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PROCESS FOR THE DEPOSITION OF TITANIUM CARBIDE COATINGS

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Fig. 1



Fig. 2



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PROCESS FOR THE DEPOSITION OF TITANIUM CARBIDE COATINGS

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The object of the invention relates to a process for improving the deposition of titanium carbide coatings at elevated temperature from an atmosphere which contains at least one titanium halide such as titanium bromide, titanium iodide, titanium chloride in the form of a vapor or gas, hydrogen, and at least one volatile nitrogen- and oxygen-free carbon compound such as hydrocarbons and halogenized hydrocarbons and comprises that the deposition of the titanium carbide coatings is effected in the presence of chromium and carbon, preferably in the form of one or more carbides containing chromium, such as chromium carbides, chromium-iron-carbides etc.

The invention is based on the unexpected discovery that chromium in the presence of carbon has a favorable influence on the deposition of the titanium carbide coatings on iron-base materials such as alloyed steels, plain carbon steels and cast irons. Chromium and carbon may be present on the surface of the workpiece to be coated with titanium carbide; it may also be sufficient, however, if chromium and carbon are present at other points in the reaction zone, being that part of the reaction chamber wherein the deposition of the titanium carbide coating actually takes place.

The process according to the invention may be carried out under conditions permitting the formation of at least one carbide containing chromium.

The process 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 or which has at least been enriched with chromium and carbon at its surface. Such base materials include steels having a diffusion chromium layer, which have been hardened by diffusing carbon therein, as well as steels having chromium and carbon contents sufficient to enable a formation of chromium carbide. Thus the deposition of titanium carbide may be promoted by selecting as base material a steel which has at least on its surface a content of at least 0.3% carbon and at least 1% chromium. Higher contents of carbon and chromium will increase the reaction-promoting effect.

The base materials apparent from the following table have proved per example suitable for the application of titanium carbides thereon by the process of the invention.

	C	Cr	Mo	Ni	V	W	Co	Fe
	(by weight-percents)							
(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	------	------	------	rest.
(7)	1.6	13.5	1.0	------	------	------	2.0	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	1.2	------	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 still contain the usual amounts of silicon and manganese. In most of these steels chromium and carbon are found as double or mixed carbides also containing iron and tungsten, molybdenum and vanadium. The steels 1, 2, 6, 10, 11, 12, 13 and 15 according to the table and besides 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 particularly suitable. The deposition of titanium carbide coatings at temperatures of 900–1050° C. on such steels results in work-pieces 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 get 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.

In a particularly simple embodiment materials containing sufficient amounts of chromium and carbon are coated with carbide layers in the same treating space as the material which is free of chromium and/or carbon or contains only small amounts of said elements.

It has been found that the reaction-promoting effect of carbides containing chromium can be used successfully for the deposition of titanium carbide coatings on carbon steels or cast-iron with flaky or spheroidal graphite, which are free of chromium or contain only very small amounts of chromium, if chromium and carbon are present in the reaction zone. In this case it has been possible to deposit well-formed titanium carbide coatings on said materials at temperatures of 900–1100° C. out of gas mixtures which contain titanium tetrachloride and volatile carbon compounds such as hydrocarbons and halogenized hydrocarbons, such as monochlorobenzene. In these cases it has proved particularly suitable to add chromium and carbon in the form of steels containing at least 1% chromium, preferably more than 5% chromium, and at least 0.5% carbon, preferably 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, e.g. 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.

A carbon steel which is free of chromium itself may be coated in the presence of small lumps of chromium. These chromium lumps may be annealed together with the carbon steel to be coated in a hydrocarbon-containing hydrogen stream at 900–1200° C. before the actual deposition of titanium carbide. To promote the reaction some hydrogen halide may be added to the stream. This will cause the formation of the various phases of the chromium-carbon system on the surface of the chromium.

For economic reasons it will often be advantageous to use chromium- and carbon-containing steels rather than pure chromium carbides for promoting the reaction.

The process according to the invention enables the formation of titanium carbide layers which are thicker and smoother than those obtained by the previously known or proposed processes. The presence of chromium and carbon in elementary form, particularly as carbides containing chromium, promotes the formation of a titanium

carbide layer in 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 regarding 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 somewhat decrease as the thickness of the carbide layer formed is increased.

Titanium carbide coatings free of uncombined titanium or uncombined carbon may be obtained by reacting a titanium halide in a gas mixture containing hydrogen and a quantity of volatile hydrocarbons which is not in excess of that which corresponds to the hydrogen-hydrocarbon equilibrium at the depositing temperature in the presence of the surface upon which the carbide coating is to be deposited, and the quantity of metal halide in said gas mixture is not in excess of that equivalent to the volatile hydrocarbons.

Particularly dense coatings of pure titanium carbide, which have a high luster, will be obtained if the starting reactants (including the base material) are freed from oxygen, oxygen compounds and nitrogen, e.g. by reducing the partial pressure of gases in the metallic base to below 10^{-2} mm. Hg when measured at temperatures of 800 to 1000° C. and depositing the carbide coating on the thus prepared metallic base.

For estimating the amount of the hydrocarbon compound which does cause deposition of elementary carbon, such as soot, it is assumed the said hydrocarbon splits completely up into methane at the temperature of the deposition of titanium carbide coatings. The thus produced methane should not exceed the amount of methane corresponding to the equilibrium between methane, hydrogen and carbon at the temperature of the deposition of the coatings. The amounts of methane corresponding to the equilibrium between methane, hydrogen and carbon are known at different temperatures and are published in technical tables. For estimating e.g. the amount of benzene in the starting gas mixtures which will not cause deposition of elementary carbon at temperatures of 950–1000° C., it is found the amount of methane corresponding to the equilibrium of methane, hydrogen and carbon does not exceed 1.5–2% per volume at said temperature and at atmospheric pressure. From the aforementioned assumption about the splitting-up of hydrocarbons at high temperatures follows the amount of benzene which does not exceed 0.25–0.33% per volume of the starting gas mixtures for the deposition of the titanium carbide coatings.

The amount of titanium halogenide being equivalent to the volatile hydrocarbon is easily calculated by the assumption that every atom of carbon of said carbon compound will be able to form one molecule of titanium carbide by combining with one atom of titanium.

In the following the invention is demonstrated by some examples:

Example 1

In automatic machine tools, adjusting elements of high resistance to wear are required. In order to ensure a high wear resistance of said adjusting elements, the elements may be formed of steel and provided with a titanium carbide coating. The performance of the process according to the invention may now be described more fully with reference to an example consisting in the application of titanium carbide coatings to such adjusting elements.

The adjusting elements are made from a steel which has approximately the following composition: 4–8% chromium, 0.8–1.5% carbon, 0.8–2% molybdenum, balance iron. The adjusting elements are first freed from adhering dirt, residual matter from the machining, such as cooling fluids, and residual oxides, and are annealed in a vacuum of about 10^{-2} to 10^{-4} mm. Hg at temperatures of 900–950° C. to free them from dissolved gases, particularly from nitrogen. Then the adjusting elements are introduced with the aid of a holding device into the reaction zone of the reaction chamber of the titanium carbide deposition plant. The reaction chamber is now closed with the aid of a flange, through which the supply and discharge lines for the gases extend. Thereafter the air is evacuated out of the reaction chamber, and the latter is filled with purified hydrogen. The reaction zone of the chamber is flushed with hydrogen and is heated to the reaction temperature at the same time; thus any residual oxides still present will be reduced. After the reaction zone has reached the reaction temperature of 950–1000° C. it is supplied with a mixture of titanium chloride and hydrogen and with a mixture of methane and hydrogen. As a result, titanium carbide coatings are deposited on the workpieces and partly also on those parts of the holding device being introduced into the reaction zone.

The reaction time will depend on the desired thickness of the surface-layers and the area of the entire surface to be coated with titanium carbide. In this connection it must be taken into account that with an increase in the amount of deposited titanium carbide the rate of deposition will decrease somewhat owing to a lack of a sufficient equilibrium adjustment. In order to provide a surface of 800 sq. cm. with a titanium carbide coating 15 microns thick, the reaction space has to be supplied with about 21 grams titanium tetrachloride and 250 litres of a mixture of hydrogen and methane, containing about 1.5% methane by volume. These gases are supplied within about three hours. Thereafter the supply of titanium tetrachloride and methane is discontinued and the reaction chamber while being flushed with hydrogen is cooled to room temperature by being externally cooled by means of a stream of air, then the adjusting elements coated with titanium carbide are removed from the reaction space. The adjusting elements will then have lustrous coatings of practically pure titanium carbide in the said thickness of layer. The steel which has been used is particularly suitable for having titanium carbide deposited thereon and has the additional advantage that under the cooling conditions described it assumes practically its maximum hardness, amounting to a Rockwell C hardness number of 61 to 62. For this reason the adjusting elements thus treated consist of hardened steel having a titanium carbide coating of even much greater hardness.

It is obvious that the process is not restricted to the application thereof to adjusting elements but lends itself to the deposition of titanium carbide coatings in the manner which has been described on workpieces of any desired shape, particularly on tools.

Particularly uniform and dense coatings may be deposited in the manner described on steels which contain about 11–15% chromium, 1.5–2.5% carbon. After this material has been provided with a titanium carbide coating it may be hardened to a Rockwell C hardness number of about 64–66 by a known additional heat treatment in a non-oxidizing atmosphere and has been used with good results for cold-working tools such as cold-drawing dies and powder-pressing dies. But the additional heat treatment in a non-oxidizing atmosphere may be avoided by making said tools of steels containing 10–15% chromium, 1.5–2.5% carbon and additions of tungsten and/or molybdenum totalling 1.3–3%. Those steels have Rockwell C hardness numbers of 60–65, depending upon the size and shape of the tools, after being treated for the deposition of the titanium carbide coatings in the manner as described before.

On the other hand, an attempt to deposit titanium carbide coatings on plain carbon steels in the absence of chromium and carbon under conditions which are perfectly identical in all other respects to those of Example 1

will result in a much reduced deposition of titanium carbide whereas considerable quantities of unconsumed titanium tetrachloride and methane leave the reaction tube together with the waste gas. This applies also to steels which contain chromium but are practically free of carbon, e.g. to stainless steels containing about 18% chromium and 8–10% nickel.

Example 2

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

The workpieces, such as guide members for wires and threads, are made by known methods from plain carbon steel or cast-iron. They are free from adhering dirt, surrounding 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. The turnings of steels containing about 12% chromium and 2% carbon are particularly suitable as a chromium-carbide containing material. The introduced workpieces and the turnings form a loose material. After the workpiece and the chromium-carbide containing material have been introduced the reaction crucible is closed as has been described in Example 1. It is then heated to the reaction temperature of 950–1000° C. while being flushed with hydrogen. Then the gaseous reaction components are introduced. After the titanium carbide coatings have been deposited and the reaction material has cooled down it is 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 occur. In order to compensate such losses the reactants are added at least with such an excess as is 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, is 400 sq. cm. and that of the added chromium-carbide material is 200 sq. cm., 160 litres of hydrogen containing 15 grams vaporized titanium tetrachloride and 160 litres of hydrogen containing 0.3% by volume of vaporized monochlorobenzene are supplied to the reaction zone to form titanium carbide layers having a thickness of about 15 microns. These starting gas-mixtures are supplied within 2½–3 hours. The supply of the starting gas-mixtures is performed in such a manner that the titanium tetrachloride containing hydrogen and the monochlorobenzene containing hydrogen are introduced separately from each other into the reaction zone of the reaction chamber by means of two separated lines.

When polished sections of the coating zone of the treated samples are examined by means of a microscope a chromium-carbide containing inter-layer is found between the titanium-carbide coating and the base material. The titanium-carbide coating has a thickness of 15 microns and the inter-layer may be as thick as 5 microns.

Example 3

A variation of the procedure explained in Example 2 will be described in the present example. The workpieces, e.g. of nodular cast-iron are prepared as described by Examples 1 and 2, introduced into the plant together with the turnings, and heated to the reaction temperature of 950–1000° C., as has been described in Example 2. After the reaction temperature has been reached some (0.1% p.vol.) purified hydrogen chloride is added to the hydrogen stream. To avoid a decarburization of the steels or cast-iron this hydrogen chloride may be replaced by monochlorobenzene vapor in a concentration of up to about 0.3% by volume. In that gas mixture the workpieces of chromium-free steel or cast-iron are annealed for about 1½ hours together with turnings of steel containing about 12% chromium and 2% carbon and only thereafter the titanium carbide is deposited thereon as has been described in Example 2, followed by cooling the workpieces.

By this way of deposition titanium carbide layers about 20–25 microns thick on a chromium-carbide containing interlayer, which may be as thick as 35 microns, are obtained on cast-iron with spheroidal graphite on an area of about 400 sq. cm., the spherulites originally contained adjacent to the surface being entirely or partly transformed to titanium carbide and chromium carbides.

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

The structure of the coatings applied according to Examples 2 and 3 is shown in Figs. 1 and 2, respectively with a 300-fold magnification.

Fig. 1 shows a coating produced according to Example 2. In this figure a_1 is the titanium carbide coating, b_1 the chromium-carbide containing interlayer and c_1 the cast-iron base material.

Fig. 2 shows a coating which has been deposited according to Example 3. In this figure a_2 is the titanium carbide coating, b_2 the chromium-carbide containing interlayer, c_2 the base material consisting of cast-iron with spheroidal graphite, and e and f respectively are spheroidal graphite completely or partly transformed into spheroidal carbides.

In the examples the titanium was supplied to the reaction zone in the form of titanium tetrachloride. In a similar manner the titanium may be introduced by means of any other titanium halide.

It is to be pointed out that the invention is not limited to the use of only those steels and volatile carbon compounds mentioned by the examples and titanium chloride. It is to be understood that every other steel containing more than 0.3% carbon and 1% chromium may be used as base material. In similar manner as described by the examples titanium may be introduced by means of any other titanium halide while carbon may be supplied by any other nitrogen- and oxygen-free carbon compound. The deposition temperature for the treating of high-alloyed steels, such as those of the type 15 of the table, may be as high as 1200° C.

What is claimed is:

1. In a method for the deposition of titanium carbide coatings, the steps which comprise heating an iron base material up to a temperature of 900–1200° C. in a chamber, reacting titanium halide with hydrogen and at least one volatile carbon compound of the group consisting of hydrocarbons and hydrocarbon halides in contact with chromium and solid carbon in said chamber at said temperature to deposit a titanium carbide coating over said material.

2. A method as in claim 1 in which said chromium and said solid carbon is present as a carbide containing chromium.

3. A method as in claim 1 in which said chromium and said solid carbon are present at least on the surface of the material to be coated.

4. A method as in claim 3 in which the base material to be coated is a steel containing at least on its surface at least 1% chromium and at least 0.3% carbon.

5. A method as in claim 4 in which said steel contains more than 5% chromium and more than 1% carbon.

6. A method as in claim 4 in which said steel contains 1–3% molybdenum and tungsten.

7. In a method for the deposition of titanium carbide coatings, the steps comprising heating an iron base material which contains carbon and contains substantially no chromium up to a temperature of 900–1200° C. in a chamber containing steel which contains chromium and carbon, reacting titanium halide with hydrogen and at least one volatile carbon compound of the group consisting of hydrocarbons and hydrocarbon halides in said chamber at said temperature to deposit a titanium carbide coating on said iron base material.

8. A method as in claim 7 in which said iron base material to be coated is a plain carbon steel.

9. A method as in claim 7 in which said iron base material to be coated is cast iron.

10. A method as in claim 9 in which said cast iron is cast iron with spheroidal graphite.

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