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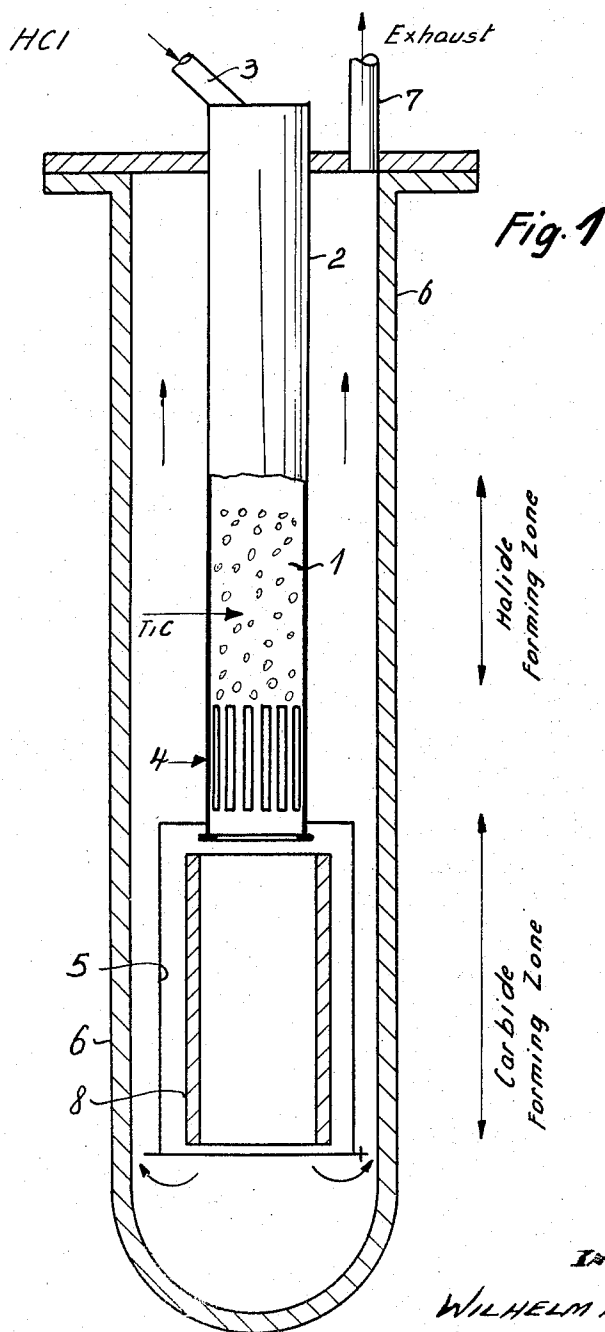
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PROCESS FOR THE PRODUCTION OF TITANIUM CARBIDE COATINGS

Filed July 21, 1959

2 Sheets-Sheet 1



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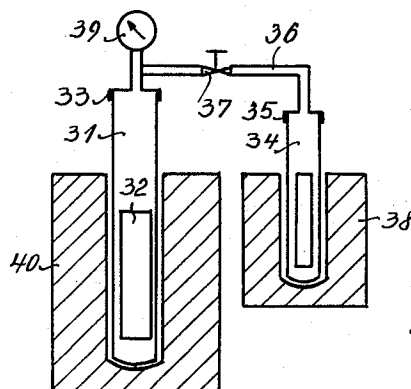
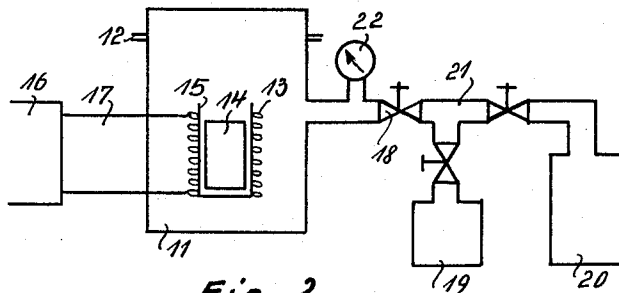
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PROCESS FOR THE PRODUCTION OF TITANIUM CARBIDE COATINGS

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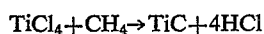
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11 Claims. (Cl. 117—49)

The present invention relates to an improved process for the production of dense titanium carbide coatings which firmly adhere to the surfaces of the base to which they are applied.

It is already known that titanium carbide can be produced by a gas phase reaction. It is furthermore known that titanium carbide coatings can be deposited from a gas mixture containing tetrachloride and a volatile hydrocarbon, such as methane, according to the equation:



in the presence of hydrogen. Such coatings according to prior suggestions were produced on filaments for incandescent lamps by heating the filaments to temperatures over 1400° C. and passing a gas mixture containing titanium tetrachloride, hydrocarbon and hydrogen over the heated filaments, whereby titanium carbide deposited on the filaments.

In view of the high reaction temperatures employed, namely, 1400° C. and higher, the material to be coated therefrom, the filaments for incandescent lamps, could only consist of high melting elements, such as tungsten, molybdenum or graphite. The coatings produced possessed a glass-like brittleness so that they were not used previously for tools or machine parts. In themselves the coatings did not possess good cohesion because they contain elemental carbon in addition to the carbide. As a result, such coatings tend to scale off, even under relatively slight pressures and impacts. Also, in view of the very high temperatures at which such coatings are deposited they are very coarse grained which according to experience leads to unfavorable mechanical properties. At times such coatings also contain excess titanium which impairs the sliding properties of such coatings.

It is an object of the invention to provide a process for the production of titanium carbide coatings which are especially wear resistant and which on sliding friction against metal surfaces do not tend to seize.

It is also an object of the invention to provide a process for the production of titanium carbide coatings on ferrous metal bases.

It furthermore is an object of the present invention to provide a process for the production of titanium carbide coatings on hardenable steels.

According to the invention the titanium carbide coatings are deposited at temperatures between 900 and 1200° C. which renders it possible to provide such coatings on materials, particularly ferrous metals, upon which titanium carbide coatings have previously not been deposited. This renders it possible to provide titanium carbide coatings on many objects for use in varied branches of technology and particularly on tools and machine parts.

As in usual coating procedures, it is desirable to clean and prepare the surfaces of the base to be coated. It has been found desirable, in addition, especially when objects of larger dimensions are to be coated for example, those having a cross-section greater than 5–10 mm., to subject the objects to be coated to a degasification in a vacuum of

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at least 10^{-3} mm. Hg at temperatures over 800° C. until the pressure in the degasification chamber will not rise above 10^{-3} mm. Hg when the vacuum pumps are shut off, that is, until the partial pressure of the gases in the objects at such temperatures does not exceed 10^{-3} mm. Hg. Such degasification prior to deposit of the titanium carbide coatings has been found to provide for an extremely firm bond between the coating and the base. The lower the pressure and therefore the higher the vacuum, the more rapid and complete is the degasification. The desired vacuum can be achieved and maintained with pumps, such as rotating or diffusion pumps, or also in a known manner with metals having a good absorptive capacity for gases, such as titanium, zirconium or rare earth metals. When such absorptive metals are employed they are preferably introduced into the degasification chamber in the form of shavings or a sponge so that the large surfaces afforded thereby cause easier absorption of the gases.

The degasification described does not merely serve to remove gases adhering to the surfaces of the base to be coated. For this purpose degasification in high vacuum would not be required as removal of gases adhering to the surface could be effected merely by heating the base under hydrogen. The essential purpose of such degasification is rather the removal of the gases dissolved in the base, particularly nitrogen and oxygen. When these gases are not removed from the base they will tend to diffuse to the surface of the base during the deposition of the titanium carbide coatings because of the high temperatures employed and react with the titanium carbide which has already deposited. Investigations have shown that very thin intermediate layers are formed thereby which considerably reduce the adherence of the titanium carbide coating on the base.

Instead of thus pretreating the base materials it is possible to use base materials whose content of reactive nitrogen and/or oxygen has been reduced to values comparable to those obtained by the described pretreatments by the addition of special alloying constituents, for example, of titanium, or by special means adopted during their manufacture, such as by melting in a vacuum.

It is not necessary that the degasified objects to be coated be maintained under a vacuum until application of the titanium carbide coating, as the gases which have been removed are not taken up again even when the objects are stored in air at room temperatures, as the gases which are primarily concerned are those which were taken up by such objects at high temperatures or in the molten state. However, as the degasification is normally effected at high temperatures, it is expedient to carry out the decomposition of the titanium carbide coating immediately thereafter to avoid the necessity of reheating the objects for such coating operation.

In order to insure that the titanium carbide coatings are in themselves firmly coherent, care is taken according to the invention that no free carbon is occluded therein so that the coatings exclusively consist of titanium carbide. This object is most assuredly attained when the quantity of hydrocarbon contained in the reaction gas mixture is selected to be not higher than that which corresponds to the equilibrium between hydrocarbon on one hand and hydrogen and carbon on the other hand ($2\text{H}_2 + \text{C} \rightleftharpoons \text{CH}_4$) at the temperature employed for the deposition of the titanium carbide coating.

In selecting such a concentration for the hydrocarbons it is impossible for free solid carbon to deposit from the gas mixture in addition to titanium carbide. The concentration which cannot be exceeded can be determined from known tables in which the concentrations of the components for such equilibrium gas mixtures are given. It is to be taken into consideration that at the high depositing temperatures of 900–1200° C. employed all hydro-

carbons essentially are decomposed to methane and that higher hydrocarbons are present in only inconsequential quantities. For example, according to Landolt, Bornstein, Roth, Scheel, Physical Chemical Tables, 5th ed., 3rd supplement, part 3, Springer Verlag, 1936, pages 2626 to 2630, it will be seen that in equilibrium mixtures at the temperatures indicated and at a partial hydrogen pressure of 1 atmosphere the following partial pressures and quantities of methane are present.

TABLE 1

Temp., ° C.	p_{CH_4} at—	Vol. Per- cent
900.....	$3.9 \cdot 10^{-2}$	3.75
1,000.....	$2.0 \cdot 10^{-2}$	1.96
1,100.....	$1.2 \cdot 10^{-2}$	1.18
1,200.....	$7.1 \cdot 10^{-3}$	0.70

Consequently, for example, when benzene is employed in addition to hydrogen in the starting mixture, a benzene content of 0.33 vol. percent corresponds to a methane content of about 2 vol. percent, which does not exceed that of the equilibrium mixture at 1000° C.

Practical investigations have, however, shown that the quantity of hydrocarbon contained in the gas mixture can slightly exceed that equivalent to the equilibrium at the temperature employed for the deposition of the titanium carbide coating without causing deposition of elemental carbon. The following table gives actual vol. percent and partial pressures of hydrocarbons with reference to methane at a partial hydrogen pressure of 1 atmosphere which cannot be exceeded if deposition of elemental carbon is to be avoided.

TABLE 2

Temp., ° C.	Vol. Per- cent	p_{CH_4} at—
900.....	4.5	$4.72 \cdot 10^{-2}$
1,000.....	3.5	$3.63 \cdot 10^{-2}$
1,100.....	2.5	$2.57 \cdot 10^{-2}$
1,200.....	1.5	$1.51 \cdot 10^{-2}$

It will be seen that the highest permissible hydrocarbon partial pressures drop linearly between 900 and 1200° C.

Elemental carbon which is contained in or on the base to be coated with titanium carbide does not influence the tenacity of the coating produced as long as such elemental carbon itself is firmly coalesced. Even if this carbon reacts along with the gas mixture it is never incorporated in the carbide coating as elemental solid carbon and therefore does not influence the strength of the coating obtained. The critical factor always is that, at the temperature employed for the deposit of the carbide coating, the hydrocarbon concentration in the gas mixture does not exceed the limits indicated above.

The partial pressures and concentrations of hydrocarbon (methane) indicated above are only valid for a hydrogen partial pressure of 1 atmosphere in the gas mixture, as the equilibrium at higher pressures is displaced towards the hydrocarbon and as a consequence when the reaction is carried out at a higher total pressure of the partial pressures, the concentration of the hydrocarbon in the gas mixture increases corresponding to the equilibrium. The hydrocarbon partial pressure rises proportionately to the square of the partial pressure of the hydrogen in that when the partial pressure of hydrogen is 2 atmospheres the methane pressure is 4 times as high as given in Tables 1 and 2 and when the hydrogen partial pressure is 3 atmospheres the methane pressure is 9 times as high. The concentration of the methane, however, does not increase in the same proportion but somewhat slower corresponding to the following equation

$$\text{Vol. percent } CH_4 = \frac{p_{CH_4}}{(p_{CH_4} + P_{H_2})} \cdot 100$$

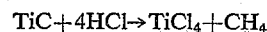
According to the invention therefore at a hydrogen partial pressure of X expressed in atmospheres, the partial pressure of the hydrocarbon with reference to methane in the hydrogen-hydrocarbon mixture should not be greater than 0.047 times X^2 at 900° C. and 0.015 times X^2 at 1200° C., the values for intermediate temperatures being interpolated linearly.

It is expedient to select a concentration of titanium halide, preferably titanium tetrachloride, in the reaction mixture which is no greater than that which is equivalent to the hydrocarbons introduced. This can easily be calculated from the quantity of hydrocarbon introduced as every atom of carbon corresponds to 1 molecule of titanium halide. The use of an excess of titanium halide over that indicated is not detrimental at the depositing temperatures of 900–1200° C. employed according to the invention, but such excess is superfluous as it is retained in the exhaust gases and unnecessarily increases the cost of the process. At higher depositing temperatures, however, such excess of titanium halide would cause deposition of elemental titanium from the gas phase and inclusion thereof in the titanium carbide coating. This would cause a deterioration in the sliding and wear properties of the coating and increase the danger of seizing upon sliding frictional contact with metal surfaces. The depositing temperatures employed according to the invention avoid this danger and provide a way to produce coatings having especially good wear resistant properties.

The exceedingly low concentration of hydrocarbon employed in the gas mixtures according to the invention unexpectedly cause the titanium carbide coatings produced to deposit very uniformly and finely grained upon the base and with very low surface roughness ($1-2\mu$) when the base has been suitably prepared. As a suitably prepared base, a base is to be understood whose surface has been at least finely machined, ground or polished. The slight surface roughness of such base is evened out during the deposit of the coating.

A number of possibilities are available for the production of the gas mixtures containing the reaction partners in the concentrations desired according to the invention. It is first of all naturally possible to admix all three reaction partners, namely, hydrogen, hydrocarbon and titanium halide, outside of the apparatus and then introduce such gas mixture into the reaction space. It is also possible to produce two different starting mixtures, namely, one of hydrogen and hydrocarbon and another of hydrogen and titanium halide, and to introduce these mixtures separately into the reaction space, the necessary quantities of both starting mixtures being controlled with the usual measuring apparatus.

It is also possible to produce a gas mixture in which the concentration of the hydrocarbon is not greater than corresponding to the equilibrium at the depositing temperature directly in the coating apparatus. This can be achieved by passing a gas mixture of hydrogen with about 5–10% of HCl over titanium carbide at temperatures of 500–800° C. In this way equivalent quantities of titanium tetrachloride and methane are formed in the gas mixture according to the following equation:



When the temperature of this gas mixture is raised to the depositing temperature of, for example, about 1000° C., the equilibrium is displaced towards the side of the titanium carbide and HCl and the titanium carbide deposits upon the base. The concentration of the hydrogen chloride which leads to the production of titanium tetrachloride should not exceed a certain upper limit which depends upon the depositing temperature, in order that a gas mixture is obtained which at the depositing temperature does not contain a hydrocarbon concentration greater than that of the equilibrium or respectively a hydrocarbon concentration required to prevent deposition of elemental carbon. Therefore the concentration

of the HCl employed for the production of titanium tetrachloride at temperatures between 600 and 800° C. should not exceed the following values with reference to the depositing temperature of the titanium carbide.

Table 3

Dep. Temp. ° C.:	HCl vol. percent
900	18
1000	14
1100	10
1200	6

In this embodiment of the invention the quantity of the titanium tetrachloride in the gas mixture is also equivalent to that of the hydrocarbon at the depositing temperature.

In the accompanying drawings:

Fig. 1 shows one form of apparatus suitable for carrying out the process according to the invention;

Fig. 2 shows a form of apparatus suitable for degasifying the base materials which are provided with titanium carbide coatings according to the invention; and

Fig. 3 shows another form of apparatus suitable for degasifying the base materials which are provided with titanium carbide coatings according to the invention.

Referring to Fig. 1, solid titanium carbide 1 is held in chamber 2. HCl together with hydrogen is introduced into space 2 through inlet 3 which, at the temperature maintained in chamber 2, namely 500 to 800° C., reacts with the solid titanium carbide to form titanium tetrachloride and volatile hydrocarbons. The gases containing titanium tetrachloride and hydrocarbons pass through the narrow openings in place 4 and reach chamber 5 which contains the workpiece 8 whose surfaces are to be coated with titanium carbide and is maintained at a temperature of 900 to 1200° C. At these higher temperatures, the equilibrium between the titanium tetrachloride, the volatile hydrocarbons, the hydrogen and hydrogen chloride is displaced to favor carbide production and the titanium carbide formed thereby deposits upon the surfaces of workpiece 8. The hydrogen chloride, hydrogen and the residues of the titanium tetrachloride corresponding to the equilibrium, which are extraordinarily small, leave the reaction furnace 6 through outlet 7.

A gas mixture in which the quantity of hydrocarbon is not greater than corresponds to the equilibrium with hydrogen and free carbon at the depositing temperature can also be produced by passing hydrogen over elemental solid carbon at the depositing temperature. In this case only so much hydrogen reacts with the carbon to produce a quantity of hydrocarbon which is just in equilibrium with the hydrogen at the depositing temperature.

The titanium halide, for example, titanium tetrachloride, required for this gas mixture can either be introduced therein in appropriate quantity from outside or it can also be produced in the reaction vessel. Hydrogen chloride can be used for the production of titanium chloride, hydrogen bromide for the production of titanium bromide and hydrogen iodide or iodine vapor for the production of titanium iodide.

In this way the gas mixture can either be produced within or outside of the depositing apparatus. When the gas mixture of hydrogen and hydrocarbon is produced in the manner just described above, the titanium halide vapor is produced independently thereof either within or outside of the apparatus. The individual components of the reaction gas mixture can be mixed in the required quantities before they are introduced into the apparatus. According to the most expedient embodiment, however, the gas mixture containing the titanium halide and the gas mixture containing the hydrocarbon are introduced separately into the reaction space so that they are only mixed with each other immediately before the depositing reaction. In this instance the gas mixtures introduced are preheated to the depositing tem-

perature during their passage through the supply conduits.

Halogen substituted hydrocarbons can also be employed as starting materials instead of pure hydrocarbons. These, insofar as higher hydrocarbons are concerned, are also cracked at the temperatures employed. The halogen atoms in these compounds are replaced by hydrogen in view of the high hydrogen content of the gas mixture so that the final result again is that pure hydrocarbon and hydrohalide are present. It is preferable not to employ too highly halogenated hydrocarbons as in such instance the quantity of hydrohalide becomes too high and reduces the yield of titanium carbide.

It is possible to produce good titanium carbide coatings when taking the measures described above. The quality of the coating, especially with regard to the uniformity of thickness and their surface quality can, however, be still improved, particularly with regard to coatings produced on ferrous workpieces.

The improved coatings can be obtained, when care is taken that the reaction space employed for the deposit of the titanium carbide coating contains chromium and carbon in the solid phase, preferably in the form of one or more compounds of chromium, such as chromium carbide or double carbides, such as chromium iron carbides, for example, $(\text{FeCr})_3\text{C}$, $(\text{FeCr})_7\text{C}_3$, $(\text{FeCr})_{23}\text{C}_6$ and the like or such double carbides in which the iron is replaced by W, Mo and the like. Such chromium and carbon may be contained in the article to be coated or be located in the reaction space outside of such article as will be more fully described below.

One special process to improve the coatings according to the invention may be carried out by depositing the titanium carbide coatings on a base material which is in itself capable of promoting the deposition of titanium carbide. For this purpose the titanium carbide coatings are deposited on a base material which contains chromium and carbon at least on its surface in a quantity sufficient to enable a formation of chromium carbide, that is, 1% Cr and 0.3% C. Such base materials include steels having a diffusion chromium layer, which has been hardened by diffusing carbon therein, as well as steels containing chromium and carbon. Higher contents of carbon and chromium will increase the reaction promoting effect.

The base materials given in the following table have proved, for example, suitable for the application of titanium carbide coatings according to the invention.

TABLE 4

	C	Cr	Mo	Ni	V	W	Co	Fe
	(percent by weight)							
(1)-----	0.3	2.5	-----	-----	0.55	4.5	-----	rest.
(2)-----	0.3	2.5	-----	-----	0.35	9.0	-----	rest.
(3)-----	0.33	5.15	1.45	-----	0.25	-----	-----	rest.
(4)-----	0.55	1.1	0.45	1.7	0.1	-----	-----	rest.
(5)-----	2.1	11.5	-----	-----	-----	0.7	-----	rest.
(6)-----	0.42	1.3	-----	4.0	-----	-----	2.0	rest.
(7)-----	1.6	13.5	1.0	-----	-----	-----	-----	rest.
(8)-----	1.6	11.5	0.8	-----	0.3	-----	-----	rest.
(9)-----	2.3	12.5	1.2	-----	4.0	-----	-----	rest.
(10)-----	1.0	5.0	1.3	-----	0.3	-----	-----	rest.
(11)-----	1.25	4.5	3.5	-----	3.3	9.0	10.5	rest.
(12)-----	2.1	12.0	0.5	-----	0.4	1.0	1.0	rest.
(13)-----	1.2	8.9	0.2	-----	0.2	1.2	-----	rest.
(14)-----	2.1	13.0	0.4	-----	-----	0.7	1.0	rest.
(15)-----	0.9	4.0	1.0	-----	2.5	12.0	3.0	rest.

Besides the aforementioned elements these alloyed steels may also contain silicon and manganese, preferably the usual amounts up to 0.5% Si and 0.5% Mn. In most of these steels chromium and carbon are found as double or mixed carbides which also contain iron and eventually tungsten, molybdenum and vanadium. The steels 1, 2, 6, 10, 11, 12, 13 and 15 according to the table and in addition those containing 1.5-2.5% carbon, 10-15% chromium with additions of tungsten and/or molybdenum totalling 1.3-3.0% have proved to be particu-

larly suitable. The deposition of titanium carbide coatings at temperatures of 900–1050° C. on such steels results in workpieces having a very hard coating on a base material of good hardness without additional heat treatments. The above-mentioned steels having 1.5–2.5% carbon, 10–15% chromium, 1.3–3.0% molybdenum and/or tungsten are specially advantageous because they assume hardness degrees as high as 63–66 Rockwell hardness numbers without any additional heat treatment and do not tend to change their dimensions during the deposition of the coatings.

When chromium and carbon are not contained in the workpiece which is to be coated, it is also possible to provide the improving action of these elements on the coatings obtained by providing another material containing these elements in the reaction space. For example, it was found that equally good results can be attained when the object to be coated is surrounded with turnings or other material which contains chromium carbide at least at its surface.

In these cases it has proved particularly suitable to add chromium and carbon in the form of steels containing at least 5% chromium, and at least 1% and more carbon to the reaction zone of the coating chamber.

In these cases the process can be carried out in a very simple manner by surrounding the workpieces which are to be coated with titanium carbide with turnings, for example, of a steel containing 12% chromium and 2% carbon, and by subjecting the workpieces thus surrounded to the action of a gas mixture consisting of at least one titanium halide, hydrocarbons and hydrogen at temperatures of about 950–1050° C. In most cases this practice causes the formation of a thin inter-layer (about 5–10 microns thick), which contains chromium carbide and is disposed between the base material and the titanium carbide coating obtained. When the gaseous reaction mixture is introduced the chromium carbide is transferred from the surrounding material to the workpieces to be coated by the halogen of the titanium halide or the hydrohalide contained in such mixture to produce a thin chromium carbide coating on the workpieces. The titanium carbide coating is then deposited over such chromium carbide coating and possesses the improved properties engendered by the intermediate chromium carbide coating. No special measures are required in order to insure that the intermediate chromium carbide coating is formed first, as this occurs automatically when the gaseous reaction mixture is introduced into the reaction space. If thicker intermediate layers of chromium carbide (over about 5 microns) are desired, it is expedient first to introduce hydrogen containing very small quantities of hydrogen halide (under 1%) into the reaction space and then later when the desired chromium carbide coating has been formed to introduce the gaseous reaction mixture. However, when very thick intermediate chromium carbide layers are not desired, it is also possible to add the hydrogen halide directly to the gaseous reaction mixture or to use halogenated hydrocarbon as a starting component of the gaseous reaction mixture.

If the workpieces to be coated contain carbon but no chromium, it is also possible to produce the desired intermediate chromium carbide coating by having small pieces of pure chromium present in the reaction space. In this instance a coating is formed on the pure chromium which contains the various phases of the chromium carbon system. This chromium carbide coating is then transferred to the workpieces by the halogen contained in the gaseous reaction mixture in the same manner as described above, and forms the desired intermediate coating thereon. It is, however, more economical to employ chromium containing steels, such as the turnings mentioned above, instead of pure chromium for this purpose. This embodiment of the process according to the invention enables the formation of titanium carbide layers which are thicker and smoother than those obtained without

the presence of chromium carbide. The presence of chromium and carbon in solid form, particularly as carbides containing chromium, promotes the formation of a titanium carbide layer to such a degree that a thicker layer is formed in a shorter time. The presence of chromium and carbon enables also the formation of the titanium carbide layers at lower temperatures than those required in a treating space which is free of chromium and carbon. Depending on the other process conditions, such as rate of gas inflow, concentration, workpiece surface and chromium and carbon contents, the process according to the invention is suitable for producing layers which are 10–30 microns thick in 2–3 hours. The rate of deposition will decrease somewhat as the thickness of the carbide layer formed increases.

Ferrous metals, above all, come into consideration as the material of the base which is to be provided with a titanium carbide coating according to the invention. In general, it may be pointed out that selection of the material for the workpiece to be coated depends more upon the intended use of the coated workpiece than on the coating procedure. In some instances, however, materials which in themselves are not suitable for certain purposes can be rendered suitable therefor by the application of a titanium carbide coating according to the invention, for example, cast iron thus coated becomes suitable for tools for oxide ceramics. The ferrous materials can be steels of any composition. However, chromium carbide containing steels, such as have been exemplified above, are especially suited for the application of the titanium carbide coatings according to the invention.

Most steels after deposit of the coatings at 960 to 1000° C. possess hardnesses without special quenching measures, which depending upon the particular steel involved and coating conditions lie between 400 to 700 kg./mm.² VPN_{30kg.} or between 42 and 59 HRC. The coated objects therefore consist of a relatively moderately hard base and a very hard coating. They are usable, without further hardening of the base, for such workpieces, tools and machine parts which are subjected to sliding friction at low pressures or erosion or corrosion in a small region at high pressures. They can, for example, be used for stone bearings, fine machine bearings, tactile parts of measuring instruments, valve gates, valves, movable parts of machines, especially internal combustion engines, and powder pressing tools. They also can be used with special advantage for parts of spinning machines, such as thread guides and the like.

When workpieces, tools and machine parts are to be subjected to sliding friction at high pressures, such as, for example, drawing tools, heavy duty bearings and the like, it is expedient to subject the base, which, for example, can be a dimensionally stable steel, after application of the coating to a hardening heat treatment. A protective atmosphere preferably is employed for such heat treatment, namely, a medium which is free of oxygen and oxidizing substances, preferably, nitrogen and/or hydrogen, which has been purified with magnesium, calcium or titanium or their nitrides or a high vacuum under 10⁻³ mm. Hg. For example, after the carbide coating has been produced, preferably employing depositing temperatures equal to the hardening temperatures, the reaction by-products, such as the hydrogen halides, are removed from the reaction space and the coated objects then quenched with oxygen free hydrogen and/or nitrogen. The cooling or quenching to effect hardening, preferably, is carried out directly after the carbide coating operation. The quenching may be effected by transferring the coated object to a cooled portion of the reaction space or by introduction into a quenching bath or a warm bath, for example, of lead or a lead zinc alloy with subsequent cooling in air. When ledeburitic chromium steels (1.5–2.5% C, 10–15% Cr) are concerned

the hardening can also be effected, if the reaction chamber is formed of stainless steel, by cooling the contents of such chamber by the introduction into water upon completion of the coating operation.

The ferrous metal objects to be coated preferably are suspended in the reaction space in such a way that they warp as little as possible. In addition to warping other dimensional changes can also occur which are caused by the different structural states of the base material. For example, precise measurements indicate that the dimensions of a steel workpiece depend upon whether it is in the soft annealed, that is, pearlitic, in the martensitic or in a tempered martensitic state. The changes in dimensions caused by the different structural states of the steel in most instances are greater than the change in dimensions caused by the deposit of the titanium carbide coating. Therefore in most instances the thickness of the deposited coating can be disregarded in the dimensioning of the workpieces.

Workpieces for which very narrow tolerance limits are required in the finished state, that is, after the coating, must be given special handling in their preparation for the coating and if necessary in their aftertreatment. Ledeburitic chromium steels are best suited for workpieces of this type as these have the lowest tendency for warping. In the preparation of such base material, it is first normalized, that is, heated for a short period above the usual austenitizing temperature and cooling down from such temperature slowly. Thereafter the workpieces are roughed out, for example, by turning, milling, planing and the like. The roughed out workpieces are then hardened to the ultimate hardness desired. Then they are precision processed to their desired end measurements, for example, by grinding, fine grinding and if necessary fine polishing. Thereafter the workpieces are degasified and provided with a titanium carbide coating as described above. The usual holding temperature of the steel of 980–1020° C. is selected as the depositing temperature for the titanium carbide coating. In the hardening of the workpieces after deposit of the titanium carbide coating, the cooling is so accelerated that the steel base hardens out completely. Surprisingly at this stage the dimensions of the workpieces, despite the presence of the coating are somewhat below the lower tolerance limit when the tolerances permitted are especially small for special purposes.

In order to restore the dimensions of the workpiece to within the tolerance limits they are cooled without prior tempering to temperatures below –60° C. (about –70 to –80° C. in the case of ledeburitic chromium steels) to convert the residual austenite contained therein to martensite. After such deep cooling the dimensions of the workpieces are larger than before such cooling and in some instances when narrow tolerance limits are concerned they may be above the upper tolerance limit. When such workpieces are then tempered their volume decreases and their dimensions return to within the tolerance limits. In such tempering it should be taken into consideration that the decrease in size engendered thereby is greater the higher the temperature thereof and the longer the workpieces are subjected to such tempering. If the dimensions of the workpieces are only slightly above the upper tolerance limit a low tempering temperature, for example, about 100–150° C., and a short tempering period, for example, about 30 minutes, would be selected. On the other hand, if the dimensions of the workpieces are further above the upper tolerance limit, higher temperatures and longer tempering periods would be of advantage. These procedures for correcting the dimensions of the workpieces are well withstood by the titanium carbide coatings without crack formation or spalling off despite their glass like brittleness often described in the literature.

The procedure described above which is especially ad-

vantageous for ledeburitic chromium steels can also be used with other steels and even cast iron, if these materials have a propensity for a stabilization of the residual austenite. For example, in this connection an alloyed cast iron with spherulitic graphite structure of the composition 3–4% C, 2.8–3% Si, 0.5–1.2% Mn, 0.3 to about 1.5% Mo, 3–5% Ni and the remainder Fe has proved suitable. The residual austenite can, however, also be stabilized artificially, by selecting a reaction temperature for the deposit of the titanium carbide coating, somewhat above the usual hardening temperatures, whereby the stabilization of the residual austenite is promoted.

The titanium carbide coating process according to the invention is not only adapted for coating the above mentioned steels and cast iron (whether the graphite be in the usual lamellar form or spherulitic form) but also other non-ferrous materials. When such coating is deposited over a cast iron base thicker coatings are obtained in a shorter period of time than when such coating is deposited over steel. The formation of the titanium carbide coating is the faster the more finely the graphite is distributed at the surface of the workpieces to be coated.

The process according to the invention is especially adapted to produce titanium carbide coatings on non-ferrous material, such as ceramic materials and graphite. These non-ferrous materials usually require higher temperatures for the deposition of the coatings, within the limits given, than steel or cast iron.

By deposition of titanium carbide coatings on ceramics and graphite which are known normally to be poor conductors at room temperature, they are converted to usable electric conductors and can, for example, be employed as heating elements.

Sintered hard metal alloys (cemented carbides) are also suited as materials for the workpieces to be coated according to the invention. Those which contain chromium carbide are particularly suited. Workpieces of this material provided with titanium carbide coatings are especially suited for such applications where sliding friction occurs at very high pressures.

Prior to the deposit of the coatings, the workpieces are generally prepared by turning and grinding to the measurement desired. When ferrous materials are concerned it is preferable to harden them before grinding, as the best surface smoothness can be obtained when they are ground in the hardened state and therefore also the smoothest coatings will be attained thereover.

When special surface forms, such as, for example, in files and similar apparatus, are desired, the desired surface profiles are provided before deposition of the titanium carbide coating and preferably before degasification of the base. It is, however, also possible first to prepare a blank, degasify and if desired harden such blank and only then provide the desired profile just before deposit of the titanium carbide coating.

Tools with somewhat roughened surfaces are often very desired in a large number of pressing operations in powder metallurgy, especially in oxide ceramics. The necessary surface roughness can either be worked in but often can be achieved much better by selection of suited base materials for the deposit of the titanium carbide coating. For example, the titanium carbide coatings obtained on cast iron with or without spherulitic graphite usually exhibit a greater roughness than those obtained on steels. Such roughness, depending on the fineness of the finish of the original surface, can lie between 3.5 and 8 μ . Such surfaces with unpolished titanium carbide coatings have been found particularly suited for the protection of pressing apparatus which in oxide ceramics work against strongly abrasive powders, such as porcelain powder.

Titanium carbide coatings according to the invention which are free of occlusions of metallic titanium, were provided on drawing dies. Smooth iron rods could be drawn through such dies without the use of a lubricant

with a 40-45% reduction without occurrence of welding or seizing. This cannot be accomplished with dies of known sintered hard metals or of steel.

To facilitate the understanding of the invention, the same will be described hereinafter with reference to some examples, though the invention is in no way restricted thereto. Some of the examples will be described in conjunction with Figs. 1-3 of the drawings.

Example 1

The degasification was carried out in a commercially available high-vacuum annealing furnace as is shown in Fig. 2. The furnace consisted of a water cooled steel crucible 11, which could be vacuum-tightly closed by means of flange 12. The crucible contained a high-frequency coil 13, which also was water cooled and which served for heating specimens 14 by induction. These specimens 14 were held in a ceramic container 15. The necessary high-frequency current was supplied to the coil from generator 16 by way of the leads 17 sealed through the crucible wall. The interior of the crucible was connected by a vacuum-tight conduit 21, which was as wide as possible, through the high-vacuum valve 18 to the pump station consisting of a mercury diffusion pump 19 and a rotary pump 20. Such conduit incorporates the measuring conduit for the vacuum gauge 22.

The degasification process included the following operations: The specimens 14 to be degasified, which consisted of cast iron, were placed in container 15, which was then inserted in the high-frequency coil 13. Then the crucible 11 was closed by flange 12 and while the valve 18 was open rotary pump 20 was started to evacuate the crucible. After the pressure in the system was reduced to about 10^{-2} mm. mercury, the mercury-vapor pump 13 was started, whereby the pressure in the system was reduced to about 10^{-4} to 10^{-5} mm. mercury. Then the heating of the specimens was started by gradually supplying and increasing the high-frequency current, whereby the specimens were slowly heated up. The pressure rise resulting from the heating of the gases still contained in the system was absorbed by the pumps.

When the specimens had reached temperatures of about 600-650° C. a rapid, an almost sudden liberation of gas from the specimens was observed, whereby the pressure in the system increased to above 10^{-2} mm. mercury in spite of the operation of the pumps. As the sudden liberation of gas began, the mercury-vapor pump was stopped immediately and the evacuation was continued only with the rotary pump whereas the temperature of the specimens was held constant at about 650-700° C. After the pressure in the system had been reduced again to about 10^{-2} mm. mercury, the mercury-vapor pump was started again. After a vacuum of 10^{-4} to 10^{-5} mm. mercury had been reached the temperature was slowly increased to about 900-950° C. The specimens were maintained at that temperature and the operation of the pumps was continued until upon disconnection of the pumps by closing of the valve 18 did not effect an increase in the pressure in the system above 10^{-3} to 10^{-4} mm. Hg. Then the high-frequency current was shut off and the specimens were allowed to cool in the plant. The workpieces were removed from the degasifying plant in a cold condition and were provided with titanium carbide coatings, if desired after a finish-machining treatment. The periods of pump operation could be substantially reduced if getters such as titanium chips or titanium sponge were added to the workpieces in the container during the degasifying process described hereinbefore. At the annealing temperatures the gases escaping from the specimens were absorbed at a high rate by said getters.

To provide a workpiece with the titanium carbide coatings a cylindrical piece, which had been treated as described to liberate the included gas, was placed in a holder of a reaction chamber wherein the coating of titanium carbide is to be deposited. The chamber was

tightly closed and evacuated and subsequently hydrogen was introduced into the evacuated chamber. When the pressure of the hydrogen within the chamber reached atmospheric, a stream of hydrogen was passed through the chamber at a velocity of 10 liters per hour and the chamber was carefully heated. The water ensuing from the reduction of the oxide traces was flushed out of the reaction chamber by the stream of hydrogen flowing therethrough. When the cast iron workpiece reached a temperature of 950° C., the stream of hydrogen was replaced by a hydrogen stream containing 2% vaporized titanium tetrachloride and 2% methane and this stream was introduced into the reaction chamber through a distributor surrounding the workpiece. The temperature of the workpiece was gradually raised to 980° to 1000° C. and the reaction conditions were then maintained for about four hours. The stream of titanium tetrachloride was then replaced by a stream of pure hydrogen while the heat was proceeded for a little while longer. Thereafter the heating of the reaction chamber was cut off and the reaction chamber cooled to room temperature. The workpiece thus treated received a uniform gray coating of titanium carbide about 30-40 μ thick.

Example 2

This example relates to an embodiment of the invention wherein a degasification was performed only by chemical means, without use of pumps.

The plant employed for this purpose is shown in Fig. 3. It comprises two annealing crucibles of quartz, which can be vacuum-sealed by flanges and are interconnected by a vacuum-tight conduit. The connection between the two crucibles may be controlled by a valve. The specimens 32 to be degasified, which consisted of ledeburitic chromium steel, were placed in the crucible 31, which is then closed by the flange 33. The crucible 34 was filled with a material which will violently absorb oxygen and nitrogen at high temperatures, e.g., chips of titanium or calcium or magnesium. Then the crucible 34 was closed by flange 35 and valve 37 was opened to connect the crucible 34 through the vacuum conduit 36 to the crucible 31. Then the heating unit 38 was passed over the crucible 34 to heat the latter slowly to temperatures of about 600-650° C. At about 400° C. the getter metals began to absorb gas at a progressively increasing rate. The reduction of pressure was observed at vacuum gauge 39. After the pressure had dropped to below about 10^{-3} mm. Hg the heating unit 40 was passed over the crucible 31 to heat the same slowly to temperatures of 900-950° C. A short pressure drop was again observed at temperatures of 600-700° C. After the crucible 31 had been kept at temperatures of 900-950° C. so long that the vacuum was maintained below 10^{-3} to 10^{-4} mm. Hg, the valve 37 was closed and the crucible 31 was allowed to cool to room temperatures. The workpieces were then removed from the crucible and were given titanium carbide coatings as described below.

To provide degasified drawing tools of steel containing 12-13% chromium and 1.9-2.5% carbon with a titanium carbide coating, the drawing tools were micro-finished, i.e., they were polished and given a bright luster especially at the working surfaces. Then they were introduced, by means of a holding device, into a reaction vessel consisting of quartz, which was tightly closed. The air contained in the reaction vessel was expelled and replaced by hydrogen. Then the reaction zone was heated up to the reaction temperature of 900-1000° C. by means of an electric heating aggregate. During heating and during the period required for heating up the workpieces to reaction temperature, purified hydrogen was passed through the reaction vessel. After the workpieces were heated up to reaction temperature, a mixture of hydrogen and hydrocarbons was introduced instead of pure hydrogen, which mixture was prepared by passing hydrogen over carbon at a temperature of 1000° C. For example,

such gas mixture was obtained by filling a quartz tube with carbon, heating such tube up to 1000° C. and passing the hydrogen at this temperature through the tube over the carbon. Then the thus obtained gas mixture which contained 1.9% methane was introduced into the reaction vessel instead of hydrogen.

After introducing the mixture of hydrogen and volatile hydrocarbons, 2 vol. percent titanium tetrachloride was simultaneously introduced into the reaction vessel. The thus obtained gas mixture of titanium tetrachloride, hydrogen and volatile hydrocarbons reacted on the surfaces of the drawing tools, forming a titanium carbide coating. The period required for this treatment depended upon the thickness of the desired coatings. When the reaction was stopped after three hours by suspending the supply of titanium tetrachloride and volatile hydrocarbons, feeding only hydrogen into the reaction zone and cooling in hydrogen to room temperature, coatings of a thickness of about 15–20 μ were obtained on the drawing tools. These coatings were distinguished by a very high surface quality. The surface roughness was around 1.5–2 μ and below.

After applying the coatings, the base metal had a hardness which, according to the cooling speed, was between 450 and 500 kg./mm.²=VPN₃₀ kg.. As this degree of hardness was too low for drawing tools, the base metal was subsequently hardened in the following manner:

The coated tools were put into a steel container, which was only a little wider than the outer diameter of the tools. A few calcium and/or magnesium chips and a small quantity of titanium nitride were placed in the steel container. Then the air in the container was expelled with purified nitrogen and the container welded tight. Subsequently, the container with the drawing tools was slowly heated up to the hardening temperature of the respective tool steel, namely, 940–980° C. for the steels employed in the present example. This temperature was maintained for about 1½ to 2 hours. Then the container with the drawing tools was removed from the heating furnace and quenched in water. After cooling, the container with the drawing tools was put into a holding furnace and exposed to a temperature of 170 to 200° C. for a period of about 2 to 2½ hours to effect tempering of the base metal of the drawing dies. When the container was opened it was found that the titanium carbide coatings had not suffered any damage by such heat treatment, and exhibited the same high polish as before. The heat treatment caused the base metal to assume a hardness of 780 to 840 kg./mm.²=VPN₃₀ kg.. After final polishing during 10–15 minutes, preferably on a band polishing machine, the drawing tools were ready for use.

The heat treatment in the closed tempering bomb in the manner as described above was effected without difficulty, there was no danger of the bomb—even if thin-walled—being burst by excess pressure, as the calcium and/or magnesium chips absorb the nitrogen, and, as the case may be, also traces of oxygen and water vapor contained in the bomb, so that even a considerable reduction in pressure will occur in the container.

Example 3

Deep drawing dies or pistons from steel containing 12% chromium, 2% carbon, 1% tungsten, 0.5% molybdenum and 1% cobalt were to be provided with titanium carbide coatings. For this purpose, a method was chosen in which the titanium halides were formed inside of the reaction vessel, an apparatus as shown in Fig. 1 being used for this purpose. The pistons were to possess a diameter of 27.070 mm. with a tolerance plus 0.010 mm. and minus 0.005 mm.

The steel was first normalized by heating for three hours at 1030° C. followed by slow cooling. Then blanks having the shape of the deep drawing pistons were formed therefrom by turning. The dimensions of the blanks were somewhat above (+0.2 mm.) the desired finished

dimensions. The blanks were then hardened in a known manner by annealing at 980° C. and cooling with compressed air and then tempering at 200° C. in an oil bath. After this treatment the hardness of the blanks was 850 kg./mm.²=VPN₃₀ kg.. The blanks were then ground to the final diameter of 27.07 mm. and polished with a 1 μ diamond paste.

The reaction vessel consisted of heat resistant steel. A rather narrow steel tube, closed at the bottom with a screenplate, was inserted in this vessel. Titanium carbide was placed on this screenplate. A device for holding the workpieces to be provided with a coating was provided below the screenplate. A two-part heating aggregate was used for heating the apparatus, one part of which served for heating the halide forming zone, i.e., the zone containing the titanium carbide, whereas the other part served for heating the carbide forming zone, where the coatings were to be deposited, i.e., the zone containing the workpieces. A lower temperature was maintained in the halide forming zone than in the carbide forming zone.

The pistons, after being degasified according to the invention and micropolished, were introduced into the reaction zone by means of the holding device, then the tube with the screenplate and the titanium carbide was placed above and the apparatus tightly closed. After expelling the air from the reaction vessel, hydrogen was passed through the reaction vessel in such a manner that the hydrogen first flowed over the titanium carbide and then over the cylinders to be coated. By means of the two heating aggregates, the reaction vessel was heated in such a manner that the halide forming zone was heated up to a temperature of 600 to 700° C., and the carbide forming zone up to a temperature of 1000° C. After these temperature conditions were reached, the hydrogen flow was somewhat throttled, and 10 vol. percent hydrogen chloride mixed therewith. In this way, a gas mixture of hydrogen chloride and hydrogen was formed, which reacted in the halide forming zone with the titanium carbide, forming a gas mixture consisting of hydrogen chloride, hydrogen, 2½–3% titanium chloride and the same amount methane with a little hydrocarbon chloride. This gas mixture flowed through the screen into the carbide forming zone, where it contacted with the surface of the machine parts to be coated, and it was heated up to the elevated temperatures. Firmly adhesive, highly smooth titanium carbide coatings deposited on the cylinders, and a gas mixture mainly consisting of hydrogen and hydrogen chloride escaped from the carbide forming zone. After a reaction period of 2½ hours, the supply of hydrogen chloride was stopped and the apparatus briefly flushed with hydrogen. The reaction vessel was cooled down to room temperature by dipping it into water. When the reaction vessel was opened it was found that the workpieces were covered with a titanium carbide coating of a thickness of about 6–10 μ . The coatings exhibited a high luster and had only a very slight surface roughness of about 1½ μ .

The diameter of the deep drawing dies after deposit of the titanium carbide coating was about 27.053 mm. They were placed in acetone without prior tempering and cooled to –70 to –80° C. by gradual addition of Dry Ice and maintained at this temperature for about one hour. The deep drawing dies were then removed from the cooling bath, slowly raised to room temperature and measured. Their diameter then was about 27.090 mm. and the steel base had a hardness of 900 kg./mm.²=VPN₃₀ kg.. Therefore before the deep cooling they were below the lower tolerance limit and afterwards they were above the upper tolerance limit.

The deep drawing dies were then tempered in oil at 200° C. After cooling down to room temperature their diameter was between 27.072 and 27.075 mm., whereas the hardness of the base material was 830 kg./mm.²=VPN₃₀ kg.. The dimensions therefore were within

the tolerance limits while the hardness of the base remained at a satisfactory value. The well coalesced titanium carbide coating withstood the deep cooling and tempering without cracking or peeling off.

Example 4

The improved deposition of titanium carbide coatings on a base material which contained carbon but contained no chromium or only very small amounts of chromium, such as in plain carbon steels and cast iron with flaky or spheroidal graphite, will be described in the following example.

The workpieces, such as guide members for wires and threads, were produced by known methods from plain carbon steel or cast iron. They were freed from adhering dirt, surrounded by chromium-carbide containing material and introduced with the aid of a holding device of comb-like type into the reaction zone of the reaction crucible of the titanium carbide depositing plant. Turnings of steels containing about 12% chromium and 2% carbon were particularly suitable as a chromium-carbide containing material. The introduced workpieces and the turnings formed a loose material. After the workpieces and the chromium-carbide containing material had been introduced, the reaction crucible was closed. It was then heated to the reaction temperature of 950–1000° C. while being flushed with hydrogen. Then the gaseous reaction components were introduced. After the titanium carbide coatings had been deposited and the reaction material had cooled down it was removed from the reaction crucible.

If titanium carbide coatings of predetermined thickness are desired, it must be taken into account that titanium carbide will also deposit on the added chromium-carbide containing material, whereby losses of reaction gas occur. In order to compensate such losses the reactants were added at least with such an excess as was sufficient to coat also the added material with a layer having the same thickness as the layer on the workpiece. For instance, if the surface area, e.g., of the thread guides, was 400 sq. cm. and that of the added chromium-carbide material was 200 sq. cm., 160 liters of hydrogen containing 15 grams vaporized titanium tetrachloride and 160 liters of hydrogen containing 0.3% by volume of vaporized monochlorobenzene forming 1.8% methane were supplied to the reaction zone to form titanium carbide layers having a thickness of about 15 microns. These starting gas mixtures were supplied over a period of 2½–3 hours. The supply of the starting gas mixture was affected by introducing the titanium tetrachloride containing hydrogen and the monochlorobenzene containing hydrogen separately from each other into the reaction zone of the reaction chamber over two separate lines.

When polished sections of the coating zone of the treated samples were examined by a microscope, a chromium-carbide containing inter-layer was found between the titanium-carbide coating and the base material. The titanium-carbide coating had a thickness of 15 microns and the inter-layer was as thick as 5 microns.

Such composite materials are particularly favorable because the chromium-carbide containing inter-layer has a coefficient of thermal expansion which lies between those of titanium carbide and cast iron and will substantially reduce the stresses set up on cooling. At the same time a favorable gradation of the hardness from the hardness of titanium carbide (micro-hardness about 3200–3300 kg./sq. mm.) via the hardness of the chromium-carbide containing inter-layer (micro-hardness about 1300–1500 kg./sq. mm.) to the much lower hardness of the cast iron is provided.

The following example will serve to illustrate an embodiment of the process according to the invention in which the degasification of the base and deposit of the titanium carbide coating is carried out without intermediate cooling to room temperature with reference to

the coating of graphite electrodes. The apparatus employed essentially was the same as that shown in Fig. 3, except that valved conduits were provided in flange 33 for the introduction of the reaction gases (hydrogen, titanium halide and volatile hydrocarbons) and for withdrawal of the exhaust gases during the coating operation. As the temperatures employed during the coating operation were about 1050° C. ($\pm 10^\circ$ C.) the supports for the graphite electrodes to be coated were also of graphite to provide sufficient strength at the high temperatures employed.

Example 5

Finely polished graphite electrodes were introduced into the degasification crucible 31 with the aid of their graphite supports. In this instance crucible 31 also served as the crucible in which the coating operation was effected. Air was pumped out of crucible 31 until a reduced pressure of 10^{-2} mm. Hg was achieved. The pump was then turned off and crucible 31 was then connected by opening valve 37 with evacuated crucible 34 which contained titanium turnings as a getter.

Then the heating unit 28 was passed over crucible 34 to heat the latter slowly to temperatures of about 600–650° C. At about 400° C. the getter metals began to absorb gas at a progressively increasing rate. The reduction of pressure was observed at a vacuum gauge 39. After the pressure had dropped to below about 10^{-3} mm. Hg the heating unit 40 was passed over crucible 31 to heat the same slowly to temperatures of 1000–1050° C. The specimens were maintained at that temperature and the degasification of the specimens was continued until disconnection of vessel 34 by closing valve 37 did not cause an increase in the pressure in the vessel 31 above 10^{-3} mm. Hg.

Valve 37 was then kept closed and the valved conduit serving to introduce a mixture of hydrogen and methane (96.5% hydrogen and 3.5% methane) was opened to fill crucible 31 with such mixture. After the gas pressure in such crucible exceeded atmospheric pressure by about 0.05 atmosphere the exhaust gas conduit was opened and the graphite electrodes heated under a stream of such gas mixture to 1150° C. Thereafter, a stream of a mixture of titanium tetrachloride and hydrogen (3.5% titanium tetrachloride and 96.5% hydrogen) was also introduced in the same quantity and rate as the hydrogen methane mixture. Upon mixture of both gas mixtures in crucible 31 a gas mixture resulted in which the titanium tetrachloride and methane content was half of that in the original individual gas mixture.

Although a portion of the reaction mixture reacted at the surface of the graphite supports the graphite electrodes received titanium carbide coatings of a sufficient thickness of 8–10 μ after a reaction period of about 2 hours.

After the reaction period indicated the supply of the titanium tetrachloride hydrogen mixture was cut off while the hydrogen methane mixture was permitted to continue to pass through the crucible. Heating element 40 was then withdrawn from crucible 31 and such crucible cooled down with compressed air. After cooling to room temperature the graphite electrodes were removed from the crucible and were found to have been coated with a firmly adherent highly lustrous titanium carbide coating.

This application is a continuation-in-part of applications Serial No. 493,710, filed March 11, 1955, Serial No. 586,198, filed May 21, 1956 and Serial No. 655,590, filed April 29, 1957.

We claim:

1. In a process for the deposit of titanium carbide coatings on surfaces of objects by reacting a reaction gas mixture containing hydrogen, a volatile hydrocarbon and a titanium halide, the step which comprises reacting at a temperature between 900° and 1200° C. a reaction gas mixture containing a volatilized titanium halide, hydro-

gen and a hydrocarbon in the presence of the surface of the object upon which the titanium carbide coating is to be deposited, the proportion of the hydrocarbon to the hydrogen in such gas mixture being such that the partial pressure of the hydrocarbon, with reference to methane, in atmosphere, does not exceed 0.047 times X^2 at 900° C. to 0.015 times X^2 at 1200° C., X being the hydrogen partial pressure in atmospheres in said gas mixture, the maximum hydrocarbon partial pressure at temperatures between 900° and 1200° C. being interpolated linearly, in order to deposit a firmly adherent titanium carbide coating which is free of elemental carbon and elemental titanium inclusions on such surface.

2. In a process for the deposit of titanium carbide coatings on surfaces of objects by reacting a reaction gas mixture containing hydrogen, a volatile hydrocarbon and a titanium halide, the steps which comprise degasifying the object to be coated in a vacuum of at least 10^{-3} mm. Hg at a temperature over 800° C. until the partial pressure of the gases in such object does not exceed 10^{-3} mm. Hg and reacting at a temperature between 900° and 1200° C. a reaction gas mixture containing a volatilized titanium halide, hydrogen and a hydrocarbon in the presence of the surface of the degasified object upon which the titanium carbide coating is to be deposited, the proportion of the hydrocarbon to the hydrogen in such gas mixture being such that the partial pressure of the hydrocarbon, with reference to methane, in atmospheres, does not exceed 0.047 times X^2 at 900° C. to 0.015 times X^2 at 1200° C., X being hydrogen partial pressure in atmospheres in said gas mixture, the maximum hydrocarbon partial pressures at temperatures between 900° and 1200° C. being interpolated linearly, in order to deposit a firmly adherent titanium carbide coating which is free of elemental carbon and elemental titanium inclusions on such surface.

3. The process of claim 2 in which the object to be coated is a ferrous metal object and in which such ferrous metal object to be coated is surrounded by a ferrous metal material containing at least 5% of chromium and 1% of carbon when subjected to said reacting gas mixture, whereby a chromium carbide containing intermediate layer is formed on such object prior to the deposit of the titanium carbide coating thereon.

4. The process of claim 3 in which the object to be coated is a cast iron object.

5. The process of claim 2 in which the object to be coated is a ferrous metal object which at least at its surface contains at least 1% of chromium and at least 0.3% of carbon.

6. The process of claim 2 in which the object to be coated is a ferrous metal object and such object after completion of the deposit of the titanium carbide coating thereon is given a heat treatment in an inert medium free of oxygen and oxidizing substances.

7. The process of claim 2 in which the object to be coated is a steel object containing at least 1% of carbon and at least 5% of chromium and such object is quenched in an inert medium directly after completion of the deposit of the titanium carbide coating thereon.

8. The process of claim 2 in which the object to be coated is a ferrous metal object and such object after deposit of the titanium carbide coating is without intermediate tempering cooled to a temperature below -60° C. and subsequently tempered.

9. The process of claim 2 in which the reaction gas mixture is prepared by passing hydrogen over carbon at the temperature employed for the deposit of the titanium carbide coating and the resulting mixture of hydrogen and hydrocarbon is admixed with the titanium halide.

10. The process of claim 2 in which the quantity of titanium halide in the reaction gas mixture is not in excess of that equivalent to the quantity of hydrocarbon contained therein.

11. The process of claim 2 in which said degasification is effected in the presence of titanium shavings.

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