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Bloom et al.

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[54] APPARATUS FOR FORMING A REFRACTORY COATING ON THE INNER PERIPHERY OF A TUBULAR OBJECT

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[52] **U.S. Cl.** **118/48,** 118/65

[51] **Int. Cl.** **C23c 11/00**

[58] **Field of Search** 118/48–49.5, 620, 118/642, 641, 643, 306, 317, 318; 117/106, 95–97

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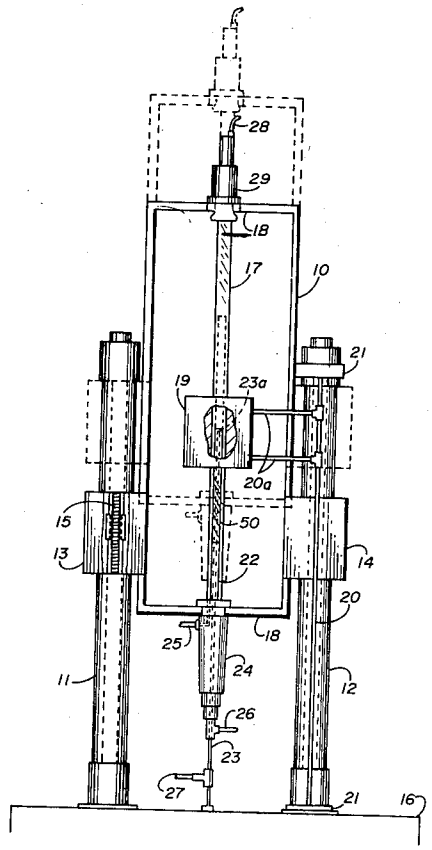
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[57] **ABSTRACT**

Means to vapor-coat the inside of a tubular object includes an annular heater surrounding a portion of the object, a lance-nozzle extending within the object. The nozzle is transversely aligned with and fixed with respect to the heater. Means effect relative longitudinal motion between the tubular object and the aligned heater and nozzle.

12 Claims, 3 Drawing Figures



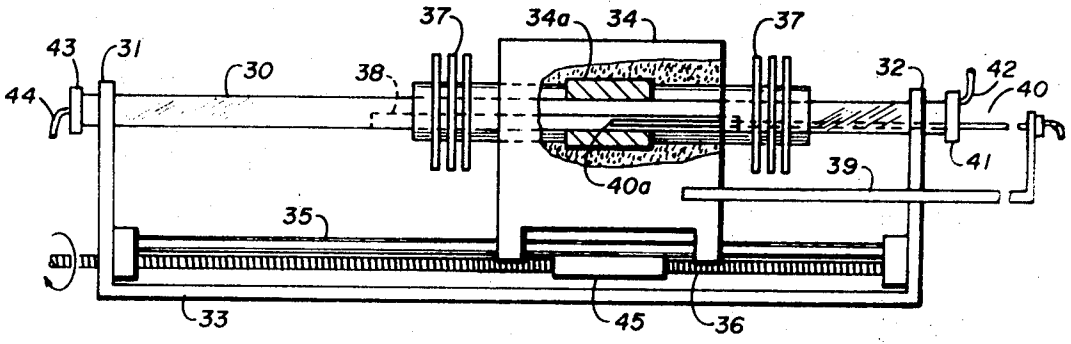


FIG. 3

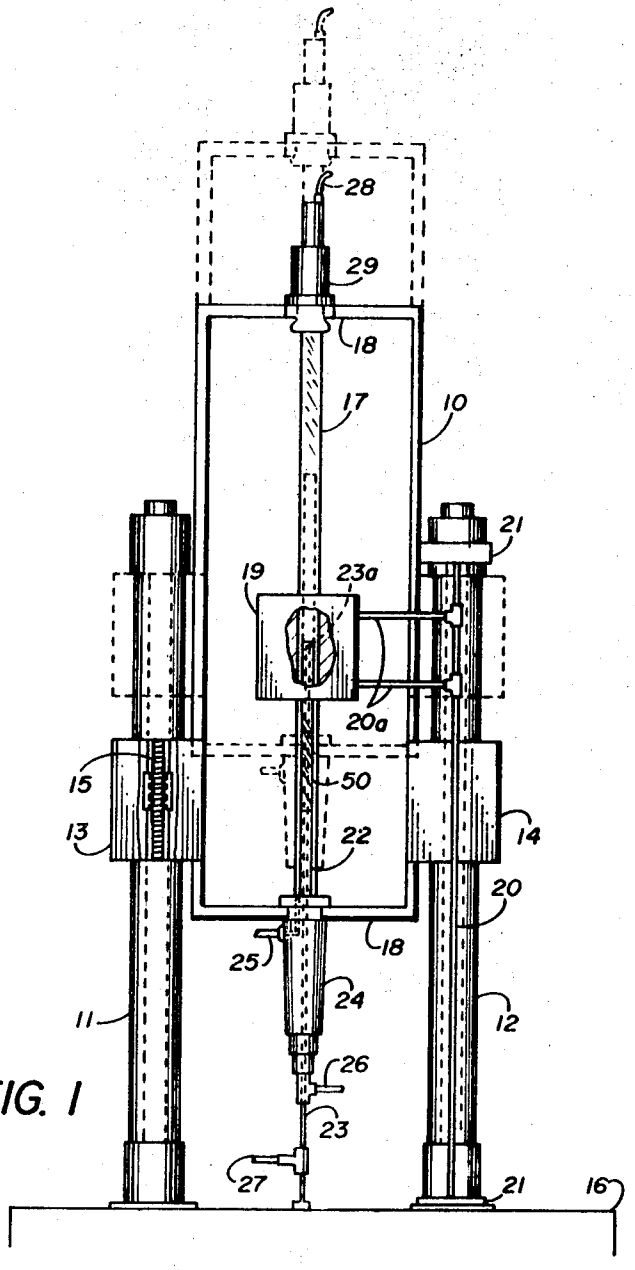


FIG. 1

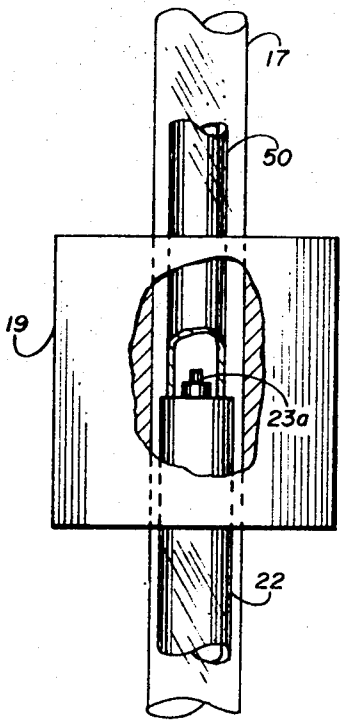


FIG. 2

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APPARATUS FOR FORMING A REFRACTORY COATING ON THE INNER PERIPHERY OF A TUBULAR OBJECT

This invention relates to coatings and coating techniques. In another aspect, this invention relates to an apparatus for forming a refractory coating on the inner periphery of a tubular object.

It is known to coat the interior of certain tubular objects such as gun barrels and rifle barrels with wear-resistant metals such as chromium and alloys thereof. However, the conventional coatings have proven somewhat inefficient in preventing damage to the interior of tubular objects which are subjected to extreme and continuous abrasive and/or thermal conditions.

Various processes are known in the art for depositing a refractory coating such as titanium carbide on a substrate. However, the processes have not been adapted for coating the interior of tubular objects.

Recently a process has been developed for coating substrates with a solid-solution carbonitride of a metal selected from silicon, boron, and transition metals in groups IVB, VB and VIB of the Periodic Table, for example, titanium carbonitride. This recently developed process is described in copending patent application Ser. No. 769,356 filed Oct. 21, 1968 now abandoned. This process can occur either at low temperatures, thus permitting the application of a hard coat to a metal without loss of hardness and temper which has been imparted to the metal by previous heating steps, or at higher temperatures for materials having compatible thermal behavior in any step required after the coating operation. Not only can the metal carbonitride exhibit greater toughness than materials such as titanium carbide or titanium nitride, but the deposition rate obtainable with the metal carbonitride is from about 2 to 10 times that of titanium carbide, for example. This process includes the steps of heating the substrate to at least the decomposition temperature of the reactants (generally from about 400° to about 1,200° C.) and then passing a gaseous stream containing the reactants over the substrate to thereby yield the reactants at the temperature of the body to permit the reaction of the metal, carbon, and nitrogen, thereby forming a solid solution of the metal carbonitride on the body.

The reactants generally include a metal halide, e.g., titanium tetrachloride, molecular nitrogen and/or an easily decomposable nitrogen-containing compound, an easily decomposable carbon-containing compound (alternatively, an easily decomposable nitrogen and carbon-containing compound can be used), and molecular hydrogen as a reducing agent.

The metal carbonitride coating applied by this recently developed method is a solid-solution material having the metal carbon and nitrogen within a single phase crystal lattice. In addition to the great hardness of the material, the strong bonding present gives a relatively large surface energy to the material. This large surface energy is believed to render the material less likely to wet and adhere to the molten materials such as glass.

Even more recently, a technique has been developed whereby vaporous reactants can be utilized to deposit the solid-solution layer of a metal carbonitride on the inner periphery of a tubular object. This technique is disclosed in copending application Ser. No. 850,351 filed Aug. 15, 1969.

Therefore, one object of this invention is to provide an apparatus for depositing a layer of a refractory material on the inside periphery of a tubular object.

Another object of this invention is to provide an improved apparatus for forming a solid-solution layer of a metal carbonitride on the inner periphery of a tube.

According to the invention, an apparatus is provided for forming a smooth, continuous layer of a refractory material such as a metal carbonitride on the inner periphery of a tubular object comprising a heater means for uniformly heating a circumferential section of the tubular object in combination with an elongated nozzle means for depositing vaporous reactants directly within the heated tubular section, and means to move the tubular object relative to the outlet of the nozzle and the heater means in a manner so that successive, contiguous sections of the tubular object are thereby heated and positioned adjacent the outlet of the elongated nozzle means.

This invention can be more easily understood from a study of the drawings in which:

FIG. 1 is a front elevational view, partially in section, of a preferred embodiment of this invention;

FIG. 2 is a partial detail view of a portion of the apparatus as illustrated in FIG. 1 in moved position; and

FIG. 3 is a side elevational view of another embodiment of this invention.

Now referring to FIG. 1, a preferred apparatus of this invention is illustrated wherein the dotted line portion illustrates a moved position thereof. Frame **10** is disposed between guide members **11** and **12**. Guide members **11** and **12** generally comprise semicylindrical members having rotatably mounted worm gears **15** positioned therein which cooperate with threaded rear portions of guide blocks **13** and **14**. Worm gears **15** are attached to a suitable actuation means (not shown) such as an electric motor or a hand crank which will impart a simultaneous rotating motion thereto. Thus, as worm gears **15** are rotated, the engagement between the gears and the threaded portions of blocks **13** and **14** will cause frame **10** to move in a vertical plane. Quartz tube **17** is mounted between support members **18** of frame **10** and is positioned through annular heater **19**. Annular heater **19** is suspended from rod **20** by arms **20a**. Rod **20** is disposed between fixed members **21** which extend from guide member **12**. Annular heater **19** can be any suitable heating device such as an electric resistance heater.

The lower portion of quartz tube **17** is positioned over tube seating section **22** which is adapted to receive an open end of a tubular object to be treated. Elongated nozzle **23** is slidably mounted through tube closure member **24** and tube seating section **22** with its lower end attached to platform **16**. The outlet end **23***a* of nozzle **23** extends to a fixed position adjacent the middle of annular heater **19**. Inlet conduit **25** communicates through tube closure member **24** with the interior of quartz tube **17** and functions to introduce a purge gas therethrough. Reactant inlet conduits **26** and **27** communicate with nozzle **23** to introduce vaporous reactants thereto. Outlet conduit **28** communicates through top closure member **29** to the upper region of quartz tube **17** to remove vaporous reactants and purge gases therefrom.

FIG. 3 is an elevational view of another embodiment of this invention for coating the interior of a tubular object which is disposed in a horizontal plane. Quartz tube **30** is positioned between support members **31** and **32** of frame **33**. Heater **34** is slidably mounted on guide rods **35** which are positioned between support members **31** and **32**, and is adapted to receive quartz tube **30** therethrough. Worm gear **36** is rotatably mounted between support members **31** and **32** and operatively attached to a suitable means such as an electric motor or hand crank (not shown) for imparting rotational motion thereto. Worm gear **36** is in threadable contact with portion **45** of heater **34** such that rotation of worm gear **36** will cause heater **34** to move in a horizontal plane on guide rods **35**. Radiator means **37** are operatively connected to the annulus through heater **34** for receiving quartz tube **30**, and function to dissipate excess heat into the atmosphere and away from a tubular object **38** which is positioned therewithin.

Guide arm **39** extends in an attached position from heater **34** to receive one end of elongated nozzle **40**. Elongated nozzle **40** is positioned eccentrically through quartz tube closure member **41** in a slidable relationship and extends within quartz tube **30** to a point adjacent the center of the heat zone **34a** within heater **34**. In this manner, elongated nozzle **40** will also extend within tubular object **38** laying within quartz tube **30**. Inlet conduit **42** communicates through quartz tube closure member **41** to the interior of quartz tube **30** for introducing a purge gas therein. Tube closure member **43** is operatively attached to the opposite end of tube **30** and carries outlet conduit **44** operatively extending therethrough for receiving ex-

haust purge and reactant gases from the interior of quartz tube **30**.

The two above described devices can be utilized to deposit a solid solution of a metal carbonitride on the interior of a suitable tubular object such as a gun barrel or any other suitable tube, the interior of which is frequently subjected to extreme frictional and/or thermal conditions. Specifically, it has been recently discovered that in order to obtain a continuous uniform layer of a solid solution metal carbonitride on a substrate in a vapor phase deposition process, it is necessary that a non-equilibrium condition exist between the vapor phase reactants adjacent the substrate and the reactants on the substrate. The apparatus of this invention can thereby be used to coat the interior of a tubular object according to this newly discovered process whereby relatively cool vaporous reactants are introduced immediately adjacent the interior surface of a heated tube, i.e., successively along contiguous heated segments of the tube.

In the operation of the apparatus as illustrated in FIG. **1**, a suitable tubular object **50** is initially positioned within quartz tube **17** in operative position upon tube seating section **22**. Nozzle **23** extends up within the tube so that the outlet **23***a* thereof is positioned in the center of annular heater **19**. The driving means for worm gears **15** is actuated to lower frame **10** to the position as illustrated in solid line in FIG. **1** such that the top of tube **50** is positioned within annular heater **19** with outlet **23***a* of elongated nozzle **23** positioned adjacent thereto.

Next, annular heater **19** is actuated to heat the segment of tube **50** therewithin to a suitable deposition temperature for vaporous chemical reactants. Additionally, a purge gas such as hydrogen is passed through quartz tube zone **17** via conduits **25** and **28**. The hydrogen will clean the surface of the tubular object **50** by reducing action. Next, a vaporous reactant stream is passed into elongated nozzle **23** from conduits **26** and **27**. This vaporous stream generally contains molecular hydrogen, a carbon-containing compound which readily decomposes at the deposition temperature (temperature at which heater **19** heats the inner periphery of tube **50**), a metal-containing compound which readily decomposes at the deposition temperature, molecular nitrogen, and/or a nitrogen-containing compound which readily decomposes at the deposition temperature. Alternatively, the nitrogen and carbon can be supplied from a single compound containing both nitrogen and carbon which readily decomposes at the deposition temperature.

Suitable metal-containing reactant compounds include metal halides. A preferred group of the metal halides is represented by the generic formula $Me(x)_n$ where n is a valence of Me, x is a halogen, e.g., fluorine, chlorine, bromine, and iodine, and Me is selected from silicon, boron, and transition metals in groups IVB, VB, and VIB of the Periodic Table as set forth on page B-2 of the *Handbook of Chemistry and Physics*, Chemical Rubber Company, 45th Edition, (1964). Generally, the transition metal tetrahalides such as titanium tetrachloride are most preferred. However, the transition metal dihalides and trihalides can be useful in some applications, particularly the higher temperature coating operations.

Suitable carbon-containing reactant compounds include cyclic and acyclic hydrocarbons having up to about 18 carbon atoms which readily decompose at the deposition temperature. Examples of suitable hydrocarbons include the paraffins such as methane, ethane, propane, butane, pentane, decane, pentadecane, octadecane, and aromatics such as benzene and halogen substituted derivatives thereof.

Suitable reactant compounds containing both carbon and nitrogen include aminoalkenes, pyridines, hydrazines, and alkylamines. Some specific examples include diaminethylene, triaminoethylene, pyridine, trimethylamine, triethylamine, hydrazine, methylhydrazine, and the like.

The apparatus of this invention will allow the coating process to occur under conditions whereby the interior of the tube to be coated is maintained at the proper deposition temperature (the temperature whereby the vaporous reactants will decompose and form in the reactive state). Additionally, the vaporous reactant stream in the tube adjacent the heated periphery is maintained substantially below the decomposition temperature of the reactant compounds in a manner so that unwanted products will not form in the vaporous state which are deleterious to the application of a smooth and continuous solid-solution metal carbonitride coating on the substrate.

The temperature to which the tube is heated will depend upon the particular reactants employed, but will generally vary within the temperature range of at least 400° to about 1,200° C. Preferably, reactants are selected which will decompose and react within the temperature range of about 550° to about 750° C., and the most improved results occur with the reactants which decompose within the range of about 650° to 700° C. The preferred reactants include a titanium tetrahalide, e.g., titanium tetrachloride, an amine, e.g., trimethylamine, hydrogen and nitrogen.

The temperature at which the vaporous reactant atmosphere in the tube adjacent the heated periphery has to be maintained will vary somewhat with the reactants being utilized. However, it is preferred to maintain a temperature of this atmosphere of vaporous reactants below about 400° C. since this is the temperature at which substantial decomposition of most of the reactant compounds will occur. It is generally preferred that the temperature of the vaporous reactant atmosphere within the tube adjacent the heated periphery be maintained between 300° and 400° C.

Thus, the reactants flowing from outlet **23***a* of elongated nozzle **23** are relatively cool with respect to the surroundings of the heated section of tube **50** into which they are emitted. For example, they are maintained at a temperature in the range of about 300° to about 400° C. Thus, non-equilibrium temperature conditions exist between the reactants contacting the heated section of tube **50** and the reactant vapor atmosphere therewithin. The reactants then contact the heated interior tube surface, decompose and react to form a solid-solution layer of metal carbonitride therewithin. Outlet purge and reactant vapors are constantly being withdrawn through tube closure member **29** via conduit **28**.

Worm gears **15** are actuated to move frame **10** upwardly at a slow rate. This action will cause tubular object **50** to be sequentially heated along the relatively small deposition zone as frame **10** moves upwardly and thereby provides a very uniform, continuous solid-solution metal carbonitride coating on the interior surface thereof. The rate of movement of frame **10** will depend upon such factors as the thickness of tubular object **50**, the heat output of annular heater **19**, and the flow conditions of the various reactants. The rate of movement should be such that newly heated sections of tubular object **50** adjacent the outlet **23***a* of elongated nozzle **23** will be heated to the proper deposition temperature. It is noted that as frame **10** moves upwardly, both heater **19** and elongated nozzle **23** will remain in a stationary position, and the outlet **23***a* of elongated nozzle **23** will always be positioned within the heated section of tubular object **50** disposed within annular heater **19**. The upward movement will continue until frame **10** reaches the position as illustrated in dotted line, FIG. **1**. This position is clearly illustrated in FIG. **2** wherein the lower end of tube **50** is positioned within heater **19** and the outlet **23***a* of nozzle **23** is contained therewithin.

An example of a typical procedure for coating the inner periphery of a steel tube having a ¼ inch inside diameter and a length of 8 inches with the apparatus as illustrated in FIG. **1**, will include the heated inner periphery of the tube **50** being maintained at about 1,000° C; a flow of reactants entering nozzles **26** and **27** consisting of 0.032 liters/minute of propane, 0.182 liters/minute of $TiCl_4$, 0.23 liters/minute of nitrogen, and 0.188 liters/minute of hydrogen; while frame **10** carries tube **50** through annular heater **19** upward at the rate of 0.05 inches/minute.

Now referring to FIG. **3**, an alternate embodiment of this invention is illustrated in detail. The basic difference between the apparatus as illustrated in FIG. **3** from that which has been

described in relation to FIG. 2 is that the tubular object 38 to be coated is positioned within the horizontal quartz tube 30 in the manner illustrated in FIG. 3. The deposition procedure in using this apparatus is substantially the same as that described above. After tubular object 38 is positioned within quartz tube 30 in a manner so that one end thereof is positioned within heater 34, and outlet 40*a* of elongated nozzle 40 is positioned within such open end of object 38, heater 34 is actuated and hydrogen is passed through tube 30 via inlet conduit 42 and outlet conduit 44. After the tube segment is heated to the proper deposition temperature, worm gear 36 is actuated by the driving means to cause heater 34 carrying elongated nozzle 40 to move along the length of tube 38 (to move to the right as illustrated in FIG. 3). It is noted that radiators 37 comprise fins connected to cylindrical body portions which encircle quartz tube 30 and are made of a highly heat-conductive metallic material. Thus, in operation, they will conduct heat away from quartz tube 30 and dissipate the heat into the atmosphere, thus avoiding any thermal damage to tube 38 which is resting within cylindrical tube 30. In this manner, only that portion of tube 38 which is positioned within heat zone 34*a* of heater 34 will be subjected to a high deposition temperature, and the other portions thereof will be constantly cooled by heat conduction and radiation.

An example of the typical procedure for coating the inner periphery of a gun barrel approximately 17 inches in length with the apparatus illustrated in FIG. 3 will include the heated periphery of tube 38 being maintained at about 1,000° C.; a flow of reactants entering nozzle 40 consisting of titanium tetrachloride in hydrogen at 0.32 liters per minute, hydrogen at 1.1 liters per minute, nitrogen at 0.23 liters per minute, propane at 16 cc. per minute; while heater 34 and elongated nozzle 40 move along the length of the gun barrel at the rate of 0.075 inch per minute.

While this invention has been described in relation to its preferred embodiments, it is to be understood that various modifications thereof will be apparent to one skilled in the art upon reading the specification, and it is intended to cover such modifications as fall within the scope of the appended claims.

We claim:

1. An apparatus for depositing a layer of refractory material on the inside periphery of a tubular object by vapor phase deposition comprising:
   a. heater means for uniformly heating a circumferential section of said tubular object;
   b. an elongated nozzle means for delivering vaporous reactants to form said refractory material, being fixedly positioned relative to said heater means so that the outlet thereof extends within the heated circumferential section of said tubular object; and
   c. means to move said tubular object relative to said heater means and elongated nozzle means at a speed such that sequential sections of said tubular object moving through said heater will be uniformly heated.

2. The apparatus of claim 1 further comprising a tubular reactor positioned through said heater means and enclosing said tubular object.

3. The apparatus of claim 2 wherein said tubular reactor is positioned in a vertical plane through said heater means.

4. The apparatus of claim 3 further comprising a tube seating section positioned in the lower region of said tubular reactor and adapted to receive said tubular object and hold said tubular object in a vertical position within said tubular reactor, said elongated nozzle means being slidably mounted concentrically through said tube seating section.

5. The apparatus of claim 4 further comprising means to pass a gas through said tubular reactor to prevent backstreaming of said vaporous reactants.

6. An apparatus for depositing a layer of refractory material on the inside periphery of a tubular object by vapor phase deposition comprising:
   a. heater means for uniformly heating a circumferential section of said tubular object;
   b. an elongated nozzle means for delivering vaporous reactants to form said refractory material, being fixedly positioned relative to said heater means so that the outlet of the nozzle extends within the heated circumferential section of said tubular object;
   c. a tubular reactor positioned through said heater means and enclosing said tubular object, said tubular reactor being suspended in a horizontal plane; and
   d. means for simultaneously moving said heater means and said nozzle means along the length of said tubular reactor.

7. The apparatus of claim 6 wherein said elongated nozzle is slidably mounted through one end of said tubular reactor and adapted to extend within a tubular object laying therein in said horizontal plane.

8. The apparatus of claim 9 further comprising means to cool said tubular reactor and tubular object (at points adjacent) near each end of said heater means.

9. An apparatus for depositing a layer of refractory material on the inside surface of a tubular object by vapor phase deposition comprising:
   a. a frame member movably secured to a guide member;
   b. a tubular quartz deposition chamber fixedly mounted to said frame member;
   c. an annular heater means circumventing said chamber and fixedly secured to said guide member;
   d. a seating member secured within said deposition chamber for supporting said tubular object within said chamber;
   e. an elongated nozzle extending into said chamber and within said tubular object having an outlet fixedly positioned near the longitudinal and radial center of said annular heater means;
   f. inlet means for introducing vaporous reactants into said nozzle near the lower end thereof;
   g. outlet means for releasing residue vaporous reactants from said chamber near the upper end thereof; and
   h. means for vertically moving said chamber so that a tubular object therein is sequentially uniformly heated and a refractory material is deposited on the inside surface of said tubular object.

10. An apparatus for depositing a layer of refractory material on the inside surface of a tubular object by vapor phase deposition comprising:
   a. a frame member having a support member at each end thereof;
   b. a tubular quartz deposition chamber extending between the support members and fixedly secured thereto;
   c. an annular heater means circumventing said chamber and movably secured to said frame member, said heater means including radiator means for the dissipation of heat;
   d. an elongated nozzle extending into said chamber having an outlet positioned near the longitudinal and radial center of said heater means;
   e. inlet means for introducing vaporous reactants into said nozzle near one end of said chamber;
   f. outlet means for releasing residue vaporous reactants from said chamber near the other end thereof; and
   g. means for simultaneously horizontally moving said heater means and said nozzle so that a tubular object in said chamber is sequentially uniformly heated and a refractory material is deposited on the inside surface of said tubular object.

11. The apparatus of claim 10 further including means for introducing a purge gas into said deposition chamber near said one end thereof to prevent backstreaming of said vaporous reactants.

12. An apparatus for depositing a layer of refractory material on the inside surface of a tubular object by vapor phase deposition comprising:
   a. heater means for uniformly heating a circumferential section of said tubular object;
   b. an elongated nozzle means for delivering vaporous reactants to form said refractory material fixedly positioned

relative to said heater means so that the outlet thereof extends within the heated circumferential section of said tubular object;

c. tubular reactor means positioned in a vertical plane through said heater means and enclosing said tubular object;

d. frame means for retaining and moving said tubular reactor and tubular object therein vertically relative to said heater means and elongated nozzle means at a speed such

that sequential sections of said tubular object moving through said heater will be uniformly heated; and

e. a seating section positioned in the lower region of said tubular reactor and adapted to receive said tubular object and hold said tubular object in a vertical position within said tubular reactor, said elongated nozzle means being slidably mounted concentrically through said tube seating section.

* * * * *