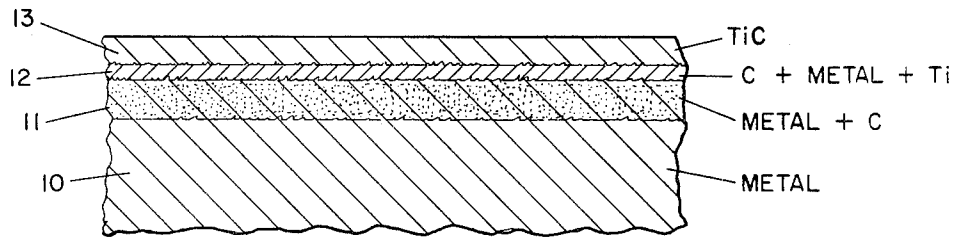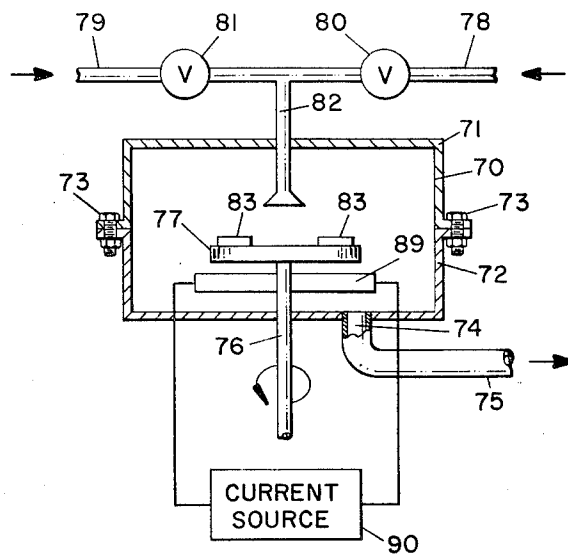FIG. 2

FIG. 1

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3,684,585
METHOD FOR FORMING ADHERENT TITANIUM
CARBIDE COATINGS ON METAL OR COMPOS-
ITE SUBSTRATES
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ABSTRACT OF THE DISCLOSURE

Disclosed is a method for forming adherent coatings
of titanium carbide on metal or composite substrates
which includes the steps of carburizing the surface of the
substrate and reacting a titanium halide with a volatile
hydrocarbon to form an interlayer comprising a mixture
of Ti and C in the material of the substrate, and thereafter
depositing a coating of TiC on the interlayer by chemical
vapor deposition.

This invention relates to the formation of titanium
carbide coatings on metal and composite substrates. More
particularly it relates to the formation of titanium carbide
by the reaction of a titanium halide with a hydrocarbon
gas at elevated temperatures to form a dense, adherent
coating of titanium carbide on metal and composite sub-
strates, and more particularly to methods of treating such
substrates prior to the deposition of titanium carbide
thereon for the formation of a tenacious bond between
the substrate material and the titanium carbide coating.

Formation of titanium carbide by the vapor phase reac-
tion of a titanium halide and a volatile hydrocarbon is
well known. Since titanium carbide has a low coefficient
of friction and a hardness approximately equivalent to one-
half of that of diamond, it is highly desirable to form
titanium carbides on tools, machine parts, wear surfaces
and the like which are subject to excessive wear and
abrasion, thereby substantially lengthening and improving
their serviceable life. However, while the reactions in-
volved in vapor phase reaction of titanium halides and
volatile hydrocarbons are well known, prior attempts to
form titanium carbides on tool steels and the like have
met with very limited success. Since the reaction tempera-
tures required for the vapor phase formation of titanium
carbide are quite high, extreme difficulty is encountered
in forming an adherent coating on a material which has a
coefficient of thermal expansion largely different from the
coefficient of thermal expansion of titanium carbide. Fur-
thermore, serious heat treatment problems can arise
through the heating of certain tool steels to the tempera-
ture required for the reaction under conventional
methods.

Prior workers in the field have encountered serious
problems, such as spalling of the coating, granulation of
the deposit, and extremely low deposition rates. Also,
using conventional methods of deposition of titanium
carbide, uniform, continuous titanium carbide coatings
could not be deposited on certain materials.

In accordance with the method of this invention ex-
tremely hard, dense, impermeable coatings of titanium
carbide may be formed on practically any steel surface
and composite surfaces such as sintered tungsten carbide
in cobalt or the like. Firmly adherent, dense, impermeable
coatings of titanium carbide may be formed on these sur-
faces by the reaction process described hereinafter if the
surface of the substrate is first carburized sufficiently to
form a layer of carbon-rich material at the surface. Due
to the prior carburization of the surface of the substrate

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sufficient reactive carbon is present at the carbide-forming
surface to promote the formation of an integrally bonded
titanium carbide coating. In the process described herein
an interlayer containing carbon, the material of the sub-
strate, titanium and/or titanium carbide is formed adja-
cent the surface of the substrate being coated. Titanium
halides in the gas phase react with the more active carbon
the carburized surface in a gas-solid reaction to form
titanium and titanium carbide in the carburized surface
forming an interlayer on which titanium carbide is de-
posited and firmly adheres. Through the carburization of
the surface and formation of the interlayer prior to depo-
sition of the titanium carbide coating, an integrally bonded
dense, impermeable bulk coating of titanium carbide is
uniformly deposited on the surface of the substrate at
rates up to as high as 0.001 inch per hour at temperatures
as low as 950 C. The process of this invention, therefore,
may be advantageously utilized to deposit dense, imper-
meable, firmly adherent coatings of titanium carbide on
most steels and other materials such as cemented carbides
and the like to produce wear surfaces and machine tools
having extremely hard, non-galling surfaces, thereby sub-
stantially lengthening and improving their serviceable life.
Other features and advantages of the invention will be-
come more readily understoood from the following de-
tailed description taken in connection with the appended
claims and attached drawings in which:

FIG. 1 is a schematic drawing of a process system for
producing titanium carbide coatings on substrates in ac-
cordance with the present invention; and

FIG. 2 is a diagrammatic illustration of a sectional
view of a portion of a substrate coated with titanium
carbide in accordance with the process of this invention.

While the empirical reaction for the vapor phase re-
action of a titanium halide and a hydrocarbon is well
known, previous attempts to produce dense, impermeable,
adherent coatings of titanium carbide on metal substrates
have generally failed. It is believed that prior failures to
produce the desired titanium carbide deposits are the
result of failure to understand the kinetics and thermo-
dynamics of the intermediate reactions and interfering
reactions involving the reactants and the constituents of
the base material. For example, it has been reported that
certain carbide-forming materials, such as chromium, are
required in the substrate to promote the reaction of car-
bon and titanium to form titanium carbides.

It has been unexpectedly discovered, however, that the
decomposition of titanium halides in the presence of a
volatile hydrocarbon and hydrogen is substantially in-
fluenced by the presence of carbon in the surface being
coated. Furthermore, the carbon must be in a reactive
or available condition at the surface. Thus some carbide-
forming constituents of ordinary steels, such as chromium,
may actually interfere with the decomposition reactions
by combining with the carbon and rendering it less re-
active with respect to the titanium halides. In order to
promote the titanium halide decomposition reactions car-
bon must be present in the system in a form which is
available to react with the titanium halides.

The rate of deposition of titanium carbide by the gas
phase reaction of titanium halides and a hydrocarbon in
hydrogen will be largely dependent upon the concentra-
tion of reactants at the surface of the substrate and the
activation energies of the individual reactions. The activa-
tion energies will be primarily controlled by the physical
state of the solid surface such as the defect crystalline
structure rather than the surface composition. For ex-
ample, most surfaces on which a chemical reaction is
proceeding contain active sites on which the reaction has
a low activation energy as compared to other sites in the
surface. These active sites are often associated with crys-

talline defects such as the exposed edge at the surface between two crystal planes or at a dislocation. The reaction proceeds preferentialy at these active sites, depositing a second solid phase which grows from these sites. High concentrations of reactive carbon are made available at or near the surface of the substrate by carburizing the surface prior to deposition of titanium carbide thereon, thereby producing a surface enriched in reactive carbon which promotes the gas-solid reaction and the formation of TiC by reacting titanium from the gas phase with carbon in the solid phase.

The preferred process for carburizing the substrate surface prior to deposition of the titanium carbide coating thereon and the process for forming titanium carbide is described hereinafter with reference to FIG. 1. The apparatus includes a sealable deposition chamber 70 comprised of an upper portion 71 and a lower portion 72. The upper and lower portions are removeably secured together by conventional means such as bolts 73, clamps or the like. Chamber 70 has an exhaust port 74 connected to an exhaust line 75 which is in turn connected to a conventional vacuum pump or the like for removing gases from the deposition chamber. A rotatable table 77 is mounted on a shaft 76 which passes transversely through the bottom of the deposition chamber 70 and is adapted for rotation by conventional means. Rotatable table 77 is preferably constructed of a relatively inert material such as graphite or the like while the deposition chamber may be constructed of steel or any other suitable material.

A radiant heater 89 is secured below rotatable table 77 and interconnected with a suitable power source 90 for heating the material in the deposition chamber. Reactants are injected into the reaction chamber through lines 78 and 79 by way of control valves 80 and 81, respectively, and injected into the deposition chamber by way of nozzle 82. Nozzle 82 projects into the upper portion of the deposition chamber and directs the reactants toward the surface of the rotatable table 77.

The substrate workpieces 83 to be coated are positioned on rotatable table 77 as illustrated in FIG. 1. Alternatively, workpieces 83 may be supported on suitable racks, hangers or the like within the deposition chamber.

The deposition chamber is closed and sealed, evacuated and refilled with purified hydrogen through inlet 79, valve 81 and nozzle 82. When the chamber 70 is filled with dry hydrogen exhaust port 74 is opened and hydrogen allowed to flow through the chamber 70 at a rate of about 25 to about 50 liters per minute.

With hydrogen flowing through the chamber 70 at essentially atmospheric pressure heater 89 is activated by passing current therethrough from current source 90. The workpiece 83 is heated to a temperature between about 900° and 1200° C. in the flowing hydrogen and maintained at this temperature for about 15 to about 30 minutes to assure complete cleaning and outgasing of the workpieces. Throughout the cleaning and following deposition process, rotatable table 77 is rotated at a rate of about 1 to about 15 r.p.m. and is uniformly heated by radiant energy from the heater 89. All workpieces 83 are therefore maintained at a relatively constant temperature.

After the workpieces have been thoroughly cleaned as described above, a mixture of a volatile hydrocarbon and hydrogen is introduced into the chamber to carburize the surface of the workpieces 83. In the preferred practice of the invention the ratio of hydrocarbon to hydrogen is about 0.01:1 carbon to hydrogen (1 carbon atom per 100 H_2 molecules). The hydrocarbon is cracked or decomposed at the heated workpiece surface depositing pure carbon thereon. The carbon deposited on the workpiece diffuses into the surface, thereby carburizing the workpiece surface. The above condition is maintained for about 5 to about 45 minutes whereby a carburized

layer is formed adjacent the surface of the workpiece which is approximately 0.005 inch thick, depending on the rate of diffusion of the carbon into the material of the workpiece and the temperature of the workpiece.

It will be readily understood that various volatile hydrocarbons may be used in the carburization process described. It has been found convenient, however, to use a mixture of hydrogen and monochlorobenzene for the carburization step. This gas mixture may be used as hydrocarbon source in the subsequent deposition process by simply adjusting the monochlorobenzene concentration and the hydrogen flow rate.

After the carburization step is completed a reactant gas containing hydrogen and monochlorobenzene is introduced into the chamber 70 through line 79, valve 81 and nozzle 82. Simultaneously with the introduction of hydrogen and monochlorobenzene gas, a mixture of hydrogen and titanium tetrachloride ($TiCl_4$) is introduced through line 78, valve 80 and into nozzle 82.

In the preferred practice of the invention, the composition of reactant gas entering the deposition chamber 70 through nozzle 82 is approximately 0.75 to about 1.5 mole percent $TiCl_4$, 0.125 to about 0.25 mole percent monochlorobenzene, and the remainder hydrogen.

It will be understood that within the gas composition ranges given it is preferred to introduce sufficient hydrocarbon to maintain at least a stoichiometric ratio of carbon to titanium in the reactant gas stream. Therefore it will be apparent that the mole ratio of C_6H_5Cl to $TiCl_4$ should be at least 1:6 under these preferred conditions. Throughout the deposition process the temperature of the workpiece 83 is maintained at a temperature between about 900° C. and about 1200° C. Under these conditions a uniform, dense coating of titanium carbide is formed on the workpiece surface at a rate of about 0.0001 to about 0.001 inch per hour.

It has been observed, however, that the titanium carbide coating does not bond directly to the surface of the substrate but, instead, is bonded thereto through an intermediate layer or interlayer as illustrated diagrammatically in FIG. 2. It is believed that the formation of the interlayer as described hereinafter is the result of carburization of the metal substrate surface prior to the deposition reaction and contains material of the substrate, carbon from the carburization process, and titanium from the titanium halide gas. It is further believed that the titanium carbide-forming reaction takes place, not in the gas phase, but with free carbon atoms or reactive carbides in the interlayer which act as active sites for the formation of titanium carbide.

Carburization of the surface prior to the deposition of titanium carbide thereon results in the formation of an interlayer which affects the concentration of chemical reactants at the surface. For example, carbon can form carbides with iron and cobalt substrates, and at high temperatures, is soluble and diffused into the substrate. The chemical potential of carbon at the surface changes as a result of diffusion thereof into the body of the substrate, dissolution thereof into the metal from the gas phase carbon source, and reaction with a titanium halide to form titanium carbide. The carbon potential at the surface of the substrate therefore is increased by dissolution of carbon into the metal from the gas phase carbon source. Conversely, the carbon potential is decreased by diffusion of the carbon into the body of the substrate or reaction of carbon with a titanium halide to form a titanium carbide. Accordingly, if the carbon potential is initially near zero, then the rate of reaction of carbon with the titanium halide will likewise be near zero. Any titanium carbide formed would be by direct reaction between the gas phase carbon source and the titanium halide at the surface. Such a direct reaction, however, must compete with the dissolution rate of carbon into the metal from the gas phase carbon source. The presence of carbon-free metal at the surface therefore will inhibit

the direct reaction. Also, since the substrate surface does not participate in the direct reaction, a chemical bond between the resulting titanium carbide and the substrate surface would not be expected.

By carburizing the surface prior to the deposition reaction, in accordance with the principles of this invention, reaction conditions on the surface are vastly changed. With an abundance of free carbon or reactive carbides at the reaction surface the rate of reaction of carbon with titanium halide to form a titanium carbide is greatly increased due to the increased carbon potential. Accordingly, the rate of titanium carbide deposition during the initial coating period will be greatly increased. Furthermore, since the substrate surface participates in this reaction, a strong chemical bond is achieved between the coating and the surface. It is further believed that the initial reaction actually forms a ternary system, Ti-C-M, where M represents the metal substrate. This ternary system forms as an interlayer between the surface of the metal and the titanium carbide coating and acts as a source of active carbon sites for the formation of TiC.

It will be observed that where the substrate is a steel the ternary system will be Ti-C-Fe and will consist primarily of a two phase mixture of α iron and $(Ti,Fe)_3C$. In this system the carbide, M_3C, is essentially Fe_3C in which titanium has been partially substituted for iron in the lattice. Therefore the interlayer provides a surface upon which titanium carbide may be formed and to which the titanium carbide is chemically bonded.

It should be observed that similar conditions will exist where the substrate is a cemented carbide such as tungsten carbide in cobalt.

While the reaction of titanium halides and volatile hydrocarbons in hydrogen is known to produce titanium carbide, the intermediate reactions are not fully understood. It is known, however, that the following reactions occur readily at 1000°: [1] $H_2 + TiCl_4 \rightarrow 2TiCl_3 + 2HCl$ [2] $2TiCl_3 \rightarrow TiCl_2 + TiCl_4$.

It is known that $TiCl_2$ disproportionates to Ti and $TiCl_4$. Where the reaction gas is introduced in the form of $TiCl_4$, such disproportionation will be inhibited. The following reaction [3], however, is thermodynamically favored. [3] $2TiCl_2 + C$ [solid solution] $\rightarrow TiC + TiCl_4$ [gas].

The equilibrium constant for reaction [3] is

$$K = \frac{P_{TiCl_4}}{A_c}$$

when A_c is the carbon potential. At 1200° K., for example, $K = 2.7 \times 10^4$. Since this reaction would be favored even at extremely low carbon potentials, a somewhat linear relation between intial reaction rate and carbon concentration would be expected and, in fact, is observed. Consequently the initial rate of reaction and formation of titanium carbide is largely governed by the concentration and potential of carbon at the substrate surface prior to the deposition reaction. Upon injecting the titanium halide and hydrocarbon into the system, the interlayer is formed upon which the titanium carbide readily forms by virtue of the reaction of $TiCl_2$ with the carbon in the substrate surface. The interlayer, therefore, not only provides means for promoting the reaction between $TiCl_2$ and carbon to initiate and promote the reaction and formation of titanium carbide, but also provides an intermediate bonding agent chemically attaching the titanium carbide coating to the substrate surface.

The thickness and composition of the interlayer is, of course, determined by the composition of the substrate materials and the degree of carburization prior to the formation of titanium carbide thereon. Furthermore, the separate regions in the finished product, as illustrated in FIG. 2, do not show distinct boundaries. For example, the substrate material, illustrated at 10 in FIG. 2, is first carburized at the surface to form a carbon-rich layer 11. Since the carbon is diffused and dissolved in the sur-

face of the substrate, the transition from the virgin metal to the carburized surface is not clear and distinct, but is a gradual transition. Likewise, the formation of the ternary interlayer 12, which is formed by both titanium from the gas phase and metal and carbon from the solid phase, is merely a change in the composition of the surface of the original substrate and the transition from region 11 to region 12 is likewise not clear and distinct.

As titanium precipitates from the vapor phase reaction and enters the interlayer 12, a titanium carbide layer 13 forms on the surface of the interlayer. Since the transition from the interlayer of pure titanium carbide is gradual, the precise transition point is difficult to establish. It should be noted, however, that upon inspection of a section of a substrate coated as described herein, each of the layers 11, 12 and 13 are clearly observed. Furthermore, while the exact point of transition from one layer to the other is not easily determined, it should be noted that the surface of layer 13 is a reproduction of the original surface of the metal substrate. Therefore if the metal substrate was originally a smooth polished surface, the surface of the titanium carbide layer 13 formed as described herein will also be a smooth polished surface.

In the following examples, identical steel specimens were subjected to identical reaction conditions except for the carburization step.

EXAMPLE I

A specimen of 4130 steel was cleaned and placed in deposition apparatus such as that described with reference to FIG. 1. The steel specimen was heated at 1050° C. in flowing hydrogen for 30 minutes. A gaseous mixture of monochlorobenzene, titanium tetrachloride and hydrogen having a carbon to titanium ratio of 1:1 was then introduced into the reaction chamber and continuously flowed through the chamber for four hours. Throughout the reaction process the temperature of the substrate was maintained at about 1050° C. A titanium carbide coating about 0.0002 inch thick formed non-uniformly on the steel substrate. No interlayer between the steel surface and the coating was formed.

EXAMPLE II

A second specimen of 4130 steel identical to the one used in Example I was treated similarly and placed in the same apparatus. The steel specimen was heated at 1050° C. in flowing hydrogen for 30 minutes. Immediately thereafter, a mixture of hydrogen and monochlorobenzene wherein the carbon to H_2 ratio was 0.01:1 was passed through the deposition chamber for 35 minutes while maintaining the specimen at 1050° C. to carburize the surface of the steel specimen. Immediately thereafter deposition conditions were established as set forth in Example I and maintained for four hours. A uniform adherent coating of TiC 0.00041 inch was formed on the specimen. Upon sectioning and inspection an intermediate layer was observed between the carburized surface of the specimen and the coating. The coating was bonded to the interlayer which was in turn bonded to the steel surface, the interlayer forming a chemical bond to the TiC and the steel.

Specimens of 410 steel were treated as described in Examples I and II and produced similar results.

Using the process described herein, uniform coatings of TiC have been formed on the full range of carbon steels, such as the 1000 series steels, 410 stainless steel and the 4000 series steels. Likewise similar results have been obtained on selected chromium, molybdenum and nickel containing steels. The process has also been found to be effective for forming TiC coating on cemented tungsten carbide and cemented tungsten and titanium carbides in cobalt, and other materials such as powder metallurgy materials, martensitic stainless steels, age hardening steels, and most tool steels. In all cases the immediate prior carburization of the substrate surface

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causes formation of the described interlayer which promotes formation of uniform adherent coatings of TiC.

While the invention has been described with particular reference to specific embodiments thereof, it is to be understood that the form of the invention shown and described in detail is to be taken as the preferred embodiment of same, and that various changes and modifications may be resorted to without departing from the spirit and scope of the invention as defined by the appended claims.

What is claimed is:

1. The method of forming a dense, continuous adherent coating of titanium carbide on the surface of a metal substrate comprising the steps of:

    (a) carburizing the surface of said substrate by depositing pure carbon thereon in amounts sufficient to form a surface layer enriched in free carbon;

    (b) reacting a titanium halide with a volatile hydrocarbon to form an interlayer at the surface of said substrate, said interlayer comprising titanium, reactive carbon and the metal of the substrate; and

    (c) depositing a coating of titanium carbide on said interlayer by reacting a volatile hydrocarbon and a titanium halide in hydrogen at the surface of said interlayer.

2. The method set forth in claim 1 wherein:

    (a) the surface of said substrate is carburized by

        (i) heating said substrate to a temperature between about 900° C. and about 1200° C. in a hydrogen atmosphere; and

        (ii) decomposing a volatile hydrocarbon at the heated surface of said substrate; and

    (b) said interlayer is formed by reacting a titanium halide with carbon in the surface of said substrate, thereby producing titanium and titanium carbide which is dissolved in the surface of said substrate.

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3. The method set forth in claim 2 wherein said volatile hydrocarbon is a mixture of monochlorozenzene and hydrogen and the composition of said mixture is about one carbon atom per 100 H_2 molecules.

4. An article of manufacture comprising:

    (a) a metal substrate having carbon disposed in a region adjacent the surface thereof;

    (b) an interlayer formed in said region and adjacent the surface of said substrate, said interlayer containing titanium, titanium carbide, carbon and the metal of said substrate; and

    (c) a dense adherent continuous coating of titanium carbide bonded to said interlayer.

5. The article of manufacture defined in claim 4 wherein said metal substrate is steel and said interlayer contains a carbide of titanium and iron.

6. The article of manufacture defined in claim 4 wherein said metal substrate is tungsten carbide in cobalt and said interlayer contains titanium, titanium carbide, carbon, tungsten and cobalt.

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