

Nov. 5, 1968

U. E. KUNTZ
VAPOR COATING CONDUCTIVE FILAMENTS
UTILIZING UNIFORM TEMPERATURE

3,409,469

Filed March 5, 1964

4 Sheets-Sheet 1

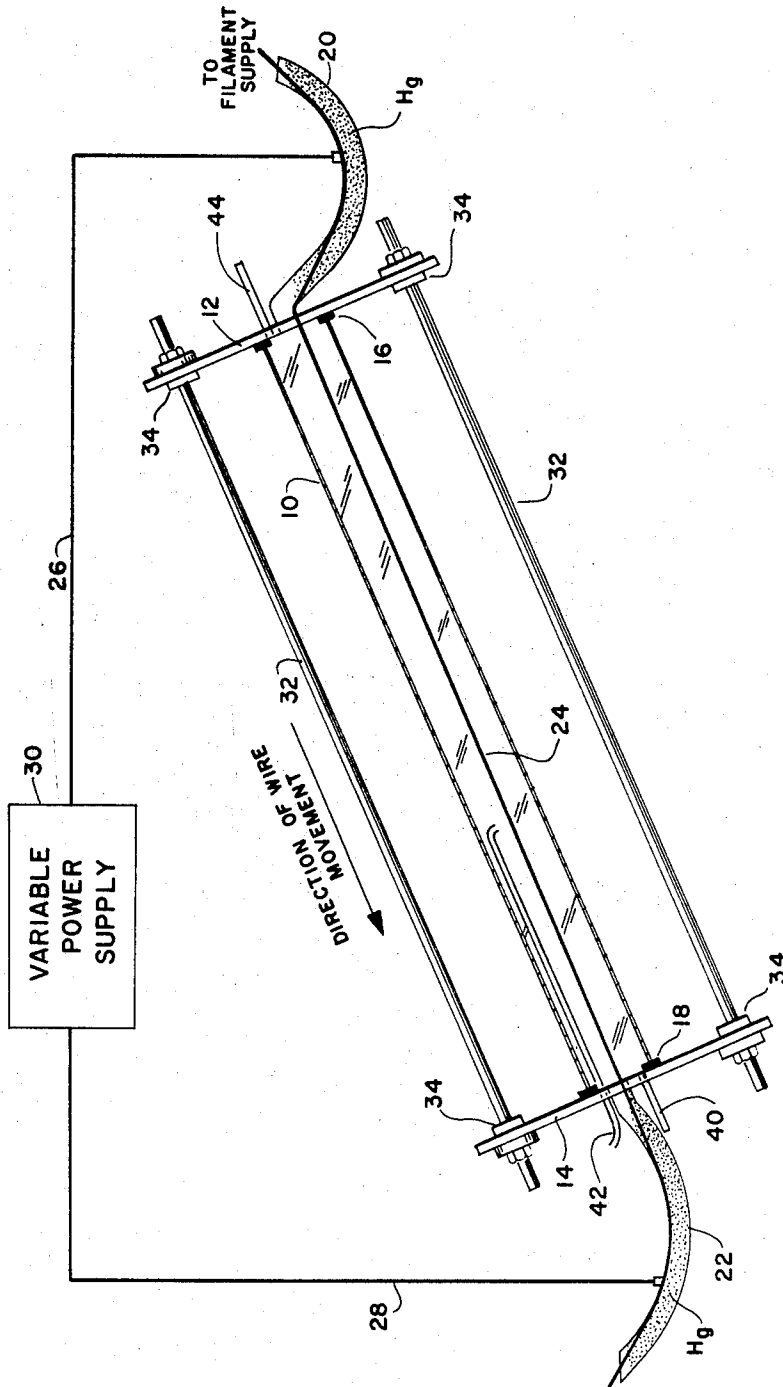


FIG. - I

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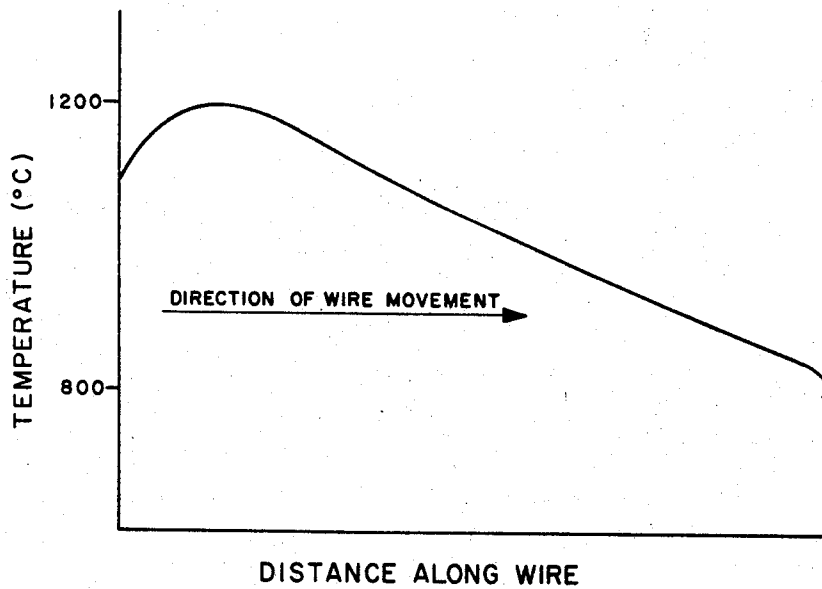


FIG.- 2

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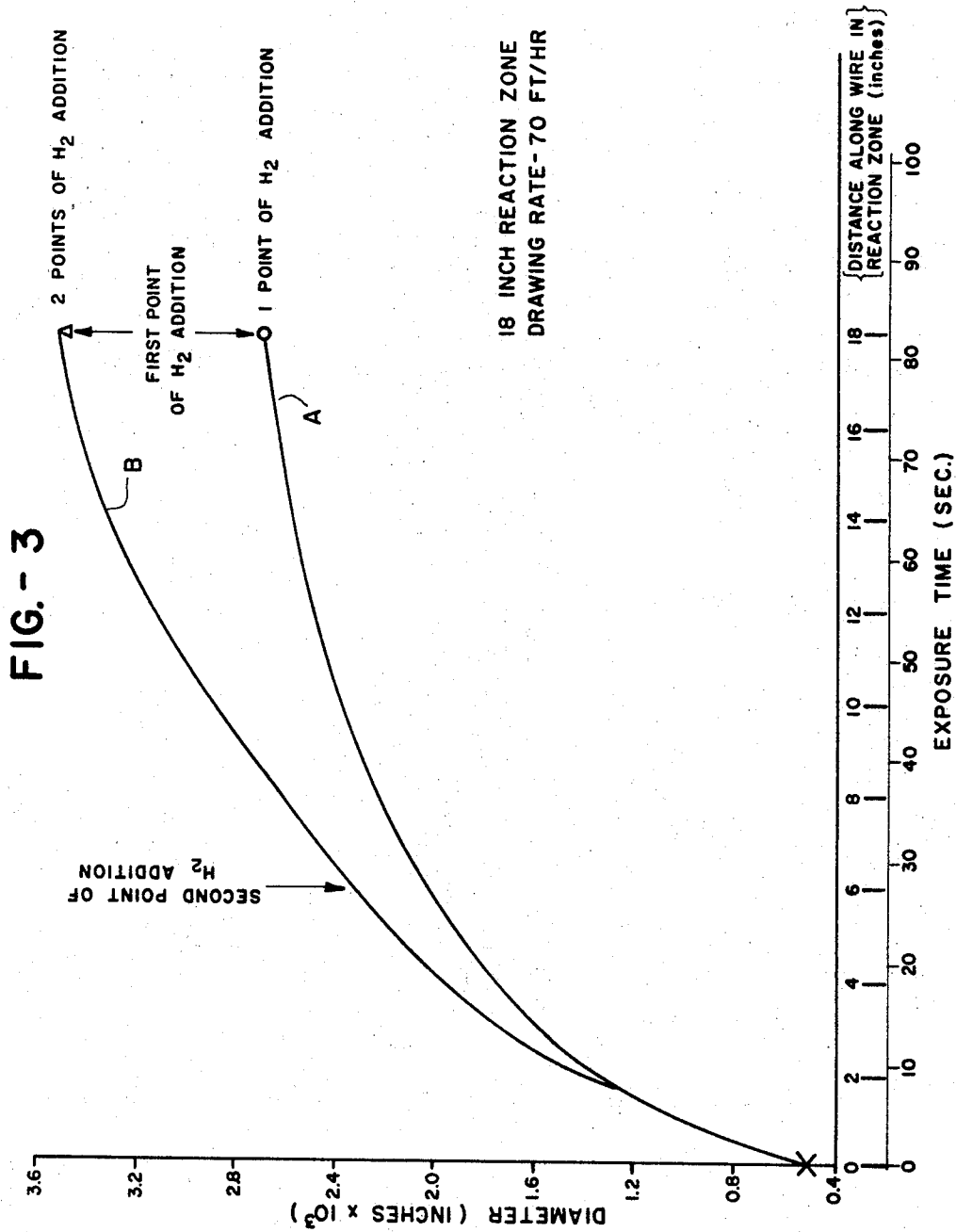
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4 Sheets-Sheet 3



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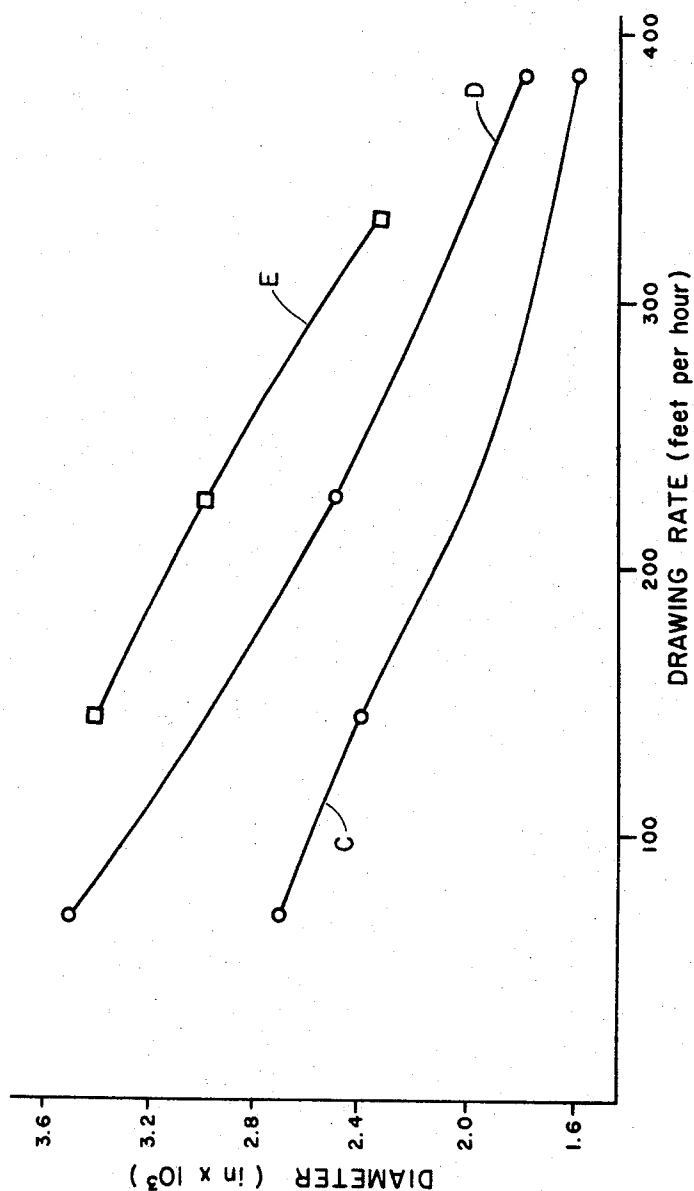
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FIG. - 4



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VAPOR COATING CONDUCTIVE FILAMENTS UTILIZING UNIFORM TEMPERATURE

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ABSTRACT OF THE DISCLOSURE

This invention is directed to the deposition of a coating on a substratum by contact of a heated surface of the substratum with vaporized chemicals which react on contact with the hot surface to deposit the coating. According to the invention, the rate of coating deposition may be enhanced by regulating the heat dissipation from selected areas of the filament by means independent of the filament heating means to thereby cause the filament to have a substantially more uniform temperature profile throughout the coating chamber.

In conventional procedures for applying coatings on electrically conducting wires, filaments, and similar substrata, the wire, filament or the like is intensely heated, and the hot surface thereof contacted with vaporized chemicals, e.g., compounds of metals or other elements, alone, or in combination with inert and/or other reaction gases. The vaporized chemicals react on contact with the hot surface to deposit the desired chemical element or compound on the heated wire or filament in a uniform layer. The technical procedure in such a method where either stationary or continuously advancing wires, filaments, or the like are acted upon, is to heat the latter within a reaction chamber between two current supply contacts until a temperature high enough for reaction of the vaporized chemicals is reached. The chemicals will be supplied to the reaction chamber in the vaporized state, alone, or in combination with other inert, reducing or reaction gases.

It is an object of the present invention to increase the rate of deposition in coating processes of the type described.

An important object of the invention is to increase the rate at which continuously advancing wires or filaments may be drawn through the reaction chambers of coating processes of the type described.

A further object of the invention is to provide long straight conducting filaments or wires having uniform coatings of metals or other compounds thereon.

Other objects of the invention will in part be obvious and will in part be made clear hereinbelow.

The invention will be better understood by reference to the specification and accompanying drawing in which:

FIGURE 1 is a side view in schematic and, for the most part, cross section of a depositing apparatus for coating continuous filaments;

FIGURE 2 is a graph showing a normal temperature profile during continuous coating of a filament; and

FIGURES 3 and 4 are graphs showing the improvement in deposition and drawing rates achieved by practicing the present invention.

The rate of coating the conducting wire or filament generally increases with temperature, the higher the temperature, the greater the coating rate.

The temperature to which the wire or filament can be heated is limited at the upper end by its melting point. At the lower, the temperature of the wire or filament constituting the substratum on which the coating is superimposed must be at least hot enough to cause reaction

of the vaporized chemical to occur on the surface of the wire or filament.

It is the temperature range between these two limits that constitutes the effective coating temperature range; and within the coating temperature range, the rate of deposition is a function of and increases with temperature.

In continuous processes to which this invention is particularly concerned, a continuous conducting filament or wire is pulled or drawn through a reaction chamber containing the vaporized coating compound or compounds.

In continuous operation, it has been discovered that the temperature of the wire tends to vary along its length; with the result that the rate of deposition decreases in the cooler regions of the wire or filament. In normal operation, because of the variation of temperature along the wire, the deposition rate is limited by the wire cold spots, and tends to become a function of the lowest temperature along the wire.

The temperature variation of the wire as it traverses the reaction chamber may be attributed to the fact that as the coating builds up, the wire diameter increases, and, also, the resistivity of the substratum (i.e., initial wire plus coating) changes. Both of these phenomena lead to a temperature variation at the surface of the substratum exposed to or "looking at" the coating vapors.

As has been brought out above, deposition of the coating material occurs on the hot surface so that the surface coating builds up as the filament passes throughout the coating chamber. In other words, the surface at which deposition occurs undergoes continual change as the filament traverses the reaction chamber and it is this change which leads to the temperature variation at the surface which has been described.

In general, other things being equal, the wire temperature at any particular point in the reaction zone may be stated to be a function of the coating thickness.

In normal or conventional operation, the variation in temperature along the wire length means in effect that the coating rate becomes a function of that temperature at which coating will proceed on the cold spots without the hot spots melting or softening.

According to this invention, a substantially uniform temperature profile is maintained along the wire, such that the average wire temperature is considerably higher than can normally be obtained using standard procedures. Since the rate of deposition is a function of temperature, for a given coating thickness, Δt , the higher, substantially uniform temperature may readily be translated into a higher drawing rate.

An apparatus suitable for carrying out the method is schematically shown in FIGURE 1, which is a view partly in section.

The apparatus comprises a reaction chamber 10, which may be made of glass or quartz, closed at both ends by plates 12 and 14, and sealed by gaskets 16 and 18. Closure plates 12 and 14 are provided with centrally disposed conduits 20 and 22 made of, for example, stainless steel. Conduits 20 and 22 are filled with mercury, and a filament or wire 24 to be coated is fed from a filament supply roll (not shown) through the mercury seal of conduit 20, thence through the reaction chamber 10. The coated filament is then drawn through the mercury seal in conduit 22, where it is cooled, and then wound on a take-up spool (not shown).

Suitable electrical leads 26 and 28 make electrical contact between the mercury seal in conduits 20 and 22 and a suitable variable power supply 30.

With the arrangement of parts shown in FIGURE 1, the wire is not bent until after it has passed into the mercury seal in conduit 22 and has been cooled. Such cooling is necessary if straight wires are desired. The posi-

tioning of the apparatus at an angle to the horizontal is also important, since it not only aids in the production of straight filaments, but also permits the use of metal tubing for the mercury seal, thus simplifying construction. Care should however be used to insure that the coated filament does not touch the metal of the mercury seal before it enters the mercury pool. If such contact occurs, arcing will result with damage to the filament.

Rods 32 fastened to the plates 14 and 12 by suitable fastening means 34 hold the assembly together.

The reaction chamber 10 is provided with gas ports 40 and 44 for feeding and exhausting the various gas streams, as will more clearly be brought out hereinbelow. Although single gas ports or conduits are shown at 40 and 44, multiple ports at each of these locations are contemplated.

One or more conduits 42 are slideably mounted on end plate 14 for insertion into and movement transversely within the reaction chamber 10. If desired, of course, other suitable mountings for conduit 42 may be employed. For example, it may be supported on end plate 12.

There will now be described procedures for improving the temperature profile across the wire as it passes through the reaction zone, or vapor deposition chamber.

It should be emphasized that the temperature regulating means and techniques to be described are auxiliary to the resistance heating caused by the power input to the wire being coated. At the same time, it will be appreciated that the auxiliary temperature regulating techniques and means are generally independent of the filament heating means.

Essentially, what is needed is to cool the hot spots or hot end of the wire, or to heat the cold spots or cold end of the wire by some means other than regulating power input to the wire.

The hot spots may be cooled in a variety of ways. Thus, a gas or gases having an average coefficient of thermal conductivity higher than that of the reactant gases may be added or injected at selected spots along the continuous filament to increase the rate of heat dissipation from said spots, thereby leading to temperature reduction thereat. The gas may be one of the reactant gases, or a gas inert to the reactant gases.

For example, when the reactant gases or vapors comprise a metal halide in combination with a reducing gas, such as hydrogen, and are caused to flow from the cold to the hot end of the wire, hydrogen can be injected at one or more points along the hot end of the wire to increase the rate of heat dissipation thereat. Hydrogen, because of its high coefficient of thermal conductivity, is especially suitable for this purpose.

Conversely, the temperature of the normally cold spots along the wire may be raised by injecting adjacent thereto a gas or mixture of gases, having an average coefficient of thermal conductivity which is lower than that of the reactant gases. The injected gases here would serve to reduce the rate of dissipation of heat from the wire, thereby causing the wire to maintain its heat in the vicinity of the point of injection and to increase in temperature. When the reactant gas comprises metal halide plus a reducer, such as hydrogen, for example, and is caused to flow from the hot toward the cold end of the wire, the metal halide, which has a comparatively low coefficient of thermal conductivity with respect to either hydrogen or a mixture of metal halide and hydrogen, could be injected at a point or points along the cold end of the wire to cause the cold end to increase in temperature.

In the apparatus shown in FIGURE 1, the temperature regulating gas could be injected via one or more tubes of the type depicted at 42.

In another embodiment of the invention, a more uniform high temperature profile may be produced by reducing the cross sectional area of the reaction zone adjacent the wire hot spots and increasing its cross sectional area adjacent the wire cold spots. This leads to an

increased rate of gas flow (and consequent increased heat dissipation) in the vicinity of the hot spots, and a decreased rate of gas flow (and consequent decreased heat dissipation) in the vicinity of the cold spots, thus serving to promote a substantially uniform temperature profile across the wire.

In FIGURE 1, for example, assume that the wire would be hottest at the end adjacent closure plate 12. In carrying out the embodiment under discussion, the tube 10 could then be reduced in diameter at this end, to thereby cause an increase in gas flow thereat. The tube 10, for example, could be frusto-conical in shape, with the apex adjacent the hot end of the wire.

In still another embodiment of the invention, the reaction chamber 10 could be provided with a variable heat exchange means which could be regulated to increase or reduce heat dissipation from spots along the wire or filament as required. Such heat exchange means, for example, could take the form of resistance coil wrapped around the reaction chamber 10. The desired cooling of hot spots or heating of cold spots described above could then be achieved by suitably regulating the power input to the resistance coil at selected portions along the reaction chamber.

In carrying out the process, the chemical compound or compounds required to form the desired coating are supplied to the reaction chamber in vapor form, and may be admixed with other gases, e.g., inert gases, reducing gases, or the like, as required. In any event, the coating gas stream may conveniently be supplied in such a way that the vapors within the reaction chamber are in close proximity to the wire, filament, or the like undergoing coating.

Preferably, the filament or wire is conducted through a tube having a relatively small cross sectional area, so that the vapors are concentrated across and in intimate contact with the hot filament.

Among the coating compounds that may be used to deposit elements may be mentioned compounds of metals, such as platinum, tungsten, uranium, vanadium, tantalum, or metalloids, such as silicon, boron and the like; or carbon.

The chemical compounds used in depositing conducting elements will typically comprise halides, e.g., chlorides, fluorides, iodides, or bromides of the described metals or metalloids.

A reducing gas such as hydrogen will also ordinarily be included as part of the reactant gas or vapor mixture when halides of the metals or metalloids are employed.

Inert gases, such as helium, neon, argon, krypton, xenon, and the like may also be included, if desired.

Chemical compounds as distinguished from elements, which may be deposited, include electrically conducting nitrides, carbides, oxides, phosphides and sulfides of such elements as silicon, titanium, zirconium and the like. Typical of such compounds are titanium nitride, zirconium carbide, and the like.

When the described chemical compounds are to be deposited, vapors of phosphorous, sulfur, oxygen, carbon and the like, or compounds of such elements, will be included as part of the reactant gas stream.

For instance, when making a coating of zirconium carbide, using zirconium tetrachloride, a certain amount of a carbon containing gas, e.g., methane will be added to the reactant gas to produce a coating of zirconium carbide.

As a further example, in order to obtain a deposit of hafnium boride, a mixture of hafnium chloride, hydrogen and boron tribromide may be passed into the reaction zone. Hafnium boride will then be deposited on the moving filament with the formation of hydrogen chloride and hydrogen bromide.

Any suitable conducting wire or filament may be used as the substratum on which deposition occurs. Thus, the wires or filaments may be any of the metals or metalloids mentioned above, or carbon, or even conductive glass, and

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the like. Typical substrate filaments may then be composed of tungsten, silicon, boron, platinum, uranium, vanadium, rhenium, tantalum carbon conductive glass and the like.

Ordinary glass metal or any other material may be used for the reaction chamber as the latter is only slightly heated during operation. In most cases, a simple glass cylinder provided with an inlet and an outlet for the reactant gases, as well as an opening for the wire or the like, which is to be coated, and the necessary electrical contacts, will be sufficient.

The invention is particularly applicable to a continuous process for coating a tungsten filament with boron, and will be described for purposes of illustration with specific reference to such a system.

Example 1

This example was performed to show that the rate of coating a tungsten wire with boron is a function of temperature, and increases with temperature.

Using the apparatus shown in FIGURE 1, a continuous filament of tungsten wire having an initial diameter of about 0.5×10^{-3} inch was heated to incandescence by resistance heating and continuously drawn through the reaction chamber at the rate of 70 feet per hour in the direction shown by the arrow, FIGURE 1. The length of the reaction zone was 12 inches. Hydrogen and boron trichloride were fed through port 40, and the gas stream was continuously exhausted through gas vent tube 44. In all cases the wire was drawn through the reaction chamber at the same rate, while the flow of hydrogen and boron trichloride was maintained constant. The potential across the wire in separate runs was varied between 0 and 380 volts. Above 380 volts the wire coated unevenly and broke. The experimental results are given in Table I.

TABLE I

Potential across wire (volts):	Final diameter (inches $\times 10^{-3}$)
0	0.5
300	2.0
350	2.7
380	3.2

It will be clear from Table I that the higher the potential, the greater the deposition rate.

Given the procedure and materials of Example 1, and utilizing the highest temperature which permits continuous operation with even coating, it can be demonstrated that the temperature of the wire across the reaction zone will vary along its length as shown in FIGURE 2, which is a theoretical plot of distance along wire versus temperature for a coating procedure of the type described in Example 1. The adverse effect of this uneven temperature distribution on coating rate has been described hereinabove and is illustrated by Curve A, FIGURE 3, described below.

Example 2

Using the apparatus shown in FIGURE 1, a continuous filament of tungsten wire having an initial diameter of about 0.5×10^{-3} inch was heated to incandescence by resistance heating and continuously drawn through the reaction chamber at the rate of 70 feet per hour in the direction shown by the arrow, FIGURE 1. The length of the reaction zone was 18 inches.

Two separate runs were made. In each run, hydrogen and boron trichloride were fed through port 40, and the gas stream was continuously exhausted through gas vent tube 44.

In the first or control run A, hydrogen was introduced only at the wire outlet end via port 40 (i.e., admixed with the boron trichloride). In the second run B, following the teaching of this invention, hydrogen gas was injected via port 40 (admixed with boron trichloride) and hydrogen gas was also injected downstream in the reaction chamber via conduit 42.

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The difference in results is shown by FIGURE 3, which is a plot of both exposure time and distance along wire in the reaction zone, as abscissae, versus wire diameter as ordinate, for each run.

The following table shows the location of the points at which hydrogen was injected for each run.

TABLE II

Run	Length of Reaction Zone, in.	H ₂ Injection	
		No.	Location, ¹ in.
A.....	18	1	18
B.....	18	2	$\begin{cases} 18 \\ 6 \end{cases}$

¹ Distance in inches along wire in reaction zone from inlet end of wire.

In the runs, the highest temperature which would permit continuous operation with even coating was used.

As can plainly be seen from FIGURE 3, Curve B, the downstream addition of hydrogen to cool the wire at its inlet, i.e., its hot end, leads to a drastic increase in the deposition rate as compared to Curve A, in which downstream addition of hydrogen was not employed.

Example 3

The procedure of Example 2 was repeated to provide data for the curves shown in FIGURE 4, which brings out the importance of hydrogen addition at downstream points on drawing rate.

In FIGURE 4, wire diameter is plotted as a function of drawing rate for different reaction zone lengths, and different locations of hydrogen injections.

In making the runs on which FIGURE 4 is derived, the procedure of Example 2 was followed, with the exception that the reaction zone length and hydrogen injections were as follows:

TABLE III

Curve	Length of Reaction Zone, in.	H ₂ Injection	
		No.	Location, ¹ in.
C.....	18	1	18
D.....	18	2	$\begin{cases} 18 \\ 6 \end{cases}$
E.....	16	3	$\begin{cases} 16 \\ 10\frac{1}{2} \\ 5\frac{1}{2} \end{cases}$

¹ Distance in inches along wire in reaction zone from inlet end of wire.

Here again, the highest temperature which would permit continuous operation with even coating was used in each of the runs.

As will be clear from FIGURE 4, Curves D and E, downstream hydrogen additions to cool the hot end of the wire have a pronounced influence on the drawing rate, as compared to Curve C, in which downstream cooling of the wire was not employed.

As will be apparent from Examples 1-3, by judicious choice of electrical power, flow rate, and downstream hydrogen injections a more uniform temperature profile across the wire is obtained. This results in higher deposition rates and faster drawing rates (see FIGURES 3 and 4).

In the examples, if desired, the wire could be drawn in the direction of the gas stream (i.e., co-currently) and boron trichloride additions could be made upstream, as brought out hereinabove.

The invention in its broader aspects is not limited to the specific improvements, steps, methods, products and apparatus described, but departures may be made therefrom within the scope of the accompanying claims without departing from the principles of the invention and without sacrificing its chief advantages.

What is claimed:

1. In a method for coating electrically conducting filaments by drawing the filament continuously through an enclosed, elongated reaction chamber containing chemical vapors reactable on contact with a hot surface of the

filament to form the desired coating material, the filament being heated by filament heating means to produce a surface temperature at least high enough to cause the chemical vapors, upon contact therewith, to react to form a coating on the surface of the filament, the improvement for increasing the rate of deposition of the coating material which comprises regulating the rate of heat dissipation from selected areas of the filament, by means independent of the filament heating means, to thereby cause the filament to have a substantially more uniform temperature profile throughout the reaction chamber.

2. The improvement of claim 1 wherein the chemical vapors are caused to flow from the cold toward the hot end of the filament, and wherein the temperature profile of the filament is rendered substantially uniform by injecting into the reaction chamber adjacent the normally hot end of the filament a gas having a higher coefficient of thermal conductivity than the vapors to increase the rate of heat dissipation from said end and thereby reduce the filament temperature thereat.

3. The improvement of claim 1 wherein the chemical vapors are caused to flow from the hot toward the cold end of the filament, and wherein the temperature profile of the filament is rendered substantially uniform by injecting into the reaction chamber adjacent the normally cold end of the filament a gas having a coefficient of thermal conductivity which is less than that of the vapors, to reduce the rate of heat dissipation from said end and thereby increase the temperature of the filament thereat.

4. The improvement of claim 1 wherein the temperature profile of the filament is rendered substantially uniform by increasing the velocity of the chemical vapors adjacent the hot end of the filament to increase the rate of heat dissipation from said end and thereby reduce the temperature thereat.

5. The improvement of claim 4 wherein the increase in vapor velocity at the hot end of the filament is achieved by a gradual reduction in reaction chamber cross section from the cold to the hot end of the filament.

6. The improvement of claim 1 wherein the chemical vapors comprise an admixture of metal halide and hydro-

gen and are caused to flow from the cold toward the hot end of the filament, wherein hydrogen gas is injected adjacent the hot end of the filament to increase the thermal conductivity of the vapors of said end and thereby increase the heat losses and reduce the temperature thereat.

7. The improvement of claim 1 wherein the chemical vapors comprise a mixture of metal halide and hydrogen and are caused to flow from the hot toward the cold end of the filament, and wherein metal halide is injected adjacent the normally cold end of the filament to reduce the coefficient of thermal conductivity of the gases at said end, and thereby reduce the heat losses and increase the temperature thereat.

8. The improvement of claim 1 wherein the vapors comprise a mixture of metal halide and hydrogen.

9. The improvement of claim 1, wherein the filament heating means is electrical resistance heating.

10. The improvement of claim 9 wherein the metal halide is boron trichloride and the reducing gas is hydrogen.

11. The improvement of claim 1 wherein the filament is tungsten, the vapors comprise a mixture of boron trichloride and hydrogen and are caused to flow from the cold toward the hot end of the filament, and wherein the rate of heat dissipation from the filament is regulated by introducing hydrogen adjacent the hot end of the filament to increase the thermal conductivity of the vapors at said end and thereby increase the heat losses and reduce the temperature thereat.

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