2])^{1/2}}$$

An analysis of the rate dependency of the forward equation will show that:

1. Decreasing the H_2 concentration two orders of magnitude decreases the reaction rate only one order of magnitude.
2. Decreasing the CO_2 concentration two orders of magnitude decreases the reaction rate two orders of magnitude.
3. Adding CO to the amount of about 0.3 mole CO per mole of mixture decreases the reaction rate three orders of magnitude.

Therefore, changes in the H_2 concentration have the least effect on the reaction rate and changes in the CO concentration have the largest effect on the reaction rate. Consequently, if H_2O is considered an essential intermediate, then the following observation can be made: if it is desired to maintain the rate of formation of water as nearly constant as possible throughout the run and also to control the over-all reaction by allowing one of the reagents to be almost completely depleted, then these objectives can be best accomplished by:

1. allowing the hydrogen to be almost depleted, and;
2. adding enough CO to the feed gas so that the relative change in CO concentration is small.

If the reaction must occur at a maximum rate it is obvious that any CO present must be removed at once.

Experimental results to date indicate that homogeneous vapor phase formation of Al_2O_3 "smoke" is competing with the heterogeneous phase surface deposition of Al_2O_3 . Thermodynamic calculations and experimental observations show that water vapor reacts very rapidly with aluminum chloride at low temperatures. Therefore, postulating that Al_2O_3 is deposited on the surface only when an AlCl_3 or Al_2Cl_6 molecule strikes a surface-sorbed H_2O molecule or a H_2O molecule very near the surface, it will be advantageous to depress the rate of water formation and also the dependence of the rate of water formation on reagent concentration in all areas removed from the surface, such that water vapor will primarily be formed at or immediately adjacent to the hot surface. The addition of a small amount of CO to the feed gas should be very beneficial in reducing the rate of formation of Al_2O_3 smoke assuming the above proposition to be correct. In summary, based on the "water-gas" reaction behavior, it would appear desirable to have a low concentration of CO_2 , a high CO/ CO_2 ratio, and a fairly high AlCl_3 concentration in the feed gas.

Analyzing the temperature dependent portion of rate equation, it is apparent by inspection that the reaction will proceed very rapidly if $\frac{12,480}{T} \leq 10.98$, or $T \geq 1137^\circ\text{K} = 1588^\circ\text{F}$.

The relative rates of the forward reaction are tabulated below.

Rate of H_2O Formation	$^\circ\text{K}$	Temperature $^\circ\text{C}$	$^\circ\text{F}$	T ($^\circ\text{F}$) Increase For A Tenfold Rate Change
R	1137	864	1588	167
$R \times 10^{-1}$	1044	771	1421	144
$R \times 10^{-2}$	964	691	1277	126
$R \times 10^{-3}$	894	621	1151	103
$R \times 10^{-5}$	779	506	944	67
$R \times 10^{-10}$	594	321	611	41
$R \times 10^{-15}$	480	207	406	28

The analysis indicates that the rate of formation of water vapor can be kept more uniform despite local changes in gas concentration if the proper starting gas compositions are selected. It is also indicated that the formation of water vapor can be depressed strongly by proper control of the CO-content, perhaps under the correct conditions so strongly that the rate becomes appreciable only when the gas is heated to temperatures approaching the temperature needed for a reaction on the work surface. This implies that the formation of H_2O will occur primarily at or near the hot surface if the bulk of the gas remains cool and the boundary layer can be kept thin. Discussion of viscosity and flow characteristics required to attain low gas temperatures and low stagnant or laminar flow film thicknesses will be found in subsequent paragraphs of this report.

3.3 Gas Properties

The vapor plating of alumina was shown to consist of the reaction of aluminum chloride with gaseous hydrogen and carbon dioxide to form gaseous carbon monoxide and hydrogen chloride reaction products. The change in composition as the reaction progresses results in an appreciable change in the physical properties of the gaseous mixture. The effect of changes in gas bulk temperature as the gas is heated in passing over the work surface are superimposed on the effects of the chemical composition changes.

The variations in physical properties, as a result of temperature changes and changes in composition induced by the reaction, have been computed using statistical mechanics. For example, simple additive relationships do not hold for determining the viscosities, thermal conductivities and diffusivities of mixtures of gases. The equations employed in the calculations are presented in Appendix B. A qualitative discussion of the importance of each of the properties is given on the following page.

Viscosity is an important factor because it determines the rate of heat transfer and the rate of diffusion of reagents and reaction products across the laminar boundary layer. Viscosity variations also influence the thermally induced transfer of heat by turbulence. Turbulent heat transfer, of course, will result in an appreciably higher rate of transfer than laminar heat transfer. In particular the concentration of hydrogen will materially affect the viscosity of the mixture.

It is well known that the Reynolds number is the dimensionless parameter which is essential in deciding if a flow should be expected to be laminar or turbulent. The Reynolds number is a function of the kinematic viscosity of the mixture, i. e. the viscosity divided by the density of the vapor. The variation in kinematic viscosity as a function of changes in gas composition and temperature therefore is obviously an important factor in determining the rate of heat transfer, the bulk and local gas temperature, and therefore the gaseous phase reactions.

Diffusivity coupled with the concentration gradient will determine the rate at which reagents are transported to the reaction site and the rate at which reaction products are carried away from there. Both surface catalyzed and homogeneous gaseous phase intermediate reactions have been postulated as part of the over-all reaction. Diffusivity values are important considerations for all of these reactions.

The specific heat of the gas mixture is an important variable because the rate of heat transfer divided by the heat capacity of the gas determines the rate of temperature change of the gas. The importance of the water-gas reaction has been discussed in a preceding section. The rate of this reaction is strongly temperature dependent and consequently the length of time required to heat up the gas becomes a very important factor.

The Prandtl number is another useful value in determining rates of heat transfer under both laminar and turbulent flow conditions. The Prandtl number is normally not sensitive to changes in gas composition, but in the present case where aluminum chloride and hydrogen are present which both have somewhat exceptional properties, the Prandtl number may well show a significant variation with changes in gas composition. Therefore, a plot of Prandtl number as a function of gas composition at varying temperatures represents useful information.

The equations, procedure and other data pertinent to the computations of the properties are presented in Appendix B. The amount of physical property data generated is too voluminous to be presented in the context of the present report. The total results are, however, available under Reference 25.

An insight into the results of the calculations can, however, be gained from the chart presented in Figure 3.3. The variation of diffusivity, thermal conductivity and fluidity are presented at one selected temperature level (i. e. 900°C) for three gas compositions. The sizable decrease in the value of the diffusivity for all gas compositions is apparent and should be attributed to the decrease in hydrogen concentration. These changes are of importance because the diffusivity controls the rate at which the reagents reach the surface. It should be noted particularly that the gas composition changes as the gas passes over the work surface. With the substantial changes in physical properties a problem must be anticipated in maintaining uniform work surface temperatures and in obtaining coatings of uniform thickness.

The problem of maintaining uniform work surface temperatures will be discussed in the next paragraph.

3.4 Heat Transfer

In paragraph 3.2 it was postulated that the rate controlling reaction in the alumina

Fig. 3.3 – Variation of feed gas physical properties with changes in initial composition

vapor plating process is the formation of water vapor by reacting hydrogen and carbon dioxide. This reaction is promoted by high temperatures. In the present process the objective is to obtain a uniform coating deposited on the surface.

It is a reasonable assumption that the formation of Al_2O_3 in the vapor phase can be suppressed by maintaining a low temperature in the process gas and that the deposition on the surface to be plated can be promoted by raising the surface temperature. It was further assumed that a uniform surface temperature would promote the formation of a uniform coating.

The formation of a coating on both the inside and outside diameter of a tube was desired. Consequently the model postulated for the analysis represented a muffle surrounding a tube. The process gas was assumed to flow both through and around the tube. The details of the model are shown in Figure 3.4.

The electrical properties of BeO render it impossible to generate heat internally by induction or resistance heating. Therefore the heat input into the tube was accomplished by thermal radiation from the muffle.

Figure 3.4 shows a hollow cylinder surrounded by an enclosing pipe. The hollow cylinder has the same inside diameter as the 5-inch-long beryllia tube and its outer diameter was so chosen that the cross-sectional area of the hollow cylinder would be the same as that of the beryllia tube with its hexagonal outer boundary. The pipe which surrounded the model tube had a diameter such that its cross-sectional area would be equal to the "cell" area in the actual heater configuration. Heat was assumed to flow from the pipe wall of radius r_3 to the outer surface of the model hollow cylinder by thermal radiation. Convective heat transfer to the gas stream w_2 takes place from the pipe wall and the outer hollow cylinder wall. Heat is transferred by conduction through the hollow cylinder wall and leaves the inner wall of radius r_1 by convection into the gas stream flow w_1 .

A thermal boundary layer starts building up from the leading edge of the model tube in the flow passages filled by the flow rates w_1 and w_2 . This build-up takes place on both the inner and outer surfaces of the tube and on the pipe wall. The resultant variation of the laminar heat transfer coefficient as a function of the distance x for the two flows w_1 and w_2 was taken from curve 3, Figure 3, Reference 27. The two flow rates w_1 and w_2 merge at the exit of the tube into a single flow rate w_{tot} and the flows w_1 and w_2 were determined assuming the pressure drops through the central hole in the tube and in the outer annulus flow passage be the same.

The results of this investigation are shown in Figures 3.5 through 3.12. In all of the figures three independent variables are employed: the distance from the tube inlet, a thermal conductivity ratio $\bar{k}$, and the product of Reynolds number and Prandtl number $N_{\text{Re}} \cdot \text{Pr}$. The thermal conductivity ratio is the ratio of the thermal conductivity of the beryllia to that of the gas. In the $N_{\text{Re}} \cdot \text{Pr}$ product, the Reynolds number is based on the total weight flow w_{tot} , the diameter of the enclosing pipe $D_{\text{H, tot}}$, and the cross sectional area of the enclosing pipe A_{tot} .

Figures 3.5 through 3.12 have all been compiled for an outer tube wall temperature $T_{w,2} = 1040^\circ\text{C}$, and a gas inlet temperature $T_{\text{en}} = 205^\circ\text{C}$. Figures 3.5 and 3.6 show the variation of radial temperature drop through the wall $T_{w,2} - T_{w,1}$ as a function of distance along the sample for the two conductivity ratios 1000 and 100. The value of $N_{\text{Re}} \cdot \text{Pr}$ is shown as parameter on the curves. It is noted that the radial temperature difference through the beryllia is less than 4 degrees for points farther than 1 inch from the inlet, except for the case where the conductivity ratio equals 100.

Figures 3.7 and 3.8 show the temperature of the radiating muffle surface $T_{w,3}$ as a

Fig. 3.4 - Model for Heat Transfer Analysis

RADIAL ΔT THROUGH TUBE WALL VS. DISTANCE
AT VARIOUS FLOW RATES FOR A
"TYPICAL" GAS COMPOSITION

FIGURE 3.5

RADIAL ΔT THROUGH TUBE WALL VS DISTANCE
AT VARIOUS FLOW RATES FOR A
VERY HIGH CONDUCTIVITY GAS

FIGURE 3.6

REQUIRED RADIANT WALL TEMPERATURE
FOR UNIFORM (EXTERIOR) SAMPLE
TEMPERATURE FOR TYPICAL GAS

FIGURE 3.7

REQUIRED RADIANT WALL TEMPERATURE
FOR UNIFORM (EXTERIOR) SAMPLE
TEMPERATURE FOR VERY HIGH
CONDUCTIVITY GAS

FIGURE 3.8

function of axial distance. The excessive temperatures that must be maintained on the muffle in the inlet section of the system in order to maintain $T_{w,2} = 1040^\circ\text{C}$ are apparent.

The variation of gas temperature in the center hole of the tube $T_{b,1}$ with distance through the tube is shown in Figures 3.9 and 3.10. It will be noted that at any given distance x through the tube, the average gas temperature $T_{b,1}$ increases with decreasing value of $N_{Re} \cdot Pr$. It is also pointed out that the results are almost independent of the conductivity ratio k . The same observations are correct for the gas flowing through the annulus between the muffle and the tube, as shown in Figure 3.11.

The required power input for conductivity ratio of 1000 is shown in Figures 3.12. The power input required for maintaining $T_{w,2} = 1040^\circ\text{C}$ can be obtained experimentally at distances more than one-half inch from the inlet of the tube. In the entrance region of the tube, however, the variation of the required power is too rapid to permit realization. This is due to the fact that the heat transfer coefficient is decreasing from a high value at the entrance of the tube to its fully developed value further down the tube; for conductivity ratios less than 1000 progressively larger power inputs are required.

The analogy between heat transfer and mass transfer makes it possible to replace the Prandtl number in the correlation for the heat transfer coefficient by the Schmidt number in the correlation for the mass transfer coefficient²⁸. The mass transfer rate $\dot{m}$ is then given by

$$\dot{m} = b (C_s - C_w)$$

where,

- b = mass transfer coefficient
- C_s = concentration in the stream
- C_w = concentration at the wall

The above equation is limited in its application to regions of uniform temperature²⁸. Several observations, however, appear warranted. Assuming that a uniform wall temperature of the surface has been achieved then a uniform coating will only develop if $\dot{m}$ is constant along the surface. This condition could be satisfied if the values of b and $(C_s - C_w)$ could either be constant or show mutually compensating variations as a function of distance along the tube. From the similarity of the variation of physical properties and diffusion coefficients as a function of temperature it may be readily deduced that the values of the mass transfer coefficient must decrease in the direction of flow similar to the change in value of the heat transfer coefficients. In addition the reagent concentrations will decrease along the tube effecting a decrease in the value of $(C_s - C_w)$. Thus the layer will vary in thickness along the tube, being thicker toward the inlet end of the tube.

The means to decrease this variation include providing a gas mixture which would result in relatively small concentration variations along the length of the tube and also operating at larger flow rates which would result in the same effect. It is obvious that larger flow rates would result in a less efficient use of chemicals and also would require larger heat inputs, making it less likely that uniform work surface temperatures will be obtained.

The excessive heat inputs required at the leading edge of the tubes indicate that it is unlikely that satisfactory coatings can be deposited in that region.

3.5 Thermal Stress Analysis

Thermal stresses are induced in the tubes due to three reasons:

1. deposition of the coating at elevated temperatures

TEMPERATURE OF GAS INSIDE TUBE
VS.
DISTANCE THROUGH TUBE
AT VARIOUS FLOW RATES FOR A
"TYPICAL" GAS COMPOSITION

FIGURE 3.9

TEMPERATURE OF GAS INSIDE TUBE
vs.
DISTANCE THROUGH TUBE
AT VARIOUS FLOW RATES FOR A
VERY HIGH CONDUCTIVITY GAS

FIGURE 3.10

TEMPERATURE OF GAS OUTSIDE TUBE
VS.
DISTANCE THROUGH TUBE
AT VARIOUS FLOW RATES FOR A
"TYPICAL" GAS COMPOSITION

FIGURE 3.11

REQUIRED POWER INPUT FOR
UNIFORM (EXTERIOR) SAMPLE
TEMPERATURE FOR A "TYPICAL"
GAS

FIGURE 3.12

2. nonuniform temperatures due to internal heat flows.
3. stress relaxation at high temperatures.

The above items will be discussed separately below.

3. 5. 1 Coating Stresses for High Temperature Deposition

The coating is deposited on the tube when the tube is at a uniform or nearly uniform elevated temperature. It is assumed that the coating and the tube are stress free at the time the coating is being formed. In general the tube and the coating will have different thermal expansion properties and consequently upon cooling or heating the clad and substrate will have a tendency to shrink or expand by different amounts. Continuity between the clad and substrate can then only be maintained by assuming that internal stresses are generated in the body which restore dimensional compatibility between the various parts.

3. 5. 2 Thermal Stresses Due to Nonuniform Temperature

Thermal stresses can also result in an isotropic body due to internal nonuniformities of the temperature. These temperature variations could result from internal heat generation or external heat input. Again elements that are initially stress free when at uniform temperature become incompatible as the temperature distribution in induced and internal stresses result.

The computer program discussed in Reference 29 is designed to solve these problems for tubular elements having a circular cross section. Three concentric regions having different physical properties are possible and an arbitrary temperature profile can be specified.

A more sophisticated analysis including the effects of a hexagonal external contour and the end effects resulting from the finite length of the tubes is incorporated in Program ANP 602 (cf. Reference 30).

3. 5. 3 Stress Relaxation and Residual Stress

It is important to observe that all of the above stress analyses are based on the theory of elasticity. Experimentally it has been observed, however, that at elevated temperatures a substantial amount of plastic strain can occur in materials which exhibit brittle behavior at room temperature. It has been experimentally demonstrated that the stress relaxation phenomenon can cause failure of elements at room temperature subsequent to their exposure to thermal stress for extended periods at high temperature³⁰.

The above observation may be explained as follows: A stress free element is raised to high temperature and a thermal stress condition is induced in the element. This condition is maintained for an extended period and the result will be that the induced stresses gradually decrease by plastic strain or stress relaxation. Upon subsequent cooling to room temperature without allowing sufficient time for relaxation the aforementioned plastic strains will result in a stressed condition of the element, the stresses being called residual stresses. The residual stresses are opposite in sign to the original elastic thermal stresses and in the case of BeO they are larger in absolute magnitude than the original elastic stresses. In the case of BeO the strength at room temperature is less than at elevated temperatures and therefore failure at room temperature due to residual stresses is very likely. This phenomenon is discussed in a more quantitative manner in Reference 30.

4. 0 EXPERIMENTAL STUDIES

A series of experiments was conducted to determine the influence of the process variables on the rate of deposition and the structure of the coating. The experiments were

the following: (1) the factorial experiment (Series A), (2) flow rate effects experiment (Series B), and (3) surface temperature effects experiment (Series C). The experiments and the results will be discussed in detail in the following paragraphs.

4.1 Factorial Experiment (Series A)

The factorial experiment was conducted to determine the effects of varying eight controllable process variables at two control levels. The variables and the selected levels are presented in Table 4.1. The test apparatus is shown in Figure 4.1 and the flow diagram is shown in Figure 4.2.

The values in Table 4.1 were selected for the following reasons:

- a. Aluminum chloride: the extreme low (0.0035) and extreme high (0.040) mole concentrations bracketed all conditions expected to be useful.
- b, c. Hydrogen and carbon dioxide: the concentration ranges (0.3 - 0.662) allowed sufficient variation to detect major changes in the results induced by variations in hydrogen or carbon dioxide concentration. The flow rates were also selected to fit within available equipment limitations because problems were encountered in freezing of CO₂ valves and also because the samples could not be maintained at the proper temperature at the higher flow rates. The initial objective was to obtain a range of Reynolds Numbers from 25 to 4000, because the transition from laminar to turbulent flow occurs at about $N_{Re} = 2100$. Equipment limitations made routine testing at higher values of the Reynolds number impractical.
- d, e. Carbon monoxide and hydrogen chloride: the presence of these reaction products can inhibit or reverse the reaction. Consequently both carbon monoxide and hydrogen chloride were added to the feed gases so that the effect of these reaction products could be identified. The specific level for carbon monoxide (2 liters per minute or 0.047 to 0.1 mole concentration) were equivalent to the amount of carbon monoxide which would be present if enough water vapor were formed to react with all the aluminum chloride. Moreover, carbon was employed in the construction of some of the chemical reactor components and it was known that the carbon dioxide-carbon monoxide reaction might yield terminal carbon monoxide concentrations which were appreciably higher than those to be expected from the stoichiometric action of aluminum chloride with water. It was known that carbon monoxide formed in this manner would serve as a depressant on the water gas reaction and it was expected that the presence of carbon monoxide could in turn depress the rate of aluminum oxide formation.

The value selected for the hydrogen chloride concentration was based on the quantity of aluminum oxide which would be formed if all of the aluminum chloride feed was reacted completely.

- f. Coating time: the coating times were set such that the tests could be completed in a minimum of time compatible with obtaining a measurable coating. It was decided to investigate coating times of 20 and 40 minutes to prove that the rate of deposition was constant and to establish the reproducibility of the tests.
- g. Coating temperature: coating surface temperatures of 1000°C and 1100°C were selected because the higher temperature assures the formation of alpha-alumina and previous experiments had indicated that relatively good coating rates were obtained at those temperatures. Also, those temperatures were well suited to the available process equipment and appeared to produce appreciable differences in the crystal habit of the deposit.
- h. Precoating: the use of a precoating deposited at a lower temperature was expected to increase the number of nucleation sites and it was expected that an extremely fine crystalline form of high temperature alumina might be produced if

Fig. 4.1 - Experimental vapor coating apparatus (U-37557)

$$T_1 \approx T_2 \approx 150^\circ\text{C}$$

$$800^\circ\text{C} \leq T_3 \leq 1430^\circ\text{C}$$

Fig. 4.2 – Vapor deposition flow diagram

the sample were precoated. Normally a fairly coarse grained alumina deposit resulted from coating at a single high temperature. The precoat temperature was chosen as 850°C since the rate of deposition at that temperature was expected to be acceptably rapid and also because literature references reported those deposits to be extremely fine grained.

TABLE 4.1
SELECTED LEVELS FOR PROCESS CONTROL VARIABLES
(SERIES A)

- a. Aluminum chloride feed rate
 - A. 2 g/minute (0.0035 - 0.008 initial Al_2Cl_6 mole concentration)
 - B. 10 g/minute (0.020 - 0.040 initial Al_2Cl_6 mole concentration)
- b. Hydrogen feed rate
 - A. 10 l/minute (0.30 - 0.495 initial mole concentration)
 - B. 20 l/minute (0.498 - 0.662 initial mole concentration)
- c. Carbon dioxide feed rate
 - A. 10 l/minute (0.30 - 0.495 initial mole concentration)
 - B. 10 l/minute (0.498 - 0.662 initial mole concentration)
- d. Carbon Monoxide
 - A. None added
 - B. 2 l/minute (0.047 - 0.10 initial mole concentration)
- e. Hydrogen Chloride
 - A. None added
 - B. 0.2 l/minute (0.0047 - 0.01 initial mole concentration)
- f. Coating Time
 - A. 20 minutes
 - B. 40 minutes
- g. Coating Temperature
 - A. 1000°C
 - B. 1100°C
- h. Pre-Coat
 - A. None
 - B. 20 minutes at 850°C

The following results or responses of the experiment were analyzed:

- a. Deposition rate in grams per minute.
- b. Alpha count (counts per minute) from inside surface at entrance of tube.
- c. Alpha count (counts per minute) from inside surface at exit of tube.
- d. Alpha count (counts per minute) on outside surface of tube from side which was upward in the experiment.
- e. Alpha count (counts per minute) on outside surface of tube from side which was downward in the experiment.

+ = High Level
- = Low Level

TABLE 4.2
COMBINATIONS AND RESULTS OF FACTORIAL EXPERIMENT

LEVELS									RESPONSES				
Combination	Single or Multiple Temperature	CO ₂	CO	HCl	AlCl ₃	H ₂	Time	Temp	Alpha Count				Average Deposition Rate (gms/min)
									Inside		Outside		
									Entrance	Exit	Up	Down	
									(counts/min)				
1	-	-	-	-	-	-	-	-	190	878	12019	8354	.007
2	+	-	-	+	+	+	-	+	90	1040	6521	6066	.0012
									2880	23239	26923		
3	-	+	+	+	+	-	+	-	47	600	31924	25331	.0021
									307	1510	29143	21716	
4	+	+	+	-	-	+	+	+	372	1470	23889	36269	.0005
									2099	2684	26536	25472	
5	+	-	-	+	-	-	+	-	2485	1945	58909	43284	.002
									42	158	4898	1911	
6	+	+	+	-	+	-	-	-	54	526	4014	5160	.0008
									1423	2165	36046	28606	
7	-	-	-	-	+	+	+	+	2457	2905	28434	35067	.004
									26	1034	8424	18153	
8	-	+	+	+	-	+	-	+	23	620	6224	10402	.0002
									3079	3025	5463	44835	
9	+	-	+	-	-	-	-	+	3159	3070	58639	55183	.0034
									73	1575	42621	49887	
10	-	+	-	-	-	+	+	-	1389	28009	28746		.0041
									66	170	1492	2979	
11	-	-	+	+	+	+	-	-	46	362	3666	6542	.0025
									570	2142	15193	14593	
12	+	+	-	+	+	-	+	+	660	1942	20202	19894	.0016
									693	975	15687	22401	
13	-	+	-	-	+	-	-	+	650	815	18132	19828	.0027
									573	1958	25078	47272	
14	+	+	-	+	-	+	-	-	310	2160	35540	29179	.0013
									1231	640	12363	17174	
15	-	-	+	+	-	-	+	+	808	1410	17468	18105	.0062
									60	1268	3829	16592	
16	+	-	+	-	+	+	+	-	86	1118	41838	49498	.0004
									845	709	8026	11710	
17	-	-	-	-	+	-	+	-	666	678	7720	8424	.0033
									103	1003	20625	21229	
18	-	+	+	+	-	-	-	-	71	954	17622	14738	.0028
									206	1902	7427	8777	
19	+	-	-	+	-	+	+	+	138	958	7053	11601	.0030
									32	980	21764	15786	
20	+	+	+	-	+	+	-	+	5	1006	22200	23340	.0011
									2181	2859	59451	72112	
21	-	-	-	-	-	+	-	+	2092	2455	38976	32372	.0028
									594	2612	58535		
22	+	-	-	+	+	-	-	-	871	2537		38029	.0015
									564	2854	26791	32367	
23	+	+	+	-	-	-	+	-	259	2707	51114	45651	.0009
									658	1460	22394	28728	
24	-	+	+	+	+	+	+	+	650	1428	20075	26775	.0024
									504	1090	8746	9779	
25	-	+	-	-	+	+	-	-	371	1158	9203	13501	.0037
									400	1208	8733	9230	
26	+	+	-	+	-	-	-	+	504	1238	15688	10676	.0014
									1201	2109	59796	55534	
27	-	-	+	+	-	+	+	-	1805	2312	27312	30936	.0027
									26	864	5276	4186	
28	+	-	+	-	+	-	+	+	22	560	12050	17061	.0062
									5	7	2655	3990	
29	+	-	+	-	-	+	-	-	0	50	1963	1428	.0017
									618	2242	9538	80677	
30	-	+	-	-	-	-	+	+	366	2714	13157	18394	.0004
									2602	1319	27327	31027	
31	-	-	+	+	+	-	-	+	138	958	27126	25832	.0055
									62	734	14547	8445	
32	+	+	-	+	+	+	+	-	66	770	16945	16412	.0006
									490	1805	8323	18281	
									400	1737	9564	15733	

+ = High Level
- = Low Level

TABLE 4.2 (Cont'd)
COMBINATIONS AND RESULTS OF FACTORIAL EXPERIMENT

LEVELS									RESPONSES				
Combination	Single or Multiple Temperature	CO ₂	CO	HCl	AlCl ₃	H ₂	Time	Temp	Alpha Count				Average Deposition Rate (gms/min)
									Inside		Outside		
									Entrance	Exit	Up	Down	
									(counts/min)				
33	+	+	-	-	-	-	-	-	76	1613	24875	18287	.0039
34	-	-	+	-	-	+	+	+	62	1640	12094	8726	.0038
									70	2352	11660	3203	
35	+	-	+	+	+	-	+	-	82	2420	10449	17097	.0054
									41	257	7006	8343	
36	-	+	-	+	+	+	-	+	82	137	5801	12307	.0025
									58	458	10645	5698	
37	-	-	+	-	+	-	-	-	98	670	17019	8007	.0038
									494	1030	25614	38525	
38	-	+	-	+	-	-	+	-	523	1318	31967	45614	.0027
									39	704	4730	7497	
39	+	-	+	+	-	+	-	+	55	439	3380	5379	.0052
									1123	950	18455	32094	
40	+	+	-	-	+	+	+	+	680	1830	16142	42439	.0035
									18	206	399	351	
41	+	-	-	-	-	+	+	-	34	164	1897	882	.0008
									1133	1408	16905	19193	
42	-	+	+	-	-	-	-	+	943	1341	32340	34034	.0022
									1270	2631	62189	64411	
43	-	-	-	+	+	-	+	-	1422	2158	28438	32913	.0055
									38	1668	5461	2604	
44	+	+	+	+	+	+	-	-	42	1668	9701	6375	.0016
									2693	1751	17100	12251	
45	-	-	-	+	-	+	-	-	2619	1662	18522	14408	.0034
									239	1211	22321	24132	
46	+	-	-	-	+	-	-	+	481	1004	27240	26541	.0041
									54	562	7132	7898	
47	-	+	+	-	+	+	+	-	32	660	9031	8534	.0037
									66	856	19617	23382	
48	+	+	+	+	-	-	+	+	48	718	37549	25416	.0030
									51	1019	13171	33577	
49	+	-	+	+	-	-	-	-	25	841	40507	18400	.0045
									62	726	3764	2523	
50	+	+	-	-	+	-	+	-	32	602	9922	3826	.0031
									27	549	1338	1850	
51	-	-	+	-	+	+	-	+	36	672	8578	5468	.0051
									242	1034	68266	52046	
52	-	+	-	+	-	+	+	+	304	1030	53446	51674	.0052
									110	1310	14847	36215	
53	-	-	+	-	-	-	+	-	98	2086	4264	16076	.0036
									170	916	25947	23727	
54	-	+	-	+	+	-	-	-	158	740	28400	34975	.0051
									94	230	1707	1581	
55	+	+	-	-	-	+	-	+	114	238	1875	1192	.0032
									73	1385	4196	6317	
56	+	-	+	+	+	+	+	+	79	1029	8224	10307	.0038
									113	726	5174	2954	
57	-	-	-	+	-	-	-	+	421	145	4756	4227	.0103
									37	317	781	3479	
58	+	-	-	-	+	+	-	-	45	135	678	1731	.0043
									40	900	5803	2323	
59	-	+	+	-	+	-	+	+	34	490	4079	2285	.0024
									382	1434	22704	14603	
60	+	+	+	+	-	+	+	-	270	1380	16959	32024	.0005
									2738	3158	15841	15409	
61	+	-	-	-	-	-	+	+	2678	3020	35534	28390	.0032
									26	241	4817	4135	
62	-	+	+	-	-	+	-	-	35	652	9785	7008	.0022
									625	1563	25404	30170	
63	-	-	-	+	+	+	+	-	561	1921	26887	36370	.0063
									204	1131	30370	23908	
64	+	+	+	+	+	-	-	+	166	1340	30012	42161	.0016
									295	1567	36609	35066	
									555	1581	31176	17418	

The 64 combinations and their responses are shown in Table 4.2. Two tubes were used in each combination.

The conclusions listed below were derived from the experiments.

Deposition rate: the average deposition rate for the sixty-four combinations on the 10-square-inch tube surface was 0.0031 gram per minute. Changing from a low to a high level of the control variable had a highly significant effect on deposition rate for the following factors or interactions of the factors:

<u>Factor or Interaction</u>	<u>Level of factor or interaction which gave higher deposition rate</u>	<u>Average change in deposition rate per tube from one level to the other (g/min)</u>
CO ₂	Low - 10 liters/minute	0.0017
Single or Mult. Temp.	Low - Single Temperature	0.0013
Single or Mult. Temp. × CO × HCl Interaction	High - (Single Temp, no CO added, 0.2 liters/min HCl)	0.0012
Single or Mult. Temp. × H ₂ × Time Interaction	Low - (Single Temp, 10 liters/min H ₂ , 20 minutes)	0.0010
H ₂	Low - 10 liters/minute	0.0008
CO	Low - no CO added	0.0005
Temperature	High - 1100°C	0.0005
HCl	High - 0.2 liters/minute	0.0002

Changing from a low level to a high level of AlCl₃ or time had no significant effect on the deposition rate. The following combination of the eight factors at the levels investigated is estimated to yield the highest deposition rate i.e., approximately 0.010 gram per minute:

Single Temperature
10 liters/minute CO₂
No addition of CO
0.2 liters/minute HCl
2 grams/minute AlCl₃
10 liters/minute H₂
20 minutes coating time
1100°C surface temperature

It will be noted that Combination No. 57 in the experiment has these levels of the factors and had an average rate of 0.010 gram per minute.

Alpha Count, inside, entrance: average count from the inside surface at the entrance of the tube was 282 counts per minute. Changing from a low level to a high level had a highly significant effect on the alpha count for the following factors or interactions of the factors.

<u>Factor or Interaction</u>	<u>Level of factor or interaction which gave lower alpha counts</u>	<u>Average change in alpha count per tube from one level to the other (counts/min)</u>
CO ₂	Low - 10 liters/minute	108
CO	Low - No CO added	89
Time	High - 40 minutes	55
H ₂	Low - 10 Liters/minute	52
Single or Mult. Temp. × CO × H ₂ Interaction	Low - (Single Temp, no CO added, 10 liters/min H ₂)	34
Single or Mult. Temp. Temperature	Low - Single Temperature	21
	High - 1100°C	3
AlCl ₃	High - 10 grams/minute	3

Changing from a low level to a high level of HCl had no significant effect on the count. The following combination of the eight factors is estimated to give a zero alpha count.

Single Temperature
 10 liters/minute CO₂
 No addition of CO
 No addition of HCl
 10 grams/minute AlCl₃
 10 liters/minute H₂
 40 minutes coating time
 1100°C Surface temperature

The above is supported by observing that Combination No. 38 in the experiment had a zero count, subtracting a background count of 20 counts, and had levels of the factors similar to the recommended combination with the exception that multiple temperatures were used and 2 liters/minute of CO was added; Combination No. 8 with the highest count disagrees with the recommended combination on 6 out of 8 levels of the factors.

Alpha Count, inside, exit: average alpha count from the inside surface at the exit of the tube was 1135 counts per minute. Changing from a low level to a high level had a highly significant effect on the count for the following factors or interactions of the factors.

<u>Factor or Interaction</u>	<u>Level of factor or interaction which gave lower alpha counts</u>	<u>Average change in alpha count per tube from one level to the other (counts/min)</u>
CO ₂ × HCl × AlCl ₃ Interaction	High - (10 liters/min CO ₂ , no HCl added, 10 grams/min AlCl ₃)	44
Time	High - 40 minutes	41
Single or Mult. Temp. × Temp. Interaction	High - (Mult. Temp., 1100°C)	31
Single or Mult. Temp. × CO × HCl Interaction	High - (Mult. Temp., no CO added, no HCl added)	29

<u>Factor or Interaction</u>	<u>Level of factor or interaction which gave lower alpha counts</u>	<u>Average change in alpha count per tube from one level to the other (counts/min)</u>
Single or Mult. Temp. $\times$ H ₂ $\times$ Time Interaction	Low - (Mult. Temp., 10 liters/minute H ₂ , 40 minutes)	28
CO ₂	Low - 10 liters/minute	23
AlCl ₃ $\times$ Temperature Interaction	High - (10 grams/minute AlCl ₃ , 1100°C)	21
CO	Low - no CO added	19
H ₂	Low - 10 liters/minute	15
AlCl ₃	High - 10 grams/minute	11

Changing from a low level to a high level of single or multiple temperatures, HCl, or temperature had no significant effect on the count.

The following combination of the eight factors is estimated to give a zero count.

Multiple Temperature
 10 liters/minute CO₂
 No addition of CO
 No addition of HCl
 10 grams/minute AlCl₃
 10 liters/minute H₂
 40 minutes coating time
 1100°C surface temperature

Combination No. 28, which had the lowest count, averaging approximately 15 after subtracting a background count of 20, had levels of the factors similar to the recommended combination with the exception that 2 liters/minute of CO was added. Combination No. 8 with the highest count disagrees with the recommended combination on 7 out of 8 levels of the factors.

Alpha count, outside: no significant difference was found between the counts taken on the sides which were upward in the experiment and the counts taken on the downward sides and consequently the results were averaged. Average outside alpha count was 16,913 counts per minute. Changing from a low level to a high level had a highly significant effect on the count for the following factors or interactions of the factors.

<u>Factor or Interaction</u>	<u>Level of factor or interaction which gave lower alpha counts</u>	<u>Average change in alpha count per tube from one level to the other (counts/min)</u>
CO	Low - no CO added	911
Single or Mult. Temp. $\times$ H ₂ $\times$ Time Interaction	Low - (Mult. Temp., 10 liters/minute H ₂ , 40 min.)	705
Time	High - 40 minutes	621
CO $\times$ HCl Interaction	High - (No CO added, no HCl added)	553

<u>Factor or Interaction</u>	<u>Level of factor or interaction which gave lower alpha counts</u>	<u>Average change in alpha count per tube from one level to the other (counts/min)</u>
CO ₂ × CO × H ₂ Interaction	Low - (10 liters/min CO ₂ , no CO added, 10 liters/min H ₂)	537
Time × Temperature Interaction	High - (40 minutes, 1100°C)	474
Single or Mult. Temp. × CO × HCl Interaction	High - (Multiple Temp., no CO added, no HCl added)	387
AlCl ₃ × Temperature Interaction	High - (10 grams/min AlCl ₃ , 1100°C)	357
Temperature	Low - 1000°C	289

Changing from a low level to a high level of single or multiple temperature, CO₂, HCl, AlCl₃, or H₂ had no significant effect on the count.

The following combination of eight factors is estimated to give the lowest alpha count on the outside surface of the tube:

Multiple temperature
 10 liters/minute CO₂
 No addition of CO
 No addition of HCl
 10 grams/minute AlCl₃
 10 liters/minute H₂
 40 minutes coating time
 1100°C surface temperature

The temperature was set at 1100°C because two interactions showing 1100°C to be the desirable level were more significant than the temperature factor showing 1000°C as the desirable level.

Combination No. 40 showing the lowest count had levels of the factors similar to the recommended combination with the exception that 20 liters/minute of CO₂ and 20 liters/minute of H₂ were employed. Combination No. 8 with the highest alpha count disagrees with the recommended combination on 7 out of 8 levels of the factors. A pictorial representation of the changes in weight gain caused by each of the control parameters is shown in Figure 4.3.

It may be noted that the optimum conditions were almost identical for each of the five sets of dependent variables. These conditions are listed in Table 4.3. The changes in weight gain caused by deviations from the recommended levels are presented in Table 4.4.

TABLE 4.3

OPTIMUM OPERATING CONDITIONS

Gas flow rate: CO₂ ten liters per minute and H₂ ten liters per minute
 HCl and CO not added
 AlCl₃ ten grams per minute
 Surface temperature 1100°C

Fig. 4.3 – Averaged effects of controlled variables on Al_2O_3 deposition rate

TABLE 4.4
ANALYSIS OF EXPERIMENTAL DATA - TEST SERIES A

Recommended Levels of Controlled Variables

a. Sample Weight Gain (Basic Depressed Rate 0.003 g/min)

<u>Recommended Level</u>	<u>Improvement</u>
Low CO ₂	+50%
Low CO	+50%
Low H ₂	+25%
High Temp.	+25%
High HCl	+25%

b. Sample Thickness - ID inlet (Unit Depressed thickness - 282)

<u>Recommended Level</u>	<u>Improvement</u>
Low CO ₂	+25%
Low CO	+25%
Low H ₂	+15%
High AlCl ₃	+ 1%
High Temp.	+ 1%

c. Sample Thickness ID exit (Unit Depressed Thickness - 1135)

<u>Recommended Level</u>	<u>Improvement</u>
Low CO ₂	+25%
Low CO	+20%
Low H ₂	+15%
AlCl ₃	+ 5%
High Temp.	+ 5%

d. Sample Thickness - Outside

<u>Recommended Level</u>	<u>Improvement</u>
Low CO	+50%
Low CO ₂	+25%
Low H ₂	+15%
AlCl ₃	+ 5%
CO ₂ - Temp.	+15%

A matter of primary importance is the crystal structure of the coating. Relatively thin coatings were obtained and the extremely fine crystallite size made it extremely difficult to employ standard micrographic examination. Furthermore, the coatings formed at temperatures between 800°C and 900°C are soft and difficult to polish. Thermal soaking above 1200°C will harden the coating, but only by converting the deposit to the α -corundum form, defeating the objective of examining the coating in its original form.

The number of samples checked by X-ray diffraction was limited to sixteen which could provide a reasonable insight into the relative effects of variations in reaction temperature, feed gas composition, etc. The results of these studies showed the deposit to be amorphous in nature at coating temperatures below 1000°C. The diffraction patterns further showed that at 1000°C, kappa alumina was the preferred deposit form. The identified crystalline forms of alumina and the approximate transformation temperatures taken from Reference 31 are presented in Figure 4.4. It was observed that the concentrations of aluminum

Fig. 4.4 - Crystalline Forms of Al_2O_3 ³¹

chloride and hydrogen chloride and also temperature affected the size of the crystallites. It must be noted however, that temperature, as expected, had a stronger effect on the degree of crystallinity and type and size of crystal than had the other factors.

The conditions selected for obtaining a maximum weight gain were also usually the conditions which yielded a coating consisting almost entirely of the preferred type deposits, i. e., α - corundum.

4.2 Flow Rate Experiment (Series B)

In a second experiment (Series B) appreciably higher gas flow rates were employed. The higher flow rates were made possible by a rather severe modification of the process equipment. Deposition rates were much lower than those of Figure 4.5, but curves were similar in shape. It is apparent that the rates of deposition decrease markedly with the increase in flow rate all other things being held constant; also the nature of the deposits was generally much less satisfactory.

4.3 Surface Temperature Experiment (Series C)

In the third experiment (Series C) appreciably higher temperatures (1300°C and 1400°C) were employed in forming the coating. The conditions and results are presented in Table 4.5. Generally, the rates of deposition were found to be inferior and the continuity of the coatings was also less satisfactory. These results are attributed at least partially to the much higher rate of reaction between carbon and carbon dioxide to form carbon monoxide. The rate of this reaction becomes appreciable above 1100°C. The occasional inconsistencies observed in deposition rate might logically be attributed to differences in the amount of exposed (uncoated) graphite. It is recommended that all exposed graphite surfaces be precoated with alumina deposited at low temperatures (850-1000°C).

TABLE 4.5
EXPERIMENTAL DESIGN AND RESULTS FOR EXPERIMENT C
(20 Minute Coating Period)

Independent Variable	CO ₂ (l/min)	AlCl ₃ (g/min)	H ₂ (l/min)	Temp (°C)	Weight Gain (gms/min)
Test					
C-1	3.5	2	7	1200	.0056
C-2	3.5	2	15	1200	.0036
C-3	7	2	7	1200	.0011
C-4	7	2	15	1200	.0003
C-5	3.5	0.5	7	1200	.0006
C-6	3.5	0.5	15	1200	.0009
C-7	7	0.5	7	1200	.0055
C-8	7	0.5	15	1300	.0002
C-9	3.5	2	7	1400	.0042
C-10	3.5	2	15	1380	-
C-11	7	2	7	1400	-
C-12	7	2	15	1370	.0095
C-13	3.5	0.5	7	1370	.0002
C-14	3.5	0.5	15	1370	.0053
C-15	7	0.5	7	1340	.0004
C-16	7	0.5	15	1370	.0016
C-17	7	10.+	15	1340	.0055

Fig. 4.5 - Effect of Al_2Cl_6 concentration on the deposition rate of Al_2O_3 .

The results of Experiments B and C indicated higher coating temperatures and higher gas flow rates in conjunction with the construction of the apparatus and the gas compositions studied to be generally undesirable.

The undesirability of higher reaction surface temperatures was attributed at least in part to the use of graphite in the coating system. The experiments definitely showed that the presence of carbon monoxide depressed the rate of deposition. It is known from the experimental studies of Graven and Long²⁴ that the rate of the water gas reaction is strongly depressed by increases in the carbon monoxide concentration. The same study also shows that high hydrogen concentrations will depress the reverse reaction rate.

4. 4 General Discussion of Experimental Results

It is apparent from the present studies that the rate of deposition was practically independent of the partial pressure of aluminum chloride in the range of 0.004-0.040 moles per mole of feed gas. The comparison of alumina deposition rates for the aluminum chloride feed rates of 2 versus the 10 grams per minute (See Figure 4. 5) showed the relative insensitiveness of the deposition rate within this range. The changes in deposition rates as a function of variations in gas flow rates are attributed to changes in the N_{Re} and the heat transfer rate rather than to any change in the aluminum chloride concentration.

The foregoing observations on the insignificance of variations in aluminum chloride concentration is of particular interest in relation to the reaction mechanism, i. e., the kinetics of the vapor plating reaction. If the sorption of the aluminum chloride or the collision of the aluminum chloride with the reaction surface were the key step, then the deposition rate should have been strongly affected by any variations in aluminum chloride concentration. The deposition rate was, however, independent of the aluminum chloride concentration and it varied inversely with the carbon monoxide concentration and consequently it seems much more likely that the water gas reaction was the rate controlling step. The Graven-Long²⁴ and Fenimore-Jones³² experiments show that both the water gas reaction and the water-aluminum chloride reaction are not surface catalyzed. It appears, therefore, that the gas temperature and water vapor concentration are the primary and virtually only rate controlling factors in the subject alumina deposition reaction. Within the concentration ranges and operating conditions of interest in this investigation, the definite depressions in deposition rate as a function of increases in carbon dioxide concentrations were not observed until reaction zone temperatures were increased to or above 1100°C.

The carbon dioxide-carbon reaction does not proceed as was noted previously at an appreciable rate until temperatures in excess of 1100°C are achieved. It seems likely that above 1200°C the actual carbon monoxide concentrations would be appreciably higher than would be present either from reacting all of the aluminum chloride or from the carbon monoxide added to the feed gas, or both. The extensive erosion of the graphite components observed in experiments at elevated temperatures and the intense burn-off flame, which matched in color and configuration that of gas having a high carbon monoxide concentration, supported the assumption of extensive reaction between the graphite and the CO_2 to form CO.

The normal increases in coating rate induced by temperature increases were not observed when coating temperatures of 1300°C and 1400°C were employed. Grain sizes of the Al_2O_3 deposited at temperatures in the range of 1400°C were excessive. Furthermore, at these higher temperatures the deposited Al_2O_3 was concentrated in the first inch or so of the tube being coated. The experimental results make it appear that the carbon monoxide generation at these high temperatures had depressed the rate of water vapor formation much more than the water vapor formation rate was increased by the rise in temperature. Subsequent pilot runs showed that, as predicted (see 4. 3), the effects of CO from the graphite

parts could be suppressed by using excess H_2 (in the $H_2:CO_2$ ratio range of 8-10:1).

It was initially expected that it would be desirable to add carbon monoxide to the feed gas in order to depress the coating rate and render it less sensitive to temperature changes. The extreme increase in deposition time make this appear undesirable. It is recommended for future applications, however, that a system employing reduced pressures be studied in order to increase the probability that the alumina and water vapor molecules strike the surface prior to being swept out of the reaction chamber.

Assuming that the apparatus must be run at atmospheric pressure, the ideal configuration is one in which only the surface to be coated is at reaction temperature. This temperature should be as uniform as possible, and the gas flow immediately adjacent to the sample surface should be heated sufficiently to produce an appreciable reaction rate. The surface area of exposed high temperature carbon or graphite should be kept to a minimum if carbon dioxide is to be employed to generate water vapor. It was expected originally that carbon surfaces would be quickly coated by alumina but it appears that the rate of formation of carbon monoxide at or near these surfaces is sufficient at higher temperatures to inhibit the formation of alumina. Therefore a low temperature pre-coat of alumina deposited at 800 to 850°C seems desirable if graphite is to be used. It also appears advisable to give the coated graphite a thermal aging treatment at 1200°C, cool and repeat the cycle to prevent spalling of the coating.

4.5 Summary of Conclusions for Series A, B and C

The experimental work reported above has established the following:

- a. the thermochemical and kinetic feasibility of the reaction over a wide range of temperatures and gas compositions.
- b. a range of coating rates (0.0001 inch - 0.0020 inch/hr)
- c. the over-all reaction rate:
 - varies inversely with the CO conc.,
 - varies inversely with the initial CO_2 conc.,
 - varies inversely proportional to the N_{Re} and therefore directly proportional to the gas temperature,
 - is independent of the $AlCl_3$ concentrations.
- d. the reaction is apparently a gaseous phase, non-surface catalyzed reaction and therefore depends primarily on the local temperature, the presence of a suitable oxygen bearer and the absence of carbon monoxide which would tend to compete with the $AlCl_3$ for any oxygen donors present.
- e. a set of conditions whereby alpha alumina having a density equal 4.00 to 4.02 g/cc can be deposited at rates of about 1.1 mils per hour.

5.0 PILOT PRODUCTION STUDIES

A pilot line operation for the coating of tubes on the bore was operated to more clearly define the process parameters and to produce tubes clad on the bore for test and evaluation purposes.³³ Coatings were produced with an average thickness of about 0.0010 inch and about 0.0006 inch.

The apparatus employed in these experiments is shown schematically in Appendix C, Figure C-3.

It is to be noted that a graphite susceptor-holder was used to hold the tubes to be coated on the I. D. This equipment coated from 12 to 16 tubes simultaneously and was later expanded to coat 60 tubes at one time.

A study was made of gas composition variation within the rather narrow limitations suggested by the theoretical and experimental work described previously. From these

studies, the following set of operating conditions were established to produce a coating of 0.006-inch-thickness:

Coating temperature (°C)	1120 ± 5
Coating time (hours)	2
Volume ratio H ₂ /CO ₂	10/1
Gas flow (l/min/tube)	0.5 ± 0.02
AlCl ₃ temperature (°C)	115 ± 2
AlCl ₃ flow rate (g/min)	0.4 ± 0.1

(The H₂/CO₂ ratio was shifted to 10/1 in order to suppress the amount of CO generated by the CO₂-C reaction).

The flow of gas through the tubes was from one end for one hour and then the tubes were reversed for the gas flow to enter the opposite end for one hour.

Using these fixed conditions and coating 15 tubes simultaneously, a pilot run was made on about 700 tubes 4½ inches long and with a bore of 0.197 inch. The weight gain per tube was measured and one tube from each run was sectioned to measure the cladding thickness. These data are shown in Table 5.1. A histogram of percent of 15 tube groups (runs) falling in a given average coating thickness is shown in Figure 5.1. A typical longitudinal profile of coating thickness is shown in Figure 5.2.

The average variation on weight gain within a given 15 tube lot was about ± 5 percent. Variations between runs was believed to be caused by inability to maintain constant AlCl₃ vaporization rates (probably because of particle size variation between lots of AlCl₃).

Non-destructive testing of these coated tubes using procedures prescribed for ceramic tubes (see Ref. 30 for details) showed an over-all yield of 70 percent. The rejects, based on subjecting all tubes to all tests, were as follows:

Statiflux rejects	12 percent*
Zyglo rejects	16 percent*
Ultrasonic rejects	19 percent*

A defective coating is shown in Figure 5.3.

The factors which were used as checks on the product of these runs were the following:

1. Weight gain of each tube.
2. Deviation of weight gain between tubes in each run.
3. Ceramographic examination.
 - a. thickness of coating
 - b. matrix-coating bond
 - c. continuity and uniformity
 - d. density of coating
4. Non-destructive examination
 - a. Statiflux and Zyglo crack detection
 - b. Ultrasonic inspection for subsurface flaws

The ceramographic examination of the control specimens shows the Al₂O₃ coating to be well bonded and consisting of high density α -alumina. The uniformity of the coating from end to end was checked by transverse sections on the basis of a ten percent sample. The results of these examinations showed the coatings to have an average measured thickness of 0.6 ± 0.15 mils. A typical profile obtained in this manner is shown in Figure 5.2. For purposes of comparison, a section of a defective coating is shown in Figure 5.3.

*Some tubes show defects by more than one test.

TABLE 5.1
RESULTS OF RUNS TO PRODUCE THIN Al_2O_3 COATINGS

Run No.	Avg. Wt. Gain (g)	Avg. Deviation (g)	Calc. Thickness (mils)	Avg. Measured Thickness (mils)	Spread (mils)	Coating Thickness	
						Max. (mils)	Min. (mils)
1	0.201	± 0.008	1.1	0.7	0.4	0.9	0.5
2	0.205	± 0.004	1.1	0.9	0.3	1.1	0.8
3	0.122	± 0.004	0.7	0.5	0.2	0.6	0.4
4	0.133	± 0.004	0.7	0.5	0.3	0.6	0.3
5	0.092	± 0.004	0.5	0.4	0.2	0.5	0.3
6	0.104	± 0.004	0.5	0.5	0.1	0.5	0.4
7	0.122	± 0.003	0.7	0.4	0.1	0.4	0.3
8	0.175	± 0.003	0.9	0.7	0.2	0.8	0.6
9	0.120	± 0.004	0.7	0.5	0.2	0.6	0.4
10	0.091	± 0.007	0.5	0.5	0.1	0.6	0.5
11	0.159	± 0.008	0.85	0.8	0.4	1.0	0.6
12	0.131	± 0.005	0.65	0.6	0.4	0.8	0.4
13	0.161	± 0.004	0.8	0.6	0.3	0.8	0.5
14	0.164	± 0.005	0.8	0.6	0.3	0.8	0.5
15	0.149	± 0.005	0.7	0.6	0.4	0.8	0.3
16	0.158	± 0.003	0.75	0.5	0.1	0.5	0.4
17	0.160	± 0.004	0.8	0.5	0.2	0.6	0.4
18	0.195	± 0.005	0.95	0.7	0.4	0.9	0.5
19	0.115	± 0.005	0.6	0.6	0.4	0.9	0.5
20	0.113	± 0.002	0.6	0.5	0.2	0.6	0.4
21	0.152	± 0.004	0.7	0.7	0.4	1.0	0.6
22	0.138	± 0.003	0.7	0.8	0.2	0.9	0.7
23	0.098	± 0.009	0.5	0.35	0.2	0.4	0.2
24	0.152	± 0.009	0.8	0.5	0.3	0.6	0.3
25	0.194	± 0.006	1.0	0.6	0.3	0.8	0.5
26	0.229	± 0.003	1.2	0.75	0.3	0.9	0.6
27	0.164	± 0.003	0.9	0.6	0.4	0.8	0.4
28	0.142	± 0.003	0.8	0.4	0.2	0.5	0.3
29	0.123	± 0.002	0.7	0.4	0.2	0.5	0.3
30	0.122	± 0.006	0.7	0.4	0.2	0.5	0.3
31	0.162	± 0.012	0.9	0.7	0.3	0.9	0.6
32	0.126	± 0.006	0.7	0.5	0.2	0.6	0.4
33	0.129	± 0.006	0.7	0.6	0.3	0.8	0.5
34	0.121	± 0.005	0.65	0.6	0.4	0.8	0.4
35	0.123	± 0.008	0.7	0.5	0.2	0.6	0.4
36	0.171	± 0.008	0.9	0.8	0.4	1.0	0.6
37	0.167	± 0.007	0.9	0.8	0.3	1.0	0.7
38	0.153	± 0.009	0.8	0.8	0.2	0.9	0.7
39	0.184	± 0.005	1.0	0.8	0.4	1.0	0.6
40	0.101	± 0.005	0.5	0.4	0.2	0.5	0.3
41	0.156	± 0.005	0.8	0.5	0.3	0.6	0.3
42	0.142	± 0.003	0.8	0.6	0.4	0.8	0.4
43	0.163	± 0.005	0.9	0.5	0.2	0.6	0.4
44	0.188	± 0.005	1.0	0.7	0.2	0.8	0.6
45	0.141	± 0.008	0.8	0.6	0.2	0.8	0.6
46	0.144	± 0.004	0.8	0.5	0.4	0.8	0.4
47	0.170	± 0.008	0.9	0.6	0.4	0.8	0.4
48	0.195	± 0.005	1.0	0.7	0.3	0.9	0.6
49	0.157	± 0.004	0.8	0.6	0.3	0.7	0.4
50	0.166	± 0.003	0.9	0.7	0.3	0.9	0.6

1
SN 18388

2
SN 18389

3
SN 18390

4
SN 18391

Mounted Sections - 250x

Average Measured Thickness - 0.5 mil

Fig. 5.2 - Longitudinal profile by transverse sections of thin Al₂O₃ coatings.

Fig. 5.3 - Defective Coating Area

6.0 CONCLUSIONS

A thin, uniform, well bonded, crystalline coating of Al_2O_3 can be applied readily to the I. D. of the fuel tubes. By using the conditions determined in this work and with the control of parameters as shown for the operating conditions, a coating can be produced which meets the following specifications:

average measured thickness (mils) 0.6

average measured variation in thickness (mils) ± 0.15

The recommended operating conditions for future coating work are as follows:

6.67 gr AlCl_3 per tube used in 120 minutes

0.5 l/min gas flow per tube

ratio H_2 : CO_2 by volume varying between 10:1 and 8:1

2050° F work surface temperature

120 minutes coating time, the gas flowing 60 minutes in each direction

(The above process produced a coating 0.0015 inches thick distributed over a bore surface of 3.7 square inches.)

Approximately fifteen percent of the AlCl_3 is used in depositing Al_2O_3 on the work surface.

A detailed set of operating instructions for the coating process is presented in Appendix C.

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APPENDIX A

Computation of The Moles of Product Al_2O_3 Formed Per Mole of Reagents and Products in the Feed Gas as a Function of Temperature for Equilibrium Conditions

The procedure follows the steps listed below:

1. Define the over-all reaction.
2. Determine the free energy of reaction as a function of temperature.
3. Determine the equilibrium constant as a function of temperature.
4. Determine the equilibrium amount of products as a function of temperature and feed gas composition (i. e., reagent concentrations).

STEP 1 - Define the Over-all Reaction

Equation A1 holds true at temperatures above 800°C and probably at temperatures above 658°C . Equation A2 is correct between room temperature and 600°C :

In order to simplify the preliminary analyses the latter equation will not be discussed.

Equation A2 would have to be considered in an analysis of the process kinetics because boundary layer temperatures may be encountered varying from 200°C to 1200°C .

STEP 2 - Determine the Free Energy of Reaction

The free energy is given by equation A3, thus

$$\Delta(F_T) = \Delta(\sum F_{iT}) = \Delta(\sum [H_{iT} - TS_{iT}]) \quad (\text{A3})$$

where,

$$H_{iT} = \int_{t=0^\circ\text{K}}^{t=T} C_{pi} dt + \text{heats of transition} = \int_{298}^T C_{pi} dt + H_{i298} + \quad (\text{A4})$$

$$+ \sum \Delta H_i \text{ transition} \\ 298 < t < T$$

$$S_{iT} = \int_{t=0^\circ\text{K}}^{t=T} \frac{C_{pi}}{t} dt + \text{entropies of transition} = \int_{298}^T \frac{C_{pi}}{t} dt + S_{i298} + \quad (\text{A5})$$

$$+ \sum \Delta S_i \text{ transition} \\ 298 < t < T$$

$$C_{pi} = a_i + b_i \times 10^{-3} T + c_i \times 10^{-6} T^2 + \frac{d_i \times 10^5}{T^2} \quad (\text{A6})$$

These equations can be solved using data from the tables in ANL 5750²³. The arithmetical manipulations for solving equation A3 are rather cumbersome and therefore the following simplified procedure will be employed.

Insert values for ΔF_{ii} taken from ANL 5750, Figures 1c, 1d, 3a, and 3c into equation A7 (See Table A1 for derivation).

$$\Delta(F_T) = [3\Delta F_{Al_2O_3} + 6\Delta F_{HCl} + 3\Delta F_{CO} - 6\Delta F_{AlCl_3} - 6\Delta F_{CO_2}] \quad (A7)$$

The calculations are tabulated in Table A2.

TABLE A1

METHOD OF SELECTING MULTIPLYING FACTORS

ΔF_{AlCl_3}	$2AlCl_3$	=	$2Al + 3Cl_2$	+ 6 (Cl)
ΔF_{CO_2}	$3CO_2$	=	$3C + 3O_2$	+ 6 (O)
ΔF_{CO}	$3C + 3/2O_2$	=	$3CO$	- 3 (O)
$\Delta F_{Al_2O_3}$	$2Al + 3/2O_2$	=	Al_2O_3	- 3 (O)
ΔF_{HCl}	$3Cl_2 + 3H_2$	=	$6HCl$	- 6 (Cl)
Adding

Employing the sign convention as defined in ANL 5750, the reaction will go to the right when ΔF is negative.

STEP 3 - Determine the Equilibrium Constant as a Function of Temperature (Figures 3.1 and 3.2)

It is known that the equilibrium constant K_T is given by equation A8, thus

$$-\Delta F = RT \ln K_T \quad (A8)$$

where

R = gas constant
T = absolute temperature

or rearranging,

$$K_T = e^{-\Delta F/RT} \quad (A9)$$

Since ΔF has been tabulated as calories/mole, R is expressed as calories per mole ($R = 1.987 \text{ cal/}^\circ\text{K-mol}$). The values for K_T derived using this equation are tabulated in Table A2.

Plotting the function ΔF as a function of the temperature T, it is possible to derive equations A10 and A11 for the variation ΔF as a function of temperature.

It follows that:

$$-\Delta F = 22,500 + 27T \quad (A10)$$

for

$$500^\circ\text{K} < T < 931^\circ\text{K}$$

and

$$-\Delta F = 7200 + 42T \quad (A11)$$

for

$$1000^\circ\text{K} < T < 1800^\circ\text{K}$$

TABLE A2

CALCULATION OF FREE ENERGIES AND EQUILIBRIUM CONSTANTS FOR THE
REACTION $2\text{AlCl}_3 + 3\text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{Al}_2\text{O}_3 + 3\text{CO} + 6\text{HCl}$ AS A FUNCTION OF TEMPERATURE

Temp °K	Temp °F	$(-)\frac{1}{2}\Delta F$ Al_2O_3	$(-)\frac{1}{2}\Delta F$ CO	$(-)\Delta F$ HCl	$(-)A =$ 1+2+3	$(-)\Delta F$ AlCl_3	$(-)\Delta F$ CO_2	$(-)B =$ 4+5	$(-)\frac{1}{6}\Delta F_T =$ B - A	$(-)\Delta F$ K cal	$\frac{-\Delta F}{RT}$	$\frac{K_T}{10^{10}}$	Temp °F
300	80	63.5	16.5	23	103.	51	49	100	3	18	30.2	1,340	80
400	260	62.2	17.65	23.15	103.	49	49	98	5	30	37.8	2,700,000	260
500	440	60.9	18.8	23.3	103.	48	49	97	6	36	36.3	600,000	440
600	620	59.6	19.95	23.45	103.	47.6	49	96.6	6.4	38.4	32.2	10,000	620
700	800	58.3	21.1	23.6	103.	47.2	49	96.2	6.8	40.8	29.4	600	800
800	980	57.0	22.25	23.75	103.	46.8	49	95.8	7.2	43.2	27.2	67	980
900	1160	55.7	23.4	23.9	103.	46.4	49	95.4	7.6	45.6	25.5	12.2	1160
1000	1340	54.4	24.55	24.05	103.	45.8	49	94.8	8.2	49.2	24.8	6.	1340
1100	1520	53.1	25.7	24.2	103.	45.1	49	94.1	8.9	53.4	24.5	4.46	1520
1200	1700	51.8	26.85	24.35	103.	44.4	49	93.4	9.6	57.6	24.2	3.3	1700
1300	1880	50.5	28.	24.5	103.	43.7	49	92.7	10.3	61.8	23.9	2.45	1880
1400	2060	49.2	29.2	24.65	103.	43.0	49	92.0	11.	66.	23.7	2.01	2060
1500	2240	47.9	30.4	24.8	103.	42.3	49	91.3	11.7	70.2	23.5	1.65	2240
1600	2420	46.6	31.6	24.95	103.	41.6	49	90.7	12.4	74.4	23.4	1.49	2420
1700	2600	45.3	32.8	25.1	103.	40.9	49	89.9	13.1	78.6	23.3	1.35	2600
1800	2780	44.	34.	25.25	103.	40.2	49	89.2	13.8	82.8	23.2	1.22	2780

Because ΔF is negative over the entire range of temperatures by the ANL 5750 convention, the reaction wants to go to the right at all the temperatures listed. It was assumed in the previous derivation that the value for $R = 1.987 \text{ cal/}^\circ\text{K-mol}$.

The equations A10 and A11 may be substituted into equation A9 to show the variation of K_T as a function of temperature, thus

$$K_T = e^{13.58 + \frac{11,300}{T}} \quad (\text{A12})$$

for

$$500^\circ\text{K} < T < 931^\circ\text{K}$$

and

$$K_T = e^{21.15 + \frac{3620}{T}} \quad (\text{A13})$$

for

$$1000^\circ\text{K} < T < 1800^\circ\text{K}$$

STEP 4 - Determine the Equilibrium Amount of Product as a Function of Temperature and Feed Gas Composition (i. e., Reagent Concentrations)

Given a chemical reaction of the type

it is known that the equilibrium constant K_T is given by

$$K_T = \frac{D^d E^e F^f}{A^a B^b C^c} = K(a, b, c, d, e, f, T), \text{ where } \sum P_i = 1 \quad (\text{A15})$$

where a, b, e , etc. are the mole fractions of the components in the gas phase of the reaction; the values for K_T are usually given for $\sum P_i = 1$, i. e., the total pressure of the gas is one (1) atmosphere.

In the present reaction given by equation A1, the Al_2O_3 phase condenses, consequently

$$K_T = \frac{(p_{\text{CO}})^3 (p_{\text{HCl}})^6}{(p_{\text{AlCl}_3})^2 (p_{\text{CO}_2})^3 (p_{\text{H}_2})^3} \quad (\text{A16})$$

Upon reacting x moles of AlCl_3 it follows in the conventional manner that

$$K_T = \frac{(e + \frac{3}{2}x)^3 (f + 3x)^6}{(a - x)^2 (b - \frac{3}{2}x)^3 (c - \frac{3}{2}x)^3} \left[1 + \frac{1}{2}x \right] \quad (\text{A17})$$

where

$a = p_{\text{AlCl}_3}$ = partial pressure of AlCl_3 in the feed gas

$b = p_{\text{CO}_2}$ = partial pressure of CO_2 in the feed gas

$c = p_{\text{H}_2}$ = partial pressure of H_2 in the feed gas

$e = p_{\text{CO}}$ = partial pressure of CO in the feed gas

$f = p_{\text{HCl}}$ = partial pressure of HCl in the feed gas

and

$$a + b + c + e + f = 1$$

Sample calculation:

Assuming the following initial conditions:

$$T = 1000^{\circ}\text{K} = 727^{\circ}\text{C} = 1340^{\circ}\text{F}$$

$$p_{\text{AlCl}_3} = 152\text{mm Hg} = 0.2 \text{ mol fraction, equilibrium vapor pressure at } 158^{\circ}\text{C} = 316^{\circ}\text{F from Figure A1}$$

$$p_{\text{H}_2} = p_{\text{CO}_2} = 370\text{mm Hg} = 0.40 \text{ mol fraction}$$

$$p_{\text{CO}} = p_{\text{HCl}} = 0$$

The final equilibrium composition will be:

$$a = 0.2 - x$$

$$b = 0.4 - \frac{3}{2}x$$

$$c = 0.4 - \frac{3}{2}x$$

$$e = \frac{3}{2}x$$

$$f = 3x$$

Substituting these values into equation A17 it follows that

$$K_T = \frac{\left(\frac{3}{2}x\right)^3 (3x)^6}{(0.2 - x)^2 \left(0.4 - \frac{3}{2}x\right)^3 \left(0.4 - \frac{3}{2}x\right)^3 \left[1 + \frac{1}{2}x\right]} \quad (\text{A18})$$

From the results presented in Table A2 it can be seen that the value of $K_T = 10^{10.76}$ for $T = 1000^{\circ}\text{K}$.

By trial and error it follows that

$$x = 0.1999 \quad \lg K_T = 11.06$$

$$x = 0.19985 \quad \lg K_T = 10.70$$

The final concentrations are, consequently,

$$\begin{aligned} \text{AlCl}_3 &= \frac{1.5}{1.1} \times 10^{-4} \text{ moles/mole exit gas} \\ &= 0.1037 \text{ mmHg partial pressure} \end{aligned}$$

The results of similar calculations for other temperatures and feed gas compositions are presented in Table A3.

TABLE A3
EQUILIBRIUM AlCl_3 VAPOR PRESSURE FOR DIFFERENT
FEED GAS COMPOSITIONS AND TEMPERATURES

T(°C)	P_{AlCl_3}	P_{CO_2}	P_{H_2}	P_{HCl}	P_{CO}	P_{AlCl_3}
	← Feed Gas atmospheres →					← Exit Gas (mmHg) →
317	0.2	0.4	0.4	0	0	0.00207
727	0.2	0.4	0.4	0	0	0.1037
1127	0.2	0.4	0.4	0	0	0.138
317	0.2	0.35	0.35	0.1	0	0.0276
727	0.2	0.35	0.35	0.1	0	1.38
1127	0.2	0.35	0.35	0.1	0	2.07
317	0.2	0.3	0.3	0.1	0.1	4.15
1127	0.2	0.3	0.3	0.1	0.1	12.78
317	0.2	0.3	0.5	0	0	0.69
1127	0.2	0.3	0.5	0	0	3.45

APPENDIX B

Computations of Physical Properties

The purpose of this program is to determine the physical properties of the gas as a function of temperature and degree of completion of the reaction for different starting compositions. The compositions of the gas were computed as outlined in Appendix A. The results were obtained from the computer in printed form or, if desired, in punched card form, the latter to be used on the veri-plotter.

A sufficient statement of the chemical problem involved in the following calculations for the purpose of this Appendix is that the primary reactions occurring in the vapor plating of alumina are the following:

In addition to these reactions H_2O is produced as an intermediate. The gaseous constituents of concern are Al_2Cl_6 (or AlCl_3), H_2 , CO_2 , CO , HCl , and H_2O . The relatively small instantaneous amount of H_2O makes its contribution to the general properties of the gaseous mixture insignificant; its diffusivity within the mixture is, however, of considerable interest.

For each starting composition and at each temperature there exists a cutoff point, expressed in terms of the reacted amount of Al_2Cl_6 (or AlCl_3), beyond which the reaction will not proceed. The cutoff point was computed for each starting composition and at each temperature as discussed in Appendix A. The reaction will not proceed to the point where all of the Al_2Cl_6 (or AlCl_3) is exhausted but it was considered informative to carry the mathematical model to the exhaustion of these constituents.

Each of the following quantities was computed as a function of temperature and degree of completion of reaction for each starting composition.

1. Diffusivity between each component and mixture.
2. Viscosity, μ .
3. Molar heat capacity, C_p .
4. Heat capacity, c_p .
5. Thermal conductivity.
6. Ratio of specific heat to viscosity.
7. Reciprocal of the kinematic viscosity.
8. Prandtl number.
9. Reciprocal of the square of the kinematic viscosity.

The cutoff is computed for each temperature and for each starting composition.

The following equations were employed in the calculations:

1. Diffusivity

(a) For components other than H_2O :

$$D_{i, \text{mix}} = \frac{1 - y_i}{\sum_{k=1}^5 y_k / D_{ik}} \quad (\text{where } k \neq i)$$

where,

$$D_{ik} = \frac{.001858 T^{3/2} \left[\frac{1}{m_i} + \frac{1}{m_k} \right]^{1/2}}{\rho \sigma_{ik}^2 \Omega_d}$$

y_i = instantaneous mole fraction of component i

T = temperature in degrees Kelvin

m_i = molecular weight of component i (see tables)

ρ = pressure in atmospheres

$\sigma_{ik} = \frac{1}{2} (\sigma_i + \sigma_k)$ = Lennard-Jones force constant or collision diameter (see tables)

$$\Omega_d = \Omega_d \left(\left\{ \frac{k}{e} \right\}_i^{1/2} \left\{ \frac{k}{e} \right\}_k^{1/2} T \right) \text{ (see tables)}$$

(b) For H_2O :

$$D_{H_2O, \text{mix}} = \frac{1}{\sum_{k=1}^5 y_k / D_{H_2O, k}}$$

where the $D_{H_2O, k}$'s are defined similarly.

2. Viscosity

$$\mu_{\text{mix}} = \frac{\sum_{i=1}^5 \mu_i y_i}{\sum_{k=1}^5 y_k \Phi_{ik}}$$

where

$$\Phi_{ik} = \frac{\left\{ 1 + \left[\frac{\mu_i}{\mu_k} \right]^{1/2} \left[\frac{m_k}{m_i} \right]^{1/4} \right\}^2}{2\sqrt{2} \left[1 + \frac{m_i}{m_k} \right]^{1/2}}$$

μ_i = viscosity of component i (at temperature T)

3. Heat Capacity - C_p

$$C_{p_{\text{mix}}} = \sum_{i=1}^5 y_i C_{pi}$$

where

C_{pi} = heat capacity of component i (at temperature T)

4. Heat Capacity - c_p

$$c_p = \frac{C_{p_{\text{mix}}}}{m}$$

where

$$m = \sum_{i=1}^5 y_i m_i$$

5. Ratio of c_p to viscosity

$$\frac{c_{p \text{ mix}}}{\mu \text{ mix}}$$

6. Thermal Conductivity

$$K_{\text{mix}} = \sum_{i=1}^5 \frac{K_i y_i}{\sum_{k=1}^5 y_k \phi_{ik}}$$

where

$$\phi_{ik} = \frac{1}{4} \left\{ 1 + \left[\frac{\mu_i}{\mu_k} \left(\frac{m_k}{m_i} \right)^{3/4} \left(\frac{T + S_i}{T + S_k} \right) \right]^{1/2} \right\}^2 \left[\frac{T + S_{ik}}{T + S_i} \right]$$

K_i = thermal conductivity of component i (at temperature T)

$$S_i = 1.5 T_{bi}$$

T_{bi} is the boiling point of component i (see tables)

$$S_{ik} = (S_i S_k)^{1/2}$$

7. Reciprocal of the Kinematic Viscosity

$$\frac{1}{\nu} = 0.1 \frac{\rho_{\text{mix}}}{\mu_{\text{mix}}}$$

where

$$\rho_{\text{mix}} = \frac{12.2}{T} \text{ m.}$$

8. Prandtl Number

$$N_{\text{pr mix}} = 2.42 \frac{\mu_{\text{mix}} c_{p \text{ mix}}}{K_{\text{mix}}}$$

9. Reciprocal of the Square of Kinematic Viscosity

$$\left(\frac{1}{\nu} \right)^2 = 0.01 \left[\frac{\rho_{\text{mix}}}{\mu_{\text{mix}}} \right]^2$$

The instantaneous mole fractions are given by:

$$T < 660^\circ \text{C}$$

$$y_{H_2} = \frac{b' - 3x'}{1 + 2x'}$$

$$y_{CO} = \frac{e' + 3x'}{1 + 2x'}$$

$$T \geq 660^\circ \text{C}$$

$$y_{H_2} = \frac{b - \frac{3}{2}x}{1 + \frac{1}{2}x}$$

$$y_{CO} = \frac{e + \frac{3}{2}x}{1 + \frac{1}{2}x}$$

$$T < 660^{\circ}\text{C}$$

$$y_{\text{CO}_2} = \frac{c' - 3x'}{1 + 2x'}$$

$$y_{\text{HCl}} = \frac{d' + 6x'}{1 + 2x'}$$

$$y_{\text{Al}_2\text{Cl}_6} = \frac{a' - x'}{1 + 2x'}$$

$$T \geq 660^{\circ}\text{C}$$

$$y_{\text{CO}_2} = \frac{c = \frac{3}{2}x}{1 + \frac{1}{2}x}$$

$$y_{\text{HCl}} = \frac{d + 3x}{1 + \frac{1}{2}x}$$

$$y_{\text{AlCl}_3} = \frac{a - x}{1 + \frac{1}{2}x}$$

The primed and unprimed quantities are related as follows:

$$a = \frac{2a'}{1 + a'}$$

$$b = \frac{b'}{1 + a'}$$

$$c = \frac{c'}{1 + a'}$$

$$d = \frac{d'}{1 + a'}$$

$$e = \frac{e'}{1 + a'}$$

$$x = \frac{2x'}{1 + a'}$$

x is the mole fraction of Al_2Cl_6 (or AlCl_3) reacted.

μ_i and K_i are computed as follows:

$$\mu_i(T) = \mu_i(T') \frac{f_1(1.33 \text{ Tr}_i)}{f_1(1.33 \text{ Tr}'_i)}$$

$$K_i(T) = K_i(T'') \frac{f_1(1.33 \text{ Tr}_i)}{f_1(1.33 \text{ Tr}''_i)}$$

where T' and T'' are reference temperatures taken to be 200°C and 0°C respectively.

f_1 = viscosity temperature function (see tables)

$$\text{Tr}_i = \frac{T}{T_{c_i}}$$

where

T_{c_i} = critical temperature of component i (see tables)

The Cp_i are computed as follows:

$$\text{Cp}_{\text{H}_2} = 6.62 + 0.81 \times 10^{-3} T$$

$$\text{Cp}_{\text{CO}} = 6.6 + 1.2 \times 10^{-3} T$$

$$\text{Cp}_{\text{CO}_2} = 7.70 + 5.3 \times 10^{-3} T - 0.83 \times 10^{-6} T^2$$

$$\text{Cp}_{\text{HCl}} = 6.7 + 0.84 \times 10^{-3} T$$

$$\text{Cp}_{\text{Al}_2\text{Cl}_6} = 39.6 - \frac{5.38 \times 10^5}{T^2}$$

$$\text{Cp}_{\text{AlCl}_3} = 19.8 - \frac{2.69 \times 10^5}{T^2}$$

In addition, the cutoff, $x_{\max}$, is computed as the solution to one of the equations:

$$T < 660^{\circ}\text{C}$$

$$e^{13.58 + \frac{11,300}{T}} = \frac{(d' + 6x')^6 (e' + 3x')^3}{(a' - x') (b' - 3x')^3 (c' - 3x')^3 (1 + 2x')^2}$$

$$T \geq 660^{\circ}\text{C}$$

$$e^{21.15 + \frac{3620}{T}} = \frac{(d + 3x)^6 (e + \frac{3}{2}x)^3}{(a - x) (b - \frac{3}{2}x)^3 (c - \frac{3}{2}x)^3 (1 + \frac{1}{2}x)^2}$$

The assumed values for the various quantities are listed below:

	m_i	$\left\{\frac{k}{e}\right\}_i (1/^{\circ}\text{K})$	$\sigma_i (\text{\AA})$
H ₂	2.016	.03003	2.968
CO	28.000	.009091	3.59
CO ₂	44.000	.005263	3.996
HCl	36.465	.002778	3.305
Al ₂ Cl ₆	266.682	.002045	8.87
AlCl ₃	133.341	.001855	6.664
H ₂ O	18.016	.002809	2.649
	$\mu_i (\text{Cp})$ at 200°C	$S_i (^{\circ}\text{K})$	$T_{c_i} (^{\circ}\text{K})$
H ₂	.012	30.3	33.9
CO	.0246	124.5	134.0
CO ₂	.022	291.0	304.0
HCl	.0222	283.5	324.5
Al ₂ Cl ₆	.0076	679.5	700.0
AlCl ₃	.009	679.5	635.0
	$K_i \left(\frac{\text{Btu}}{\text{hr} - \text{ft}^2 - ^{\circ}\text{F}/\text{ft}} \right)$ at 0°C	T_b	$S - 1.5 T_b$
H ₂	.0966	20	30
CO	.0134	83	124
CO ₂	.0084	194	290
HCl	.01015	189	284
Al ₂ Cl ₆	.00136	453	680
AlCl ₃	.00175	453	680
H ₂ O		373	560

The values of the collision integral, Ω_d , and the viscosity temperature function, f_1 , are based on the Lennard-Jones Potential²⁸.

The initial or feed gas compositions were assumed as given in mole fractions in Table B1.

TABLE B1
INITIAL OR FEED GAS COMPOSITIONS

Case	AlCl ₃	H ₂	CO ₂	CO	HCl
1	.01	.98	.01		
2	.01	.495	.495		
3	.01	.01	.98		
4	.01	.88	.01	.1	
5	.01	.445	.445	.1	
6	.01	.01	.88	.1	
7	.01	.88	.01		.1
8	.01	.445	.445		.1
9	.01	.01	.88		.1
10	.01	.01	.78	.1	.1
11	.01	.395	.395	.1	.1
12	.01	.01	.78	.1	.1
13	.1	.8	.1		
14	.1	.45	.45		
15	.1	.1	.8		
16	.1	.7	.1	.1	
17	.1	.4	.4	.1	
18	.1	.1	.7	.1	
19	.1	.7	.1		.1
20	.1	.4	.4		.1
21	.1	.1	.7		.1
22	.1	.6	.1	.1	.1
23	.1	.35	.35	.1	.1
24	.1	.1	.6	.1	.1
25	.05	.9	.05		
26	.05	.478	.478		
27	.05	.05	.9		
28	.05	.8	.05	.1	
29	.05	.425	.425		.1
30	.05	.05	.8	.1	.1
31	.24	.36	.36	.04	
32	.2	.3	.3	.1	.1

The results of the above calculations are available under Reference 25.

A representative set of results is presented in the Figures B1 through B5 inclusive. The variations in the physical properties from the feed gas to the completely reacted gas compositions are apparent. The discontinuity in some of the curves at approximately 660°C results from the thermal decomposition of Al₂Cl₆ into AlCl₃.

Fig. B1 - Diffusivity of hydrogen as a function of gas temperature and composition

Initial Composition:

H₂ - 80 vol %
CO₂ - 10 vol %
AlCl₃ - 10 vol %

Fig. B2 - Diffusivity of carbon dioxide as a function of gas temperature and composition

Initial Composition:

H₂ - 80 vol %

CO₂ - 10 vol %

AlCl₃ - 10 vol %

Fig. B3 - Diffusivity of aluminum chloride as a function of gas temperature and composition

Initial Composition:

H₂ - 80 vol %

CO₂ - 10 vol %

AlCl₃ - 10 vol %

Fig. B5 - Prandtl number and thermal conductivity as a function of gas composition and temperature

APPENDIX C

Fabrication Procedures For Alumina Coating Of The Bore Of Tubes By Vapor Deposition

This appendix presents the preliminary fabrication procedures and specifications for coating the I. D. of fuel tubes with Al_2O_3 by vapor deposition. The process as detailed represents the status of the process at the conclusion of the production series.

1. GENERAL

The processing of tubes for coating consists of two types of operations. The first one is the preparation of tubes for coating and the second is the actual coating procedure. The preparation of the tubes is a procedure for thoroughly cleaning of the tubes. The coating procedure itself consists of two consecutive one-hour exposures of the tubes to the coating atmosphere. A flow sheet for the entire process is shown in Figure C1.

2. CRITICALITY

The danger of assembling a critical mass of U^{235} is eliminated by limiting all lots to 300 tubes, five inches long or their equivalent. In no case can a batch of tubes exceed 200 grams of contained UO_2 . All such batches must be separated from every other batch by at least one foot edge to edge distance at all times.

3. HEALTH HAZARDS

The cautious handling of the tubes should be emphasized since both UO_2 and BeO are toxic. All handling must be done wearing gloves, and used gloves must be handled as contaminated waste.

The anhydrous aluminum chloride used in this process is not toxic, but it is an irritant to the skin, eyes, and mucous membranes, due to the fact that it forms hydrochloric acid on contact with water. The dry material should be handled in an exhausted hood at all times, except when placing the material in the apparatus.

4. TUBE PREPARATION

a. General

The purpose of this operation is to thoroughly clean, weigh, and batch the tubes prior to coating. It is essential that only good, crack-free tubes be introduced into this operation. It is recommended that the inspection for cracks be done by statiflux and ultrasonic scan prior to receipt for coating.

b. Equipment Required

1. Ultrasonic cleaning unit
2. Water rinse facility
3. Drying oven
4. Mettler balance
5. Dry Box
6. Diamond tipped Vibro-tool

c. Procedure

1. The tubes, as received, are loaded in the basket for the ultrasonic cleaner. A convenient load for the cleaner is about 60 tubes.
2. The loaded basket is hung in the ultrasonic cleaning tank.
3. Turn on "Main Line" switch and then turn on the "Plate Power" switch.
4. Adjust both control knobs, if necessary, to keep meter readings between the red lines.

Fig. C1 - Flow Diagram of Production Process

5. Run for five minutes.
6. Turn off transducers and power.
7. Remove basket from tank.
8. Rinse thoroughly with water.
9. Remove tubes from basket, drain, and place in drying oven.
10. Dry for 15 minutes at 105°C.
11. Remove tubes from oven and allow to cool.
12. Make up batches of 15 tubes each, sealing each unit of 15 tubes in a plastic bag.
13. The batched tubes are placed in a dry box and numbered with run number and tube number using a diamond tipped Vibro-tool.
14. Each batch is then entered in a log book by batch number and individual tube number.
15. Weigh each tube and record weight.
16. Identify each bag of batched, numbered and weighed tubes with the batch number and the phrase "Ready for 1st Pass."

5. TUBE COATING

a. General

The purpose of this operation is to apply a dense, uniform, and continuous Al_2O_3 coating to the I. D. of the ceramic tubes. This is accomplished by heating the tubes to 1100°C and passing the reacting gas mixture through them. The gas mixture is passed through from one end for half the application time and from the other end for the other half of the application time.

b. Equipment Required

1. 30 KW M. G. set or equivalent induction heating power source.
2. Vapor coating rig as shown in Figure C2.
3. Filtered, acid-proof exhaust system.

c. Raw Materials

1. Aluminum chloride, anhydrous, granular, reagent grade.
2. Hydrogen, dry.
3. Carbon dioxide, dry.

d. Procedure for Coating I. D. of Ceramic Tubes

1. Weigh out 150 ± 10 grams of AlCl_3 , record weight and place AlCl_3 in vapor pot.
2. Place pot in furnace well.
3. Place aluminum support tube over well.
4. Place $\frac{3}{4}$ -inch-long BeO spacers inside susceptor openings.
5. Place tubes in the susceptor openings in their numerical order clockwise from the scribed line on top of the susceptor. On first pass, place the end of the tube bearing the run number toward the top of the susceptor with the number toward the outside.
6. Place $\frac{3}{4}$ -inch-long BeO spacers on top of each tube.
7. Place susceptor on the support tube in such a way that the scribed line on it coincides in rotation with that of the scribed line on the base.
8. Place the fused quartz tube over the entire assembly.
9. Place asbestos cord in the joint of the quartz tube and the furnace base.
10. Apply Sauereisen No. 31 over the cord making a seal at the tube base joint.
11. Fasten induction coil to power leads.
12. Turn on water supply to induction coil.
13. Attach gas exit line to No. 1 water trap.

Fig. C2 - Rig for Al_2O_3 Vapor Deposition on Bore of Tubes

14. Start purge with CO₂. Adjust flowmeter setting to 2. At this time begin taking data for run and recording it on data sheet. See sample run data sheet Figure 4.
15. Adhere to the time schedule defined in Table C1 for rest of run.

TABLE C1
COATING TIME SCHEDULE

Time Interval Minutes	Time Elapsed Minutes	Operation to Perform	Remarks
	0	Start purge	CO ₂ setting -2
5	5	Increase purge flow	CO ₂ setting -10
5	10	Change gas mixture and check for leaks	CO ₂ setting -2 H ₂ setting -4
5	15	Start M-G set	Set power at 13 KW
10	25	Increase preheat and pot variacs. Reduce M-G - Set power to about 7.5	Setting for each -60
20	45	Reduce preheat and pot variac settings	Preheat to 50, pot to 40
5	50	Switch both CO ₂ and H ₂ to sweep	CO ₂ -2 H ₂ -4
50	100	Reduce preheat and pot variac settings	Reduce both settings to 10
10	110	Switch to purge and blow air on vapor pot	CO ₂ -2 H ₂ -4
20	130	Power off	
35	165	H ₂ turned off, CO ₂ setting increased	CO ₂ -10
10	175	Shut off CO ₂ and open furnace according to following steps	CO ₂ -10

1. Turn off water supply to induction coil.
2. Remove coil from power leads.
3. Remove exit line.
4. Break seal at furnace base.
5. Remove quartz tube.
6. Remove susceptor.
7. Remove $\frac{3}{4}$ -inch spacers and ceramic tubes from susceptor with forceps.

8. The tubes are then brushed, cleaned and weighed as in procedure for tube preparation - Steps 1-11.
9. Remove alundum support tube from base.
10. Remove AlCl_3 pot from furnace well.
11. Weigh AlCl_3 , record weight, and weight loss during run in record book.
12. Clean and brush furnace thoroughly.
13. Re-insert tubes with run number inside and down for second pass and repeat above procedure.
14. Record all temperatures and M-G set meter readings at 10 minute intervals during course of coating time schedule.

6. INSPECTION

a. General

The purpose of the inspection procedures is to eliminate those tubes not satisfactory for reactor use. The following criteria are used for this purpose:

1. Total weight gained in coating must correspond to required thickness of coating.
2. α count on the I. D. must be less than 50 cpm.
3. There are to be no cracks detected by either statiflux or ultrasonic scan.
4. There are to be no bond defects as determined by ultrasonic scan.
5. There are to be no obvious flaws such as gross deposition of coating, chips, pin holes, or gouges as determined by a visual I. D. and O. D. inspection.

b. Procedure

1. The total weight for each tube is checked and tabulated; any tube which has either too little or too much weight gain is rejected.
2. The tubes are visually inspected for obvious flaws, rejecting tubes showing gross deposition of coating as evidenced by white deposits on the I. D. or tubes with chipped ends when chip extends across wall of tube.
3. The I. D. of the tubes is then checked for α count, rejecting tubes giving an α count of 50 cpm or higher.
4. The tubes are checked for external cracks by statiflux, rejecting tubes exhibiting cracks by this method.
5. The tubes are checked ultrasonically for internal cracks, rejecting tubes registering cracks.
6. The tubes are checked by ultrasonic scan for bond defects, rejecting tubes showing a bond defect.

The tubes passing all of the above inspection routines are then packaged as "acceptable" tubes.

7. PACKAGING AND STORING

a. General

The purpose of this step is to package accepted tubes and dispose of rejected tubes.

b. Procedure

1. Record the uncoated weight of all tubes that have passed inspection and record tabulation in duplicate.
2. Place tubes in a plastic bag and seal with masking tape. Place the tubes with a copy of the weight tabulation into a one-gallon can. Place can in storage area and retain file copy of weight tabulation.
3. Record uncoated weight of all rejected tubes and tabulate in duplicate.

4. Package as above for passed tubes and place can in scrap area.
5. Storage areas must be arranged so that each gallon can is at least a one-foot separation edge to edge from all other cans. This separation must be positively maintained.

8. ACCOUNTABILITY

a. General

Since the UO_2 in the tubes is accountable, an accurate set of records must be maintained to account for the material on hand.

b. Procedure

1. Maintain record of all incoming material.
2. All coated tubes, both "passed" and "rejected", should be recorded, employing standard accountability procedures to prevent excessive accumulation of material.
3. Data for each phase of the accountability can be taken from the process records.
4. It is essential to maintain accurate and up-to-date records.

9. WASTE DISPOSAL

a. General

These procedures are to cover the disposal of contaminated waste generated by the processing and the disposal of chemical waste from the process. The contaminated waste is generated in both the scrubbing bottles and the ultrasonic cleaner. The chemical waste is in the form of the residual chloride from each run.

b. Procedures

1. Scrubber Flasks

- a. Once a day remove flasks from coating rig.
- b. Place in exhausted hood and neutralize acid by adding sodium hydroxide pellets until solution is neutral as registered on pH indicator paper. The pellets must be added slowly to prevent excessive heating and boiling of the solution.
- c. Pour neutral solution into liquid contaminated waste drum, observing safety practices for handling beryllium.

2. Ultrasonic Cleaner

- a. Once a day drain cleaning tank.
- b. Put liquid into liquid contaminated waste drums.
- c. Rinse tank thoroughly with water.
- d. Put all rinse water in liquid contaminated waste drum.

3. Aluminum Chloride Waste

- a. After weighing residual chloride from each run, transfer to a dry waste jar in an exhausted hood.
- b. As each waste jar is filled, the contents are transferred to a double plastic bag and sealed.
- c. Sealed plastic bags are employed for ultimate disposal.

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GENERAL ELECTRIC