United States Patent

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[54] **METHOD FOR PRODUCING HARD COATINGS ON A SURFACE**

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[63] Continuation-in-part of Ser. No. 636,614, May 8, 1967, abandoned.

[30] **Foreign Application Priority Data**

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[52] **U.S. Cl.** ....**117/106 C**, 23/208 A

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[58] **Field of Search**...............117/106, 106 A, 106 C, 106 D, 117/107.2 R, 46 CB, 46 CC, 46 CG; 23/208 A

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[57] **ABSTRACT**

The invention is concerned with a process for producing hard coatings of titanium carbide on a surface. The process comprises subjecting the surface to be coated to a mixture a gaseous titanium halide, a gaseous hydrocarbon and hydrogen, at a temperature of 700° to 900° C. and under reduced pressure.

17 Claims, No Drawings

METHOD FOR PRODUCING HARD COATINGS ON A SURFACE

CROSS-REFERENCE TO COPENDING APPLICATION

The present application is a continuation-in-part of our copending application Ser. No. 636,614, filed May 8, 1967, now abandoned.

BACKGROUND OF THE INVENTION

A method has already been proposed for forming coatings of hard carbides of the metals of the groups III to VI of the periodic system, for instance of the metals titanium, vanadium, tungsten, on metallic or non metallic surfaces, by the reaction of halogen compounds of the respective metals with hydrogen and hydrocarbons. This known method comprises reacting a halogen compound of the carbide forming metal with a gas mixture on the surface to be coated at temperatures of from 900° to 1,200° C, the gas mixture containing hydrogen and a proportion of volatile hydrocarbon compounds which is no greater than that corresponding to its state of equilibrium with carbon and hydrogen at the deposition temperature.

This known method has the disadvantage of having to be carried out at temperatures above 900° C., i.e., at relatively high temperatures. Numerous materials, on which it would be desirable to form a hard coating, are however unable to withstand such temperatures. At such high-temperatures modifications in the structure of the workpieces may occur which may make them useless for their intended purpose. In addition, owing to differences in the thermal coefficient of expansion of the materials of the base and the coating, stresses build up in the coating which when it is cooled down from high temperatures to room temperature may become so great that a sufficient adherence of the coating is no longer assured.

OBJECT OF THE INVENTION

The purpose of the present invention is to eliminate these disadvantages of the known method. It has been found that titanium carbide can also be deposited at temperatures below 900° C., when the operation is effected under a reduced pressure.

Thus the process of the invention comprises subjecting the surface to be coated to a mixture of about 0.5 to 6 volume percent of a gaseous titanium halide, such as titanium chloride or bromide, about 0.5 to 10 volume percent of at least one gaseous hydrocarbon, such as aliphatic, cycloaliphatic, aromatic and alkylaromatic hydrocarbons, and hydrogen as the balance, at temperatures between about 700° and 900° C., and under a pressure of about 1 to 200 Torr. Preferred ranges are 1 to 5 volume percent of the titanium halide, 1 to 5 volume percent of the hydrocarbon, and pressures of 1 to 100 Torr, especially 1 to 40 Torr.

Useful hydrocarbons are the lower alkanes, e.g., from methane to the hexanes, cyclohexane, dicyclopentadiene, naphthalene and the like, which may also be substituted.

The hydrocarbon can also be replaced by another source of carbon, such as a vessel built of carbon or solid carbon as such.

The preferred flow range of the total gaseous mixture is about 1 to 100 normal liters per hour, i.e., liters calculated at 0° C., and 760 Torr.

It is characteristic for the operation of depositing TiC in in the range of temperatures of from 700° to 900° under pressures ranging from 1 to 40 Torr and with a rate of flow of the reacting gases of from 1 to 30 normal liters per hour, that the maximum rate of deposit generally occurs at lower temperatures when the pressure decreases,

that the kinetics of the deposition process are comparable with those corresponding to 1,000° C. and atmospheric pressure,

that the efficiency is notably better than in the case of deposition at higher temperatures and under atmospheric pressure, i.e., that the products of the reaction are utilized with a better yield so that the method becomes more economical,

that the coatings deposited at low temperatures under reduced pressure have mechanical properties which are as good as or are even better than those of coatings deposited at higher temperatures and under normal pressure, in particular their microhardness of from 3,000 to 4,000 Vickers degrees (kg./mm.^{2}) remains the same, the microporosity of the coatings is smaller and the resistance to corrosion better,

that the polished surfaces of TiC coatings deposited at low temperatures and under reduced pressure have a surface roughness which is smaller by a factor of 10 and can be as low as 0.1 μm. which offers the advantage that it is only in special cases that surfaces coated in this way require a subsequent treatment, respectively to final polishing,

that the method is more economical at lower temperatures than at higher temperatures, owing to the fact that the consumption of electrical power is smaller, that the time required to attain the temperature of reaction is shorter and that the life of all parts subjected to higher temperatures, including the heating device is longer,

that in contrast with effecting the deposit at higher temperatures and under normal pressure, it is possible by the application of electrical fields and the use of an appropriate distribution of the temperatures in the reactor along the reaction path of the gases, to find conditions which either allow a higher rate of deposit to be expected at workpiece temperatures between 700° and 900° C. or else are such that a deposit of TiC at temperatures below 700° C. may be obtained.

PREFERRED EMBODIMENTS

EXAMPLE 1

A steel watchcase ring is to be made absolutely impact and scratch resistant, and to that effect to be provided with a coating of titanium carbide. The ring is used polished, in its finished state. It is secured in a suitable holding device in a reaction tube made of "Inconel" alloy. The reaction tube is then securely closed and washed out with hydrogen. The reaction space is evacuated and heated by means of a resistance furnace until the workpiece has attained a temperature of 800° C. After this a mixture consisting of 90 to 98 percent hydrogen, 5 to 1 percent titanium tetrachloride and 5 to 1 percent methane is introduced into the reaction space. A pressure of 10 Torr is maintained in the reaction tube by regulating the total amount of the dose of gas introduced and the rate of suction of the vacuum pump. After 3 to 4 hours the supply of reaction gases is interrupted. After having been cooled in the vacuum down to room temperature, the watchcase ring has a bright coating of pure titanium carbide of up to 10 μm. thickness. The coating is remarkable for its considerable hardness (microhardness of from 3,000 to 4,000 HV), its perfect adherence, a surface roughness of less than 0.5 μm. and a good resistance to corrosion. After having been lightly polished to a high gloss by means of a cloth disk, the watchcase ring is ready to be mounted. During the deposit of the coating at 800° C., its initial form was maintained uncharged.

EXAMPLE 2

A workpiece of sintered aluminum oxide is to be provided with an electrically conducting coating which must in addition be wear resistant and have a hardness which is equivalent to that of aluminum oxide. The workpiece is suitably placed in a reaction tube made of "Inconel" alloy. The reaction space is securely closed and evacuated. By means of a resistance furnace the workpiece is heated to a temperature of 800° C. Hydrogen is introduced into the reaction chamber and drawn off by a vacuum pump in such a manner that a pressure of 50 Torr is obtained in the reaction space. A dose of 3 percent titanium tetrachloride and 0.5 percent naphthalene is now added to the hydrogen. After a reaction lasting from 2 to 3 hours and subsequent cooling down to room temperature, a uniform, strongly adherent coating of titanium carbide of about 15 μm. thickness has formed on the aluminum oxide.

EXAMPLE 3

A number of pivots and "endstones" of steel watch bearings are to be provided with a wear resistant, friction reducing coating of titanium carbide. The pivots and "endstones" are introduced in a carbon container into a quartz reaction tube. The tube is closed and washed out with hydrogen. A vacuum pump draws off the gas through the quartz tube and maintains therein a pressure of 20 Torr. The carbon container and its contents are heated inductively to a temperature of from 750° to 800°. A dose of about 5 percent of titanium tetrabromide is now added to the hydrogen, by enriching a partial stream of hydrogen with titanium tetrabromide in an evaporator containing liquid titanium tetrabromide. After continuing the reaction from 1 to 2 hours, a coating of titanium carbide from 10 to 12 μm. has formed on the workpieces. Owing to the fact that during the coating operation at a temperature of at most 800° C. the composition and the grain of the steel have remained unaltered, the steel core of the pivots and "endstones" may then be subjected to a subsequent hardening operation. By this means the coating of titanium carbide is made impervious to impact.

EXAMPLE 4

Cutting tools of the cemented-carbide type are covered with a wear-resistant layer of titanium carbide. To do so the tools are appropriately fixed in an "Inconel" tube serving as the reaction-kettle. After evacuating this tube and thoroughly rinsing it with hydrogen it is heated to 800°–850° C. by a tube furnace. When a constant temperature is attained, 4 percent by volume of titanium tetrachloride and 0.5 percent volume of dicyclopentadiene are added to the flow of hydrogen of 500 ml./min. calculated at normal conditions. The reaction mixture is made to move in a constant flow through the reaction kettle at a pressure of 5 Torr, this pressure being maintained by means of a vacuum pump. After 2 hours reaction time as well adherent layer of titanium carbide of 8–10 μm. thickness has been deposited on the cutting tool. These tools provide a lifetime of at least 10 times longer than those uncoated, when used on a lathe against a 1 percent carbon steel.

We claim:

1. A process for producing a surface coating consisting substantially of hard titanium carbide, comprising subjecting the surface to be coated to a mixture of 0.5 to 6 volume percent of a gaseous titanium halide, 0.5 to 10 volume percent of a gaseous hydrocarbon and the balance being hydrogen, at a temperature of 700° to 900° C. and under a pressure of 1 to 200 Torr.

2. A process for producing a surface coating consisting substantially of hard titanium carbide, comprising subjecting the surface to be coated to a mixture of 0.5 to 6 volume percent of a gaseous titanium halide selected from the group consisting of titanium chloride and titanium bromide, 0.5 to 10 volume percent of a gaseous hydrocarbon selected from the group consisting of aliphatic, cycloaliphatic, aromatic and alkylaromatic hydrocarbons, and the balance being hydrogen, at a temperature of 700° to 900° and under a pressure of 1 to 200 Torr.

3. A process according to claim **2**, where the total gas flow rate is 1 to 100 liters per hour calculated for 0° C. and 760 Torr.

4. A process for producing a coating consisting substantially of hard titanium carbide on a surface, comprising subjecting the surface to be coated to a mixture of 0.5 to 6 volume percent of a gaseous titanium halide selected from the group consisting of titanium chloride and titanium bromide, and of 99.5 to 94 volume percent of hydrogen, in a carbon container at a temperature of 700° to 900° C. and under a pressure of 1 to 200 Torr.

5. A process according to claim **2**, wherein the hydrocarbon is an aliphatic hydrocarbon.

6. A process according to claim **5**, wherein the aliphatic hydrocarbon is a lower alkane.

7. A process according to claim **6**, wherein the lower alkane is methane.

8. A process according to claim **2**, wherein the hydrocarbon is a cycloaliphatic hydrocarbon.

9. A process according to claim **8**, wherein the cycloaliphatic hydrocarbon is dicyclopentadiene.

10. A process according to claim **9**, wherein the titanium halide is titanium tetrachloride.

11. A process according to claim **8**, wherein the cycloaliphatic hydrocarbon is cyclohexane.

12. A process according to claim **2**, wherein the hydrocarbon is an aromatic hydrocarbon.

13. A process according to claim **12**, wherein the aromatic hydrocarbon is naphthalene.

14. A process according to claim **2**, wherein the hydrocarbon is an alkylaromatic hydrocarbon.

15. A process according to claim **1**, wherein the pressure is 1–100 Torr.

16. A process according to claim **2**, wherein the pressure is 1–100 Torr.

17. A process according to claim **4**, wherein the pressure is 1–100 Torr.

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