

Jan. 5, 1971

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3,553,038

METHOD FOR FORMATION OF A TITANIUM CARBIDE SURFACE LAYER ON
TITANIUM AND TITANIUM ALLOY PARTS

Filed Oct. 21, 1966

4 Sheets-Sheet 1

FIG. 1

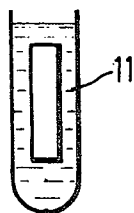


FIG. 1a

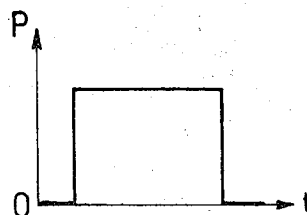
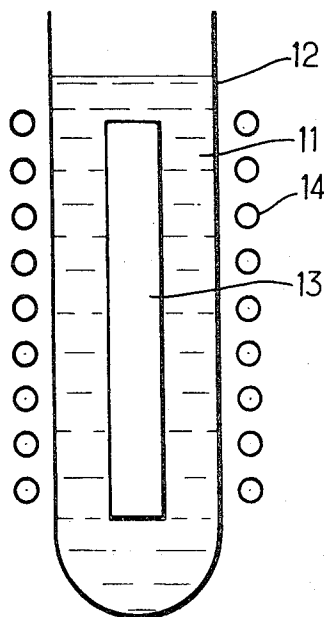


FIG. 1b



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FIG. 2

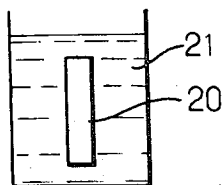


FIG. 2a

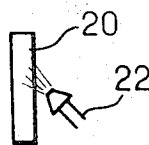


FIG. 2b

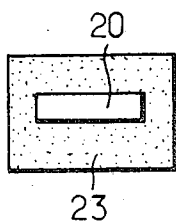


FIG. 2c

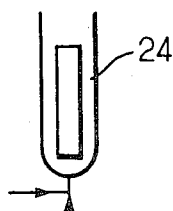


FIG. 2d

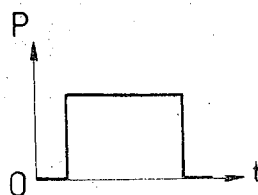
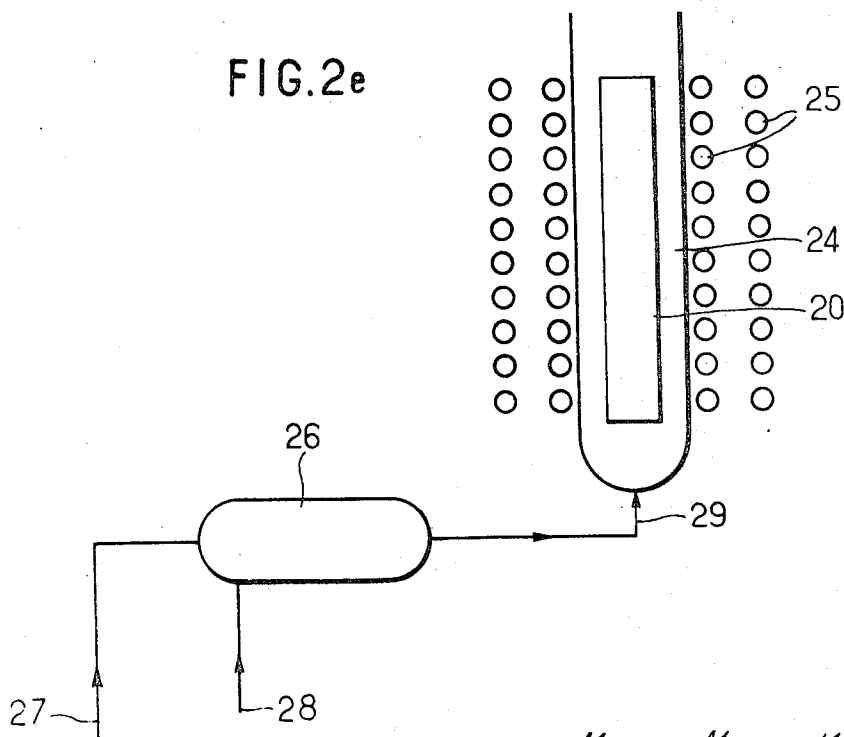


FIG. 2e



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FIG. 3

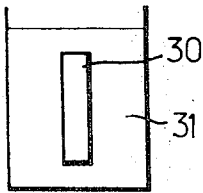


FIG. 3a

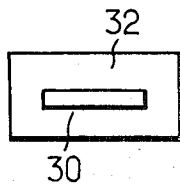


FIG. 3b

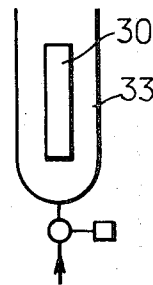


FIG. 3c

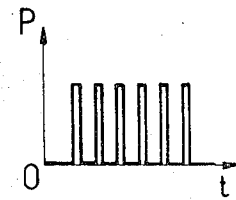
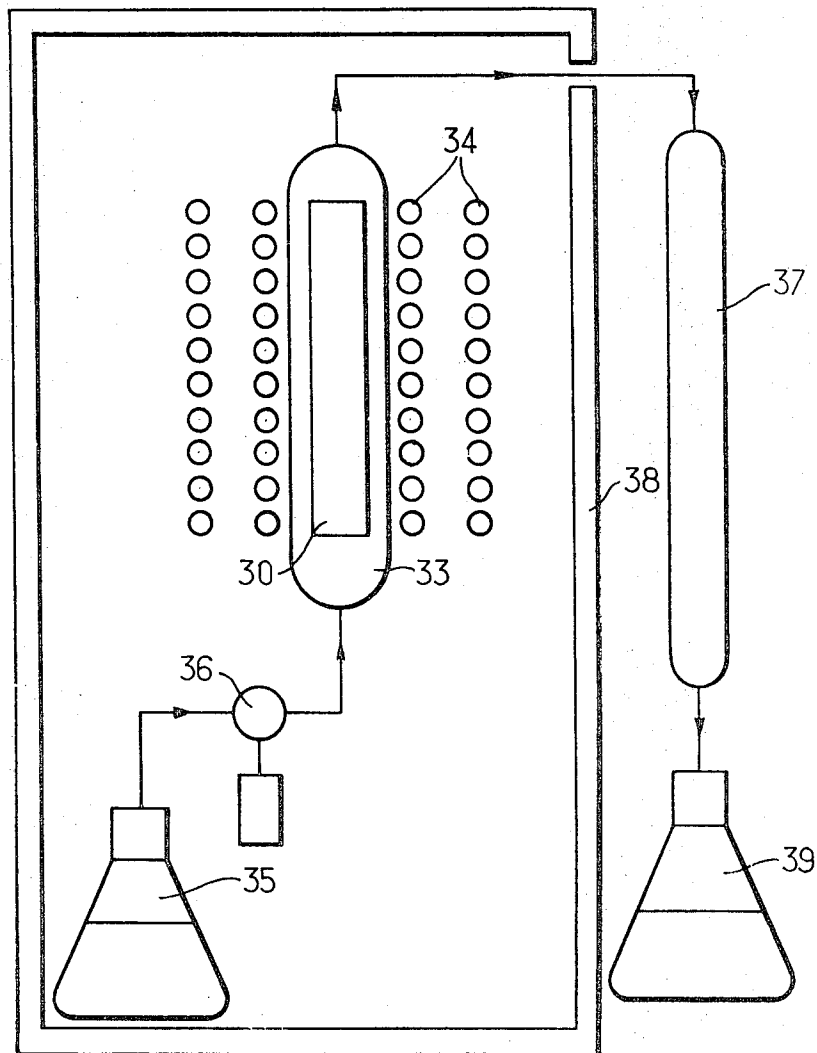


FIG. 3d



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FIG. 4

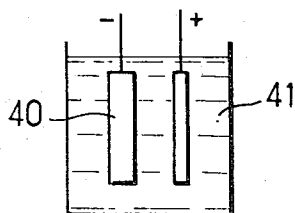


FIG. 4a.

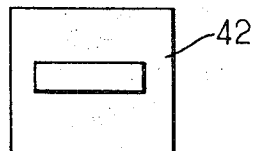


FIG. 4b

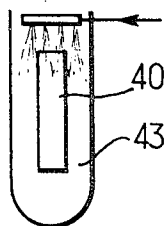


FIG. 4c

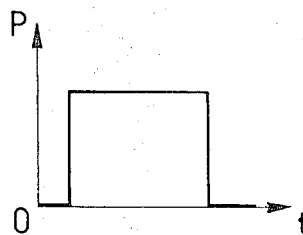
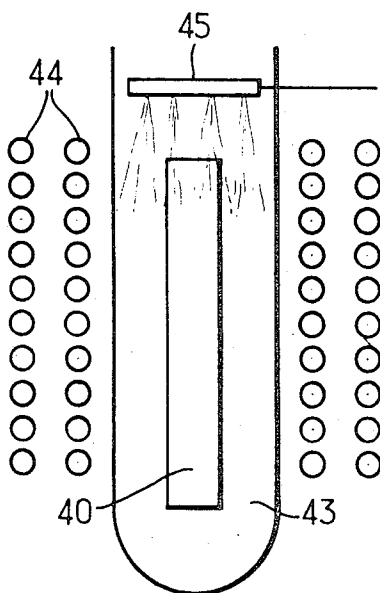


FIG. 4d



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19 Claims

ABSTRACT OF THE DISCLOSURE

A method of formation of a layer of titanium carbide at the surface of a component of titanium or titanium alloy in which the said component is associated with a fluid medium having a base of a carbon compound such as carbon disulphide or carbon tetrachloride or a mixture of these two, and is subjected in said medium to a heat treatment of short duration by high frequency current, bringing the surface of said component to a temperature higher than 1100° C. and preferably higher than 1350° C. The invention also comprises the components or parts made by this method.

The present invention relates to a method of commercial production of a layer of titanium carbide on the surface of a part of titanium or of titanium alloy.

At the present time, the use of titanium in mechanical engineering is becoming increasingly developed, but its applications are limited by the two following particular characteristics of titanium:

(1) Its easy and very rapid oxidation at temperatures below 500° C.;

(2) Its poor frictional qualities.

These two defects can be remedied, that is to say the oxidation of a titanium surface can be reduced and its seizure under considerable mechanical forces can be prevented, by proceeding to conversion of the superficial layers of the metal to titanium carbide.

Up to the present time, various methods have been proposed which all have the disadvantages, on the one hand of being too complicated and too expensive to have profitable industrial applications, and on the other hand of only permitting the production of layers of a thickness of the order of one micron or even a few fractions of a micron, which are entirely inadequate for parts in the usual applications.

The known methods generally comprise prolonged heating for at least four hours at a temperature below 1100° C.

The present invention has for its object a simple method of carburization of a part made of titanium or titanium alloy, to a suitable thickness.

According to the invention, a method of obtaining a layer of titanium carbide on the surface of a part of titanium or titanium alloy is characterized in that the part of titanium or titanium alloy is subjected, in a fluid medium with a base of a carbon compound such as carbon sulphide or carbon tetrachloride or a mixture of both, to a heat treatment of short duration by high frequency, bringing its surface to a temperature higher than 1100° C. and preferably higher than 1350° C.

The medium with a base of carbon sulphide and/or carbon tetrachloride is free from the drawbacks of hydrocarbons, in which the hydrogen is a poison for titanium, of oxygenated compounds which would form harmful oxides at a temperature above 1100° C., and of certain dangerous and costly halogenides.

The medium with a base of carbon sulphide and/or tetrachloride may be liquid or gaseous. The carbon sul-

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phide and carbon tetrachloride are in the liquid state at ordinary temperatures and are gaseous at temperatures exceeding 50° C. They may therefore be utilized in the liquid or gaseous state, diluted or not in a neutral gas. It may be advantageous to add to the medium a suspension of graphite, of sulphur or of alkaline carbides. Furthermore, a discontinuous supply of the carburizing agent may be favourable.

The method according to the invention may be carried out in various ways and in particular in the following forms of execution:

(1) The carburizing agent comprises carbon sulphide and/or carbon tetrachloride in the liquid state, filling a chamber which receives the part to be treated;

(2) The carburizing agent comprises carbon sulphide and/or carbon tetrachloride in the liquid state filling the chamber with agitation while receiving in suspension, carbon, sulphur or alkaline carbides;

(3) The carburizing agent (carbon sulphide or carbon tetrachloride or a mixture of the two) in the liquid state is spread in the form of a shower into the interior of the chamber;

(4) The carburizing agent passes through the chamber in the vapour state at a temperature higher than 50° C.;

(5) The carburizing agent in the vapour state is conveyed through the chamber by a flow of neutral gas at a temperature higher than 50° C.;

(6) The carburizing agent in the vapour state, at a temperature higher than 50° C., passes through a bed of graphite, sulphur or alkaline carbides, thus creating in the chamber a fluidized bed of these elements;

(7) The carburizing agent in the vapour state, conveyed by a flow of neutral gas at a temperature higher than 50° C., passes through a bed of graphite, sulphur or alkaline carbides, thus producing a fluidized bed of these elements;

(8) The carburizing agent is sent by short and repeated puffs into a flow of neutral gas at a temperature higher than 50° C., which passes through the chamber;

(9) The carburizing agent in the vapour state, diluted in a neutral gas at a temperature higher than 50° C., is sent into the chamber by short and repeated puffs.

According to a further characteristic feature of the invention, the heating of the part is obtained by electric currents induced in the body of the part by an appropriate inductor through which passes an electric current having a frequency of at least 0.2 megacycle and preferably of at least 0.4 megacycle, supplying a power of at least 40 kw./sq. dm. for a pre-determined short duration not exceeding 3 to 5 minutes and preferably 190 seconds.

In one form of embodiment the heating is carried out in a single continuous operation, the power being applied to the inductor continuously during the short pre-determined period.

In an alternative form, the heating is effected in a discontinuous manner by applying the power to the inductor for short periods at regular intervals, the total time of application of the power to the inductor not exceeding the pre-determined short period.

When the method according to the invention is used to treat the part of titanium or titanium alloy, it is found that with a very simple apparatus, with products of low cost and a very brief heating time at high frequency, there are obtained layers of titanium carbide which are perfectly adherent, regular, homogeneous, having a hardness greater than 1.800 HV and having a thickness exceeding 5 microns. The parts thus treated have remarkable properties of resistance both to seizure and to oxidation.

In addition, the heating is so short that the heat does not have the time to penetrate into the interior of the

part. The structure of the titanium thus remains intact beyond a small depth, and the mechanical properties of elongation, striction, resilience and elastic limit are only reduced to a negligible extent.

A test sample of titanium alloy having 6% of aluminium and 4% of vanadium, 6 mm. in diameter and 50 cm. in length, treated by the method according to the invention and set in rotation at 760 r.p.m., gripped between two jaws of 35 NCD 6 steel with a load of 1000 Newtons, rotates for 250 seconds before creeping, without either cooling or lubrication, whereas the same sample untreated seizes after 1 to 5 seconds of rotation under the same conditions.

In accordance with other arrangements of the invention, the treatment proper is preceded by a pre-treatment and/or a surface preparation.

In one method of carrying out the pre-treatment, the part is heated to a temperature comprised between 600 and 850° C. for a time comprised between 1 and 20 hours in a chamber filled with graphite, which produces a saturation in carbon in the dissolved state of the superficial layer of the part, which facilitates the subsequent carburization treatment.

In an alternative form of pre-treatment, the part is given a metallic coating having a thickness comprised between 1 and 10 microns deposited on its surface, either by electrolysis or by metallization under vacuum, or by any other suitable means, this metallic layer being then diffused at a temperature comprised between 600 and 850° C. for a time of between 1 and 20 hours. This treatment produces at the surface of the part a layer having a melting temperature higher than that of titanium or of the titanium alloy of which it is composed, which makes it possible to carry out the carburization treatment at a higher temperature. The metal deposited is chosen so that its melting temperature is higher than that of titanium and that the diagram of solidification of the mixture of the titanium with the metal does not have any eutectic. According to the invention, the metal deposited is molybdenum, tungsten or platinum.

For the surface preparation, the part is subjected to one or more of the following operations:

- (1) The part is de-greased in a chlorated solvent or preferably in acetone;
- (2) The part is subjected to chemical attack, for example by immersing it for 10 seconds in a bath having the following composition:

	Percent by volume
Hydrofluoric acid at 48%	18.5
Concentrated nitric acid	2.5
Water	79.0

- (3) The part is subjected to a super-finish of the vapour-blast type;

- (4) The part is de-gasified under a vacuum of at least 10⁻⁴ millimetre of mercury at a temperature comprised between 600 and 650° C. for a period exceeding 5 hours.

The operation No. 1 is intended to remove the greater part of the stains and dirt from the part. Operations No. 2 and No. 3 have the purpose of removing the coating of oxide which may soil the surface. Operation No. 4 removes from the part the gases which it has absorbed and which may adversely affect the carbonization treatment.

The present invention has also for its object the parts of titanium or titanium alloy obtained by the above method and having a large superficial thickness of titanium carbide, greater than 5 microns, which permit of excellent performances.

Forms of embodiment of the invention are described below, by way of non-limitative examples, reference being made to the accompanying drawings, in which:

FIG. 1 illustrates the type of medium adopted for the carburization in a first example;

FIG. 1a illustrates the method of heating adopted for the carburization in the first example;

FIG. 1b is a diagrammatic view of an apparatus for effecting the carburization following the first example;

FIG. 2 illustrates the method of de-greasing a part with a view to its carburization following a second example;

FIG. 2a illustrates a method of super-finishing the part by means of a vapour blast according to the second example;

FIG. 2b illustrates a method of pre-treatment of the part following the second example;

FIG. 2c illustrates the type of medium adopted for the carburization following the second example;

FIG. 2d illustrates the method of heating adopted for the carburization following the second example;

FIG. 2e is a diagrammatic view of an apparatus for carrying into effect the carburization following the second example;

FIG. 3 illustrates a method of de-greasing a part with a view to its carburization following a third example;

FIG. 3a illustrates a method of degasifying this part following the third example;

FIG. 3b illustrates the type of medium adopted for the carburization according to the third example;

FIG. 3c illustrates the method of heating adopted for the carburization following the third example;

FIG. 3d is a diagrammatic view of an apparatus for carrying into effect the carburization following the third example;

FIG. 4 illustrates a pre-treatment of a part for the purpose of its carburization following a fourth example.

FIG. 4a illustrates a method of diffusion under vacuum applied to this part in accordance with the fourth example;

FIG. 4b illustrates the type of medium adopted for the carburization according to the fourth example;

FIG. 4c illustrates the method of heating utilized for the carburization following the fourth example;

FIG. 4d is a diagrammatic view of an apparatus for carrying out the carburization according to the fourth example.

EXAMPLE 1

Reference will be made to FIGS. 1, 1a and 1b.

There are mixed together in parts by weight, 95% of carbon disulphide and 5% of carbon tetrachloride.

In the liquid thus obtained and stirred, there is put in suspension colloidal graphite at the rate of 50 grams per litre, which gives the mixture 11 (see FIG. 1).

In a receptacle 12 (FIG. 1b) filled with the mixture 11, there is placed a Faville test-sample 13 made from a titanium alloy TA 6 V and having a diameter of 6.5 mm. and a length of 40 mm.

Around this test-sample is arranged a copper inductor 14 composed of eight turns of 6 mm. in diameter, wound on a cylinder on 40 mm. in diameter.

The inductor is supplied with a power of 16 kw. at a frequency of 1 megacycle. The heating period does not exceed 2 seconds. This heating is continuous, as shown in the diagram of FIG. 1a, in which the time has been plotted in abscissae Ot and the power applied to the inductor in ordinates OP.

It is found that after the treatment, the test-sample of TA 6 V alloy has been carburized to a depth of 100 microns. Its maximum hardness thus obtained, measured with a micro-hardness-meter under a load of 50 grams, is 1900 HV.

EXAMPLE II

Reference will be made to FIGS. 2, 2a, 2b, 2c, 2d and 2e.

A test-sample 20 similar to the test-sample 13 of Example 1, is first subjected to de-greasing with acetone 21 (see FIG. 2) and a finishing treatment by vapour-blast 22 (FIG. 2a), and is pre-treated by being placed in a chamber filled with graphite 23 (FIG. 2b) heated for 10 hours at a temperature of 750° C.

The test-sample 20 is then placed in a chamber 24 (FIGS. 2c and 2e) at the centre of a double-winding inductor 25 consisting of two concentric layers of eight turns each of copper tube of 4 mm. in diameter, wound on cylinders of 25 mm. and 45 mm. in diameter.

A flow-rate of 20 litres per minute of a neutral gas, preferably argon, at a temperature of 120° C. is introduced at an inlet 27 of a mixer 26 which receives through another inlet 28 a flow of 4 litres per minute of carbon disulphide vapour superheated to 120° C.

The gaseous mixture thus obtained is extracted from the mixer 26 and is introduced at 29 into the chamber 24.

The treatment according to the invention is then effected with the following characteristics:

Power available at the inductor: 20 kw.;

Frequency: 0.5 megacycle;

Duration of heating: 0.8 second.

The heating (see FIG. 2d) is continuous as in Example 1.

After treatment, the test-sample shows in micrographic section a uniform and adherent layer of 0.02 mm. in thickness of titanium carbide, the hardness of which, measured on the micro-hardness-meter under a load of 50 grams, is 2400 HV.

EXAMPLE III

Reference will be made to FIGS. 3, 3a, 3b, 3c and 3d.

The carrying out of the invention in accordance with the present Example III has the advantage of providing a very accurate control of the thickness of the layer of carbide.

The test-sample 30, similar to the test-sample of the previous examples, is de-greased with acetone at 31 (see FIG. 3) and then degasified by heating to 800° C. in a vacuum furnace 32 (FIG. 3a). It is then placed in a chamber 33 (FIGS. 3b and 3d) at the centre of an inductor 34 similar to the inductor 25 of Example II.

A flask 35 containing liquid carbon disulphide is coupled to the lower extremity of the chamber 33 by an electro-magnetic valve 36. From the upper extremity of the chamber 33 passes a tube which conducts the carbon disulphide vapours into a condenser 37. The assembly comprising the flask, the valve and the chamber is enclosed in a casing 38 which is maintained at a temperature of 55° C.

The treatment in accordance with the invention is then carried out as follows: the valve 36 opens for 0.1 second in order to permit the passage of about 15 cubic centimetres of carbon disulphide vapour. When the valve is closed, a power of 30 kw. supplied by a current of 1.5 megacycles is applied for 0.1 second to the inductor 34. The cycle is repeated every 15 seconds for 5 minutes. The excess of carbon disulphide vapour which has not taken part in the reaction is condensed in the condenser 37 and is collected in a flask 39.

There can be seen in FIG. 3c a diagram showing this form of discontinuous heating.

The test-samples thus treated show by micrographic examination, a perfectly uniform layer of 56 microns having great uniformity and a hardness of 2000 HV under 50 grams.

EXAMPLE IV

Reference will now be made to FIGS. 4, 4a, 4b, 4c and 4d.

A test-sample 40 taken from an alloy TA 6 V of 12 mm. in diameter and 80 mm. in height is coated by electrolytic treatment at 41 (FIG. 4) with an electrolytic deposit of molybdenum of 7 microns in thickness and is then subjected at 42 (FIG. 4a) to a diffusion treatment at a temperature of 760° C. for a period of 18 hours under a vacuum of 10⁻⁵ mm. of mercury.

The test-sample 40 is then placed (FIGS. 4b and 4d) in a chamber 41 at the centre of an inductor 44 constituted by two layers of 10 turns of copper tube of 4 mm.

in diameter. The height of the inductor is 60 mm. and the respective diameter of the layers are 30 mm. and 50 mm.

At the upper extremity of the chamber, a spraying device 45 atomizes liquid carbon tetrachloride.

The treatment according to the invention is then carried out with the following characteristics:

Power supplied to the inductor: 70 kw.;

Frequency of the current: 1.5 megacycles;

Period of heating: 0.7 second.

The heating is continuous, as shown in FIG. 4c.

The carburized layer thus obtained has a thickness of 60 microns and a hardness of 1700 HV at 50 grams.

What I claim is:

1. A method for producing a layer of titanium carbide at the surface of a part of titanium or titanium alloy, in which said part of titanium or titanium alloy is subjected, in a fluid medium with a base of a carbon compound selected from the group consisting of carbon disulphide, carbon tetrachloride, and mixtures thereof, to a thermal treatment of short duration by high frequency current, bringing the surface of said part to a temperature higher than 1100° C.

2. A method as claimed in claim 1, in which the surface of said part is brought to a temperature higher than 1350° C.

3. A method as claimed in claim 1, in which said medium further comprises graphite, sulphur or alkaline carbides.

4. A method as claimed in claim 1, in which said fluid medium is a liquid filling a chamber adapted to receive said part to be treated.

5. A method as claimed in claim 3, in which said liquid is agitated and receives, in suspension, carbon, sulphur or alkaline carbides.

6. A method as claimed in claim 1, in which said fluid medium is a liquid atomized in the form of a spray on the part to be treated.

7. A method as claimed in claim 1, in which said fluid medium is constituted by a flow in the vapour state at a temperature higher than 50° C.

8. A method as claimed in claim 7, in which said flow is conveyed by a neutral gas.

9. A method as claimed in claim 7, in which said flow passes through a bed of graphite, sulphur or alkaline carbides.

10. A method as claimed in claim 7, in which said flow is effected in short and repeated puffs.

11. A method as claimed in claim 1, in which the heating of said part is produced by electric currents induced in the body of said part by an inductor through which passes an electric current at a frequency of at least 0.2 megacycle and preferably of at least 0.4 megacycle, supplying a power of at least 40 kw./sq. dm. for a brief pre-determined duration less than 3 to 5 minutes and preferably less than 190 seconds.

12. A method as claimed in claim 11, in which the electric power is applied to said inductor continuously during said pre-determined duration.

13. A method as claimed in claim 11, in which the electric power is applied to said inductor in a discontinuous manner during the course of successive spaced-apart periods of time, the total of which corresponds to said pre-determined duration.

14. A method as claimed in claim 1, in which said part is subjected to a pre-treatment by being heated to a temperature comprised between 600 and 850° C. for a period of between 1 and 20 hours in a chamber filled with graphite.

15. A method as claimed in claim 1, in which said part is subjected to a pre-treatment by being coated with a layer of metal such as molybdenum, tungsten or platinum, said layer having a thickness comprised between 1 and 10 microns, and being then diffused at

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a temperature of between 600 and 850° C. for a time comprised between 1 and 20 hours.

16. A method as claimed in claim 1, in which said part is subjected before treatment to a surface preparation by de-greasing in a solvent such as acetone.

17. A method as claimed in claim 1, in which said part is subjected before treatment to a surface preparation by immersion in a bath comprising hydrofluoric acid and nitric acid.

18. A method as claimed in claim 1, in which said part is subjected before treatment to a surface preparation by a vapour-blast.

19. A method as claimed in claim 1, in which said part is subjected before treatment to a surface preparation by degasifying under a vacuum of at least 10^{-4} millimetre of mercury at a temperature comprised between 600 and 850° C. for a time longer than 5 hours.

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G. K. WHITE, Assistant Examiner

U.S. Cl. X.R.

148—20.6, 32