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**W-8000 München 90 (DE)**(54) **METHOD AND DEVICE FOR PLASMA-DETONATION WORKING OF METAL ARTICLES.**

(57) A method for plasma-detonation working of metal articles provides for filling a reaction chamber (1) with a combustible gas mixture and with a powder material and introducing into the chamber (1), in particular, an element selected from groups III, IV, V, VI of the periodic system of elements, after which detonation burning of the combustible gas mixture is initiated outside the chamber (1) and the electric current is passed through the combustion products of the mixture, the powder material and the introduced element. For that purpose, in a device implementing the method, a nozzle (4) for introducing said element into the chamber (1) is provided, in particular, in the wall of the chamber (1).

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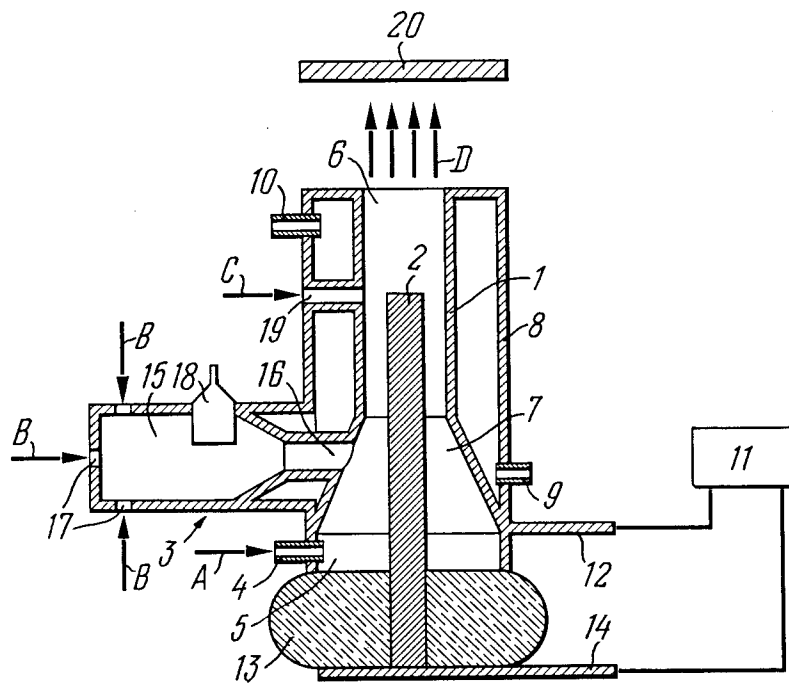


FIG.1

## Field of the Invention

The present invention relates to methods of treatment of metal products and to apparatus for effecting same and, more particularly, the invention relates to methods of plasma-detonation treatment of metal products and to apparatus for performing such methods.

## Prior Art

Known in the art is a method of plasma-detonation treatment of metal products including treatment of metal products by a plasma beam (A.G. Grigoryants, "Fundamentals of Laser Treatment of Materials", "Mashinostroenie" Publishers, Moscow, 1989).

In this method the gas-vapour layer of a surface being hardened is disintegrated by a light beam and plasma is formed which absorbs the light beam energy and acquires energy sufficient for heating the metal surface and alloying it with the plasma components.

This method is disadvantageous in a low coefficient of energy utilization (3-5%) due to the loss of energy being converted from electricity into light and then from light into hot gas energy (plasma).

Furthermore, since the plasma stream is formed in the boundary region of the product, it is difficult to add the alloying elements in the form of a gas and their mixtures.

Also known in the art is an apparatus for plasma-detonation treatment of metal products effecting the above method and comprising a solid-state pulse laser, a system of supply of gases and powdery material to the treatment zone and units for mounting and manipulation of the product (A.G. Grigoryants, "Fundamentals of Laser Treatment of Materials", "Mashinostroenie" Publishers, Moscow, 1989).

In this apparatus a laser generates a pulsed light flux directed to the surface of a product to be treated. Located in the working area of the product is an adapter having nozzles to supply powdery materials and gases. Some gases and powdery materials occurring in the laser beam having a diameter of 3-5 mm are heated and carried to the surface being hardened and interact with it. A larger portion of the gas and powdery material  $\approx 80\%$  are drawn away and do not react with the surface being hardened, and this increases the powder consumption.

In the Soviet practice there is known a method of plasma-detonation treatment of metal products including the steps of filling a reaction chamber with a combustible gas mixture and powdery material, detonation combustion of the gas mixture and passage of an electric current through the products of combustion of the combustible gas mixture and powdery material.

In this method propane (butane), oxygen and air in a ratio of 1:5:3 are used as a combustible gas mixture and fusing powders are used as a powdery material.

The introduction of a powdery material into the reaction chamber results in heating of the powdery material, accelerating it to a high velocity when it flies towards the product and forming a hardened and spray-coated layer on the product surface. In this case, the high temperature of the products of combustion (plasma) results in evaporation of elements with a low melting point constituting the powdery material, thereby deteriorating the quality characteristics of the hardened and spray-coated layers. The powdery material is destroyed resulting in poor adhesion of the layers with the product surface and low wear resistance of the final product.

In the Soviet practice there is also known an apparatus for plasma-detonation treatment of metal products effecting said method and comprising a reaction chamber, an electrode installed inside the reaction chamber and a detonation initiation source connected to the chamber.

In this apparatus the detonation initiation source is mounted in the chamber. Since the detonation is initiated directly in the chamber, a special combustible mixture with small additives of powdery material is needed to initiate the detonation. The introduction of additional powdery material into the reaction chamber disturbs the conditions of detonation combustion and makes impossible the quality plasma-detonation treatment in general, while drastically reducing the efficiency and increasing the energy consumption.

## Disclosure of the Invention

The basic object of the invention is to develop a method of plasma-detonation treatment of metal products, in which the detonation combustion of a combustible gas mixture is preceded with an additional operation imparting the powdery material extra energy and eliminating or reducing the evaporation of powdery material elements having a low melting point and to provide an apparatus for plasma-detonation treatment of metal products performing said method, which has a means to realize an additional working step of this method so as to improve the quality characteristics of the hardened and spray-coated layers,

the treatment efficiency and energy saving.

This is attained by providing a method of plasma-detonation treatment of metal products including the steps of filling of the reaction chamber with a combustion gas mixture and a powdery material, detonation combustion of the combustible mixture and passing of an electric current through the products of combustion of the combustible gas mixture and powdery material in which method, according to the invention, prior to the detonation combustion of the combustible gas mixture, the reaction chamber is filled with at least one element selected from groups III, IV, V, VI of the Periodic System or its compound, and the electric current is passed also through this element and/or its compound.

It is advisable that the initiation of the detonation combustion of the combustible gas mixture is effected outside the reaction chamber.

It is also advisable that a hydrocarbon gas is fed into the reaction chamber together with at least one element selected from groups III, IV, V, VI of the Periodic System and/or its compound.

This is also attained due to the fact that in the apparatus for plasma-detonation treatment of metal products performing the above method and comprising a reaction chamber, an electrode installed inside the reaction chamber, and a detonation initiation source connected to the chamber, according to the invention, the reaction chamber has at least one nozzle to feed at least one element selected from groups III, IV, V, VI of the Periodic System and/or its compound.

The detonation initiation source may be installed outside the reaction chamber.

The nozzle to feed into the reaction chamber at least one element selected from groups III, IV, V, VI of the Periodic System and/or its compound can serve as a nozzle to supply a hydrocarbon gas into the reaction chamber.

The nozzle to feed into the reaction chamber at least one element selected from groups III, IV, V, VI of the Periodic System and/or its compound and/or hydrocarbon gas is preferably made in the wall of the reaction chamber.

The nozzle to feed into the reaction chamber at least one element selected from groups III, IV, V, VI of the Periodic system and/or its compound and/or hydrocarbon gas is preferably made inside the electrode.

Such an arrangement of the claimed apparatus performing the method, according to the invention, enables one to introduce into the reaction chamber any amount of powdery material without affecting the possibility of initiation of the detonation combustion of a combustible gas mixture. Depending on the thermophysical characteristics of the powdery material and supplied elements, the latter are fed through the nozzles made in the reaction chamber wall or inside the electrode. This, in turn, provides sufficient time and temperature for plasma-chemical processes inside the reaction chamber and uniform reaction of the products of plasma-chemical processes on the surface of metal products being hardened.

Depending on the elements being fed, the reaction chamber can be used for synthesis of carbides, nitrides and other compounds which are implanted into a heated surface of the metal product being hardened. It is possible to decompose complex compounds into simple elements and to effect plasma-chemical synthesis in the heated layer of the product or on its surface.

Therefore, it is possible to alloy the surface of a product or spray onto its surface wear-resistant compounds increasing the life of the units operating under wearing loads.

#### Brief Description of the Drawings

The invention is further described by way of example, reference being made to the accompanying drawings, in which:

Fig. 1 is a general diagram of the apparatus for plasma-detonation treatment of metal products effecting the method of plasma-detonation treatment of metal products, according to the invention (a longitudinal section);

Fig. 2 is a longitudinal section of another embodiment of the apparatus shown in Fig. 1;

Fig. 3 is a longitudinal section of still another embodiment of the apparatus shown in Fig. 2;

Fig. 4 is a longitudinal section of one of the embodiments of the apparatus shown in Figs 2 and 3.

#### Preferred Embodiments of the Invention

The method of plasma-detonation treatment of metal products, according to the invention, consists in that the reaction chamber is filled with a combustible gas mixture and a powdery material, one element selected from the elements of group III of the Periodic System, whereupon detonation combustion of the combustible gas mixture outside the reaction chamber is initiated and an electric current flows through the products of combustion of the combustible gas mixture, the powdery material and the element fed into the

reaction chamber.

In the above-described first embodiment of the method the combustible mixture consists of the following: propane or butane (1 part), oxygen (5 parts) and air (1.5 parts), the powdery material is a fusing powder of the following composition, per cent by weight: chromium 13, manganese 1.7, carbon 0.4, boron 1.6, the rest being iron, boron being the element selected from group III of the Periodic System.

#### Example 1

The reaction chamber is filled with a combustible gas mixture: propane (1 part), oxygen (5 parts), and air (1.5 parts) and with a powdery material - a fusing powder of the following composition, per cent by weight: chromium 13, manganese 1.7, carbon 0.4, boron 1.0, the rest being iron.

After that powdery boron is fed into the reaction chamber. Then detonation is initiated in the chamber and an electric current is forced through the products of combustion of the mixture, powdery material and powdery boron. The current flowing through the combustible gas mixture heats it up to a plasma state. The powder is melted and partially evaporated.

The product surface is treated with plasma containing a vapour-drop phase until the surface is fused. In so doing, the fused layer of the product is hardened or borated with formation of iron borides.

The hardened layer thickness is up to 80  $\mu\text{m}$ , and hardness is 18000 MPa.

Formed on the hardened layer surface is a sprayed layer with a hardness of 18000 MPa.

The embodiment of the claimed method, according to the invention, is preferably used for increasing the wear resistance of stamps, cutters and other tools.

The second embodiment of the method is similar to the first one.

The distinction consists in that two elements selected from groups III and V of the Periodic System are fed into the reaction chamber.

Such elements may consist of the following pair: powdery boron and nitrogen.

#### Example 2

Introduction of nitrogen together with boron allows the thickness of the hardened layer on the surface of the product to be reduced.

The hardened layer thickness is reduced to 70  $\mu\text{m}$ , in which case the hardness of this layer and sprayed layer is unchanged.

This embodiment of the claimed method is advisable for protection of products operating under abrasive loads accompanied by corrosion processes.

Additional supply of nitrogen (element of group V) is effected for producing nitrides in the hardened layer which have high corrosion resistance.

In addition to the elements of groups III and V in the third version of the method, according to the invention, a hydrocarbon gas is fed into the chamber.

The hydrocarbon gas may consist of methane.

#### Example 3

Methane is fed into the reaction chamber together with powdery boron and nitrogen.

As a result, a hardened layer 70  $\mu\text{m}$  thick with hardness of up to 16000 MPa and a sprayed layer with a hardness of up to 20000 MPa are formed on the surface of the product.

This embodiment of the method is preferably used when protecting products operating in an abrasive medium in the presence of water, as well as for increasing the wear resistance of piston rings.

The fourth version of the method, according to the invention, is similar to the first one.

The distinction consists in that the reaction chamber is fed with another element selected from group III, e.g., aluminium.

#### Example 4

An aluminum wire is fed into the reaction chamber. The plasma treatment leads to melting of the wire end and to hardening and aluminizing of the fused surface of the product.

The thickness of the hardened aluminized layer is 60  $\mu\text{m}$ , the hardness is 7000 MPa.

The surface of the hardened layer is spray-coated by a layer of aluminum and products of its reaction with the plasma. The hardness of the sprayed layer is up to 2000 MPa.

This embodiment of the claimed method can be used to produce corrosion-resistant coatings on tubes and other products subject to atmospheric corrosion.

The fifth embodiment of the method, according to the invention, may be effected using an element of group III and compounds of the element of group III.

5 Aluminum and boron carbide may be used as such elements and compounds.

#### Example 5

10 In addition to the aluminum wire, boron carbide is fed into the reaction chamber. The product surface is treated with plasma pulses containing aluminum, boron and carbon in the form of elements and a boron/carbide compound.

Formed on the product is a hardened layer having a thickness of up to 70  $\mu\text{m}$  and hardness of up to 11,000 MPa.

15 In addition, a layer with hardness of up to 8000 MPa is sprayed onto the hardened layer surface. Insertions with hardness of up to 20,000 MPa are present in the sprayed layer.

This embodiment of the method is preferably used for protection of products from wear by hot slag due to the fact that the aluminum compounds are resistant to wear at high temperatures.

The sixth embodiment of the method, according to the invention, is effected similarly to the fifth embodiment of the method.

20 The distinction consists in that the reaction chamber is supplied with an additional element selected from group V of the Periodic System.

Such an element may be nitrogen.

#### Example 6

25 The reaction chamber is additionally fed with nitrogen, the rest being as in Example 5.

A hardened layer with a thickness of 70  $\mu\text{m}$  and hardness of 11,000 MPa and a sprayed layer with hardness of 18,000 MPa are obtained on the surface of the product.

30 This embodiment of the method, according to the invention, can be used similarly to the application of the fifth version of the method but under condition of more stringent requirements to protection against corrosion.

The seventh embodiment of the method, according to the invention, is similar to the sixth embodiment of the method.

The distinction is that hydrocarbon gas is additionally fed into the reaction chamber.

35 This gas may consist of methane.

#### Example 7

40 The reaction chamber is fed with an aluminum wire, powdery boron carbide, nitrogen and methane. It is found that, like in Example 6, the surface of the product has a hardened layer due to fusion of the surface and introduction into the melt of plasma components such as aluminum, boron, carbon and nitrogen.

Furthermore, a sprayed layer is also available. In this case, the introduction of nitrogen and methane increases the hardness of both the hardened layer and the sprayed one by 30-40%.

45 The hardened layer hardness is 12,000 MPa while the sprayed one is 20,000 MPa. The thickness of the hardened layer is up to 70  $\mu\text{m}$ .

This embodiment of the method is preferably used for protection of products from abrasive wear under the action of active corrosive media: these products include water pump components and elements of thermal boilers.

Embodiment eight of the claimed method is similar to the seventh version of effecting this method.

50 The distinction consists in that the reaction chamber is supplied with an element selected from the groups III, IV, V of the Periodic System and a hydrocarbon gas.

Such elements may consist of aluminum, silicon and nitrogen, while the hydrocarbon gas is methane.

#### Example 8

55 The reaction chamber is fed with a mixture of powders of aluminum and silicon in a ratio of 5:1. Formed on the product surface is a hardened layer with a thickness of up to 60  $\mu\text{m}$  and hardness of up to 6000 MPa.

The additional supply of nitrogen and methane into the reaction chamber increases the hardness of the aluminum silicate layer to 12,000 MPa.

The sprayed layer on the product surface has hardness of up to 10,000 MPa.

This embodiment of the method is preferably used for hardening the components of thermal boilers.

5 The ninth embodiment of the method is similar to the third embodiment of the method.

The distinction consists in that the chamber is supplied with two elements selected from group III and one element selected from group IV.

Such elements may consist of yttrium, boron and carbon, respectively.

#### 10 Example 9

The reaction chamber is fed with powdery yttrium, boron and graphite. The powders are blown into the chamber immediately before initiation of detonation. Methane is used as a transport gas.

15 After one plasma pulse has been initiated, a hardened layer is formed on the surface of the product with a thickness of up to 50  $\mu\text{m}$  and hardness of up to 9000 MPa.

A sprayed layer with hardness of up to 25,000 MPa is formed on the hardened layer.

This version is preferably used for increasing the life of various nozzles of power plant boilers.

The tenth embodiment of the method is similar to the first version of the same.

20 The distinction consists in that the chamber is supplied with one element selected from group III and another element from group IV.

Yttrium and carbon can be used as such elements.

#### Example 10

25 The introduction into the reaction chamber of powdery yttrium and carbon provides a hardened layer with a thickness of 50  $\mu\text{m}$  and hardness of 12,000 MPa on the surface of the product and a sprayed layer with hardness of 15,000 MPa.

This embodiment of the method, according to the invention, can be used similarly to the ninth embodiment of the method.

30 The eleventh embodiment of the method, according to the invention, is carried out similarly to the ninth version.

The distinction consists in that the reaction chamber is supplied with an element selected from group IV simultaneously with hydrocarbon gas.

This element may consist of carbon and methane may be used as a hydrocarbon gas.

35

#### Example 11

Carbon is fed into the chamber in the form of powdery graphite. The graphite is carried by methane.

40 On increasing the power of the plasma pulses, one observes formation of a hardened layer with a thickness of up to 70  $\mu\text{m}$  and hardness of 8000 MPa. The sprayed layer has hardness of 10,000 MPa.

This embodiment of the method is preferably used when treating products made of low-carbon steel to increase their surface hardness.

The embodiment twelve of the method is similar to the eleventh version.

45 The distinction consists in that the reaction chamber is supplied with one compound of an element selected from group VI and elements selected from groups IV and VI of the Periodic System.

This compound may consist of a compound of oxygen with iron (iron oxide) and carbon and molybdenum as said elements.

#### Example 12

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The reaction chamber is fed with a mixture powdery graphite (carbon), iron oxide and molybdenum. After hardening the product, a layer is formed on its surface having a thickness of up to 60  $\mu\text{m}$  and hardness of up to 4000 MPa.

55 An increase in the power of the plasma pulses provides a hardened layer with a thickness of up to 70  $\mu\text{m}$  and hardness of up to 6000 MPa, as well as a hardened layer with hardness of up to 6000 MPa.

This embodiment of the method is preferably used to create an antifriction layer on piston rings, crankshafts and valves.

The thirteenth embodiment of the method is similar to the eleventh version.

The distinction consists in that the reaction chamber is additionally supplied with compounds of an element selected from group V.

Ferrovandium is used as such compound.

#### 5 Example 13

Carbon in the form of powdery graphite, powdery ferrovandium and methane are fed into the reaction chamber. After the process of hardening a layer with a thickness of up to 20  $\mu\text{m}$  and hardness of up to 18,000 MPa is observed.

10 An increase in the power of the plasma pulses provides a hardened layer with a thickness of up to 40  $\mu\text{m}$  and hardness of up to 20,000 MPa.

This version of the method is preferably used to form a carbide-vandium layer on the surface of products operating in active oxidizing media.

The fourteenth embodiment of the method is similar to the first method.

15 The distinction consists in that the reaction chamber is supplied with one element selected from group IV of the Periodic System.

Silicon may be used as such an element.

#### Example 14

20

The reaction chamber is fed with powdery silicon.

After the process of hardening on the product surface there is formed a layer with a thickness of up to 90  $\mu\text{m}$  and hardness of up to 5000MPa. The hardened layer hardness is 8000 Mpa.

This embodiment of the method is preferably used for silicating the surface of the product.

25 The fifteenth embodiment of the method is similar to the eleventh version.

The distinction consists in that the reaction chamber is supplied with another element selected from group IV.

Silicon is used as such an element.

#### 30 Example 15

The supply of silicon and carbon in the form of powdery graphite into the reaction chamber provides formation of a hardened layer with hardness of up to 10,000 MPa and thickness of up to 90  $\mu\text{m}$  and a hardened layer having hardness of up to 10,000 MPa.

35 This embodiment of the method is preferably used in the same cases as the version according to Example 8.

The sixteenth embodiment off the method is similar to the eleventh embodiment of the method.

The distinction consists in that the reaction chamber is supplied with one compound of an element selected from group IV of the Periodic System simultaneously with a hydrocarbon gas.

40 This compound may be a silicon oxide while the hydrocarbon gas is methane.

#### Example 16

45 The supply of silicon oxide and methane provides a hardened layer with a thickness of up to 60  $\mu\text{m}$  and with hardness of up to 8000 MPa and a sprayed layer with hardness of up to 9000 MPa.

This version can be used for applying coatings on members operating under abrasive wear: sprockets, bushings, some components of agricultural machines.

The seventeenth embodiment of the method is similar to the second version.

50 The distinction consists in that the reaction chamber is supplied with two elements selected from groups IV and V.

Zirconium and nitrogen can be used as such elements.

#### Example 17

55 Powdery zirconium is introduced into the reaction chamber in a nitrogen flow.

After the process of hardening, the surface of the product has a hardened layer with a thickness of up to 40  $\mu\text{m}$  and hardness of 12,000 MPa and a sprayed layer with hardness of 16,000 MPa.



This embodiment of the method is preferably used for hardening of turbine blades, deflectors and other components operating in a high-temperature medium.

The eighteenth embodiment of the method is similar to the seventh embodiment of the method.

The distinction consists in that the reaction chamber is supplied with an element selected from group

5 IV.

Zirconium is used as such an element.

#### Example 18

10 The reaction chamber is fed with powdery zirconium, boron carbide, nitrogen and methane so as to obtain a hardened layer with a thickness of up to 80  $\mu\text{m}$ , hardness of up to 16,000 MPa and a sprayed layer having hardness of up to 20,000 MPa.

The nineteenth embodiment of the method is similar to the eighteenth embodiment of the method.

15 The distinction consists in that the reaction chamber is supplied with another element selected from group IV, namely: carbon.

#### Example 19

20 An additional supply of carbon into the reaction chamber provides a hardened layer on the product with a thickness of up to 80  $\mu\text{m}$  and hardness to 16,000 MPa and a sprayed layer having hardness of up to 22,000 MPa.

The twentieth embodiment of the method assumes application of only one element of group V.

Nitrogen may be used as such an element.

#### 25 Example 20

By feeding nitrogen into the reaction chamber plasma pulses are formed having nitrogen content of up to 80%.

30 The analysis of the product hardened with nitrogen plasma has shown that the surface has a hardened layer with a thickness of up to 100  $\mu\text{m}$  and hardness of up to 9000 MPa.

This version of the method can be used for nitriding various components: gear wheels, cams, pistons and synchronizers. The twenty first embodiment of the method is similar to the twentieth embodiment of the method.

35 The distinction consists in that the reaction chamber is supplied with nitrogen and hydrocarbon gas- (methane) simultaneously, and this significantly increases the hardness of the product being treated.

#### Example 21

Supply of methane into the reaction chamber increases the hardened layer hardness to 11,000 MPa.

40 The twenty second embodiment of the method is preferably carried out similarly to the twenty first version.

The distinction consists in that the reaction chamber is supplied with another element from group IV, namely: titanium.

#### 45 Example 22

The hardening of the product by a plasma pulse comprising titanium, nitrogen and methane produces on the surface of the product a hardened layer with a thickness of up to 100  $\mu\text{m}$  and hardness of up to 12,000 MPa.

50 This embodiment of the method is preferably used for hardening metal working tools.

The twenty third embodiment of the method includes supply of the reaction chamber with an element of group V, namely: ferrovanadium.

#### Example 23

55 The reaction chamber is supplied with ferrovanadium containing up to 60% of vanadium. The pulse hardening of the product by plasma containing ferrovanadium provided a hardened layer of up to 40  $\mu\text{m}$  and hardness of 8000 MPa and a sprayed layer with hardness of up to 10,000 MPa.

This embodiment of the method is efficient for producing wear-resistant coatings on the surface of the products operating under conditions of abrasive wear, such as plows, plowshares, cultivators.

The supply of a hydrocarbon gas (methane) significantly increases the hardened layer hardness.

The twenty fourth embodiment of the method includes simultaneous supply of ferrovanadium and methane.

#### Example 24

Simultaneous supply into the reaction chamber of ferrovanadium and methane increases the hardened layer hardness to 12,000 MPa with a thickness of up to 40  $\mu\text{m}$ . The sprayed layer has hardness of up to 8000 MPa.

This version of the method is similar to the previous embodiment of the method.

It is advantageous to supply the reaction chamber with still another element of group IV (carbon).

The twenty fifth embodiment of the method significantly increases the hardness thus making it more efficient.

#### Example 25

The reaction chamber is fed with ferrovanadium, methane and carbon simultaneously.

A hardened layer is obtained having the same characteristics as in Example 24 and a sprayed layer with hardness of up to 16,000 MPa.

The use of the twenty sixth embodiment of the method is of practical interest. This method includes supply of a compound of element of group V and an element of group III.

The former element may be ferrovanadium and the latter is aluminum.

#### Example 26

In order to harden the surface of the product, aluminum wire and ferrovanadium are fed into the reaction chamber. The wire surface is fused by a plasma pulse.

A hardened layer is obtained having a thickness of up to 40  $\mu\text{m}$  and hardness of up to 8000 MPa and a sprayed layer with hardness of up to 7000 MPa.

It is possible to feed the reaction chamber with two elements of group V according to the twenty seventh embodiment of the method. Niobium and nitrogen are used as such elements.

#### Example 27

A nitrogen flow carries powdery niobium into the reaction chamber. After hardening the surface by single plasma pulses, one can observe a double layer on the surface of the product: a hardened layer with a thickness of up to 50  $\mu\text{m}$  and hardness of up to 18,000 MPa and a sprayed layer with hardness of 20,000 MPa.

This method can be used for production of catalysts in the electrode industry in the electrolysis of chlorine salts.

It is possible to supply the reaction chamber simultaneously with two elements of group IV and two elements of group V of the Periodic System.

The twenty eighth embodiment of the method provides introduction of elements from group V, such as nitrogen and niobium, and from group IV, such as carbon and titanium in the form of a rod.

#### Example 28

The procedure is similar to Example 27 but the reaction chamber is also fed with carbon in the form of powdery graphite and titanium in the form of a rod.

A hardened layer is obtained having a thickness of 60  $\mu\text{m}$  and hardness of 18,000 MPa and a sprayed layer with hardness of up to 25,000 MPa. This method is used like the twenty seventh embodiment of the method.

The claimed method can be realized using an element of group VI.

The twenty ninth embodiment of the method provides supply of chromium (element of group VI) into the reaction chamber.

Example 29

The surface of the product is hardened by introducing a chromium rod into the reaction chamber.

A hardened layer is obtained having a thickness of up to 100  $\mu\text{m}$  and hardness of up to 8000 MPa.

5 The thirtieth embodiment of the method is similar to the twenty ninth embodiment of the method.

The distinction consists in that the reaction chamber is supplied with another element selected from group IV. Carbon may be used as such an element.

Example 30

10

The supply of additional carbon in the form of powdery graphite provides a hardened layer with a thickness 100  $\mu\text{m}$ , hardness of 8000 MPa and sprayed layer with hardness of 12,000 MPa.

The hardness of the obtained layers can be increased by supplying the chamber with a hydrocarbon gas (methane) according to the thirty first embodiment of the method.

15

Example 31

Simultaneous supply of chromium, carbon and methane into the reaction chamber increases the hardness of the hardened layer to 9000 MPa (thickness of 90  $\mu\text{m}$ ) and the hardness of the sprayed layer to 14,000 MPa.

20

According to the thirty second embodiment of the method, the reaction chamber is fed with one element of group VI of the Periodic System, namely: molybdenum.

Example 32

25

In order to create a hardened layer with high antifriction properties on the surface of the product, molybdenum in the form of a rod is introduced into the reaction chamber.

The product has a hardened layer with a thickness of up to 80  $\mu\text{m}$  and with hardness of 6000 MPa.

30

This embodiment of the method can be used for increasing the operating life of pistons and cylinders of internal combustion engines.

An antifriction layer on the product can be created by introducing with molybdenum another element of group VI and its compound.

Oxygen may be such an element and iron oxide may be such a compound.

35 Example 33

Simultaneous supply of molybdenum, iron oxide and oxygen methane into the reaction chamber provides formation on the surface of the products of a hardened layer with a thickness of up to 60  $\mu\text{m}$  and hardness of up to 6000 MPa and with hardness of the sprayed layer of up to 4000 MPa.

40

This embodiment is efficient for producing an antifriction layer on piston rings to increase their workability.

The thirty fourth embodiment of the method is effected similarly to the thirty third embodiment.

The distinction consists in that the reaction chamber is supplied with still another element of group VI (sulfur) and a hydrocarbon gas (methane).

45

Example 34

Everything is done as in Example 33 but the reaction chamber is supplied with sulfur carried by methane.

50

On the product there is produced a hardened layer with a thickness of 60  $\mu\text{m}$ , hardness of 6000 MPa and a sprayed layer of molybdenum and iron sulfides smelted with iron and molybdenum oxides, as well as with molybdenum and iron. The hardness of this layer is up to 2500 MPa.

Formed on the surface is a soft antifriction layer of molybdenum and iron sulfides and oxides.

Other elements of group VI, e.g. tungsten, may be fed into the reaction chamber.

55

The thirty fifth embodiment of the method provides the use of tungsten.

Example 35

Tungsten in the form of a rod is fed into the reaction chamber. The surface of the product is hardened by pulses of plasma containing tungsten.

5 A hardened layer is produced on the surface of the product with a thickness of up to 80  $\mu\text{m}$  and with hardness of up to 8000 MPa.

This embodiment may be used for improving the properties of metal products operating at high temperatures.

10 The thirty sixth embodiment of the method is realized similarly to the thirty fifth embodiment of the method.

The distinction consists in that the reaction chamber is supplied with a hydrocarbon gas, e.g., methane.

Example 36

15 Tungsten and methane are simultaneously fed into the reaction chamber.

A hardened layer is obtained with a thickness of 80  $\mu\text{m}$  and with hardness of up to 10,000 MPa and a sprayed layer with hardness of up to 14,000 MPa.

In the thirty seventh embodiment of the methods use may be made of elements of groups IV and VI (carbon and tungsten) jointly with a hydrocarbon gas, e.g., methane.

20

Example 37

Everything is done as in Example 36 but with simultaneous supply of carbon into the reaction chamber.

25 A hardened layer is obtained with a thickness of up to 80  $\mu\text{m}$ , hardness of up to 10,000 MPa and a sprayed layer having hardness of up to 18,000 MPa.

Supply of the reaction chamber with one compound of an element of group VI is of practical interest.

Formed on the surface is a hard sprayed layer which can be used for hardening screws conveyers, cutters, pistons and valves, i.e., products operating in an abrasive medium.

30 Thus, according to the thirty eighth embodiment of the method, the reaction chamber is fed with tungsten carbide as such a compound.

Example 38

Powdery tungsten carbide is fed into the reaction chamber.

35 A hardened layer is obtained having a thickness of up to 40  $\mu\text{m}$  and hardness of 8000 MPa and a sprayed layer having hardness of 18,000 MPa.

The thirty ninth embodiment of the method is effected similarly to the thirty eighth embodiment.

The distinction consists in that a hydrocarbon gas (methane) is fed into the reaction chamber simultaneously with tungsten carbide.

40

Example 39

The reaction chamber is fed with powdery tungsten carbide carried by methane.

45 A hardened layer is obtained having a thickness of up to 40  $\mu\text{m}$  and hardness of 8000 MPa and a sprayed layer having hardness of up to 20,000 MPa.

It is possible to supply the reaction chamber with compounds of elements of groups III, IV and VI and an element of group V simultaneously with the hydrocarbon gas.

50 For example, in the fortieth embodiment of the method, the chamber is fed with boron carbide, tungsten carbide and titanium nitride simultaneously, while the hydrocarbon gas is composed of nitrogen and methane.

Example 40

55 A joint supply of boron and tungsten carbides, titanium nitride, nitrogen and methane provides the surface of the product with a hardened layer with a thickness of up to 40  $\mu\text{m}$  and hardness of up to 8000 MPa and a sprayed layer with hardness of up to 22,000 MPa.

In order to obtain a hardened layer on the surface of the product according to the forty first embodiment of the method, one may feed the reaction chamber with a compound of two elements of group III of the

Periodic System, e.g., indium boride, and a hydrocarbon gas having a higher density than methane, e.g., propane-butane.

#### Example 41

5

A joint supply of indium boride and propane-butane into the reaction chamber provides formation on the surface of the product of a hardened layer having a thickness of 50  $\mu\text{m}$  and hardness of up to 20,000 MPa and a sprayed layer with hardness of up to 28,000 MPa.

This hardened layer can be used for protection of surfaces of gas turbines subject to wear.

10

Similar properties can be obtained by feeding into the reaction chamber two elements of group IV of the Periodic System, for example, zirconium carbide, according to the forty second embodiment of the method.

#### Example 42

15

The procedure is effected similarly to Example 41. Powdery zirconium is carried into the reaction chamber by propane-butane. The joint heating in the reaction chamber and plasma-chemical interaction with the surface of the product provides a hardened layer with a thickness of 60  $\mu\text{m}$  and with hardness of up to 18,000 MPa.

20

In order to create protective layers on the electrodes of the devices for electrolysis according to the forty third embodiment of the method use can be made of a compound of two elements of group V of the Periodic System, for example, niobium nitride.

#### Example 43

25

The procedure is effected similarly to Example 41.

Powdery niobium nitride is fed into the reaction chamber by propane-butane.

30

The pulse treatment of the product by the products of the plasma-chemical synthesis makes it possible to obtain a hardened layer with a thickness of 50  $\mu\text{m}$  and hardness of 16,000 MPa and a sprayed layer with hardness of 14,000 MPa.

To provide protection against abrasive wear and corrosion protection of products according to the forty fourth embodiment of the method the surface of the product may be treated by a compound of two elements of group VI of the Periodic System, for example, chromium carbide.

#### Example 44

The procedure is effected similarly to Example 41.

The reaction chamber is supplied with chromium carbide carried by propane-butane. The treatment of the surface of the product by the products of plasma-chemical synthesis results in formation of a hardened layer with a thickness of 150  $\mu\text{m}$  and hardness of up to 11,000 MPa on the surface of the product.

40

This embodiment of the method can be used for protection of some components of agricultural machinery.

45

Depending on the conditions of performing the method, according to the invention, it is possible to form a hardened layer with different properties on the surface of the metal product. In this case, depending on the requirements to the surface of the product, the reaction chamber is fed with elements of groups III, IV, V, VI and/or compound(s) of element(s) in the form of carbides, nitrides, borides, ferroalloys, silicides, as well as gases and their mixtures. The elements can be introduced in the form of powder, a rod, gas, aerosol.

50

Given below is a description of the claimed apparatus for plasma-detonation treatment of metal products performing the method, according to the invention.

The apparatus, according to the invention, effecting the claimed method comprises a reaction chamber 1 (Fig. 1), an electrode 2 installed inside the reaction chamber 1, and detonation initiation source 3 connected to the reaction chamber 1.

55

The apparatus, according to the invention, has a nozzle 4 to feed into the reaction chamber 1 an element selected from groups III, IV, V, VI off the Periodic System and/or its compound in the direction of the arrow A.

The reaction chamber 1 consists of cylindrical parts 5 and 6 and a conical part 7 between these parts and is placed into a water-cooled casing 8 having an inlet 9 and an outlet 10 for the cooling liquid (water).

The nozzle 4 is made in the wall of the cylindrical part 5 of the chamber 1.

The chamber 1 is a cathode and is connected to a power supply unit 11 through a current supply circuit 12.

The electrode 2 is incorporated into an insulator 13 serving as a bottom of the chamber 1 and as an anode connected to the power supply unit 11 through a current supply circuit 14.

The detonation initiation source 3 comprises a precombustion chamber 15 and a cylindrical channel 16 connected in series, the channel 16 being connected to the conical part 7 of the reaction chamber 1. The pre-combustion chamber 15 has a nozzle 17 to feed a combustible gas mixture in the direction of the arrows B and a spark plug 18.

The powdery material is fed into the cylindrical part 6 of the chamber 1 in the direction of the arrow C via a channel 19 made in the chamber formed by the water-cooled casing 8 and the walls of the cylindrical part 6 of the reaction chamber 1.

The treated metal product 20 is disposed at the output of the plasma pulses from the chamber 1 in the direction of the arrow D.

This embodiment of the apparatus, according to the invention, realizes the first, twentieth, twenty third, forty first, forty second, forty third and forty fourth embodiments of the claimed method, in which one element or one compound of the same is fed into the reaction chamber 1 through the nozzle 4.

In the same embodiment of the apparatus shown in Fig. 1 the nozzle 4 can be also used for supply into the reaction chamber 1 of two or more compounds selected from groups III, IV, V, VI of the Periodic System, or two and more compounds of these elements.

In this case, the apparatus shown in Fig. 1 realizes the seventeenth and twenty seventh embodiments of the method, where powdery zirconium or niobium is fed into the reaction chamber 1 in a nitrogen stream.

The nozzle 4 to supply one or more elements or one or more its compounds into the reaction chamber 1 can be also used as a nozzle to supply a hydrocarbon gas into the reaction chamber.

In this case, the apparatus according to Fig. 1 realizes the eleventh, fifteenth, sixteenth, twenty first, twenty fourth, thirtieth and thirty eight embodiments of the method, according to the invention.

Fed through the nozzle 4 into the reaction chamber 1, at the same time with the element or its compound, is a hydrocarbon gas which is used as a transport media: these are the thirty first and thirty ninth embodiments of the method.

The embodiment of the apparatus shown in Fig. 2 realizing the method, according to the invention, is made similarly to the apparatus shown in Fig. 1.

The distinction consists in that the wall of the cylindrical part 5 (Fig. 2) of the reaction chamber 1 has three additional nozzles 21, 22, 23 to supply the reaction chamber 1 with elements selected from groups III, IV, V, VI or compounds of these elements (in the direction of the arrow E for the nozzle 21).

Depending on the conditions of performing the claimed method, according to the invention, some nozzles can be closed.

Thus, with closed nozzles 22 and 23 the apparatus of Fig. 2 realizes the second embodiment of the method, in which powdery boron is fed into the chamber 1 through the nozzle 4 and nitrogen is fed through the nozzle 21.

The same embodiment of the apparatus can realize the third, thirteenth and twenty fifth embodiments of the method, when the nozzle 4 is used for injection of both the element compound and nitrogen into the chamber 1.

In this way, powdery boron and ferrovanadium are fed through the nozzle 4 in a methane stream while nitrogen and carbon in the form of graphite powder are fed through the nozzle 21.

When the nozzle 21 is closed, the apparatus of Fig. 2 realizes the ninth method of plasma-detonation treatment of metal products, in which powders of yttrium, boron and graphite are injected into the chamber 1 through the nozzles 4, 22 and 23, respectively.

The embodiment of the apparatus shown in Fig. 3, according to the invention, is similar to that shown in Fig. 2.

The distinction consists in that the apparatus has another nozzle 24 (Fig. 3) to supply the reaction chamber 1 with an element selected from groups III, IV, V, VI or compounds of these elements (in the direction of the arrow F).

The nozzle 24 is made inside the electrode 25.

This embodiment of the apparatus is used to realize the fourth, fifth, sixth, twenty sixth, twenty eighth, twenty ninth, thirty second, thirty third and thirty fourth embodiments of the method.

Thus, according to the above embodiments of the method with closed nozzles 4, 21, 22 and 23 aluminum wire is fed into the chamber 1 through the nozzle 24, with closed nozzles 21, 22 and 23 the nozzle 4 is used for additionally feeding boron carbide, with closed nozzles 22 and 23 additional gaseous

nitrogen is fed through the nozzle 21, with closed nozzles 4, 22 and 23 ferrovanadium is fed through the nozzle 21.

The embodiment of the apparatus according to Claim 4 realizing the method according to the invention is similar to the embodiment of the apparatus shown in Figs 2 and 3.

5 The distinction consists in that, in addition to the nozzles 4 (Fig. 4), 21 and 24, this apparatus has two nozzles 26 and 27 which can be used for injection of both, an element selected from groups III, IV, V, VI or its compound fed in the direction of the arrows G and H, and a hydrocarbon gas.

These nozzles 26 and 27 are made in the wall of the cylindrical part 6 of the reaction chamber 1.

10 This embodiment of the apparatus realizes the seventh, eighth, ninth, twelfth, fourteenth, nineteenth, twenty second, thirty fifth, thirty sixth, thirty seventh and fortieth embodiments of the method.

In this case, in accordance with the above listed embodiments of the method, in the eighteenth embodiment of the apparatus shown in Fig. 4, zirconium is fed through the nozzle 4 into the cylindrical part 5 of the chamber 1, methane is fed through the nozzle 21 and nitrogen and boron carbide are fed into the cylindrical part 6 of the chamber 1 through the nozzles 27 and 26, respectively the nozzle 24 still being  
15 closed in the nineteenth embodiment and carbon being fed together with methane through the nozzle 21.

The apparatus for plasma treatment of metal products performing the method, according to the invention, operates as follows.

The components of combustible gas mixture are fed through the nozzles 14 into the source 3 (Fig. 1) of initiation of detonation. In the pre-combustion chamber 15 the combustible gas mixture components are  
20 mixed and the channel 16 is filled with the mixture. At the same time, the chamber 1 is supplied with a mixture of gaseous and solid elements of groups III, IV, V and VI of the Periodic System. In this case, depending on the technology requirements, use can be made of one element or several elements in a mixture or chemical compound, and the reaction chamber 1 can be fed also with a hydrocarbon gas. Powdery material is fed into the reaction chamber 1 through a passage 19.

25 When the combustible gas mixture is ignited by the spark plug 18, a pressure of the products of combustion is produced in the pre-combustion chamber 15, which transforms into detonation condition of combustion in the cylindrical channel 16. The detonation combustion transfers into the conical section 7 of the reaction chamber 1. Here the detonation conditions are maintained due to passage of an electric current in the inter electrode gap through the products of combustion of the combustible gas mixture, the powdery  
30 material and the element. The electric current is fed from the power unit 11 via the current conductors 12 and 14 to the electrodes (cathode and anode) and then through the products of combustion of the combustible gas mixture, powdery material and introduced element.

Therefore, the detonation conditions of combustion transform into magnetogasdynamic conditions and can be as much as large with respect to the output power.

35 The electromagnetic energy in the reaction chamber 1 activates the element introduced into the chamber and this element reaches the powdery material and effect thereon plasma-chemical synthesis or interacts together with the powder with the surface of the metal product 20. The temperature conditions of the reaction chamber 1 is stabilized by means of the water-cooled casing 8 having a water inlet 9 and an outlet 10.

40 The hardening of the surface of the product 20 is effected either by a single pulse or a train of sequential pulses of the products of the plasma-chemical synthesis and plasma with a smooth movement of the product 20.

The principle of operation of the apparatus shown in Fig. 1 is identical for a plurality of elements, one compound of an element, a plurality of compounds of elements together with a hydrocarbon gas and  
45 without it.

The principle of operation of the apparatus shown in Figs 2, 3 and 4 realizing the method, according to the invention, is similar to the principle of operation of the apparatus shown in Fig. 1.

Given below is a table containing the results of concrete examples of performing the method, according to the invention, realized by the apparatus shown in Figs 1-4.

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Table

Item No.	Element(s), its(their) compounds, hydrocarbon gas in reaction chamber	Characteristic of hardened layer		Characte- ristic of sprayed layer	Fig. No.
		Thick- ness, $\mu\text{m}$	Hard- ness, MPa	Hardness, MPa	
1	Boron	80	18,000	18,000	1
2	Boron+nitrogen	70	18,000	18,000	2
3	Boron+nitrogen+methane	70	16,000	20,000	2
4	Aluminum	60	7,000	2,000	3
5	Aluminum+ boron carbide	70	11,000	8,000	3
6	Aluminum+boron carbide +nitrogen	70	11,000	18,000	3
7	Aluminum+boron carbide + nitrogen+methane	70	12,000	20,000	4
8	Aluminum+silicon+ + nitrogen+methane	60	12,000	10,000	4
9	Yttrium+boron+carbon +methane	50	9,000	25,000	2
10	Yttrium+carbon	50	12,000	15,000	4
11	Carbon+methane	70	8,000	10,000	1
12	Carbon+iron oxide+ +molybdenum	70	6,000	6,000	4
13	Carbon+ferrovanadium+ +methane	40	20,000		2
14	Silicon	90	5,000	8,000	4
15	Silicon+carbon+ +methane	90	10,000	10,000	1
16	Silicon oxide+methane	60	8,000	9,000	1
17	Zirconium+nitrogen	40	12,000	16,000	1
18	Zirconium+boron car- bide+nitrogen+methane	80	16,000	20,000	4
19	Zirconium+boron carbide+nitrogen+ carbon+methane	80	16,000	22,000	4



Table (continued)

Item No.	Element(s), its(their) compounds, hydrocarbon gas in reaction chamber	Characteristic of hardened layer	Characteristic of sprayed layer	Fig. No.	
		Thick- ness, mm	Hard- ness, MPa	Hardness, MPa	
20	Nitrogen	100	9,000	-	1
21	Nitrogen+methane	100	11,000	-	1
22	Nitrogen+methane+ +titanium	100	12,000	-	4
23	Ferrovanadium	40	8,000	10,000	1
24	Ferrovanadium+methane	40	12,000	8,000	1
25	Ferrovanadium+methane +carbon	40	12,000	16,000	2
26	Ferrovanadium+aluminum	40	8,000	7,000	3
27	Niobium+nitrogen	50	13,000	20,000	1
28	Niobium+titanium+ +nitrogen	60	18,000	25,000	3
29	Chromium	100	8,000	-	3
30	Chromium+carbon	100	8,000	12,000	1
31	Chromium+carbon+ +methane	90	9,000	14,000	1
32	Molybdenum	80	6,000	-	3
33	Molybdenum+iron oxide+ +oxygen	60	6,000	4,000	3
34	Molybdenum+iron oxide+ +oxygen+sulfur+methane	60	6,000	2,500	3
35	Tungsten	80	8,000	-	4
36	Tungsten+methane	80	10,000	14,000	4
37	Tungsten+carbon+ methane	80	10,000	18,000	4
38	Tungsten carbide	40	8,000	18,000	1
39	Tungsten carbide+ methane	40	8,000	20,000	1
40	Boron carbide+ +tungsten carbide+ +titanium nitride+ +nitrogen+methane	40	8,000	22,000	4

Table (continued)

Item No.	Element(s), its(their) compounds, hydrocarbon gas in reaction chamber	Characteristic of hardened layer		Characteristic of sprayed layer	Fig. No.
		Thick-ness, $\mu\text{m}$	Hard-ness, MPa	hardness, MPa	
41	Indium boride+ +propane-butane	50	20,000	28,000	1
42	Zirconium carbide+ +propane-butane	60	18,000	-	1
43	Niobium nitride+ +propane-butane	50	16,000	14,000	1
44	Chromium carbide+ +propane-butane	150	11,000	-	1

The claimed apparatus realizing the method according to the invention considerably improves the quality of the treated product which is clearly seen from the above Table.

In the claimed apparatus to effect the method according to the invention the detonation is initiated outside the reaction chamber, thereby increasing the stability of useful application of the electric energy in each pulse of plasma-chemical synthesis by 20-30%.

#### Industrial Applicability

The apparatus for plasma-detonation treatment of metal products effecting the method of plasma-detonation treatment can be used for surface hardening of wearable metal components in mechanical engineering, in the manufacture of internal combustion engines, compressors, pneumatic and hydraulic drives and various tools, as well as for increasing the operating life of power boilers and turbines.

#### Claims

1. A method for plasma-detonation treatment of metal products comprising the steps of filling of the reaction chamber (1) with a combustible gas mixture and a powdery material, detonation combustion of the combustible gas mixture and passing of an electric current through the products of combustion of the combustible gas mixture and powdery material, characterized in that, prior to the detonation combustion of the combustible gas mixture, the reaction chamber (1) is filled with at least one element selected from groups III, IV, V, VI of the Periodic System and/or its compound, while the electric current is passed also through this element and/or its compound.
2. A method according to Claim 1, characterized in that the initiation of detonation combustion of the combustible gas mixture is effected outside the reaction chamber (1).
3. A method according to Claim 1 or 2, characterized in that hydrocarbon gas is fed into the reaction chamber (1) simultaneously with at least one element selected from groups III, IV, V, VI of the Periodic System and/or its compound.
4. An apparatus for plasma detonation treatment of metal products comprising a reaction chamber (1), an electrode (2) installed inside the reaction chamber (1) and a source (3) to initiate the detonation connected to the reaction chamber (1), characterized in that the reaction chamber (1) has at least one nozzle (4) adapted to feed at least one element selected from groups III, IV, V, VI of the Periodic System and/or its compound to the reaction chamber (1).

5. An apparatus according to Claim 4, characterized in that the source (3) to initiate the detonation is installed outside the reaction chamber (1).

5 6. An apparatus according to Claim 5, characterized in that the nozzle (4) adapted to feed at least one element selected from groups III, IV, V, VI of the Periodic System and/or its compound into the reaction chamber (1), is used as a nozzle to supply a hydrocarbon gas into the reaction chamber (1).

10 7. An apparatus according to Claim 5 or 6, characterized in that the nozzle (4) adapted to feed at least one element selected from groups III, IV, V, VI of the Periodic System and/or its compound and/or hydrocarbon gas into the reaction chamber (1) is made in the wall of the reaction chamber (1).

15 8. An apparatus according to Claim 5 or 6, characterized in that a nozzle (24) adapted to feed at least one element selected from groups III, IV, V, VI of the Periodic System and/or its compound and/or hydrocarbon gas into the reaction chamber (1) is made inside an electrode (25).

9. An apparatus according to Claim 7, characterized in that the nozzle (24) adapted to feed at least one element selected from groups III, IV, V, VI of the Periodic system and/or its compound and/or hydrocarbon gas into the reaction chamber (1) is made inside the electrode (25).

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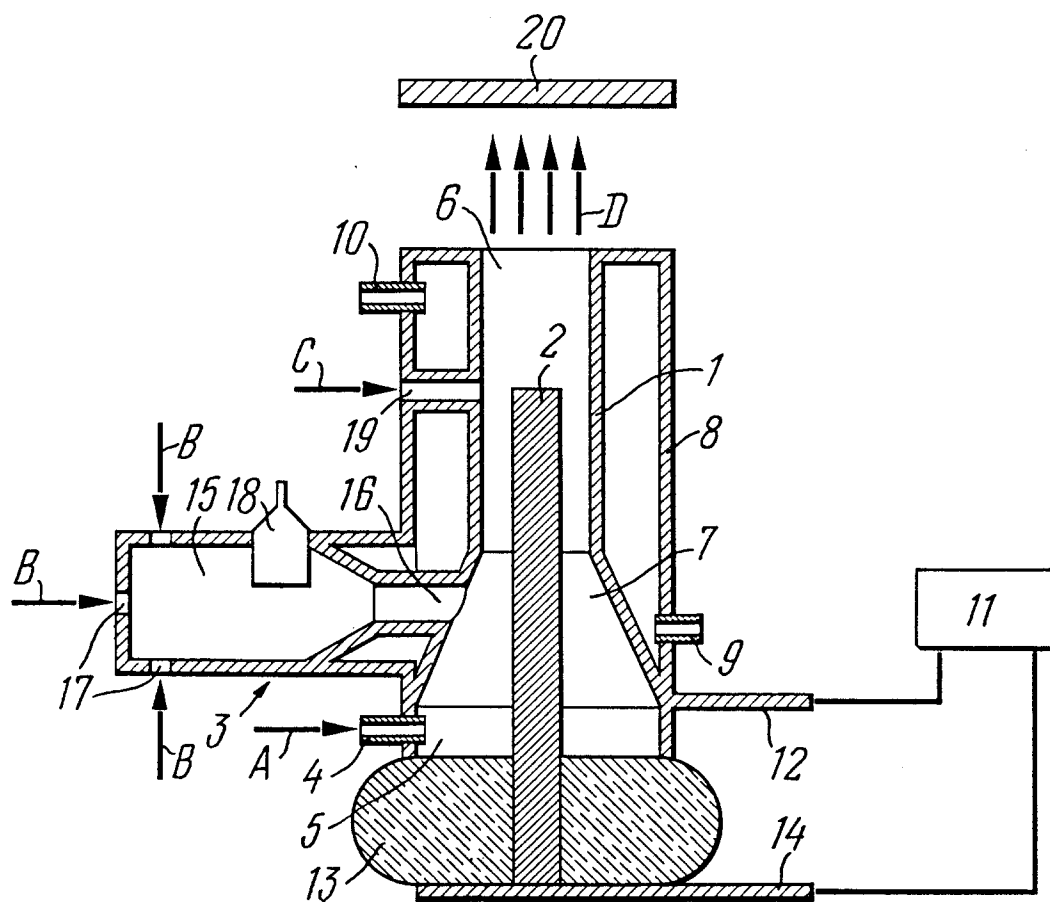
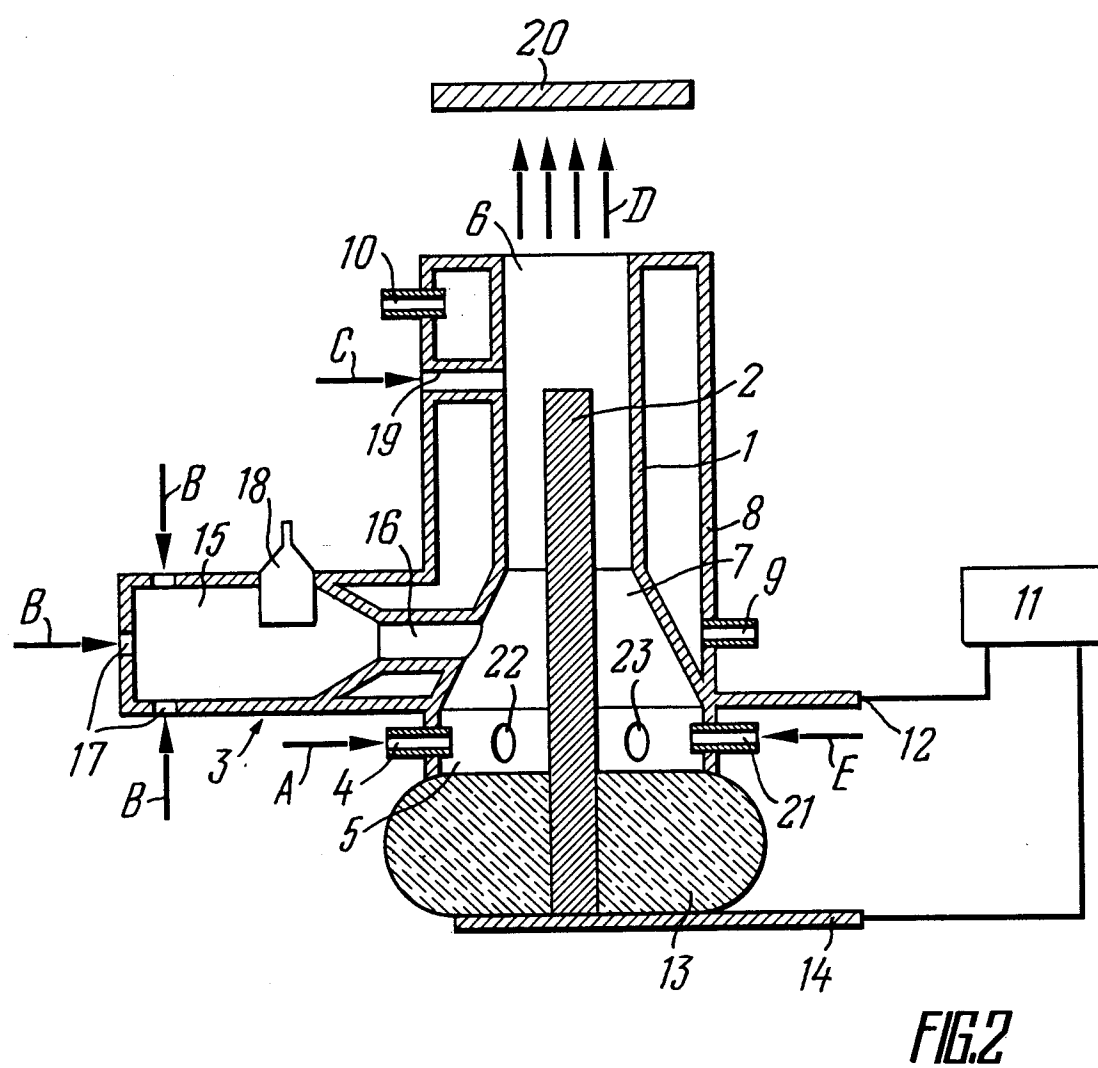


FIG. 1



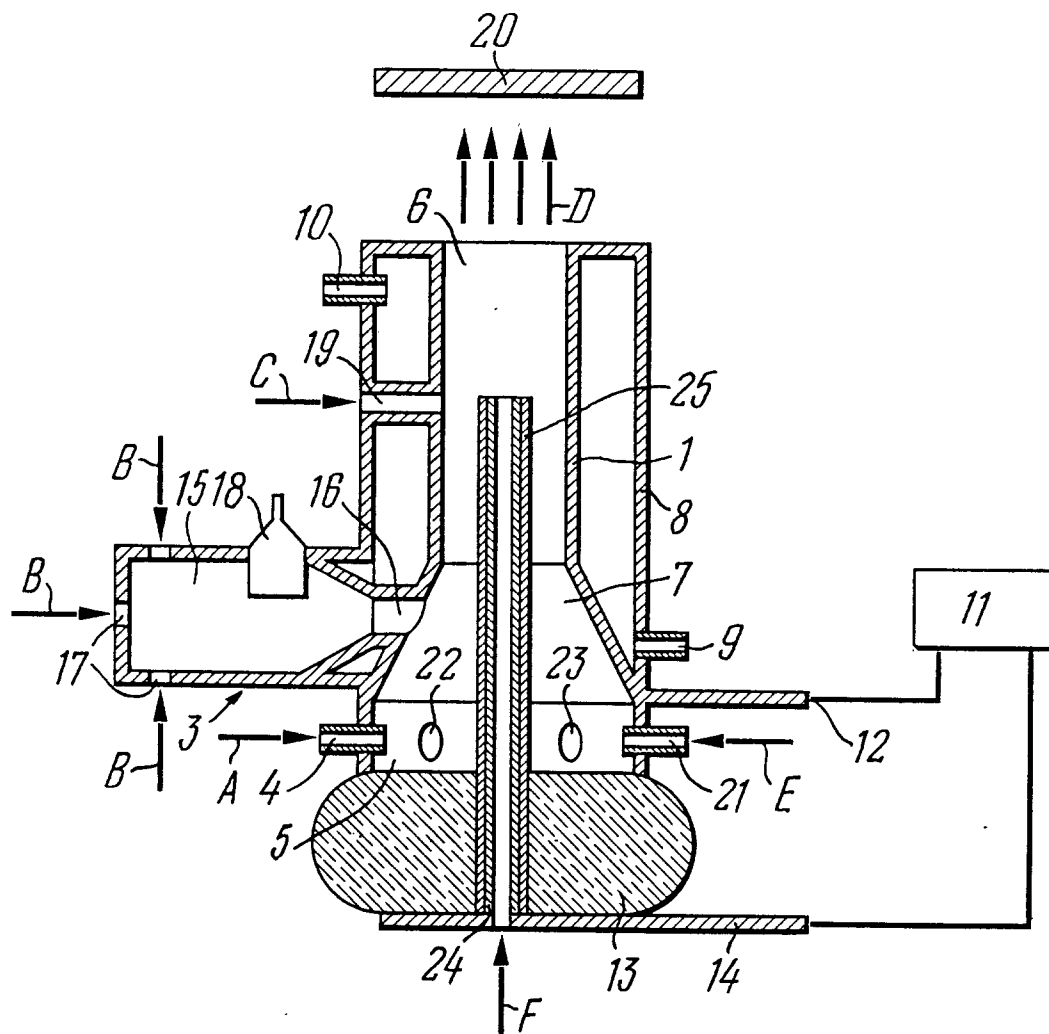


FIG.3

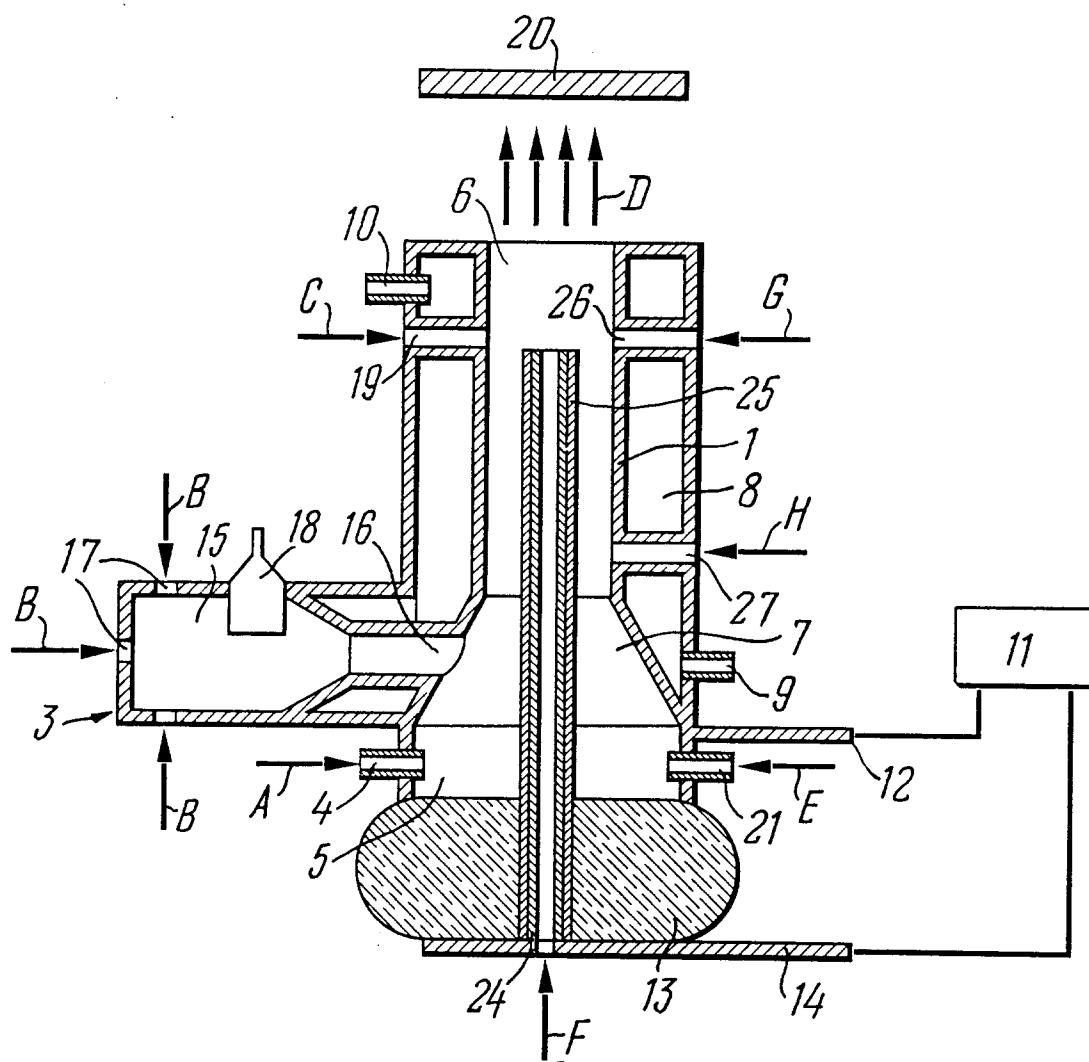


FIG. 4

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/SU 91/00051

## A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. 5 C23C 4/00, B05B 7/20

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl. 5 C23C 4/00, B05B 7/20

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	SU, AI, 747010 (NAUCHNO-ISSLEDOVATELSKY INSTITUT TEKNOLOGII AVTOMOBILNOI PROMYSHLENNOSTI) 7 November 1989 (07.11.89), the claims	1-3, 4-9
A	--- JU.S.BORISOV et al. "Gazotermicheskie pokrytia iz poroshkovykh materialov", spravochnik, 1987, Naukova Dumka, (KIEV), pages 76-78	1, 4, 7
A	--- US, A, 4172558 (A.I.ZVEREV et al.) 30 October 1979 (30.10.79), the abstract	4-9
A	--- DE, AI, 3903888 (GASTOLLIN S.A.), 16 August 1990 (16.08.90), the abstract	1, 4
A	--- EP, A3, 0297845 (GENERAL ELECTRIC COMPANY), 18 October 1989 (18.10.89) -----	8, 9



Further documents are listed in the continuation of Box C.



See patent family annex.

## \* Special categories of cited documents:

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Date of the actual completion of the international search

29 November 1991 (29.11.91)

Date of mailing of the international search report

25 December 1991 (25.12.91)

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