

[54] **FORMATION OF REFRACTORY COATINGS
ON STEEL WITHOUT LOSS OF TEMPER OF
STEEL**

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[22] Filed: **Oct. 1, 1969**

[21] Appl. No.: **862,937**

[52] U.S. Cl. 117/62, 29/195, 117/69,
117/71 M, 117/106 R, 117/106 A, 117/106
C, 117/DIG. 10, 204/35 R, 204/38 R
[51] Int. Cl. C23c 11/02, C23c 11/08, C23f 17/00
[58] Field of Search 117/71 M, 106 C,
117/106 D, 106 R, 69, DIG. 10, DIG. 12, 62;
204/38 R

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[57] **ABSTRACT**

Improved refractory coatings are provided in proc-
esses involving the chemical vapor phase deposition of
a refractory coating upon a substrate by initially coat-
ing the substrate with a continuous adherent layer of
substantially pure elemental material. For example, in
a process for the vapor deposition of titanium carboni-
tride on a substrate such as stainless steel, by the con-
tact of vaporous reactants containing titanium, car-
bon, and nitrogen, the substrate is initially plated with
a continuous adherent layer of pure nickel, and the
titanium carbonitride coating is applied over the
nickel.

4 Claims, No Drawings

FORMATION OF REFRACTORY COATINGS ON STEEL WITHOUT LOSS OF TEMPER OF STEEL

This invention relates to coatings and coating techniques. In still another aspect, this invention relates to refractory coatings formed by chemical vapor phase deposition processes. In still another aspect, this invention relates to an improved method for improving adhesion of vapor deposited refractory coatings, such as metal carbonitride coatings.

In many instances it is desirable to apply very hard, durable, and oxidation-resistant coatings to the surface of various objects such as missile nose cones, machine tools, turbine blades, and the like. For example, it is known to coat various metals with a metal carbide, or a metal nitride, or both, to increase the oxygen resistance thereof. Generally the metal substrate is heated to a vapor deposition temperature, e.g., about 900°-1,200° C and then contacted with a gaseous stream to form the refractory coating. U. S. Pat. No. 2,972,556 discloses vapor phase reactions for depositing metal carbides and metal nitrides to a substrate.

One of the problems encountered in coating metal with a carbide such as titanium carbide by the above described processes is the loss of temper in the metal. Generally, metals, and in particular steel, are first hardened by elevating the steel to about 1,000° C and then quickly quenched. The steel after quenching is tempered by elevating the temperature to about 500° C to 600° C, thus reducing its brittleness. If a hardened and tempered steel is then reheated to a temperature between 900° C and 1,200° C to permit the application of a coat of titanium carbide, the hardness and temper of the steel is lost during the reheating process. If the steel, after application of the coating, is quenched to again harden the steel, the coating may be damaged as the steel will change in size during the quenching process, which can rupture the coating, create a roughness in the coating or cause it to eventually peel from the surface of the steel. Thus, not only is the coating damaged but the steel is also weakened and does not provide as strong a support for the coating necessitating that the coating be thicker to withstand the forces to which it may be subjected.

One conventional method of imparting corrosion resistance to objects such as steel turbine blades is to coat the blades with a protective layer of a metal or metal alloy, such as a nickel-cadmium alloy. However, while these coatings are generally effective for imparting corrosion resistance to the part, they are relatively soft and ductile. Thus, in conventional operations such as when a turbine blade coated with such a metal or metal alloy contacts a particle at extremely high speeds, the coating will become dented and discontinuous. This results in a small portion of the substrate being subjected to the corrosive atmosphere, and a resultant corrosion and weakening of the metal substrate.

Recently a process has been developed for coating substrates with a solid solution carbonitride of a metal selected from silicon, boron, and transition metals in Groups, IVB, VB and VIB of the Periodic Table, for example, titanium carbonitride. This recently developed process is described in copending patent application Ser. No. 769,356 filed Oct. 21, 1968 and now abandoned. This process can occur either at low temperatures, thus permitting the application of a hard coat to a metal without loss of hardness and temper which has been imparted to the metal by previous heating steps,

or at higher temperatures for materials having compatible thermal behavior in any step required after the coating operation.

While this new process yields highly improved and beneficial coatings, it has been found that many substrates carry unwanted and undesirable impurities such as oxides on the surface thereof which are deleterious to the formation of a smooth continuous coating of refractory materials including the metal carbonitride. Most surface impurities can be removed by heat and reducing action with a material such as hydrogen. However, such processes many times result in the loss of temper in the metal parts.

Therefore, one object of this invention is to provide an improved process for applying a refractory coating to a substrate which carries surface impurities which are deleterious to the formation of coatings by conventional vapor phase deposition techniques.

Another object of this invention is to provide a method of producing a continuous refractory coating on the surface of the substrate such as a stainless steel substrate without causing damage thereto in heating operations.

A further object of this invention is to provide a method of obtaining improved adhesion of a refractory coating to a substrate material when deposition occurs at relatively low temperatures.

Still a further object of this invention is to provide a novel laminated protective coating for an object consisting of a layer of a corrosion resistant material applied to the object and covered by a layer of refractory material.

According to the invention, it has been found that continuous layers of refractory materials such as metal carbonitrides can be applied to the substrate having surface impurities thereon, such as oxides and the like, by initially coating the substrate with a continuous, adherent coating of pure elemental material. Suitable coating materials include metals which do not oxidize under ordinary conditions and/or metals whose oxides are easily reducible at low temperatures.

Thus, it has been found that refractory coatings applied to certain substrates such as stainless steel, e.g., AM-335, AM-350, and the like, under low temperature vapor phase deposition reactions have many times resulted in discontinuous and flaky coatings of the refractory material. It is believed that such flaky coatings result from the presence of surface impurities, e.g., oxides such as chromium oxide, which are relatively impossible to remove by hydrogen reduction at the lower temperatures. Attempted hydrogen reduction of these various stable oxides at the lower temperatures has been quite unsatisfactory.

Higher temperatures for the hydrogen reduction process (around 900° to 1,000° C) generally deleteriously affect the temper of the substrate and therefore defeat the purpose of the low temperature vapor phase deposition process. Therefore, it has been found that the application of a continuous adherent coat of a pure elemental substance or mixture thereof to the surface of the substrate prior to the vapor phase deposition of the refractory material thereto results in a very uniform continuous coating of the refractory material on the substrate. The adherent elemental material uniformly covers the substrate and any surface impurities thereon which would be deleterious to the application of the continuous coating of refractory material such as metal

carbonitrides. The refractory coating on the other hand, applies uniformly to the pure elemental coating.

The pure elemental coating can consist of any metal, metal alloy or mixture which does not substantially oxidize under ordinary atmospheric conditions and/or a metal, metal alloy of mixture, whose oxide is easily reducible at low temperatures (below about 800° C). Preferred materials include the metals in Group IB and IIB of the Periodic Table as set forth on page B-2 of the *Handbook of Chemistry and Physics*, Chemical Rubber Company, 45th Edition (1964). Preferred metals from these Groups include gold, silver, cadmium and copper. Additionally, metals in Group VIII of the Periodic Table can be used, e.g., nickel. Any elemental material can be applied to the substrate by any suitable process such as vapor phase deposition or electroplating, or the like, including a combination of vapor phase deposition and electroplating. Any such conventional deposition process for applying the pure material can be utilized. By substantially pure metal in this connotation it is meant that the plating process can include some surface and/or sorbed impurities, but these impurities must be removable by chemical etching, washing, or heating in an inert atmosphere or a hydrogen atmosphere.

Thus, after the initial plating process wherein the surface of the substrate to be coated with a refractory material is initially coated with an elemental material such as described above, particularly metals such as nickel or cadmium which form oxides at atmospheric conditions, but which are easily reducible at lower temperatures, the coated substrate is initially subjected to a cleaning procedure preparatory to the vapor phase deposition of the refractory coating. The substrate is initially suspended within a vapor phase treating chamber and contacted with hydrogen under reducing conditions, e.g., temperatures from about 300° to about 800° C. This will assure that any impurities contained or sorbed within the elemental coating will be bled therefrom. Next, the substrate is subjected to a liquid etching procedure to remove any scale deposits which might have accumulated thereon. This washing procedure generally comprises washing the substrate with an aqueous solution of a strong commercial detergent, and treating the washed substrate with a dilute mineral acid etch, e.g., 15 percent H₂SO₄ or HCl solution. After the acid etch, the substrate is rinsed, dried, and ready for vapor phase deposition of the refractory coating. It is generally preferable to subject the coating to a short hydrogen reduction step prior to the latter coating procedure.

The conditions of the above described pre-treatment step can vary somewhat with the substrate and initial elemental coating thereon. However, the general procedure as outlined above is necessary to remove (1) any sorbed impurities collected by the elemental coating during the initial elemental deposition process, and (2) any scale which forms, or grease which is collected on the surface of the elemental material. An example of a typical procedure wherein a stainless steel (AM-355) substrate has been initially coated with a nickel plating using a sulfamate nickel bath in an electroplating process, which bath is generally prepared from nickel sulfamate, nickel chloride, boric acid and various organic addition agents, is as follows: After the electroplating of the nickel on the stainless steel the substrate is positioned within a vapor reactor, the reac-

tor is flushed with nitrogen and then hydrogen. Next, the substrate is heated by suitable means, such as an RF coil positioned around the reactor to a temperature of about 700° C. Hydrogen is passed in contact with the heated substrate for about 30 minutes. After this time period the substrate is allowed to cool, and the interior of the reactor is flushed with nitrogen. The substrate is then removed from the reactor and placed in a beaker and submerged in an aqueous solution of a very strong commercial detergent such as an alkyl aryl sulfonate. The beaker can be placed upon an ultrasonic agitation device to thereby cause extreme agitation of the detergent against the substrate. This washing procedure is continued for at least about 10 minutes, the substrate is removed and rinsed with de-ionized water. Next, the substrate is added to a 15 percent aqueous solution of sulfuric acid and allowed to etch for about 10 minutes at room temperature. After this etching step the substrate is rinsed with de-ionized water, methanol, and then blown dry with hydrogen or an inert gas. This procedure yields a substantially pure nickel coating on the surface of the substrate. It is only necessary to lightly reduce the surface with hydrogen preparatory to the deposition of the refractory coating to remove any possible impurities which may have collected or sorbed upon the surface thereof after the cleaning step and prior to the vapor phase deposition step.

Any suitable refractory coating can now be applied to the surface of the substrate. For example, metal carbides, metal nitrides, metal silicides, and metal carbonitrides. According to a preferred embodiment of this invention, the above described low temperature process for producing a metal carbonitride coating is applied over the coating of pure elemental material. While the metal carbonitride coating can be applied over a relatively wide temperature range, it can be used effectively at the lower temperatures of from about 400° to about 750° C on substrates such as stainless steel which are particularly sensitive to the higher temperatures.

According to this preferred metal carbonitride vapor phase deposition process, the vaporous stream passed over the heated substrate generally contains molecular hydrogen, a carbon-containing compound which readily decomposes at the deposition temperature, a metal-containing compound which readily decomposes at the deposition temperature, molecular nitrogen, and/or a nitrogen-containing compound which readily decomposes at the deposition temperature. Alternatively, the nitrogen and carbon can be supplied from a single compound containing both nitrogen and carbon which readily decomposes at the deposition temperature.

Suitable metal-containing reactant compounds include metal halides. A preferred group of the metal halides is represented by the generic formula Me(x)_n, where *n* is a valence of Me, *x* is a halogen, e.g., fluorine, chlorine, bromine, and iodine, and Me is selected from silicon, boron, and transition metals in Groups IVB, VB, and VIB of the Periodic Table as set forth on page B-2 of the *Handbook of Chemistry and Physics*, Chemical Rubber Company, 45th Edition, (1964). Generally, the transition metal tetrachlorides, such as titanium tetrachloride are most preferred. However, the transition metal dihalides and trihalides can be useful in some applications, particularly, the higher temperature coating operations.

Suitable carbon-containing reactant compounds include cyclic and acyclic hydrocarbons having up to

about 18 carbon atoms which readily decompose at the deposition temperature. Examples of suitable hydrocarbons include the paraffins such as methane, ethane, propane, butane, pentane, decane, pentadecane, octadecane, and aromatics such as benzene and halogen substituted derivatives thereof.

Suitable reactant compounds containing both carbon and nitrogen include aminoalkenes, pyridines, hydrazine, and alkylamines. Some specific examples include diaminoethylene, triaminoethylene, pyridine, trimethylamine, triethylamine, hydrazine, methylhydrazine, and the like.

The temperature to which the substrate is heated will depend upon the particular reactants employed, but will generally vary within the temperature range of at least 400° C to about 1,200° C. For coating of substrates such as stainless steel which are deleteriously affected by higher temperatures, reactants are selected which will decompose and react within the temperature range of about 550° to about 750° C, and preferably reactants which decompose within the range of about 650° to 700° C. The preferred reactants include a titanium tetrahalide, e.g., titanium tetrachloride, an amine, e.g., trimethylamine, hydrogen, and nitrogen.

It is noted that a particularly preferred metal coating to be used in combination with the metal carbonitride is nickel-cadmium alloy. As discussed above, nickel-cadmium layers are conventionally applied to substrates to enhance the corrosion resistance thereof. These layers are generally quite effective in corrosion environments. However, these layers are very soft and easily damaged. It has been found that when a metal carbonitride layer is positioned over the nickel-cadmium alloy layer upon an object, the resultant laminated protective coating is far superior to either the nickel-cadmium alloy or metal carbonitride. The nickel-cadmium layer will impart excellent corrosion resistance to the surface, while the metal carbonitride, e.g., titanium carbonitride, layer imparts not only heat resistance but tremendous impact resistance to the coating. Thus, the metal carbonitride is an extremely tough substance and adequately protects not only the nickel-cadmium layer, but the substrate material.

The following examples are given to better facilitate the understanding of this invention, and are not intended to limit the scope thereof.

EXAMPLE 1

In this run eight turbine blades having a blade length of about 2 inches, a blade width of about 1 inch and a blade thickness of about one thirty-second inch were electroplated with nickel from a sulfamate nickel electroplating bath. This electroplating process yielded a nickel layer of about 100 microns in thickness.

Next, the blades were suspended on an annular platform within a vapor phase deposition chamber. The vapor phase deposition chamber consisted of a cylindrical quartz tube having enclosures at either end with means for introducing vaporous reactants at the upper end thereof and means for removing vaporous reactants from the interior of the tube positioned through the closure at the bottom end thereof. The annular platform was positioned adjacent the center of the tube and was attached to a spindle which was rotatably mounted through the bottom closure of the reactor. An RF heating coil was positioned around the quartz tube

adjacent the turbine blades such that when actuated the lower portions of the blades would be heated.

Thus, the blades were positioned on the annular platform and the interior of the reactor was flushed with nitrogen. Next, hydrogen was introduced into the interior of the reactor and displaced the nitrogen and the RF coils were actuated and thereby heated the blades to a temperature of 700°C. This hydrogen reduction continued for 30 minutes. This resulted in the desorption of impurities and/or removal of impurities from the blade surface. Next, the blades were cooled and removed from the reactor and placed in a rinse of an aqueous solution of a detergent (Alconox). The solution was subjected to ultrasonic vibrations for 2 minutes. Next, the blades were removed from the detergent mixture and rinsed with de-ionized water and placed in an acid etch vat containing 85 weight percent de-ionized water and 15 weight percent sulfuric acid. The acid etch step lasted for about 2 minutes. The blades were then removed and rinsed with de-ionized water, methanol, and blown dry with helium.

The dry, clean blades were then suspended from the annular platform within the vapor deposition reactor and allowed to reduce in hydrogen for 30 minutes at 700°C. After this time, reactants were passed through the upper closure of the deposition chamber as follows: Nitrogen was passed into the reactor at the rate of 21.32 liters per minute, hydrogen flow was adjusted to 1.17 liters per minute, 31.68 cc per minute of trimethylamine was added with the nitrogen stream, and 80 cc per minute of titanium tetrachloride was added in a 4.68 liter per minute nitrogen stream. The annular platform was rotated at 11 rpm. The reactant flow was allowed to continue over the rotating blades for a period of 1 hour and 20 minutes. The temperature of the blade portion of each of the turbine blades was maintained in a range of from 695° to 710° C (as determined by infrared pyrometry) during the 1 hour and 20 minute deposition run.

After this time, the flow of reactants was shut off, the RF coil deactuated, and the blades were allowed to cool. The blades had obtained a very smooth, continuous and uniform coating of titanium carbonitride of approximately 1 mil in thickness.

EXAMPLE 2

Five turbine blades similar to those described above, but made of Greek ascaloy AMS 5616 were initially plated with a 100 micron layer of a nickel-cadmium alloy.

After the plating procedure these blades were placed within the reactor described in Example 1, and reduced in hydrogen as described.

After the blades were cooled, they were removed from the reactor and washed in a detergent solution (Alconox) and subjected to ultrasonic vibrations for 2 minutes. The blades were then rinsed with de-ionized water and soaked for 1 hour in an aqueous solution of ammonium nitrate consisting of 12 grams of ammonium nitrate per 100cc of de-ionized water. The ammonium nitrate removes cadmium oxide from the coating surface. After the ammonium nitrate soaking, the blades were rinsed again with de-ionized water, and placed in an acid etch solution consisting of 10 percent sulfuric acid and 90 percent de-ionized water for 15 minutes. After the acid etch step, the blades were again

rinsed with de-ionized water, methanol, and blown dry with nitrogen.

Next, the blades were positioned within the reactor and allowed to reduce in hydrogen and were then subsequently coated with titanium carbonitride as disclosed in Example 1. This process yielded a very smooth continuous adherent layer of titanium carbonitride on the surface of the blades. The blades were subjected to the action of a conventional jet abrader device. The nozzle of the jet abrader was positioned six tenths inch from the titanium carbonitride coating, run 300 seconds, and the abrading action did not break through the smooth uniform coating.

EXAMPLE 3

In this example, 4 turbine blades, such as described in Example 1, made of AM—355 stainless steel were plated with a gold plating of about 10 microns by vapor phase deposition. Since gold does not form oxides at atmospheric conditions the initial hydrogen reduction and washing steps used in Example 1 were not necessary.

The blades were positioned within the reactor as described in Example 1 and subjected to hydrogen reduction and chemical vapor phase deposition of the titanium carbonitride under the same conditions as described in Example 1. A very smooth continuous coating of titanium carbonitride resulted on the blades.

Although this invention has been described in relation to its preferred embodiments, it is to be understood that various modifications thereof will now be apparent to one skilled in the art upon reading this specification, and it is intended to cover such modifications as fall within the scope of the appended claims.

I claim:

1. An improved method of applying a protective coating on a tempered steel substrate, said coating comprising a solid solution layer of a carbonitride of a material selected from silicon, boron, and the transition

metals in Groups IVB, VB and VIB of the Periodic Table, by contacting the substrate with a vaporous reactant stream including a compound of said material, a carbon-containing compound, and nitrogen, said method comprising:

- a. applying to said substrate a continuous adherent coating of a substantially pure metal or alloy selected from Groups IB, IIB and VIII of the Periodic Table;
- b. suspending said coated substrate in a vapor deposition zone;
- c. heating said substrate to a temperature of 550° – 750° C. at which said reactants will decompose; and
- d. passing said vaporous reactant stream through said vapor deposition zone to contact said coating on said substrate, thereby causing said reactants to decompose and form said carbonitride coating thereon.

2. The method of claim 1 wherein said coating is formed by steps of:

- a. applying a coating of said metal or alloy to said substrate;
- b. subjecting said metal or alloy and said substrate to an atmosphere of hydrogen and heating said substrate and metal or alloy to a temperature of less than 800° C. to remove sorbed impurities therefrom; and
- c. removing impurity deposits from the surface of said metal or alloy.

3. The method of claim 2 wherein said deposits are removed from the surface of said metal or alloy by initially contacting said metal or alloy with an agitated detergent solution, and thereafter contacting said surface with an aqueous solution of dilute mineral acid.

4. The method of claim 1 wherein said carbonitride is titanium carbonitride.

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