March 20, 1973 P. F. WOERNER **3,721,577**

PROCESS FOR THE DEPOSITION OF REFRACTORY METAL AND
METALLOID CARBIDES ON A BASE MATERIAL

Filed Aug. 26, 1968 2 Sheets-Sheet 1

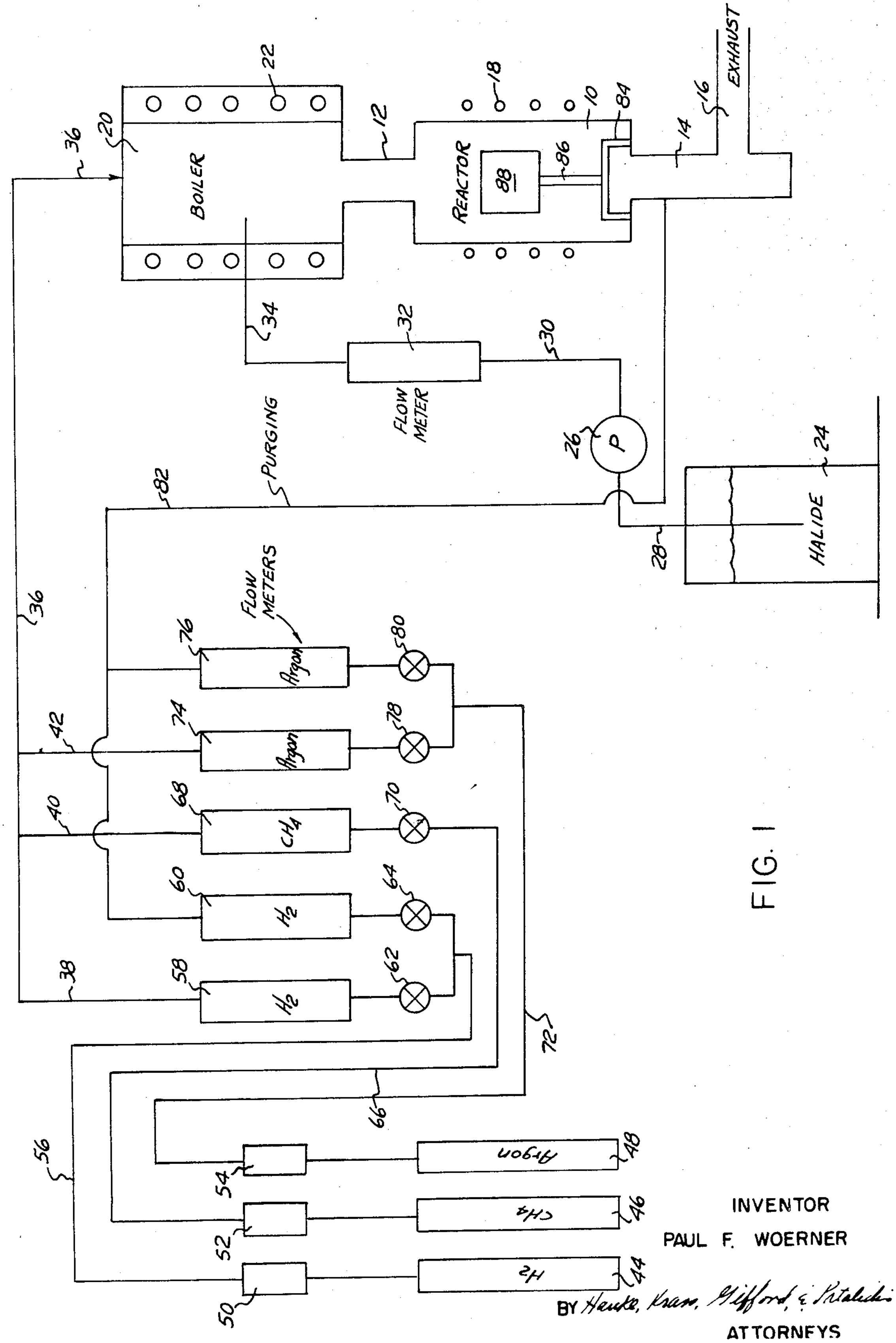

FIG. 1

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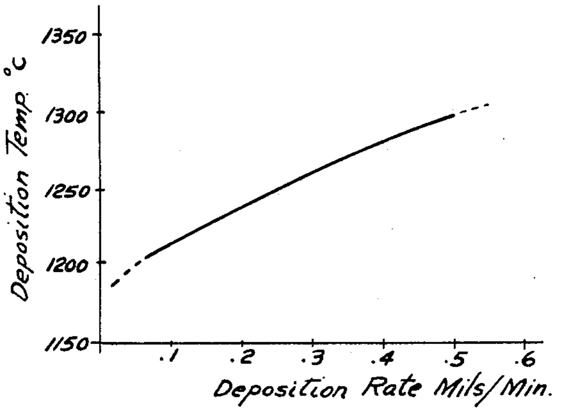

FIG.2

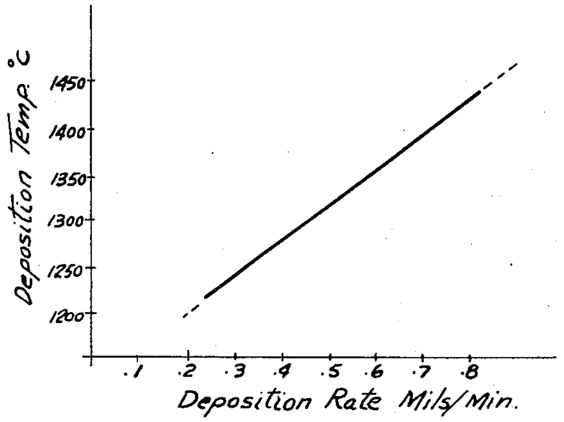

FIG.3

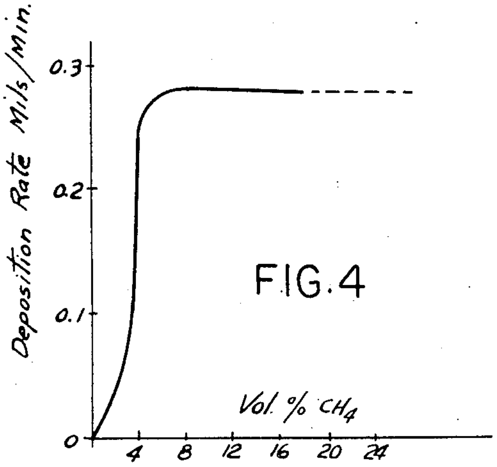

FIG.4

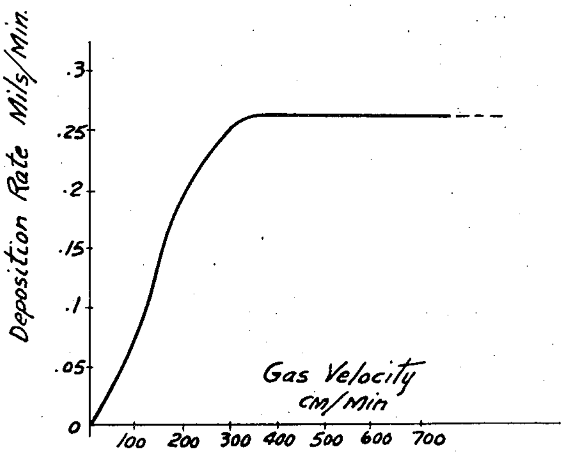

FIG.5

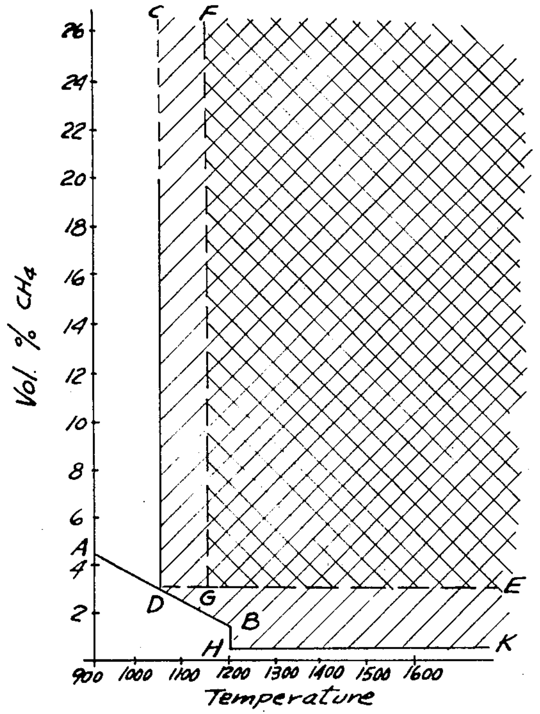

FIG.6

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Patented Mar. 20, 1973

3,721,577

PROCESS FOR THE DEPOSITION OF REFRACTORY METAL AND METALLOID CARBIDES ON A BASE MATERIAL

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Continuation-in-part of application Ser. No. 581,646, Sept. 23, 1966, now Patent No. 3,529,988. This application Aug. 26, 1968, Ser. No. 755,242
Int. Cl. B44d *1/00;* **C23c** *11/08*
U.S. Cl. 117—46 CG **10 Claims**

ABSTRACT OF THE DISCLOSURE

A process for the deposition of refractory metal or metalloid carbides on ferrous and non-ferrous base materials by heat reacting a hydrocarbon and halide vapors of the metal or metalloid to be deposited in a hydrogen atmosphere, the hydrocarbon concentration being at least .5% per volume and the temperature of reaction being at least 1050° C.

CROSS REFERENCE TO RELATED APPLICATION

The present application is a continuation-in-part application of copending application Ser. No. 581,646, filed Sept. 23, 1966, now Pat. No. 3,529,988.

BACKGROUND OF THE INVENTION

Field of the invention

The present invention belongs to the broad area of chemical vapor deposition in general, and more particularly the invention relates to a process for the deposition of carbides on a ferrous or non-ferrous base material so as to provide such base material with a hard carbide coating substantially resistant to friction, deformation, thermal shock, and to the action of most chemicals.

Description of the prior art

Chemical vapor deposition has been the subject of much research and development. A summary of the work accomplished to date may be found in "Vapor Deposition" by Carroll F. Powell, Joseph H. Oxley and John M. Blocker, Jr. (John Wiley & Sons, 1966). More specifically, chemical vapor deposition of carbides by heat reaction of a hydrocarbon with an appropriate halide, has been reported in an article entitled "Formation of Silicon and Titanium Carbides by Chemical Vapor Deposition" by M. L. Pearse and R. W. Marek, published in the Journal of the American Ceramics Society, Vol. 51, No. 2, February 1968, pages 84–87. In United States Patents Nos. 2,884,894, 2,962,388 and 2,962,399, in the name of Wilhelm Ruppert et al., there are also described processes for the production of titanium carbide coatings by heat reacting a titanium halide with a hydrocarbon in a hydrogen atmosphere.

The prior art known to applicant includes the following:

(1) Powell et al., Vapor Plating, John Wiley and Sons, Inc., New York (1966).

(2) J. R. Darnell et al., U.S. Pat. No. 3,368,914, issued Feb. 13, 1968.

(3) R. L. Heestand et al., U.S. Pat. No. 3,367,826, issued Feb. 6, 1968.

(4) Takahashi, Takehiko et al., Journal Electrochemical Society, 114, No. 12 (December, 1967), pp. 1230–1235.

(5) M. E. Weech et al., U.S. Pat. No. 3,151,852, issued Oct. 6, 1964.

(6) J. H. Oxley, et al., U.S. Pat. No. 3,178,308, issued Apr. 13, 1965.

(7) E. Newenschwander et al., U.S. Pat. No. 3,340,-020, issued Sept. 5, 1967.

(8) M. Turkat, U.S. Pat. No. 3,294,880, issued Dec. 27, 1966.

(9) Aerobraze Corporation Literature.

(10) S. J. Sindeband, U.S. Pat. No. 2,685,543, issued Aug. 3, 1954.

(11) S. J. Sindeband, U.S. Pat. No. 2,685,545, issued Aug. 3, 1954.

(12) R. L. Samuel et al., U.S. Pat. No. 3,029,162, issued Apr. 10, 1962.

(13) W. Ruppert et al., U.S. Pat. No. 2,962,399, issued Nov. 29, 1960.

(14) R. W. Marek and M. L. Pearce, Electrochemical Technology, Vol. 5, No. 5–6, May-June, 1967, pp. 185–188.

(15) G. A. Semenova, A. N. Minkevich, Izvest. VUZ.-Chern. Met. (September 1965), No. 8, pp. 168–70.

(16) W. Ruppert et al., U.S. Pat. No. 2,962,388, issued Nov. 29, 1960.

(17) M. L. Pearce and R. W. Marek, Journal of the American Ceramic Society, Vol. 51, No. 2 (February 1968), pp. 84–87.

(18) W. Ruppert et al., U.S. Pat. No. 2,884,894, issued May 5, 1959.

(19) A. Munster and W. Ruppert, Zeitschrift Für Elektrochemie, Vol. 57 (1953), No. 7, pp. 564–71.

(20) H. Wiegand and W. Ruppert, Metalloberflache, Vol. 14 (1960), No. 8, pp. 229–35.

(21) A. Munster, K. Sagel, Zeitschrift Für Elektrochemie, Vol. 57 (1953), No. 7, pp. 571–79.

(22) G. A. Semenova, A. N. Minkevich, E. V. Panchenko, S. B. Maslenkov, Metallovedenie i Term. Obra Metallov (November 1965), No. 11, pp. 37–38.

(23) Manufacturing Techniques for Application of Erosion Resistant Coatings to Turbine Engine Compressor Components, Interim Engineering Progress Report, April 1968–30 June 1968, MATC Project No. 476–8, Contract No. F 33615–68–C–1487.

(24) J. R. Darnell et al., U.S. Pat. No. 3,368,914, issued Feb. 13, 1968.

Some of the prior art methods are incapable of obtaining fully adhering carbide coatings on a base material. Semenova et al., for example, report that the coatings obtained by their methods generally flake off and are poorly adherent. Flanking may be reduced with partial success by long temperature soaks of the coated articles in order to promote diffusion, but the overall metallurgical properties of the substrate may be affected, and the practicality and economics of the process are decreased. Use of such techniques are similar to diffusionizing coatings.

Most methods of the prior art have in common operating under conditions which correspond to the thermodynamic equilibrium between hydrocarbon on one hand and hydrogen and carbon on the other hand, at the temperature used for the deposition of the coating. As a result of using low concentrations, or partial vapor pressures, of hydrocarbon and halide, using a hydrocarbon to halide volume ratio of approximately one, operating at substantially low temperatures, for example, between 900° C. and 1200° C., the prior art methods permit to obtain very low rates of deposition. Additionally, as more particularly disclosed by Ruppert et al., the prior art indicates that the presence of carbon in the base material and that the presence of chromium either in the base material or in proximity therewith permit to accomplish better results or are absolutely necessary to obtain coatings having adequate qualities of adhesion to the base material and optimum compositions. When operating upon a base material containing carbon, part of the carbon entering into the composition of the carbide is supplied by such base material and the carbon is caused to diffuse through the already existing coating once the reaction and deposition have begun. This carbon diffusion tends to exhaust carbon from the surface of the base material and limits the coatings obtained by methods of the prior art to a few microns in thickness, as the reaction tends to decrease in efficiency and even stop completely as soon as the coating becomes thick enough to prevent such carbon diffusion from the base material.

The process of Ruppert et al. is partially a chemical vapor deposition process utilizing $TiCl_4$, and CH_4 or similar hydrocarbon which decomposes into basis CH_4 and hydrogen. The concentration of $TiCl_4$ is regulated by purging a vessel containing $TiCl_4$ at a given temperature. The $TiCl_4$ exerts a vapor pressure at the control temperature and this vapor is swept into the reaction zone with H_2, or H_2 and CH_4. Deposition temperatures for coating ferrous and non-ferrous based materials are between 900° C. and 1200° C.

Ruppert is critically concerned with avoiding the formation of elemental carbon and refers in Table II of U.S. Pat. No. 3,962,388 to the ideal operating parameters as follows:

	P_{CH_4}	Vol. percent CH_4
Temperature:		
900	4.72×10^{-2}	4.5
1,000	3.63×10^{-2}	3.5
1,100	2.57×10^{-2}	2.5
1,200	1.51×10^{-2}	1.5

Stated mathematically, the hydrocarbon to hydrogen ratio should not be above $.047\times P^2H_2$ at 900° C. and $.015\times P^2H_2$ at 1200° C. These values are slightly higher than predicted from equilibrium, but were found by Ruppert et al. to be adequate, and define the limiting operating parameters according to their teachings. Ruppert states "the critical factor is always that, at the temperature employed for the deposit of the carbide coating, the hydrocarbon concentration in the gas mixture does not exceed the limits indicated above."

Semenova, Minkevich, Panchenko, and Maslenkov, have disclosed in their report appearing in Metallovedenie

Semenova et al. note the difficulty of obtaining adherent coatings on steel. In fact they state "in view of the fact that spalling of the deposit was sometimes observed on the steel specimens, control test pieces of graphite were heated simultaneously with the steel." The rate of growth of the deposit was calculated over the period of 30 min. by measuring the increase in weight of the graphite, expressed in terms of a unit area (ΔP/S mg./sq./mm."). Ruppert likewise makes such statements, and compensates by long exposure at temperature.

Generally speaking, the prior art methods for coating a base material or substrate by chemical vapor deposition have definite limitations due to long reaction times, low plating rates, dependency on diffusion of at least one constituent from the base material, and the need for surface constituents to initiate the reaction. They are limited to thin coating thicknesses within a practical time period, and are generally based on equilibrium reaction conditions or conditions close to equilibrium reaction.

SUMMARY OF THE INVENTION

The present invention, by contrast, permits base materials to be coated with refractory metal and metalloid carbides with practical rates of depositions as high as 15 to 50 mils per hour. Coatings may be formed on ferrous base materials, non-ferrous base materials and non-metallic surface materials. The resulting coating is hard, dense, wear resistant and corrosion resistant. It is generally not necessary to heat treat the base material either before or after deposition of the coating thereon, but subsequent heat treatment may be accomplished, if so desired.

The present invention relates to an improved and practical manufacturing process for producing high density carbide-containing coatings, metallurgically bonded to the base material substrate. In the process of the present invention, carbide coatings are produced by metering gaseous constituents or reagents into a work reaction chamber and, as the gaseous constituents come in contact with the heated part or substrate, thermal reduction and chemical reduction combine to produce metal or metalloid carbides which are deposited in a well-defined fixed composition. It is already known that TiC can be formed

These and the many other objects and advantages of the present invention will become apparent to those skilled in the art when the following description of some of the best modes contemplated to practice the invention is read in conjunction with the accompanying drawings wherein:

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic representation of an example of an apparatus utilized for practicing the process of the present invention;

FIG. 2 is a graph representing the deposition rate in mils/minute of carbide coatings obtained by the process of the invention as a function of the deposition temperature;

FIG. 3 is a graph similar to FIG. 2, but showing the deposition on a non-ferrous base material such as graphite;

FIG. 4 is a graph showing the deposition rate in mils/minute, on a graphite base material, of a carbide coating as a function of the volume percent of hydrocarbon;

FIG. 5 is a graph showing the deposition rate in mils/minute as a function of the gas velocity in the reactor in cm./minute at constant deposition temperature and constant methane concentration; and

FIG. 6 is a graph comparing some of the important parameters of the present invention, namely the volume percent of hydrocarbon and temperature relationship, with the same parameters as taught by the prior art.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The method of the present invention, as previously mentioned, permits to vapor deposit a firmly adhering coating of a carbide of a refractory metal or metalloid on ferrous, non-ferrous and non-metallic base materials. Although the present invention will be hereinafter described primarily relatively to the production of coatings of titanium carbide. TiC, on carbon steel, stainless steel and graphite base materials for the illustrative purpose of explaining the principles of the invention, it will be appreciated by those skilled in the art that the principles of the invention are applicable to obtaining carbide coatings of any refractory metal or metalloid, such as tungsten, zirconium, hafnium, tantalum, columbium, vanadium, thorium, etc.

In order to practice the invention, an apparatus as shown in FIG. 1 is utilized which includes a vessel or reactor **10** having an inlet **12** and an outlet **14** connected to an exhaust conduit **16**. Around the reactor **10** is disposed a heating element **18** which may be a resistance heater or preferably a radio frequency induction heater with an appropriate control means, not shown, for regulating the temperature within the reactor. The reactor **10** is preferably made of a material which is refractory, substantially inert, and which can not be heated by induction, such as alumina, or aluminum oxide.

A boiler **20** preferably made of stainless steel, has its outlet connected to the inlet **12** of the reactor **10**, and means such as heating coils **22** are disposed around the boiler for maintaining the interior thereof at a predetermined temperature. A tank or reservoir **24** provided with heating means, not shown, contains a halide of a refractory metal or metalloid which may be brought to its melting temperature by means of the heater dependent from such reservoir **24**. A pump **26** has an inlet line **28** disposed below the level of the liquid metal halide in reservoir **24** and an outlet line **30** connected through a flow meter **32** to a line **34** leading within the boiler **20**. Boiler **20** is provided with an inlet line **36** into which may be individually metered by means of lines **38, 40** and **42** adjustable flows of, respectively, hydrogen, a hydrocarbon such as methane, CH_4, and an inert gas, for example, argon. The hydrogen, the hydrocarbon and the argon gases are respectively supplied from a hydrogen tank **44**, a hydrocarbon tank **46** and an argon tank **48** from which the separate gases are permitted to flow into, respectively, gas dryer-purifiers **50, 52** and **54**. Each gas dryer-purifier **50, 52** or **54** contains a drying agent and a purifying agent capable of absorbing or removing carbon monoxide and carbon dioxide from the gas, such agents being respectively for example calcium sulphate and asbestos coated with sodium hydroxide. From the hydrogen gas dryer-purifier **50**, the dried and purified hydrogen is led by means of a line **56** into two flow meters **58** and **60** disposed in parallel, each provided with a flow regulating inlet valve as shown at **62** and **64** respectively. The output of flow meter **58** leads through line **38** into the inlet line **36** to the boiler **20**, thus permitting hydrogen to be mixed at will and in any proportion with a hydrocarbon such as methane, which after flowing from tank **46** through gas dryer-purifier **52** is led by a line **66** into a flow meter **68** through which the flow of gas may be regulated by inlet regulator valve **70**, the output of flow meter **68** being connected through a line **40** to the boiler inlet line **36**. The inert gas, such as argon, from tank **48**, after being dried and purified in gas dryer-purifier **54** flows through line **72** into two flow meters **74** and **76** disposed in parallel, the flow of inert gas being regulated therethrough by means of respectively regulator valves **78** and **80**. The output of flow meter **74** is connected through a line **42** to the boiler inlet line **36**. The outputs from hydrogen flow meter **60** and argon flow meter **76** are led into a common purging pipe **82** leading into the outlet **14** of reactor **10**, so as to permit at will to purge the exhaust of the system with inert gas, hydrogen, or mitxure of both, or, alternately, so as to permit reverse flow purge of the system.

Means are provided in the reactor **10** such as a support base **84** and pillar **86** for supporting a part, as shown at **88**, in the reactor for the purpose of such part, constituting the base material, being coated with a layer of carbide, as hereinafter explained. It is obvious that support base **84** is adequately perforated or consists of slender legs and brackets supporting pillar **86** so as not to cause an interruption of the gas flow through the boiler and, preferably, pillar **86** is made of a material such as alumina.

The base material of part **88** is prepared in the following manner. If the part is made of steel, cast iron, or the like, it is degreased and descaled if necessary, the scale and oxide layers being removed by acid etching, sand blasting or similar means. The part may also be further cleaned by being washed in water and dried, for example, in acetone or alcohol in order to remove any residual material that may be on the surface of the part. The part need not be degasified, and it is placed in the reactor **10**, being held in position on pillar **86** or by any other alternate convenient attaching means. Regulator valves **62, 64** and **70** being closed, valves **78** and **80** are opened and the whole system is purged with argon. Valve **80** is closed once the whole system is filled with argon, and hydrogen at atmospheric pressure, although higher or lower pressures may be used, is introduced into the system by opening valves **62** and **64** while closing valve **78** for interrupting the flow of argon through the system. Once the boiler **20** and the reactor **10** are filled with flowing hydrogen, at a pressure slightly above one atmosphere, the reactor heater **18** is turned on and the part **88** is rapidly heated to a temperature above 1050° C. Preferably, if the part **88** is made of steel, the part is heated to a temperature between 1100° and 1250° C., and if the part **88** is graphite, it is heated to a temperature between 1200° and 1600° C., preferably in the range of 1275° to 1325° C. If the part **88** is of quartz, the preferred range of heating temperature is 1300° to 1325° C.

With pure hydrogen still flowing through the boiler **20** and reactor **10**, liquid halide from tank **24** is directly metered by means of pump **26** through flow meter **32** and inlet pipe **34** into the heater boiler **20** where the liquid halide immediately vaporizes and mixes into the flow of pure hydrogen flowing through the boiler **20** into the reactor **10**. It is very critical for the practice of the invention that, when the part **88** is a carbon or metal base material, the sequence of introducing the metal halide into the reactor **10** before hydrocarbon is introduced therein be strictly followed, because if the hydrocarbon first flows into the reactor, excess carbon atoms will form on the surface of the part which would cause surface melting and carbon eutectic formation or add carbon to the base metal, resulting in surface melting of the part and poor adhesion of the carbide coating.

As a typical example of the present invention, if it is desired to coat a part **88** made of 410 stainless steel, with a dense, continuous and adhering titanium carbide coating, after degreasing, washing and drying of the part, purging the reactor with purified argon and with purified hydrogen, the part **88** is heated to a temperature of 1200° to 1250° C. in a flow of hydrogen. The hydrogen flow rate depends on the reactor size, and for a reactor of 50 mm. in diameter, the preferred hydrogen flow is comprised between 13,000 and 14,000 cm.^{3}/minute corresponding to a gas velocity of 660 to 735 cm./minute. Once the part **88** has reached the reaction temperature, liquid titanium tetrachloride, $TiCl_4$, is introduced into the boiler **20** where it immediately vaporizes, the boiler being maintained at a temperature between 350° and 800° C., preferably at 600° C. or thereabout. The $TiCl_4$ vapors intimately mixed with the hydrogen enter the reactor **10** and, when approaching the heated surface of the part **88** first turn to white fumes which rapidly turn to a violet color resulting seemingly from the heat and hydrogen reduction of the $TiCl_4$ to $TiCl_3$. When this happens, the hydrocarbon, preferably methane, CH_4, is added to the gas flow by opening regulator valve **70**, and the reaction is carried out for the desired length of time depending on the titanium carbide coating thickness which it is desired to obtain. For example with a deposition time of ten minutes under the conditions hereinbefore indicated, an adhering coating of titanium carbide about three mils thick is produced. The coating is metallurgically bonded to the steel and has a micro harness in excess of 3000 Knoop, ranging as high as 3800 Knoop.

After the part **88** has been exposed in the reactor or deposition chamber **10**, for the desired time interval to produce a desired coating thickness, the CH_4 flow is first stopped, and then the $TiCl_4$ flow, and the system is purged with hydrogen. The part **88** is removed from the reactor **10** via an air lock chamber, not shown, if a hot wall technique (resistance heating) is used. The coated part **88** may be removed immediately to a cooling air lock chamber and essentially gas quenched or, alternately, it may be removed and cooled in stages to retain desirable substrate properties. The choice of procedure depends on the material. If a cold wall technique (induction heating) is used the part is generally rapidly cooled in either an argon or hydrogen atmosphere in the reactor itself.

The sequence of gas introduction into the reactor is a very critical sequence, as previously mentioned, because if excess carbon atoms are allowed to form in the reactor on a steel or ferrous part, it could cause surface melting by carbon eutectic formation, or add carbon to the base metal. All gases are precisely metered. The $TiCl_4$ is directly metered into the boiler in a liquid form. Direct metering and the use of a boiler are features of the invention, differing from other known methods. The boiler serves to vaporize and also mix the other gases. Since the CH_4 and/or hydrogen are also metered directly into the boiler, and since each is controlled individually, hence the sequence of additions is readily controlled. The use of direct liquid metering of the $TiCl_4$ into the boiler permits high concentrations of the titanium-bearing molecules in the deposition zone, and permits increased deposition rates leading to a practical manufacturing process. The process of the invention is truly one of forming an overlayer or coating on any substrate of interest. The process is not limited to reactions with the surface being plated. The surface does not need to furnish any constituents to the TiC coating. Thus the process of the invention is not diffusion limited. In diffusion-limited reactions by contrast, the $TiCl_4$ is either thermally or chemically reduced and the titanium atoms combine with the carbon, furnished by the surface, forming a very thin layer of TiC (perhaps several mono-layers thick). To increase this layer thickness, more carbon must diffuse to the surface to react with the new titanium atoms. Therefore, such methods are "diffusion-time-limited."

The graph of FIG. 2 represents the deposition rate in mils per minute in function of the temperature of the part being coated in the reactor. The graph results from a series of titanium carbide coating operations according to the hereinbefore explained process, obtained on 410 stainless steel, on M2 steel, on graphite and on quartz, with a volume percent of hydrogen equal to 95.2%, a volume percent of CH_4 equal to 3.2%, and a volume percent of $TiCl_4$ equal to 1.6%, therefore at a $TiCl_4/CH_4$ ratio of .5. The total flow was 4545 cm.^{3} per minute per in.^{2} or 706 cm./min.

The graph of FIG. 2 reveals that the deposition rates in mils per minute are independent from the composition of the base material, which indicates that the process of the present invention is not diffusion limited, and that remarkable deposition rates 50 to 100 times greater than those obtainable by prior art processes are achieved by the present invention. Furthermore, the graph of FIG. 2 shows clearly the temperature influence on the rate of deposition.

When the base material is graphite, higher reaction temperatures may be used than when the base material is steel. Such higher reaction temperatures result in greater deposition rates, as illustrated by the graph of FIG. 3 showing deposition rate of TiC on graphite in function of the temperature of the base material, at a constant $TiCl_4/CH_4$ of 1.89, with a volume percent of CH_4 equal to 2.75%, a volume percent of $TiCl_4$ equal to 5.19% in 92.06 vol. percent of hydrogen, using an overall total flow rate of 5280 cm.^{2}/min.-in.^{2} through the reactor, or 812 cm./min.

FIG. 3 therefore shows the pronounced effect of temperature on the deposition rates, indicating that with higher temperatures there is a more complete pyrolysis of the hydrocarbon, thereby an increase in the number of carbon atoms impinging on the substrate surface and reacting with the metal atoms from the metal halide.

The slope of the curves of the graphs of FIGS. 2 and 3 are not identical. The slope of the curve of FIG. 3 is greater. It seems that the relationships are not truly linear with a slight increase at higher temperatures. This may be due to a greater driving force at higher temperatures making the overall reaction more favorable. Also, it has been observed that a reaction of hydrogen and $TiCl_4$ in the presence of graphite is possible at substrate surface temperatures above 900° C. with the formation of a diffusion-limited TiC coating. It is possible that initially such a deposit forms, adding to the overall coating thickness thereby increasing the deposition rate. Such a surface reaction becomes very slow at lower temperatures. Howver, it is obvious that temperature does in fact have a pronounced influence on the deposition rate.

The reaction involved in the process of the present invention is one in which pyrolysis of the hydrocarbon must occur to promote the formation of the TiC. Pyrolysis of the hydrocarbon, for example methane, is more complete at elevated temperatures and the reaction energetics are more favorable. By increasing the number of carbon atoms arriving at the deposition surface, the deposition rate is increased. This can be accomplished by increasing the volume percent of hydrocarbon into the reactor or by increasing the total flow velocity of the gas.

FIG. 4 is a chart showing the influence of the volume percent of hydrocarbon, such as CH_4, on the deposition rate of carbide expressed in mils per minute. The results represented by the curve of the chart of FIG. 4 were obtained with a constant total gas flow velocity through the reactor of 16,000 cm.^{3} per minute or 353 cm./min., the reactor diameter being 75 mm., and at a constant reaction temperature of 1250° C., a constant $TiCl_4$ flow velocity of 417 cm.^{3} per minute or 9.18 cm./min. and a constant deposition time of 30 minutes, the substrate material being graphite. The methane concentration was varied as shown from less than 2% per volume to more than 20% per volume. The graph of FIG. 4 clearly indicates that for a given temperature, maintaining a constant $TiCl_4$ and total flow velocity, the deposition rate of TiC increases as the volume percent of CH_4 increases. However, the greatest increase occurs between 2 and 3.5 volume percent of CH_4 with an apparent leveling off for a concentration of CH_4 greater than 4% per volume. This seems to be due to the fact that increasing the volume percent of CH_4 without increasing the volume percent of $TiCl_4$ results in an insufficient concentration of $TiCl_4$ not permitting enough atoms of titanium to combine with the excess atoms of carbon.

A whole series of such curves as the curve of FIG. 4 may be obtained for different temperatures. At higher temperatures maximum deposition rates are reached at lower methane concentrations because pyrolysis of methane and reaction kinetics become more favorable at elevated temperatures.

FIG. 5 represents a graph of the deposition rate in mils per minute as a function of the gas velocity in cm./min. The graph of FIG. 5 was obtained at a constant deposition temperature of 1250° C. with a constant methane concentration of 8% per volume using a reactor having a diameter of 75 mm. Runs were made using graphite as a base material and also using 410 stainless steel and M2 steel as base materials. Once again, the results achieved were the same irrespective of the base material composition. The graph clearly illustrates the influence of the gas velocity upon the deposition rate. As the gas velocity increases the deposition rate also increases until the deposition rate remains substantially constant or even decreases slightly. This leveling off of the curve is believed to be due to a temperature limitation factor, resulting from the cooling effect of the gases flowing past the substrate. FIG. 5 also clearly demonstrates that at low gas velocities approaching or corresponding to equilibrium conditions, slow deposition rates are obtained.

The deposition rates below gas velocities of, for example, 300–350 cm./min., decrease fairly rapidly, as shown in FIG. 5, whereas above 350 cm./min. the deposition rates remain fairly constant. As the gas velocity decreases, the deposition conditions begin to simulate equilibrium conditions, which would be the most obvious processing parameters derived from theory and as taught by the prior art. Use of such low gas velocities means long deposition times to build up a coating of even one mil. Such conditions are typical of the prior art. In addition, because a by-product produced by the reaction is HCl gas, if the gas velocity is very slow, it is possible to have present increased HCl concentration which slows down the deposition kinetics and impedes the arrival rate of the feed constituents to the surface of the part being coated. High surface concentrations of HCl could also lead to chemical corrosion of the substrate and make the deposition reaction gas-diffusion barrier limited. Thus the principles of the present invention are that equilibrium conditions should be avoided and non-equilibrium conditions utilized to obtain high carbide deposition rates.

Taken together, the data presented by FIGS. 2–5 clearly indicate that the deposition rate is influenced by the temperature of the base material, the volume percent of hydrocarbon in the gas flow, the volume percent of halide in the gas flow and an overall increase of the gas velocity.

The increase in carbide deposition rate on a base material obtained by practicing the method of the invention consisting in operating at high temperatures, at high concentration of hydrocarbon and halide and at high gas flow rates seem to result from the increase number of carbon atoms available at the substrate surface. By correct balance of the base material temperature, concentration of halide and hydrocarbon and total gas velocity, correct pyrolysis of the hydrocarbon with formation of carbide is effected upon the base material surface itself rather than being effected in a gas phase above the surface. If formation of carbide is effected in a gas phase above the base material surface, this results in a loosely bonded coating with much surface roughness.

Other hydrocarbons such as, for example ethane, propane, benzene, and the like may be used instead of methane, such other hydrocarbons being considered herein and referred to as methane functionally equivalent. The methane functionally equivalent hydrocarbon concentration depends on process conditions. Higher hydrocarbons such as benzene are more difficult to control than lower hydrocarbons such as methane, ethane and propane because C_6H_6 could effectively act as anywhere from zero to slightly more than 6 CH_4 groups. Higher hydrocarbons under some circumstances could pre-pyrolize in the reactor or "blow-off" most of its carbon radicals when pyrolysis begins at the surface of the substrate.

FIG. 6 is a plot of volume percent of hydrocarbon CH_4, as a function of the deposition temperature. The straight line AB running from 900 to 1200° C. for CH_4 volume percents of 4.5 to 1.5 represent the conditions outlined by the prior art, these conditions being stated to represent maximum CH_4 concentrations for the temperature range reported. Contrary to the prior art, the present invention teaches there is a minimum rather than a maximum volume percent of CH_4 concentration required at any temperature. Use of such higher concentrations yields higher deposition rates which make the invention substantially more practical. The operating parameters relative to CH_4 concentrations and temperatures of reaction are situated in the cross-hatched region of FIG. 6 bordered by line CDBHK. The lower operating temperature is 1050° C. with the volume percent of CH_4 to be no less than 3% per volume (point D). The upper temperature range is about 1600° C. with a CH_4 concentration of no less than 0.5% per volume. It is preferable that the CH_4 concentration be considerably greater than 3% per volume at lower temperatures such as 1050° C. and greater than .5% per volume at higher temperature such as 1200° C. and above. As noted on FIG. 6 the double cross-hatched region limited by dotted line FGE represents a preferred operating area, such operating conditions resulting in substantial deposition rates permitting to minimize the time at which the substrate is maintained at high temperature, thus providing a practical, efficient and economical process. Minimizing the time at high temperature also reduces the possibility of impairing or changing the metallurgical properties of the substrate.

When operating at high temperatures, the previously mentioned criticality of the sequence of additions of the reagents becomes most critical for ferrous-based parts, but operating at high temperatures results in maximum deposition rates. Furthermore when operating at high volume percent of CH_4, sufficient $TiCl_4$ must be present to react with the carbon atoms deposited on the surface of the substrate. It does not seem true that free or elemental titanium can be formed if excess $TiCl_4$ is used as suggested by the prior art. The prior art uses a $TiCl_4/CH_4$ ratio of about unity. Experimental results obtained by using the method of the present invention reveals no observed criticality in the $TiCl_4/CH_4$ ratio over a preferred range of .25 to 2.5, with limited success with ratios as low as 6×10^{-5}. Preferably, a $TiCl_4/CH_4$ ratio of less than 1 should be used. It is desirable to operate at low $TiCl_4/CH_4$ ratios for economical reasons since the cost for $TiCl_4$ is more than the cost of other constituents. Use of exceedingly high $TiCl_4/CH_4$ ratio can lead to increased formation of HCl gas in the reactor and thereby corrode the substrate, changing the over-size or causing pits on the surface.

Use of exceedingly low $TiCl_4/CH_4$ ratios, on the other hand, can lead to titanium starvation and excess carbon in the carbide coating. However, proportions of $TiCl_4$ as low as .02% per volume of the methane have been found to result in the formation of acceptable carbide coatings, the $TiCl_4/CH_4$ ratio being thus as low as 6×10^{-5}, which clearly demonstrates that operating under the conditions of the present invention permits to neglect operating under the stoichiometric composition condition recommended by the prior art.

The present invention further teaches that gas velocity is a very vital processing parameter and definitely aids in increasing deposition rates. No mention is made in the prior art concerning this parameter. Preferably, a gas velocity of above 100 cm./min. should be used to obtain high deposition rates.

The high concentration of halide in the total gas flow is provided by metering the halide in a liquid form directly into the boiler **20**, rather than adding the halide in a gaseous form into the hydrogen flow, as taught by the prior art. The following table lists commonly available metal halides and silicon halides, the state of such halides at room temperature, and their melting or sublimation temperatures, and the means of metering the halides into a boiler, in order to practice the methods of the present invention.

Compound	Room temp., state	Melting point, ° C.	Sublimation point, ° C.	Method of metering
$ZrCl_4$	Solid		331	Vapor through heated flow meter.
ZrI_4	do		431	Do.
ZrI_2	do	427		Liquid above 427° C.
$HfCl_4$	do		313	Vapor through heated flow meter.
HfI_4	do		427	Do.
$TaCl_5$	do	207		Liquid between 210–234° C.
$TaBr_5$	do	240		Liquid between 240–319° C.
$CbCl_5$	do	212		Liquid between 212–243° C.
$CbBr_5$	do		227	Liquid between 227–272° C.
VCl_4	Liquid	−24	[1] 164	Liquid between −24°–−164° C.
WCl_4	Solid	327	[1] 332	Vapor above 332° C.
WCl_5	do	244		Liquid between 244–276° C.
WCl_6	do	275		Liquid between 275–337° C.
WBr_4	do		327	Vapor.
WF_6	Gas			As gas.
ThI_4	Solid	566		Liquid between 566–837° C.
$SiCl_4$	Liquid			As liquid.
SiBr	do			Do.

[1] Boiling.

Utilizing the method of the present invention, carbide coatings have been formed on ferrous base materials, non-ferrous base materials and non-metallic materials. Ferrous-base materials include 1020, 1045, and 1095 low carbon steel, 4130, 4350, 5210, and 6150 alloy carbon steels, cast iron materials, 316, 403, 410, and 430 stainless steels, Am350, Am355, and Inconel 718, as well as M–2, M–4, M–7, M–11, T–15, D–2, D–13 and H–16 tool steels. Non-ferrous materials include tungsten, tungsten carbide, molybdenum and columbium base materials. Non-metallic materials include graphite, aluminum oxide (Al_2O_3) and other refractory oxides, boron and boride materials.

Unusual advantages of titanium carbide and other carbide-coated parts make them particularly useful for boats, fixtures, and crucibles in diffusion furnaces in the semi-conductor industry. It has been found that titanium carbide coatings obtained by the method of the invention are stable in the atmospheres used in such furnaces and that their coefficient of expansion can be matched to certain grades of graphite so that composite structures of graphite and titanium carbide do not crack on heating or cooling as a result of mismatch of thermal coefficient of expansion.

On compressor blades for engines, titanium carbide coatings reduce erosion and sometimes increase fatigue life. Erosion life is sometimes increased by a factor of 10–50. Extended erosion life is realized by applying a titanium carbide coating to the leading edge of helicopter rotor blades.

The application of a titanium or other metal or metalloid carbide coating on a ferrous-type material offers a desirable composite resulting in a very hard-wear resistant surface combined with a relatively ductile substrate retaining the original properties of the substrate combined with the desirable benefit provided by a hard surface coating.

It has been found that thin films of for example titanium carbide coatings on ferrous and non-ferrous materials, especially on ductile substrates, have unusual properties in that very thin layers exhibit less of the bulk properties, particularly brittleness. Spalling, for example, does not take place with large chunks of material loss, the thin layer coating behaving more like the substrate and exhibiting properties of the substrate.

Carbide coatings on machine tool parts such as punches, forming dies, heading dies and piercing punches, exhibit longer wear life due to the enhanced wear resistance offered by the coating obtained by the method of the present invention as compared to coatings obtained by prior art methods. Other perishable tools such as reamers, drills, end mills and cutting tools coated with carbide coating according to the present invention have a considerably increased lifetime. This results from the extreme hardness of the coatings and their resistance to wear.

It has also been found that carbide coatings and more particularly titanium carbide applied to ferrous as well as non-ferrous materials by way of the method of the present invention have considerable potential as friction material and as a friction wear pad for aircraft brakes, and motor vehicle brakes. The composite, in addition to having desirable frictional properties, possesses excellent heat transfer characteristics. It further represents a weight saving over conventional friction materials.

Due to their exceptional wear and abrasive properties carbide coatings obtained by the present invention have many applications in the dentistry field as in dental burs and the like. Such coated burs have substantially increased lifetime.

Other applications are in the textile, leather, and synthetic fiber industry as wear guides because of the greatly improved resistance to service wear.

Carbide-graphite and carbide-metal composites are excellent seal materials for water pumps, drilling equipment, and seal parts subjected to adverse wear and corrosion environments.

Having thus described the invention by way of typical examples of application thereof, what is sought to be protected by United States Letters Patent is as follows:

What is claimed is:

1. A method for the deposition of a coating of a carbide of an element wherein said element belongs to a group consisting of refractory metals and silicon, said

method comprising the steps of heating in a vessel a ferrous base material to a temperature of more than about 1200° C., circulating through said vessel a mixture of a gaseous methane equivalent hydrocarbon and of a gaseous halide of said element in a hydrogen atmosphere for depositing on the base material a carbide containing coating, the hydrocarbon concentration being at least 1.5% by volume of the mixture, the ratio of halide to hydrocarbon being at least 6×10^{-5} and the flow velocity of said mixture past said base material being at least 100 cm./minute, and introducing said halide in said vessel prior to introducing said hydrocarbon in said vessel.

2. A method for the deposition of a coating of a carbide of an element wherein said element belongs to a group consisting of refractory metals and silicon, said method comprising the steps of heating in a vessel a carbon base material to a temperature of more than about 1200° C., circulating through said vessel a mixture of a gaseous methane equivalent hydrocarbon and of a gaseous halide of said element in a hydrogen atmosphere for depositing on the base material a carbide containing coating, the hydrocarbon concentration being at least 1.5% by volume of the mixture, the ratio of halide to hydrocarbon being at least 6×10^{-5} and the flow velocity of said mixture past said base material being at least 100 cm./minute, and introducing said halide in said vessel prior to introducing said hydrocarbon in said vessel.

3. A method for the deposition of a coating of at least one carbide of an element belonging to a group consisting of titanium, zirconium, hafnium, tantalum, columbium, vanadium, tungsten, thallium and silicon, said method comprising the steps of heating a base material to a temperature above 1050° C. in the presence of a gaseous mixture containing hydrogen and at least $x\%$ per volume of a methane equivalent hydrocarbon and $y\%$ per volume of a halide of said element, wherein y is at least equal to $0.02\ x$, and $x\%$ has a value linearly varying from 3% at 1050° C. to 0.5% at 1200° C. and $x\%$ is equal to 0.5% above 1200° C., and wherein said base material contains at least one metal and said hydrogen and halide are introduced in said vessel before a mixture of said hydrogen, said halide and said hydrocarbon.

4. The method of claim **3** wherein said hydrocarbon is methane.

5. The method of claim **3** wherein $x\%$ is at least equal to 3% and $y\%$ is at least equal to $0.02\ x$ at at least 1150° C.

6. The method of claim **5** wherein said hydrocarbon is methane.

7. In a process for applying on the surface of a substrate a carbide coating belonging to the group consisting of refractory metal carbides and silicon carbide, said substrate being capable of forming a eutectic composition with carbon and said process consisting in the heat reaction of a metal halide gas and a hydrocarbon gas in a hydrogen atmosphere at a temperature which is at least proximate the eutectic temperature of said composition, the improvement characterized by introducing to the surface of substrate said metal halide gas prior to introducing to the surface of the substrate said hydrocarbon gas.

8. The method of claim **7** wherein said substrate contains carbon.

9. The method of claim **7** wherein said substrate contains a metal.

10. In a process for the deposition of a coating comprising a carbide of an element belonging to a group consisting of refractory metals and siilcon, said process comprising the step of heating a base material to a high temperature in the presence of a gaseous mixture containing hydrogen, a hydrocarbon and a halide of said element, the improvement consisting in metering said halide in a liquid form into a boiler heated to a temperature higher than the temperature of vaporization of said halide and in placing said base material in presence of said hydrogen and halide prior to placing said base material in presence of said gaseous mixture containing said hydrogen, said halide and said hydrocarbon.

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W. E. BALL, Assistant Examiner

U.S. Cl. X.R.

111—106 C

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,721,577 Dated March 20, 1973

Inventor(s) PAUL F. WOERNER

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

IN THE SPECIFICATION

Column 1, line 50, change "Pearse" to - - Pearce - -

Column 2, line 46, correct the spelling of "flaking"

Column 3, line 22, change "3,962,388" to - - 2,962,388 -

Column 8, line 24, change "706" to - - 705 - -

line 43, change "cm^2" to - - cm^3 - -

Column 10,

line 68, change "$TiCl/CH_4$" to - -

$TiCl_4/CH_4$ - -

Column 11, line 1, change "for" to - - of - -

between lines 30-50, with reference to compound "VCl_4" in the Method of Metering Column, change

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,721,577 Dated March 20, 1973

PAGE 2

Inventor(s) PAUL F. WOERNER

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

the expression "Liquid between -24° - -164°C" to

- - Liquid between -24°C and +164°C - -

IN THE CLAIMS

Column 14, line 15, correct the spelling of "silicon"

Signed and sealed this 20th day of November 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

RENE D. TEGTMEYER
Acting Commissioner of Patents