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[54] **CHEMICAL VAPOR DEPOSITION COATINGS ON TITANIUM**

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Related U.S. Application Data

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

[58] **Field of Search** ... 117/106 C, 106 R, 69, 71 M, 117/DIG. 10, DIG. 12; 148/6.3, 31.5; 29/195 A, 198

[56] **References Cited**

UNITED STATES PATENTS

2,836,514	5/1958	Munster et al.	117/106 R
2,715,576	8/1955	Payson	75/124
3,178,308	4/1955	Oxler et al.	117/107
3,356,618	12/1967	Rich	117/106
3,029,162	4/1962	Samuel et al.	148/6.3
3,054,694	9/1962	Aves, Jr.	29/195 X
3,437,511	4/1969	Hough	117/69

FOREIGN PATENTS OR APPLICATIONS

95,792	12/1959	Czechoslovakia	117/106 C
753,297	7/1956	Great Britain	148/6.3

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[57] **ABSTRACT**

A process for coating titanium-containing substrates with a dense, adherent, chemically vapor deposited coating by initially effecting a protective, adhesion-promoting, intermediate layer of the titanium surface and subsequently depositing from the vapor phase a metal nitride, carbide, or carbonitride coating on the intermediate film. For example, a titanium article may be initially nitrided to provide a titanium nitride protective layer and titanium nitride, titanium carbide, or titanium carbonitride may subsequently be deposited from the vapor phase onto this film to provide a dense, adherent, protective coating on the titanium article. The barrier layer serves to promote adhesion between the titanium substrate and the final overlay and to prevent reaction between the substrate and such a reaction ingredient as titanium tetrachloride, which is a preferred constituent for supplying titanium in the titanium carbide, nitride, or carbonitride final coating.

4 Claims, No Drawings

CHEMICAL VAPOR DEPOSITION COATINGS ON TITANIUM

This application is a division of application Ser. No. 821,506, filed May 2, 1969, now U.S. Pat. No. 3,656,995 issued Apr. 18, 1972.

This invention relates to an improved chemical vapor plating process for depositing dense, adherent coatings on titanium-containing substrates. More particularly, the invention relates to the deposition of dense, adherent, and oxidation-resistant metal carbides, nitrides, and carbonitrides on titanium articles by initially providing a protective barrier layer on the article and subsequently chemically vapor depositing these materials from selected organic compounds under carefully controlled conditions to yield superior coatings than were heretofore attainable in the art.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The term "vapor plating" as used in the art commonly includes both physical and chemical vapor plating processes. Physical vapor plating means include such processes as evaporation of metals and vacuum metallizing. The terminology "chemical vapor plating," as used throughout the instant specification and claims, is intended to exclude physical vapor plating as above defined; it is intended that this term include deposition of a selected coating by chemical reaction of a thermally activated chemical vapor plating material in a vaporized state at or near a hot titanium surface. Illustrative of chemical vapor plating reactions, as the term is used in this application, are thermal reduction, thermal decomposition, and thermal disproportionation reactions. Thermal reduction reactions include hydrogen or metal reductions of a halide and reactions of halides with a gas containing carbon, nitrogen, boron, silicon, or oxygen compounds. Thermal decomposition and disproportionation processes include decomposition of halides, oxygen-containing compounds, carbonyl compounds, and hydride compounds. A recent survey presenting a broad, unified picture of chemical vapor plating can be found in the publication *Vapor Plating* by C. F. Powell, I. E. Campbell, and G. W. Gonser, John Wiley & Son, Inc., New York, 1955. Numerous other publications describing vapor plating and, in particular, the chemical vapor plating processes of the nature with which the present invention is concerned, are known in the art.

2. Description of the Prior Art

It is known in the art that various substrates can be protected from the effects of oxidation and attrition by the deposition thereon of certain coatings having desired characteristics of hardness, adherence, and oxidation resistance. It is further known that these coatings may be deposited from selected heat decomposable chemical compounds introduced into the reaction system in the vapor phase, the constituents of which are combined in a desired manner to provide the coating needed. For example, it is known that titanium carbide coatings can be produced by a hydrogen-promoted gas phase reaction, such as from a gas mixture containing titanium tetrachloride and a volatile hydrocarbon, according to the equation

$$TiCl_4 + CH_4 \rightarrow TiC + 4HCl.$$

Such a coating, according to prior suggestions, has been produced on filaments for incandescent lamps by heating the filaments to temperatures over 1,400°C and passing thereover a gas mixture containing titanium tetrachloride, hydrocarbon, and hydrogen to form a coating of titanium carbide on the filaments.

In view of the high reaction temperatures necessarily employed in this and similar processes (1,400°C and higher), the materials to be coated, for example, filaments for incandescent lamps, were heretofore limited to high melting elements such as tungsten, molybdenum, or graphite. In addition, the deposited coatings possessed a glass-like brittleness so that they could not be used for tools or machine parts and seldom possessed good cohesion qualities, since they contained elemental carbon in addition to the carbide. As a result, such coatings tended to scale off, even under relatively slight pressure and impacts. As a further result of the very high temperatures at which such coatings were effected, they were frequently characterized by a very coarse grained structure, a consequence which frequently resulted in unfavorable mechanical properties.

In view of the foregoing limitations in the art, the impact of the instant invention on the chemical vapor deposition of selected coatings on chemically sensitive titanium-containing substrates is apparent. Accordingly, an object of this invention is to provide a process for applying an adherent, nonporous, oxidation-resistant metal carbide, nitride, or carbonitride coating on a titanium substrate. Another object of the invention is to provide a process for coating titanium and titanium alloys with an adherent, dense coating of titanium nitride, carbide, or carbonitride by initially providing an adherent, adhesion-promoting, diffused, barrier layer on the titanium or titanium alloy. Still another object of the invention is to provide a new and useful process for effecting a coating containing the above constituents by utilizing conventionally available equipment and readily procurable, as well as cheap, reactants. A still further object of the invention is the provision of a process for coating titanium or titanium alloys with a metal nitride, carbide, or carbonitride by utilizing lower reaction temperatures than were heretofore possible, deposition at these temperatures being made possible by a judicious choice of chemical reactant compounds not heretofore utilized in the art for providing such coatings.

SUMMARY OF THE INVENTION

Accordingly, in a broad aspect of the invention, there is provided a process for coating a titanium-containing substrate with a metal-carbon-nitrogen compound by initially forming a protective barrier layer on the substrate and subsequently contacting the substrate with a gaseous stream containing carbon, nitrogen, hydrogen, and a metal selected from the group boron, silicon, and the transition metals of Groups IVB, VB, and VIB of the Periodic Chart at a temperature sufficient to form the metal-carbon-nitrogen compound by reaction among the carbon, nitrogen, and metal.

The invention is characterized by convenience in that the important protective and adhesive-promoting barrier layer may be formed by a number of techniques known to those skilled in the art. Since titanium is a relatively reactive metal, formation of the protective barrier layer thereon prior to effecting the final coating has been found desirable in order to prevent, or at least

minimize, reaction between the coating constituents and the titanium itself prior to formation of the desired finished overlay, as well as to aid in achieving good adherence between this overlay and the titanium. For example, the protective layer may be formed by such techniques as electrolytic metal plating, epitaxial deposition of suitable constituents, and similar techniques, as well as by application of chemical vapor deposition processes and diffusion techniques such as nitriding. Thus, such elements as boron, aluminum, nickel, chromium, silver, gold, and similar elements, as well as suitable compounds which may be deposited by the above techniques, may be placed on, and in some cases diffused into, the surface of the titanium to protect it from reaction with the coating constituents and to provide an adhesion-promoting interface. It will be recognized that still other suitable elements and compounds known to those skilled in the art may also be utilized to provide a dense, impermeable, intermediate barrier layer on the titanium substrate.

In a preferred aspect of the invention, the protective barrier layer may be formed by exposing the substrate to a nitrogen or ammonia atmosphere at elevated temperatures to form a diffused layer of titanium nitride on the substrate. Such a technique ensures formation of an adherent and dense final coating by forming titanium nitride on and below the surface of the titanium substrate itself, due to the propensity of nitrogen to diffuse through the titanium surface and into at least a portion of the interior thereof. Such a nitriding step can be undertaken at temperatures as low as 400° to 500°C, but is preferably effected at a temperature within the range of from about 750°C to about 1,100°C in a time of at least 1½ to about 2 hours. A more desirable temperature range which has been determined for carrying out the nitriding step is from about 800°C to about 1,000°C, and a most preferred temperature to effect deposition of the intermediate barrier layer is from about 850°C to about 950° C when the nitriding span varies from about ½ to about 2 hours.

It has further been found that the preferred nitriding step of the invention may be advantageously carried out in the presence of hydrogen, particularly at temperatures above 800°C, although the exact mechanism by which the formation of titanium nitride is aided by this expedient is not known. Accordingly, the nitriding operation may be effected in the presence of hydrogen within the temperature ranges noted above to provide a suitable protective, and adherence-promoting interlayer film on the titanium substrate.

As heretofore noted, the invention is characterized by convenient flexibility in that a wide variety of materials may be utilized under proper conditions to yield the necessary reactants for coating a titanium-containing substrate with a dense, protective coating. Accordingly, after the initial barrier layer is formed, carbon may be introduced into the gaseous reactant coating stream as a hydrocarbon, and the desired metallic constituent of the coating may be included therein as a metal halide, under conditions where the gaseous stream contains hydrogen as a reducing agent and carrier gas, along with nitrogen, which also functions as a reactant constituent. It will be appreciated that the hydrogen and nitrogen may be together introduced into the reactant stream in the form of one or more heat decomposable compounds such as ammonia. Other suitable compounds for supplying one or more reactants to the deposition zone will be hereinafter discussed in various embodiments of the invention.

Accordingly, in a preferred aspect of the invention, a protective barrier layer may be formed by exposing a titanium-containing substrate having a preselected configuration to a nitrogen atmosphere at a temperature within the range of from about 800°C to about 1,000°C for about ½ to 1½ hours. Next, a gaseous reactant stream containing hydrogen, nitrogen, and carbon in the form of at least one hydrogen, and a halide of a metal of the heretoforenoted group may be charged into a suitable reactor, under appropriate temperature and reaction conditions, to form the desired metal-carbon-nitrogen compound. Under these reaction conditions, it is particularly desirable that the hydrocarbon introduced be natural gas and the metal halide titanium tetrachloride, although it will be appreciated that other hydrocarbons and metal chlorides known to those skilled in the art may be utilized with good results in the invention.

It will be appreciated that adherence between the barrier layer and substrate and, therefore, between the final coating and substrate, will be increased by suitably cleaning the substrate before applying the coating or barrier layer. For example, degreasing with known cleaning agents such as methyl-ethyl-ketone or chlorinated solvents such as trichloroethylene and carbon tetrachloride, can be utilized, along with, or independently of, a suitable etching procedure. It is preferred to use a 30 percent HNO_3 — 3 percent HF etch in combination with degreasing to ensure that TiO_2 is thoroughly cleaned from the titanium substrate. It will be recognized that other degreasing agents and etching constituents known to the skilled artisan may be utilized in the invention, although the above-noted methyl-ethyl-ketone and HF-HNO_3 cleaning combination is preferred. For example, other chlorinated solvents known to the skilled artisan can be used to degrease the titanium substrate, and such etching agents as hot caustic, exemplified by sodium hydroxide, potassium hydroxide, and/or ammonium hydroxide, can easily serve to further prepare the substrate surface.

Adherence between the final coating and substrate can be further improved by introducing hydrogen and a heat decomposable titanium compound into the nitrogen atmosphere initially present when the barrier layer selected for application is titanium nitride. This technique ensures the formation of a titanium nitride barrier layer of sufficient thickness to provide adequate protection against chemical attack of the titanium substrate, and to form a good bonding agent for the final coating.

Accordingly, when utilizing the gaseous reactants heretofore pointed out, the invention provides a process for coating a titanium-containing substrate with a solid solution layer of titanium carbonitride by initially cleaning the substrate, effecting a barrier layer thereon by exposing the substrate to a nitrogen and hydrogen atmosphere at temperatures ranging from about 850°C to about 950°C and thereafter introducing titanium tetrachloride into the nitrogen and hydrogen atmosphere for a period of time from about ½ hour to 1 hour to form a titanium nitride diffused layer thereon. Subsequent deposition of the titanium carbonitride is completed by contacting the substrate with a gaseous stream containing additional quantities of titanium tet-

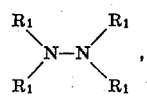
rachloride, natural gas, hydrogen, and nitrogen at a temperature within the range of from about 750°C to about 1,200°C for a time sufficient to form the desired coating on the preformed titanium nitride interlayer. It will be appreciated that in many instances the temperature range in which the final coating step may be effected will correspond to that in which the nitriding may take place. Under such circumstances, it will further be appreciated that the nitriding step may be accomplished and additional reactants necessary for forming the final coating, that is, the carbon-containing compound, metal-containing compound, and hydrogen, may simply be charged into the reactor under appropriate flow conditions. Alternatively, if a temperature adjustment for the final coating operation is necessary, it may be easily accomplished by simply introducing the appropriate reactants and then adjusting the temperature or vice versa.

As heretofore pointed out, particular substrates which may be coated according to the process of this invention may be pure titanium or titanium alloys containing substantially any number of metals other than titanium in substantially any proportion. The process is particularly well suited to coating either pure titanium or titanium alloys containing titanium as a major constituent, that is, 80 percent or greater, utilizing a gaseous stream containing titanium tetrachloride, natural gas, hydrogen, and nitrogen under heretofore-noted reaction conditions.

In an alternative embodiment of this invention, the protective barrier layer may be deposited on a titanium-containing substrate by one of the techniques disclosed above, and the final coating step may subsequently be effected utilizing a gaseous stream containing hydrogen, a metal halide, and a nitrogen-containing hydrocarbon which is heat-decomposable to yield nitrogen and carbon in the proper atomic ratio. Although many such compounds may be utilized, preferred among these are amines, such as ethylene diamine, trimethylamine, and pyridine, as well as hydrazines. Among the hydrazines which may be successfully utilized to provide carbon and nitrogen for deposition of the desired metal carbonitride coating are the following:

Hydrazine and a suitable carbon-containing compound,

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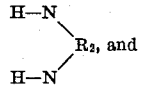
(II)

$$R_1—N=N—R_1,$$

III

$$R_1—N=N—NH—R_1,$$

IV



(V)

$$N=N=R_2,$$

wherein R_1 is selected from hydrogen and cyclic and acyclic hydrocarbon radicals each having from one to about 18 carbon atoms including the amino substitute derivatives thereof, provided at least one R_1 group is one of said hydrocarbon radicals; and wherein R_2 is selected from cyclic and acyclic aliphatic hydrocarbon radicals each having from one to about 18 carbon atoms including the aromatic and amino substituted derivatives thereof. Exemplary of specific hydrazine compounds of the above class are 1,1-dimethylhydrazine and, in combination with natural gas, hydrazine itself.

Preferred metals for incorporation into the metal carbonitride coating deposited utilizing carbon- and nitrogen-containing reactants selected from the above groups are those of the group boron, silicon, and the transition metals of Groups IVB, VB, and VIB of the Periodic Chart. Introduction of a selected metal into the coating is preferably achieved by utilizing a metal halide having the general formula $Me(X)_n$, where X is a halogen and n is a valence of metal Me, selected from the above group.

A most preferred metal of the above group for incorporation into the carbonitride coating is titanium, and a most desirable vehicle for carrying this metal to the reaction zone is titanium tetrachloride.

It will be recognized that a carrier gas, such as nitrogen, argon, or the like, may be utilized to transport the carbon- and nitrogen-containing compound to the reaction zone. Furthermore, temperatures ranging from about 400°C to about 1,200°C have been found suitable to effect the desired decomposition reaction. Additionally, where heat decomposable nitrogen- and carbon-containing compounds are utilized in the invention, the protective barrier layer is preferably deposited by exposing the titanium-containing substrate to a nitrogen atmosphere at a temperature within the range of from about 800°C to about 1,000°C during a nitrogen retention time of about ½ to 1½ hours.

Accordingly, in a most preferred aspect of this embodiment of the invention, there is provided a process for coating a titanium-containing substrate which may consist of pure titanium or a titanium alloy by the following procedure: first, exposing the substrate to a nitrogen atmosphere at a temperature within the range of from about 850°C to about 950°C for about ½ to about 1½ hours in order to form a titanium nitride diffused layer thereon; and, secondly, contacting the nitrided substrate with a gaseous stream containing hydrogen, a metal halide such as titanium tetrachloride, and at least one nitrogen-containing hydrocarbon, exemplified by hydrazine and natural gas, 1,1-dimethylhydrazine, ethylene diamine, trimethylamine, and pyridine, under temperature conditions of from about 500°C to about 1,200°C for a time sufficient to form the titanium carbonitride layer on the nitride film.

In another important aspect of the invention, the patentee has found it possible to eliminate the necessity of introducing separate metal and nitrogen-containing compounds into the reaction chamber by judiciously choosing for use in the coating process heat decomposable coating compounds which contain all of the necessary reactant constituents which are incorporated into the desired coating. For example, the carbon, nitrogen, and desired metal necessary for deposition of a metal

carbonitride overlay may be constituents of a vaporous, hydrogen-containing organic compound capable of being decomposed to yield the carbon, nitrogen, and metal in the reactive state. As in preceding embodiments of the invention, a protective barrier layer may be initially formed by convenient techniques heretofore disclosed, but is preferably prepared by exposing the substrate to a nitrogen atmosphere at elevated temperatures to form a film of titanium nitride on the substrate. Although not a necessary feature of this aspect of the invention, it is preferred to disperse the organic compound reactant within a carrier gas, such as nitrogen, hydrogen, and mixtures thereof, for easier charging into the reactor. It will be appreciated that other gases such as argon, xenon, and the like, may also be utilized in this capacity.

The carbon-, metal-, and nitrogen-containing organic compounds useful in this aspect of the invention may be represented by the generic formula $[(R)_2N]_n$ Me, wherein Me is a metal of the group boron, silicon, and the transition metals of Groups IVB, VB, and VIB of the Periodic Chart; *n* is a valence of Me; and R is selected from hydrogen and hydrocarbon radicals each having from about one to about 18 carbon atoms with at least one R group being at least one of the hydrocarbon radicals. Where such a compound is utilized to supply nitrogen, carbon, and the selected metal in the coating reaction, it has generally been found that a temperature range of from about 400°C to about 1,200°C is adequate to effect the desired decomposition or disproportionation reaction. In accordance with heretofore discussed aspects of the invention, either a pure titanium substrate or a titanium alloy may be coated utilizing such a compound, and exemplary compounds having the above formulation which may be utilized in the invention are tetrakis dimethylamino titanium, tetrakis diethylamino titanium, and tetrakis diphenylamino titanium.

It will be appreciated that the particular embodiments disclosed above for producing a metal-carbon-nitrogen coating, and more specifically, a solid solution metal carbonitride coating, may be utilized to produce various articles of manufacture which are highly useful. For example, utilizing a titanium or titanium alloy substrate having a preselected configuration and the technique of this invention, one can initially deposit an adherent, protective barrier layer on the substrate and then a homogeneous solid solution of a metal carbonitride selected from the group silicon, boron, and the transition metals of Groups IVB, VB, and VIB of the Periodic Chart on this barrier layer. A preferred article for manufacturing according to the above process is that wherein the inert barrier layer is titanium nitride and the homogeneous solid solution coating is titanium carbonitride.

Further, within the scope of this invention, is the provision of a process for coating a titanium-containing substrate with a metal nitride by initially forming a protective barrier layer on the substrate as heretofore disclosed, and subsequently contacting this substrate with a gaseous stream containing nitrogen, hydrogen, and a metal of the heretofore-noted group.

It is apparent from this and other embodiments of the invention that the nature of the coating on the titanium substrate may be varied depending upon the particular reactants included in the gaseous reaction stream. In forming the metal nitride coating in the manner disclosed immediately above, the metal is preferably introduced in the form of a metal halide to produce a desired coating. Further, in an additional embodiment of this aspect of the invention, the substrate is preferably cooled by contact with an essentially inert gas after the metal nitride is formed to preclude the possibility of embrittling the coating by a rapid temperature drop in an undesirable atmosphere.

Accordingly, in a preferred embodiment of the invention, a metal nitride coating is formed on a titanium-containing substrate by exposing the substrate to a nitrogen atmosphere to form a diffused film of titanium nitride thereon, and subsequently introducing hydrogen and a halide of a metal of the group above noted into the nitrogen atmosphere at a temperature sufficient to form the metal nitride on the intermediate titanium nitride interlayer. As heretofore described, it is desirable, but not necessary, to cool the heated substrate in an inert gas after the metal nitride is formed. The metal nitride coating may be formed at a temperature of from about 800°C to about 1,200°C and, more preferably, within the range of from about 850°C to about 1,100°C for about ½ to about 2 hours. The metal nitride interlayer may be conveniently formed at temperatures heretofore disclosed. Under these reaction conditions, the metal halide to be used is most preferably titanium tetrachloride.

In a most preferred embodiment of the metal nitride application, the substrate, which may be pure titanium or a titanium alloy, is initially exposed to a nitrogen atmosphere at a temperature within the range of from about 850°C to about 950°C for about ½ to about 1 hour to form a thin, diffused titanium nitride film on the substrate. Hydrogen may then be introduced, along with titanium tetrachloride, into the nitrogen atmosphere, and the temperature should thereafter be maintained at the above-noted level for a time interval of from about ½ to about 1 hour to effect a titanium nitride coating on the initial titanium nitride interlayer. Again, it is desirable to cool the coating in an inert gas environment, preferably nitrogen, after the final nitride coating has been deposited.

It will be appreciated that the titanium nitride deposition embodiment of the inventive process is suitable for producing articles of manufacture comprising titanium-containing substrates having a preselected configuration with an essentially chemically inert barrier layer film thereon and having a homogeneous metal nitride of the group above pointed out securely deposited on this barrier layer. More specifically, both the inner layer and the final coating are preferably titanium nitride, the inner layer serving to form a better bond between the final titanium nitride coating and the original titanium-containing substrate, which, as previously disclosed, may be either pure titanium or a titanium alloy.

In addition to the embodiments whereby titanium nitride and titanium carbonitride, as well as other metal nitrides and metal carbonitrides, may be deposited on a titanium substrate, the invention further encompasses the expedient whereby a titanium-containing substrate may be coated with a metal carbide. Such a coating may be deposited by, first, forming a protective barrier layer in the manner heretofore described, and subsequently contacting the substrate with a gaseous stream containing carbon, hydrogen, and a metal of the above-noted group. As in previously discussed aspects of the

invention, the metal is preferably introduced in the form of a metal halide; the carbon in the form of a hydrocarbon or mixtures thereof, such as natural gas; and the titanium substrate having a titanium carbide coating thereon is preferably cooled by contact with an inert gas, such as nitrogen, after the carbide coating is formed. Thus, the barrier layer may be applied by exposing the substrate to a nitrogen atmosphere at elevated temperatures, the nitrogen may then be purged from the reactant chamber, and the substrate finally contacted with hydrogen, a carbon-containing compound, and a metal of the previously noted group in order to deposit the desired carbide coating. Further, temperatures on the order of from 750° to 1,100°C are suitable for both interlayer formation and the contacting of the substrate with the coating compound, and the carbon-containing compound utilized may be natural gas, while the metal is preferably introduced in the form of a metal halide.

In a most preferred feature of applying a metal carbide coating to a titanium-containing substrate, titanium carbide is placed on the substrate by initially exposing the substrate to a nitrogen atmosphere at a temperature within the range of from about 800°C to about 1,000°C for about ½ to about 1½ hours to form a diffused layer of titanium nitride on the substrate; removing the nitrogen from contact with the substrate; and subsequently contacting the substrate with a gaseous stream containing hydrogen, natural gas, and titanium tetrachloride at a temperature within the range of from about 800°C to about 1,000°C for about one-half hour to form a titanium carbide layer on the titanium nitride film. As in previous embodiments of the invention, the titanium carbide layer may be placed on an essentially pure titanium substrate or a titanium alloy, and the substrate is preferably cooled in an essentially pure nitrogen environment after the metal carbide is formed.

It will be appreciated that the titanium carbide phase of the inventive process can be utilized to produce an article of manufacture consisting of a titanium-containing substrate (either pure titanium or a titanium alloy) having an essentially inert barrier layer, for example, a diffused layer of metal nitride, thereon (preferably titanium nitride) and a metal carbide layer on this metal nitride inner layer. The deposited metal carbide layer is preferably titanium carbide.

The disclosed embodiments of the invention may be more particularly illustrated by reference to the following examples:

EXAMPLE I

Ten samples of titanium-aluminum-vanadium alloy coupons (6 percent aluminum, 4 percent vanadium) were placed in a chemical vapor deposition reactor, which was closed and purged of air by means of a nitrogen flow. The temperature in the apparatus was raised to about 900°C and the nitrogen flow was adjusted to a rate of about 115 liters per minute for about 2 hours. Hydrogen was then metered into the reactor at a rate of about 150 liters per minute, along with natural gas in an amount equal to about 17 liters per minute. About 3 seconds after the hydrogen and natural gas were introduced into the reactor, titanium tetrachloride was metered into a vaporizer and subsequently into the apparatus at a rate of about 2.5 millileters per minute. The reactor temperature was held at 900°C for approximately 2 hours. After the elapse of this coating period, a hydrogen and nitrogen purge was metered into the apparatus, the hydrogen flow rate being about 150 liters per minute, and the nitrogen about 57 liters per minute. This purge was effected for approximately 30 minutes, after which time about 115 liters per minute of substantially pure nitrogen was introduced into the reactor for an additional 30 minutes. During this period of time, the reactor was allowed to cool and, upon reaching room temperature, the samples were removed. All of the coupons were evenly coated with titanium carbonitride, with no imperfections noted in the coating.

EXAMPLE II

Two aluminum-vanadium-titanium alloy samples of the type used in Example I were degreased with methyl-ethyl-ketone and etched for 2 to 5 minutes in a solution of 30 percent nitric acid and 3 percent hydrochloric acid at room temperature. The samples were then rinsed in cold, deionized water, flushed with hot, deionized water for about 2 minutes, and then air dried. The samples were next loaded into the chemical vapor deposition reactor, which was purged with nitrogen and heated to about 850°C under a 57 liters per minute nitrogen flow. One hundred fifty liters per minute of hydrogen were next metered into the reactor, and the samples were held at about 850°C under the flowing hydrogen and nitrogen for 5 to 10 minutes. 0.62 millileters per minute of liquid titanium tetrachloride were then metered into the vaporizer, introduced into the reactor, and allowed to flow therein for about 1 hour. The reactor temperature was maintained at 850°C and, under these conditions, a coating of titanium nitride formed on the substrate samples. Natural gas was then allowed to flow into the reactor at a rate of about 17 liters per minute, the titanium tetrachloride flow was adjusted to about 2¼ millileters per minute, and the temperature of the reactor was slowly increased to about 900°C as the titanium carbonitride coating formed. The samples were coated under the above conditions for two hours, after which the titanium tetrachloride and natural gas flows were terminated, and the samples were held for 10 minutes under a hydrogen and nitrogen purge and for a final 20 minutes under an essentially pure nitrogen flow. The reactor was then allowed to cool to about 750°C in nitrogen, after which about 300 liters per minute of helium was introduced into the reactor and the nitrogen turned off. Under these conditions, the samples were cooled to room temperature and the reactor was unloaded.

The titanium alloy samples were noted to be coated with titanium carbonitride, the coating having a shiny and smooth appearance. One sample was placed in a vise and bent until the parts separated. The coating cracked on the side in tension and spalled on the side in compression, and the area of the sample where the spalling occurred was observed to be dark in color. No apparent wear was observed after the samples were subjected to 300 seconds on a jet abrader. The substrate structure appeared to be in fair condition after an acid etch test was run. It was concluded that this coating represented a great improvement over previous coatings.

EXAMPLE III

The procedure of Example II was substantially repeated with the following modifications: after the hy-

drogen was initially charged to the reactor, it was allowed to continually flow therein along with the previously charged nitrogen for about 30 minutes before the titanium tetrachloride was metered to the reactor.

After the completion of the run, the tests noted heretofore in Example II were run on the samples, and it was found that the coating and protective barrier layer appeared to be characterized by exceptionally good adherence to the titanium alloy substrate. The coating quality was considered to be slightly better than that realized from the Example II reaction conditions.

EXAMPLE IV

The procedure of Example II was substantially repeated with the modification of depositing the titanium carbonitride coating at 880°C instead of 900°C.

Identical tests to those noted in Example II were run on the samples, and the results of these tests indicated that a titanium carbonitride coating of high quality formed on the titanium alloy, the coating being superior to all others heretofore deposited.

EXAMPLE V

A sample of substantially pure titanium in the form of a pump disc and a sample of titanium-aluminum-vanadium alloy having essentially the same compositions as those used in Examples I–IV were degreased in hot trichloroethylene vapor and loaded into a suitable chemical vapor deposition reactor. The apparatus was purged with nitrogen and heated to a temperature of 1,000°–1,050°C in the nitrogen atmosphere for about 30 minutes. The nitrogen flow rate was then adjusted to about 100 liters per minute and 67 liters per minute of hydrogen saturated with titanium tetrachloride at 30°C was metered into the reactor. The total hydrogen flow was then adjusted to 100 liters per minute, the nitrogen to the same flow rate, and the samples were coated with titanium nitride for two hours at about 1,000°–1,050°C. After the 2 hour coating period elapsed, the reactor was purged for 15 minutes with hydrogen and nitrogen at a flow rate of 100 liters per minute, respectively, after which the hydrogen was shut off and the reactor purged for an additional 20 minutes with 50 liters per minute of argon. The argon flow was then cut off and the reactor cooled under a 50 liters per minute flow of nitrogen.

The samples were unloaded and observed to be bronze in color. There were no signs of cracking or spalling on either sample, and the coatings appeared to be continuous and smooth.

EXAMPLE VI

The procedure of Example V was substantially repeated with the modification of saturating (at 30°C) 13.8 liters per minute of the initial hydrogen flow into the reactor with chlorobenzene. Additionally, the nitrogen was introduced into the reactor through a separate line from that used for charging the hydrogen, titanium tetrachloride, and chlorobenzene.

Both samples were observed to be smoothly and uniformly coated with a dark, blue-grey film of titanium carbonitride.

EXAMPLE VII

Suitable samples of titanium and titanium alloy are cleaned by application of methyl-ethyl-ketone and a nitric-hydrochloric acid etch, dried, and placed in a chemical vapor deposition reactor. The samples are heated in nitrogen to about 900°C for about 1 hour, and the nitrogen is then purged from the reactor by introduction of a hydrogen flow. After the purge is completed, titanium tetrachloride is metered into the reactor, and thereafter natural gas is introduced at a flow of about 17 liters per minute. The samples are coated with titanium carbide for about 4 hours, during which time the reactor temperature is maintained at about 900°C. After the 4 hour coating period has elapsed, the reactor is initially purged for about 10 minutes with hydrogen and subsequently purged for an additional 10 minutes with nitrogen. The reactor is then allowed to cool in a nitrogen or inert gas atmosphere. The samples are uniformly coated with an adherent film of titanium carbide.

It will be appreciated, from a consideration of the Examples and embodiments of the invention heretofore disclosed, that the concept of this invention is quite broad in scope. A key feature of the invention lies in the selective deposition of an interlayer film which serves a dual purpose — to provide a good bonding base for the final overlay film and to protect chemically sensitive titanium-containing substrates from attack by certain reactants utilized to effect the final coating. Thus, where it is desired to coat an alloy containing a relatively small percentage of titanium, the benefit provided by application of the protective barrier layer is primarily one of furnishing an adherent base to which the final coating may securely bond. On the other hand, where the substrate to be coated is essentially pure titanium or an alloy containing a high percentage of titanium, the dual function of the barrier interlayer becomes most apparent.

Since the protective barrier layer plays such an important role in the invention, it is significant that it can be deposited by many different techniques, as heretofore noted. Furthermore, various embodiments of the invention, as heretofore set forth, can be utilized in various combinations to provide the interlayer and final coating. For example, in addition to the nitriding procedure set forth as a preferred technique for depositing the protective barrier film, the procedure of Example VI can be utilized to place a protective titanium carbide film on the substrate. This procedure can be used with or without the initial nitriding step, depending upon whether or not the sample to be coated contains a relatively high percentage of titanium. Thus, referring to Example IV, after the samples are coated with titanium carbide to a suitable thickness, nitrogen can be introduced into the reaction zone in the proper amount to effect deposition of a titanium carbonitride coating on the titanium carbide intermediate film. Accordingly, if an initial nitriding or alternative metal deposition step were effected to deposit an initial protective barrier layer, the titanium-containing substrate would have deposited thereon three layers of dense, adherent material, thereby affording the desired degree of protection to the substrate.

Flexibility in the invention allows the deposition of graded coatings tailored to the physical characteristics of the substrate, such as, for example, thermal expansion coefficients, a feature which becomes quite significant should the substrate and applied coating be subjected to thermal or physical stresses.

It will further be recognized that the cooling phase of the invention is important to the production of dense,

adherent coatings, although the exact reason for this phenomenon is not known. In general, it has been found that rapid cooling in an inert gas atmosphere is effective, and particularly, in an atmosphere of argon, helium, nitrogen, or mixtures of these gases.

It will further be appreciated that the process of this invention can be conveniently carried out at atmospheric pressure, although either vacuum conditions or pressures greater than atmospheric can be utilized under circumstances where it is convenient to do so.

Further, it should be noted that the reaction vessel can be designed so as to provide a preheat of all or some of the reaction constituents in order to increase the deposition rate. Alternatively, this preheating can be effected outside of the deposition apparatus.

What is claimed is:

1. An article comprising:

a. a substrate selected from titanium and titanium alloys wherein titanium is the principal constituent having a preselected configuration;

b. a barrier layer selected from aluminum-, nickel-, chromium-, silver-, and gold-comprising layers uniformly covering said substrate; and

c. a homogeneous carbide of a metal selected from the Group boron, silicon, and the transition metals of Groups IVB, VB, VIB of the Periodic Chart, formed on said barrier layer.

2. The article of claim **1,** wherein said titanium-containing substrate is essentially pure titanium.

3. The article of claim **1,** wherein said titanium-containing substrate is a titanium alloy.

4. The article of claim **1,** wherein said homogeneous carbide of a metal is titanium carbide.

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