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3,783,007

METAL CARBONITRILE COATINGS

Original Filed Aug. 15, 1969

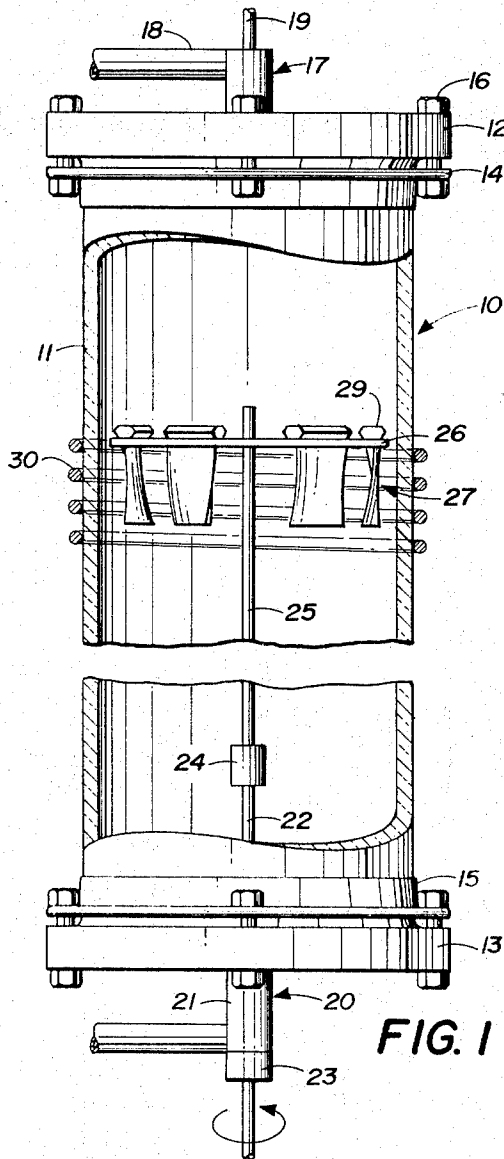


FIG. 1

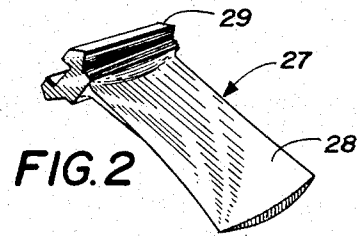


FIG. 2

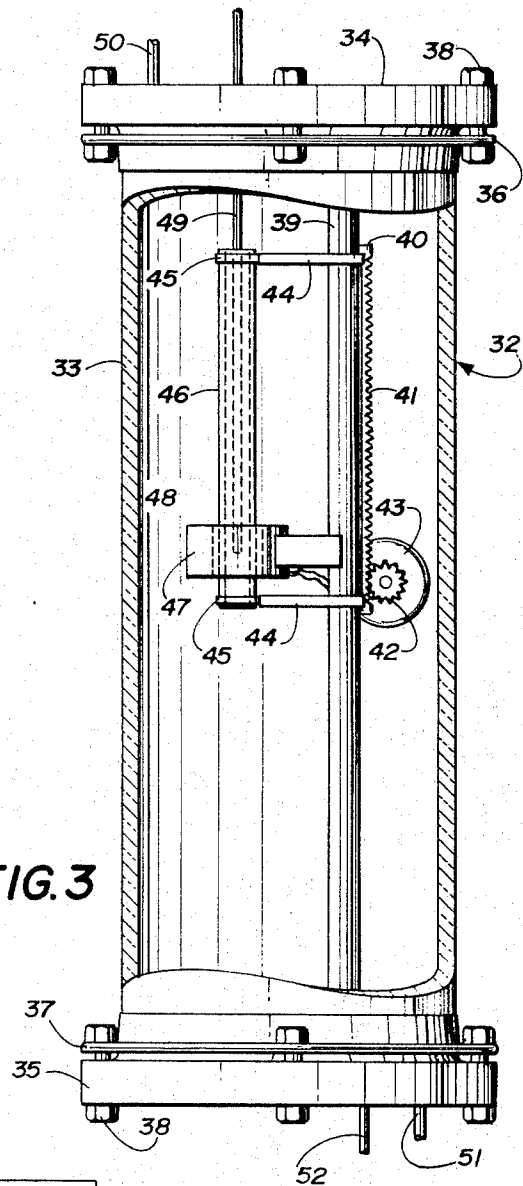


FIG. 3

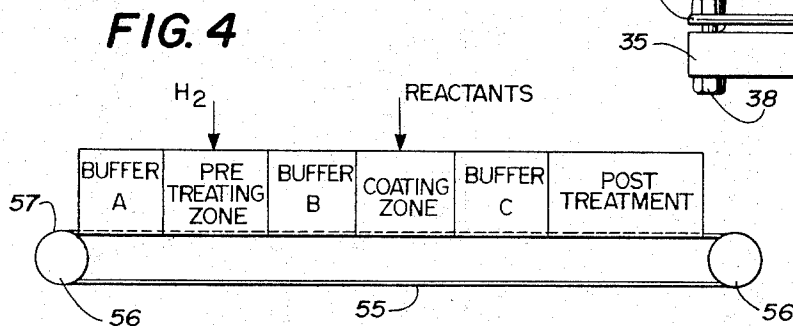


FIG. 4

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## METAL CARBONITRILE COATINGS

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Continuation of abandoned application Ser. No. 850,351, Aug. 15, 1969. This application Oct. 1, 1971, Ser. No. 185,872

Int. Cl. C23c 11/18

U.S. Cl. 117—95

9 Claims

### ABSTRACT OF THE DISCLOSURE

Metal carbonitride coatings such as titanium carbonitride, are produced upon the surface of an object by a vapor phase deposition process utilizing reactant compounds containing carbon, nitrogen, and the metal. The reactant compounds are contacted upon the surface of the heated substrate under conditions wherein the atmosphere of the reaction zone around the substrate is maintained at a temperature below the decomposition temperature of the reactant compounds so that substantially no vapor phase reaction therebetween will occur before contact is made with the heated substrate.

This application is a continuation of copending application, Ser. No. 850,351, filed Aug. 15, 1969, now abandoned.

This invention relates to coatings and coating techniques. In another aspect, this invention relates to vapor deposited coatings of metal carbonitrides.

It has been found desirable to apply very hard, durable oxidation-resistant coatings to the surfaces of various objects such as missile nose cones, machine tools, turbine blades, and the like.

Thus, it is often desirable to utilize the basic properties of a material, but to protect the material from exposure to the environment within which it must function. As mentioned in U.S. Pat. No. 2,972,556, carbon and graphite articles have exceptionally good thermal and electrical properties. However, in some applications where the thermal characteristics of the material could be utilized, such as in a missile nose cone, or a turbine blade, the material oxidizes in the air under high temperatures to which it is subjected. The material must, for such application, be coated with a more oxygen-resistant material such as a metal carbide, a metal nitride, or both, as described in U.S. Pat. No. 2,972,556, mentioned above.

Also, in the production of machine tools, for example, it is often more economical to form steel in the desired shape and coat it with a harder material such as tungsten carbide or titanium carbide. The difficult and expensive step of machining a dense, solid block of tungsten carbide or titanium carbide into a desired shape is thus avoided.

It is known that coatings such as titanium carbide can be applied to a substrate such as metal by exposing the surface of the metal to a gaseous stream of titanium tetrachloride and methane. The metal is usually heated to a temperature between 900° C. and 1200° C. and upon contacting the metal surface, the materials within the gaseous stream react to form titanium carbide which will adhere to the surface of the metal. More specific details of this reaction may be found in U.S. Pat. No. 2,962,388 and the description of equipment suitable for applying hard, dense coatings may be found in U.S. Pat. No. 2,884,894.

One of the problems encountered in coating metal with titanium carbide by the above-described process is the loss of temper in the metal. Generally, metals, and in particular steel, are first hardened by elevating the steel to about 1000° C. and then quickly quenched. The steel

after quenching is tempered by elevating the temperature to about 500° C. to 600° C. thus reducing its brittleness. If a hardened and tempered steel is then reheated to a temperature between 900° C. and 1200° C. to permit the application of a coat of titanium carbide, the hardness and temper of the steel is lost during the reheating process. If the steel, after application of the coating, is quenched to again harden the steel, the coating may be damaged as the steel will change in size during the quenching process which can rupture the coating, create a roughness in the coating or cause it to eventually peel from the surface of the steel. Thus, not only is the coating damaged, but the steel is also weakened and does not provide as strong a support for the coating necessitating that the coating be thicker to withstand the forces to which it may be subjected.

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 IV-B, V-B and VI-B 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 for continuation application Ser. No. 105,075, filed Jan. 8, 1971. 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 hardness 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° C. to about 1200° C.) and then passing a gaseous stream containing the reactants over the substrate to thereby yield 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.

The above described process for applying coatings of metal carbonitrides produces coatings which are superior to the refractory coatings heretofore known in the art. Various improvements and modifications of this process are disclosed in the copending patent applications Ser. No. 769,372 filed Oct. 21, 1968 and Ser. No. 769,385 filed Oct. 21, 1968. This invention relates to a newly discovered technique in this process whereby smooth and uniform coatings of metal carbonitride are continuously obtained.

Therefore, one object of this invention is to provide an improved process for coating a substrate with a metal carbonitride which yields a uniform and greatly improved coating of the metal carbonitride on the substrate.

Another object of this invention is to provide a novel process for coating the inner periphery of a tubular object with a metal carbonitride.

A further object of this invention is to provide a continuous process for coating substrates with a metal carbonitride.

According to the invention, it has been discovered that an improved coating of solid solution metal carbonitride on a substrate occurs in a vapor phase deposition process wherein the vapor phase deposition process is maintained under nonequilibrium conditions. Basically, it has been discovered that when reaction between the reactants occurs substantially entirely upon the substrate, and substantially no reaction occurs in the vapor phase around the substrate, a highly uniform and continuous coating of the metal carbonitride on the substrate will result.

According to one embodiment of this invention the deposition substrate is maintained at the proper deposition temperature while the atmosphere around the substrate within the deposition zone is maintained below the decomposition temperature reactants by a suitable heating means positioned outside a transparent reaction zone, which heating means will heat the substrate without directly heating the reaction zone and the vapor therewithin. Such heating means includes an RF heating coil, and a laser beam.

According to another embodiment of this invention a method is provided for coating the inside periphery of the tubular object such as a gun barrel with a smooth and continuous coating of a solid solution metal carbonitride by the basic process of this invention.

According to a further embodiment of this invention, a continuous process is provided for coating surfaces of objects with a smooth, uniform solid solution metal carbonitride layer.

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

FIG. 1 is an elevational view, partially in section, of a suitable reactor for carrying out the process of this invention;

FIG. 2 is a perspective view of a conventional turbine blade which can be coated by the process of this invention;

FIG. 3 is an elevational view of another reactor for carrying out the process of this invention; and

FIG. 4 is a schematic view illustrating a continuous process of this invention.

Thus, it has been 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 nonequilibrium condition exist between the vapor phase reactants adjacent the substrate and the reactants on the substrate. If the atmosphere surrounding the substrate is maintained under conditions which will allow the reactants to decompose and thereby occur which result in the formation of a discontinuous or nonuniform coating of the metal carbonitride on the substrate.

The vaporous stream passed over the heated substrate generally contains molecular hydrogen, a carbon-containing compound which readily decomposes at the deposition temperature, 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 IV-B, V-B, and VI-B 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 diaminoethylene, triaminoethylene, pyridine, trimethylamine, triethylamine, hydrazine, methylhydrazine, and the like.

The coating process of this invention must be conducted utilizing procedures and equipment whereby the substrate 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 reaction zone around the substrate 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 substrate is heated will depend upon the particular reactants employed, but will generally vary within the temperature range of at least 400° to about 1200° 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 reaction zone surrounding the heated substrate 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 deposition zone around the heated substrate be maintained between 300° and 400° C.

Now referring to FIG. 1, a preferred reactor of this invention is illustrated. Reactor 10 comprises a transparent ceramic (Pyrex) cylindrical member 11 disposed between end plates 12 and 13, respectively. End plates 12 and 13 are held in sealing relationship against the outer ends of cylindrical member 11 by the coaction of annular retaining rings 14 and 15, respectively, and nut and bolt assemblies 16. Inlet nozzle means 17 is operatively positioned through end plate 12 and comprises an L-shaped conduit 18 carrying a concentric conduit 19 for introducing vaporous reactants to the interior of reactor 10.

Outlet conduit means 20 is positioned through the center of end plate 13 and comprises a generally L-shaped conduit 21 adapted to receive spindle 22 concentrically within the upper leg thereof which is positioned through end plate 13. Outlet conduit means 20 carries a rotary seal 23 adjacent the intersection between the upright and outwardly extending legs of L-shaped conduit 21, which seal receives spindle 22. The lower end of spindle 22 is connected to a suitable means such as an electric motor (not shown) for imparting rotational motion thereto. Spindle 22 is made from a suitable high strength material such as stainless steel, and has coupling 24 attached to the upper end thereof which carries quartz shaft 25.

Rotating annular platform 26 is operatively connected to the upper end of quartz shaft 25 and carries means for receiving and retaining objects 27 about its periphery. Objects 27 can be conventional turbine blades such as is illustrated in FIG. 2, and are retained so that the blade portion 28 extends downwardly from platform 26 and the base portion 29 thereof either extends above or is retained within the retaining and receiving means carried by the periphery of platform 26.

RF coil 30 is wrapped around cylindrical member 11 and positioned in a manner so that energy emitted thereby will be absorbed by the lower portion of objects 27 extending below platform 26. RF coil 30 is operatively connected to a conventional generator for emitting radio frequency impulses. It must be noted that this invention is operable with any type heating means which will heat objects 27 within reactor 10 with directly heating side walls of cylindrical member 11, and the atmosphere between cylindrical member 11 and objects 27. For example, a laser beam can be utilized instead of RF coil 30.

The embodiment as illustrated in FIG. 1 can be utilized to coat any suitable substrate such as stainless steel or graphite. It is particularly effective for coating stainless steel objects such as turbine blades. FIG. 2 is a perspective view of a conventional turbine blade. As shown, the blade portion 28 comprises a twisted blade member, and is integral with base portion 29 which fits within a suitable seating means on a spindle in a turbine motor. As the conventional turbine motor rotates, the turbine blade will be forced outwardly by the action of centrifugal force and base portion 29 will seat firmly against a matching seating portion of the spindle of the turbine motor. It has heretofore been found that if base portion 29 is coated with a refractory coating material, the layer of coating will not only cause the base portion 29 to fit imperfectly in the machined seat carried by the turbine spindle, but the coating will tend to crack and flake. Even a very small flake of the refractory coating contained between the turbine spindle seat and base portion 29 will cause unwanted abrasion and wear and substantially reduce the life of the spindle seat and turbine blade.

Therefore, if it is necessary that base portion 29 not carry a refractory coating, but that the blade portion 28 carry a refractory coating to provide erosion resistance, the process of this invention as carried out within reactor 10 (FIG. 1) will provide a coating on blade portion 28 of the solid solution metal carbonitride without coating base portion 29. Likewise, any other object which has at least a portion thereof subjected to erosion and/or friction environment can be selectively coated by the process of this invention.

In operation, objects 27 are initially positioned within retaining means on the periphery of platform 26 within reactor 10, RF coil 30 is actuated, and spindle 22 is rotated to a suitable speed (about 5 to 15 r.p.m.). The rotation of spindle 22 will thereby cause annular platform 26 to rotate within reactor 10 and thereby randomize and make more uniform the heating of objects 27 and vapor contact upon objects 27. The reactor can be flushed with a suitable material such as nitrogen or hydrogen, and if desired, objects 27 can be pretreated with hydrogen. Thus, the frequency of RF coil is increased to heat the part to a suitable temperature and hydrogen passing through reactor 10 will contact objects 27 and clean the surfaces thereof by reducing action.

After the reducing procedure, the temperature of objects 27 is adjusted to a suitable vapor phase deposition temperature by RF coil 30, e.g., 650° C. Next, suitable reactants are passed through the interior of reactor 10 via inlet conduit means 17 and outlet conduit means 20. For example, a suitable reactant stream includes a vaporous mixture if trimethylamine and nitrogen passing through conduit 19 and titanium tetrachloride, nitrogen and hydrogen passing through conduit 18 of inlet conduit means 17. The vaporous reactants intermix adjacent

the outlet of inlet nozzle means 17 and become only slightly warmed due to the radiation from objects 27.

Since RF coil 30 selectively heats only the lower portion of objects 27 and does not directly heat cylinder member 11 nor the gases within the interior of reactor 10, the gaseous reactants will be maintained at a temperature below decomposition temperature of the metal, carbon, and nitrogen-containing compounds. In the reactant stream, it is generally necessary that at least two of the three compounds containing the critical compounds (carbon, nitrogen, and the metal) be intact and not decomposed while in the vapor phase prior to contact upon the heated surface of objects 27. Thus, nonequilibrium temperature conditions exist between the reactants in contact with heated objects 27 and the vaporous atmosphere within reactor 10. It has been discovered that this relationship must exist in order to prevent the unwanted formation of constituents in the vapor phase before contact is made with the heated deposition surface in order to uniformly obtain a continuous and uniform solid solution coating of the metal carbonitride.

After contact between the vaporous reactant streams and heated objects 27, exhaust gases are removed from the interior of reaction 10 via outlet conduit means 20.

Now referring to FIG. 3, another embodiment of this invention is illustrated whereby the interior surface of a tubular object such as a gun barrel can be coated with a solid solution layer of a metal carbonitride.

As illustrated, reactor 32 comprises a tubular member 33 which is preferably made of a transparent heat resistant material such as quartz and disposed between end plates 34 and 35. End plates 34 and 35 are held in sealing relationship against the ends of tubular member 33 by the action of annular rings 36 and 37, respectively, and nut and bolt assemblies 38. Track means 39 is operatively positioned between end plates 34 and 35 and carries an elongated running track for guiding and retaining rack member 40.

Rack member 40 carries teeth 41 which mesh in operative relationship with gear means 42, which in turn is driven by motor 43. Suspension arms 44 are operatively connected adjacent opposite ends of rack 40 and carry clamping means 45 for retaining tubular objects 46 therebetween. Annular heater 47 is operatively attached to suitable means such as track means 39 and held a fixed distance from end plate 35 within reactor 32. Annular heater 47 generally comprises a tubular body portion carrying an annulus 48 (shown in dotted line) for receiving tubular object 46. Annular heater 47 can contain any suitable heating element for heating tubular object 46, for example, a resistance heater.

Elongated nozzle 49 extends through end plate 34 and is positioned concentrically within annular heater 47. The end of elongated nozzle 49 generally extends to about the center of the body of annular heater 47. For example, with a body portion of annular heater 47 being 4 inches long, the end of elongated nozzle 49 will be positioned at about 2 inches therewithin.

Gas inlet conduit 50 communicates through end plate 34, and the gas outlet conduit 51 communicates through end plate 35. In addition, conduit 52 containing electrical wires communicating with motor 43 and annular heater 47 communicate through end plate 35.

In operation, a suitable tubular object 46 such as a gun barrel is clamped within reactor 32 so that elongated nozzle 49 will extend therein to a point adjacent the bottom portion thereof as illustrated in FIG. 3. Hydrogen is introduced into the interior of reactor 32 via conduit 50 and exhausted therefrom by outlet conduit 51 to thereby purge the interior of reactor tube of any oxidizing or deleterious vapors. Annular heater 47 is actuated to thereby heat a section of tubular object 46 to a suitable temperature, e.g., a temperature in the range of about 400° to about 1200° C.

After the lower segment of tubular object 46 within annular heater 47 is heated to the desired temperature,

suitable reactants are passed through elongated nozzle 49 and out the exit end thereof. These reactants are relatively cool with respect to the surroundings of the heated tube into which they are emitted, for example, they are maintained at a temperature in the range of from about 300° to 400° C. Thus, nonequilibrium temperature conditions exist between the reactants contacting the lower heated portion of tubular object 46 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.

Motor 43 is actuated to very slowly rotate gear 42 in a counterclockwise manner as viewed in FIG. 3 to thereby cause rack 41 to be moved downwardly at a correspondingly slow rate. This action will cause tubular object 46 to be sequentially heated along the relatively small deposition zone as rack 40 moves downwardly and thereby provides a very uniform continuous solid solution metal carbonitride coating on the interior surface thereof. The rate of movement of rack 41 will depend upon such factors as the thickness of tubular object 46, the heat output of annular heater 47, and the flow conditions of the vaporous reactants. The rate of movement should be such that each newly heated section of tubular object 46 adjacent the outlet of elongated nozzle 49 will be heated to the proper deposition temperature. This generally nonequilibrium procedure is necessary in order to obtain a uniform coating. For example, an unsuccessful experiment wherein an entire tubular object was heated and reactant gases introduced at one end thereof yielded a very rough and nonuniform coating on the inner periphery thereof in all portions of the tube except at the points directly adjacent the reacted inlet at the end of the tube.

Exhaust vapors passing from the lower end of tubular object 46 are passed out of reaction zone 32 via exhaust conduit 51.

The above described process which was explained in relation to FIG. 3 will allow a very hard coating of the metal carbonitride to be deposited uniformly on the inside periphery of objects such as gun barrels, rifle barrels, and conduits subjected to extreme heat and abrasive wear conditions.

Under conditions of this invention wherein the decomposed reactants on the surface of the heated substrate are in nonequilibrium with the nondecomposed reactants to the vapors surrounding the substrate, a continuous process is entirely beneficial and desirable. A schematic illustration of a continuous process for this invention is illustrated in FIG. 4. As illustrated the various treatment and reaction zones are positioned within a contiguous relationship having a continuous transporting section including continuous belt 55 driven by pulley members 56. The various treatment zones, i.e., the pretreating zone, the coating zone, and the post treatment zone, are separated from one another by a vaporous buffer zone which generally includes a zone of an inert gas, such as argon.

Thus, an object to be coated is positioned on delivery point 57 and passed through buffer zone A into the pretreating zone wherein it is heated to an elevated temperature, e.g., about 650° C. and contacted with hydrogen to reduce the surface thereof. The part passes from the pretreating zone through buffer zone B and into the coating zone. At least one reactant gas nozzle is positioned in the coating zone to impinge vaporous reactants directly upon the heated substrate to be coated. If desired, the reactant nozzles within this zone can be cooled by a suitable means such as a water jacket in order to assure that a sufficient temperature differential will result between the heated substrate to be coated and the vaporous atmosphere therearound. After the coating operation the part is passed through buffer zone C into the post treatment zone wherein it is heat treated and/or cooled. This invention can be more easily understood from a study of the following examples.

### EXAMPLE 1

A deposition run was carried out in an apparatus which substantially corresponded to that illustrated in FIG. 1. Four turbine blades very similar to that illustrated in FIG. 2 were suspended in operative manner from annular platform 26. The turbine blades were made of AM 355 stainless steel and had previously been plated by a chemical vapor phase deposition with a gold plating of about 10 microns.

The reactor was flushed with hydrogen and RF coil 30 was actuated to heat the blade portion 28 of the turbine blades. Spindle 22 was actuated to rotate annular platform 26 at 11 r.p.m. The blades within the reactor were allowed to heat to a temperature of about 700° C. over a period of 12 minutes. Next, the turbine blades were allowed to reduce in hydrogen for 15 minutes as a hydrogen stream was passed through reactor 10 from conduit 18 and out conduit means 20.

After this time, nitrogen was passed into reactor 10 via conduit 19 at a rate of 21.32 liters per minute, the hydrogen flow was adjusted to 1.17 liters per minute, 31.61 cc. per minute of trimethylamine was then added with nitrogen stream flowing in conduit 19, and 80 cc. per minute of titanium tetrachloride was added in a 4.68 liter per minute nitrogen stream flowing in conduit 18.

This flow was allowed to continue over the rotating blades (11 r.p.m.) for a period of one hour and 20 minutes. The temperature of the blade portion of each turbine blade was maintained in a range of from 650° to 665° C. (as determined by infrared pyrometry) during the one hour 20 minute deposition run. The temperature of the reactant atmosphere within reactor 10 around the turbine blades was maintained below 400° C.

After this time, the flow of reactants was shut off, RF coil deactivated, and the blades were allowed to cool. The blades had obtained the purplish color and carried a very smooth and uniform coating of titanium carbonitride. One of the blades was subjected to the action of a conventional jet abrader device. The nozzle of the jet abrader was positioned six-tenths inch from the titanium carbonitride coating, run 300 seconds, and the abrading action did not break through the smooth uniform coating.

### EXAMPLE 2

A run was carried out in the apparatus as utilized in Example 1, except two coupons made of AM 350 stainless steel and having dimensions of 1 inch by 2 inches by about 1/32 inch were suspended from annular platform 26.

These coupons were initially etched for 2.5 hours in hydrogen at a temperature of 700° C.

Next, the temperature upon the coupon was adjusted to about 650° C. and the vaporous reactants as disclosed in Example 1 (same types and flow rates) were introduced into reactor 10 and contacted the rotating coupons. The flow of these reactants through reactor 10 was continued for one hour and 45 minutes, and the average temperature maintained on the surface of the coupons was 665° C.

After the deposition run, the coupons had turned a purplish gold in color and carried a uniform and continuous coating of solid solution titanium carbonitride. One of these coupons was subjected to an abrading test as disclosed in Example 1, and the coating did not fail.

### EXAMPLE 3

A run was conducted in an apparatus similar to that illustrated in FIG. 3. Tubular object 46 was a steel tube having a length of 8 inches and an inside diameter of one-fourth inch. A steady flow of hydrogen was passed through the interior of reactor 32 via conduits 50 and 51. Annular heater 47 was actuated to heat the tube disposed therein to 1000° C.

The exit end of elongated nozzle 49 was positioned adjacent the lower end of the steel tube as illustrated in FIG. 3, and after the tube section disposed within the

annular heater 47 was heated to a temperature of 1000° C., a gaseous reactant flow was passed from elongated nozzle 49. The reactants were mixed before they were introduced to elongated nozzle 49 and contained:

0.032 liters per minute of propane  
0.182 liters per minute of  $\text{TiCl}_4$   
0.23 liters per minute of nitrogen  
0.138 liters per minute of hydrogen

Motor 43 was actuated so that rack member 40 and the steel tube moved downward at a rate of 0.05 inches per minute until the inside of the tube was coated. After the deposition process, the tube was cooled to 200° C. by passing hydrogen therethrough and then cooled to room temperature by passing nitrogen therethrough at a rate of 2 liters per minute. The resulting tube containing the internal coating was cut. A smooth uniform solid solution layer of titanium carbonitride of 1.5 mils was uniformly deposited on the inside of the tube. The coating had an average knoop hardness of 2480.

A comparative run was conducted under the same basic conditions as the above described run except that the entire tube was enclosed in an annular heater, and the reactants were introduced at one end thereof, passed therethrough and exhausted at the opposite end thereof. This run was conducted for 30 minutes until the one-fourth inch pipe plugged due to deposits formed from the reactants. The coating on the interior of the tube was nonuniform, caked, and soft except for a very small portion in the end thereof adjacent the reactant gas inlet.

While this invention has been described in relation to its preferred embodiments, various modifications will now 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.

What is claimed is:

1. The method of coating the inside of a tube with a solid solution layer of a carbonitride of a metal selected from boron, silicon, and the transition metals in Groups IV-B, V-B, and VI-B of the Periodic Table with a gaseous reactant stream having reactants including a reactive compound of said metal, a carbon-containing compound, and nitrogen or a decomposable compound of nitrogen, comprising:

(a) selectively heating only a limited section of the inside surface of said tube to a temperature at which said reactants will decompose; and

(b) selectively introducing said gaseous reactant stream directly into the heated section to contact the inner periphery thereof and to thereby cause decomposition of said reactants and formation of said solid solution layer of said metal carbonitride on said surface, while maintaining the remainder of said reactant stream at a temperature sufficiently low that substantially no decomposition of said reactants occurs until said reactants contact said heated section.

2. The method of claim 1 wherein said section is heated to a temperature in the range from about 400° to 1200° C.

3. The method of claim 2 wherein said gaseous reactant stream contains hydrogen, nitrogen, a hydrocarbon, and a halide of said metal which are reactable at the temperature of said heated section.

4. The method of claim 2 wherein said gaseous stream contains hydrogen, halide of said metal and a nitrogen containing compound which are reactable at the temperature of said heated section.

5. The method of claim 1 wherein said heated section comprises one end section of said tube and further comprising: sequentially heating contiguous sections of said tube along the length thereof toward the other end thereof while maintaining the selective introduction of said gaseous reactant stream directly into each heated section to thereby coat said sections with a solid solution layer of said metal carbonitride.

6. The method of claim 1 wherein said gaseous reactant stream is introduced from a nozzle inserted concentrically within said tube having its outlet positioned within said heated segment.

7. The method of claim 6 wherein said heated section comprises a first end of said tube and said nozzle extends from the second end of said tube with its outlet exhausting toward said first end.

8. The method of claim 7 wherein said section is heated by a stationary heat zone positioned around said tube adjacent said section.

9. The method of claim 8 further comprising moving said tube through said heat zone so that said second end thereof approaches said heat zone while maintaining said nozzle stationary with respect to said tube and heat zone, and maintaining said gaseous reactant stream passing continuously from the outlet thereof, said moving occurring at a rate such that sequential sections of said tube passing through said heat zone are heated to said temperature to thereby coat said sections with a solid solution layer of said metal carbonitride.

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