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Continuation-in-part of application Ser. No. 715,669, Mar., 1968, now Patent No. 3,519,257. This application Feb. 25, 1970, Ser. No. 13,939

[54] **PROCESS AND DEVICE FOR THE TREATMENT OF SURFACES OF WORKPIECES IN AN ANNEALING FURNACE**
9 Claims, 2 Drawing Figs.

[52] **U.S. Cl.** **263/15, 148/16**
[51] **Int. Cl.** **F27d 17/00, C21d 1/76**
[50] **Field of Search** 263/15, 52; 148/16

[56] **References Cited**

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ABSTRACT: Protective and carrier gases which are to be used in various processes in annealing furnaces are produced in situ with the aid of catalysts applied to the inner surfaces of the furnaces. Preferably the oxygen containing gas is preheated before being mixed with fuel to form the protective or carrier gas.

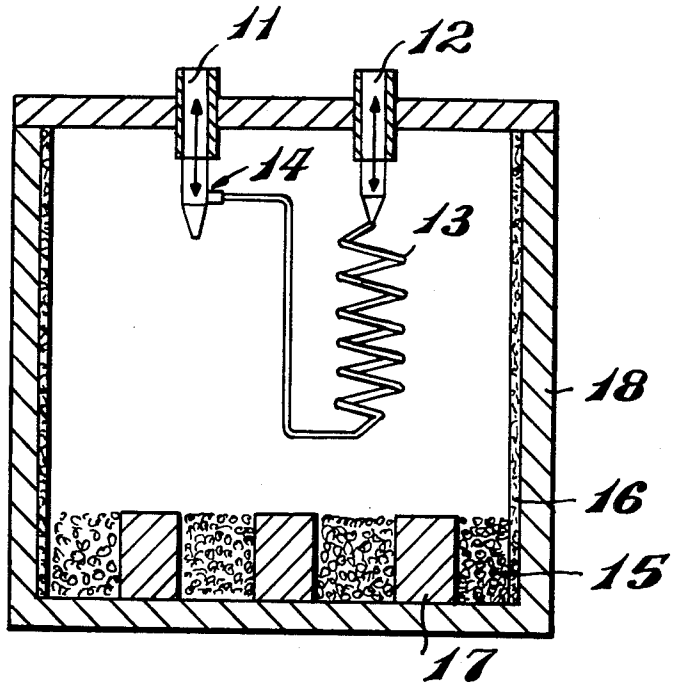

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Fig. 1.

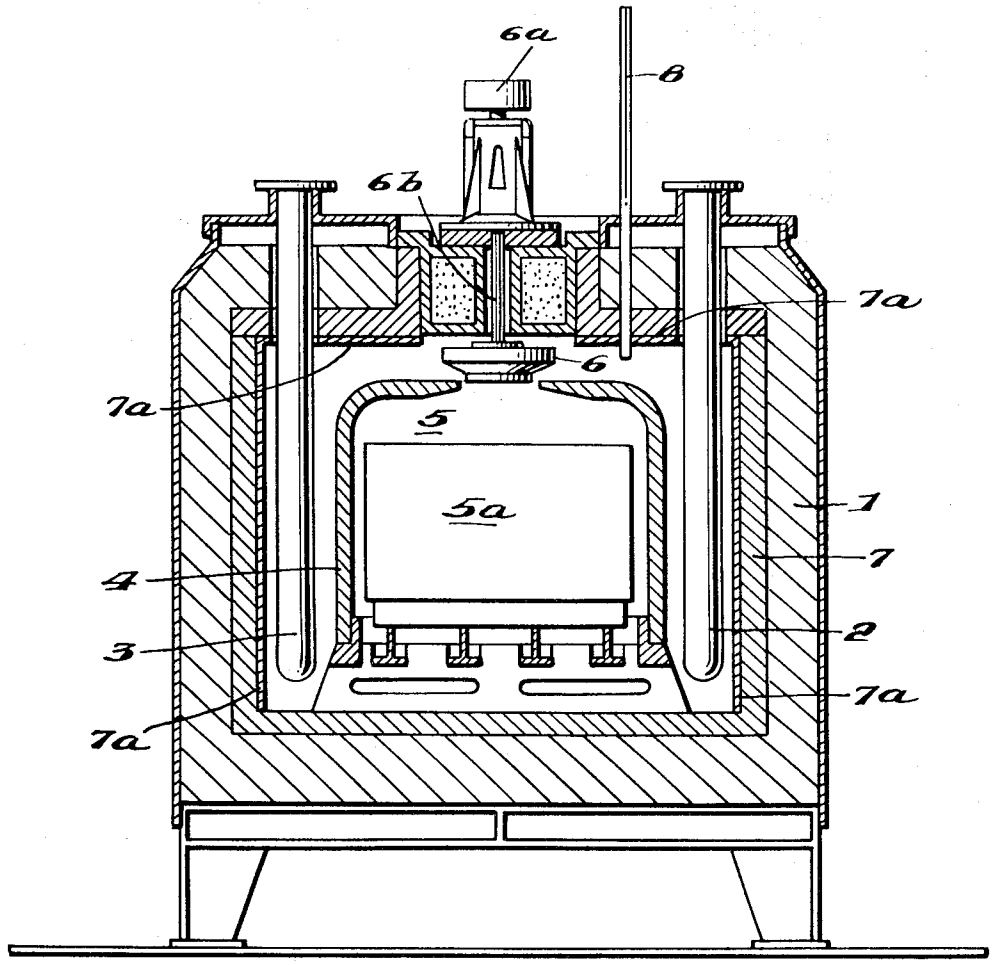

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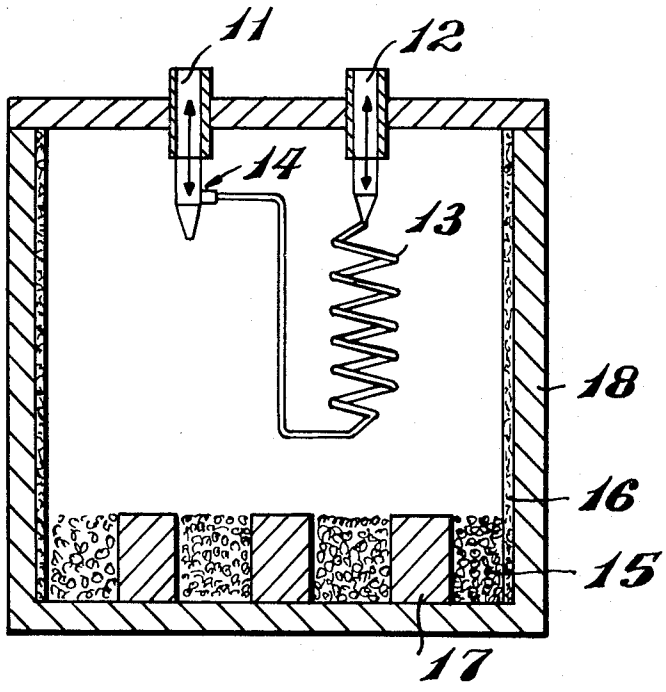
Fig. 2.



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PROCESS AND DEVICE FOR THE TREATMENT OF SURFACES OF WORKPIECES IN AN ANNEALING FURNACE

The present application is a continuation-in-part of application Ser. No. 715,669, filed Mar. 25, 1968 now U.S. Pat. No. 3,519,257, July 7, 1970. The entire disclosure of the parent application is hereby incorporated by reference.

Protective gases or carrier gases which are used in chemical processes such as the gas carburizing, gas carbonitriding and bright hardening processes, for the treatment of the surfaces of various types of workpieces including metals such as steel and steel alloys, have been produced, in general, in special generators. These gases are produced, generally, in exothermic or endothermic processes in which a hydrocarbon fuel is partially or completely combusted in air. Thus, in order to produce a protective gas endothermically, the hydrocarbon fuel is mixed with such an insufficient amount of air or oxygen for combustion that the combustion of the fuel is not as complete as would be the case in an exothermic combustion of the fuel. The protective gas generators in which these endothermic reactions are conducted have an additional heated reaction chamber in which a catalyst is placed in order to provide for improved decomposition of the fuel, particularly when the heavier hydrocarbon materials are used for this purpose.

It has been proposed several times that the protective gases be produced in suitable annealing furnaces in which they were to be used in the gas carburizing, gas carbonitriding or bright hardening processes conducted in such furnaces. When these processes were conducted, however, in the furnaces prepared in accordance with such proposals, undesirable carbon black formed on the surfaces of the workpieces which rendered the surfaces of the workpieces inactive. In addition, the dependability of the operation of the furnaces was jeopardized by the carbon black.

It has also been proposed in Keitel U.S. Pat. No. 3,075,757, to line a furnace for the bright annealing of metals with platinum or palladium and then introducing a reducing gas consisting of hydrogen or hydrogen mixed with nitrogen into the furnace.

An object of the present invention is to provide a process and device in which various types of gases may be formed in situ in annealing furnaces, and without the attendant formation of carbon black.

An important feature of the present invention resides in the use of an annealing furnace which has a catalytically active surface therein for use in the in situ formation of protective and carrier gases from fuel and oxygen.

Another important object is to improve such furnace and process by appropriate pretreatment of the oxygen.

The invention will be understood best in connection with the drawings wherein:

FIG. 1 shows an annealing furnace in which the process of the present invention may be conducted; and

FIG. 2 shows a modified annealing furnace for carrying out the process in improved fashion.

It has now been found, in accordance with the present invention, that various types of protective gases can be produced without difficulty by supplying air for combustion and fuel to an annealing furnace, if the wall of furnace, preferably a ceramic wall, is treated with a catalyst, for example nickel oxide, in such a way as to provide the wall with a layer of catalyst as, for example, by applying nickel oxide in a liquid carrier to the wall, and then vaporizing off the liquid so as to leave behind a layer of nickel oxide. Since the ceramic walls of annealing furnaces have large surface areas, the treatment of the wall with the catalyst in this way will provide a sufficiently large active surface area for the purposes of the present invention. In addition, the treatment prevents the formation of carbon black on the walls of the furnace.

FIG. 1 of the drawings shows an annealing furnace device of the present invention. The device has an outer wall **1**. The inside of the furnace is heated by steel heating rods **2** and **3**. Within the furnace there is located a gas containing muffle **4**

in which there is located area **5** in which workpiece **5a** is placed when it is to be processed in the furnace. The atmosphere within the furnace is agitated by means of a rotating ventilator **6** which is turned by means of knob **6a** which is attached to ventilator **6** by rod **6b**. On the inner wall **7** of the furnace there is a layer of catalyst **7a**. The catalyst layer can, for example, as mentioned above, be formed by placing a layer of nickel oxide on wall **7**. However, if desired, another catalyst can be used, such as platinum or palladium. Through inlet tube **8** there can be introduced into the furnace a mixture of air and fuel, such as a heavy hydrocarbon such as butane or propane. When this mixture is partially combusted in the furnace, in contact with the catalyst, a gas which can be used for carburizing the workpiece if formed. If it is desired to form a gas for carbonitriding, then ammonia can also be introduced into the furnace, simultaneously, with the hydrocarbon material.

It has proved advantageous to use catalyst preparations containing nickel, generally with a content of Ni of 3 to 6 percent; but catalysts containing precious metals may also be applied, i.e., metal catalysts, preferably a nickel or a precious metal catalyst on a suitable carrier material, e.g., finely divided aluminum oxide.

FIG. **2** shows the presently preferred annealing furnace device of the invention wherein the process and apparatus have been substantially improved by providing for the preheating of the air for combustion. In this preferred form of the invention it is especially desirable to subject the preheated air and fuel to a partial process of combustion prior to contact with the catalyst lined furnace surface. The primary advantage of preheating the air is to prevent the formation of carbon black. The oxygen, e.g. as air, is preheated to a temperature of 600° to 1,600° C., preferably about 800° C. so that there is no formation of carbon black in the annealing chamber.

As shown in FIG. **2**, fuel, e.g., hydrocarbons of one to 10 carbon atoms, are supplied to the furnace chamber through conduit **11** and air is supplied through conduit **12**. The air does not go directly into the furnace chamber but is supplied by way of air preheater **13** to mixing nozzle **14** in which a partial combustion of the gases results. This partially burned gas enters into the furnace chamber and forms, after catalytic combustion on the catalyst layer **16** of the wall **18** of the annealing furnace, the desired protective or carrier gas atmosphere.

In addition to hydrocarbon containing gas for this purpose it should be understood that liquid hydrocarbons can be employed. There can be used any of the fuel gases or liquids previously set forth.

To increase the catalyst surface additional catalyst particles **15** can be discontinuously positioned in the furnace chamber, for example, on the floor of the furnace. Most suitable is the entire space between the carrying rails **17** for the load. The invention can also be carried out in such a manner than in place of the ceramic furnace lining with a catalyst coating, e.g., nickel, nickel oxide, platinum or palladium, the furnace muffle is made of high nickel-containing, heat-resisting material whereby the high nickel-containing construction material acts partially or completely as the catalyst.

In the process as described in connection with FIG. **1** or as modified in FIG. **2**, the protective or carrier gas is formed in the furnace during the operation of the furnace under the conditions commonly employed for such processes, i.e.,

Process	Operating Conditions Temperature	Pressure
Carburizing	800°–1,100° C.	0.2–4,000 Torr
Carbonitriding	750°–1,100° C.	0.5–3,000 Torr
Bright hardening	750°–1,100° C.	0.5–3,000 Torr

The time of treatment varies between 1 and 10 hours according to the desired carbon content, depth of carburization and the strength of the nitriding layer.

The workpieces that may be treated during such processes in accordance with the present invention include all those types of materials that are commonly treated in such processes, such as, ferrous materials including steel and steel alloys. To improve hardness and resistance against wear and tear all technical parts of machinery, parts of gear, working parts, the surfaces of which may be carburized, gas carbonitrided and bright hardened, may be treated accordingly.

To carburize the surfaces of metal, city gas, generator gases, coke oven gas, methane, propane, butane and mixed power gases deriving from the aforementioned kinds of gas may be used. Furthermore, the necessary gas atmospheres may also be furnished by liquid hydrocarbons such as fuel oil, diesel oil, benzene, alcohol and the like. For nitroding or carbonitriding purposes NH_3 may also be applied in addition of the aforementioned gases.

The gases that can be formed in the furnaces in accordance with the present invention include all those commonly employed in annealing furnaces, and preferably those formed in endothermic reactions. A listing of the types of such gases, the precursors which are reacted to form such gases, and the catalysts to be employed in such reactions is as follows:

Type of gas	Precursors	Catalyst
Carburizing	(a) C_1 to C_{10} hydrocarbon + oxygen.	(a) NiO, Pt, or Pa.
Carbonitriding	(a) C_1 to C_8 hydrocarbon + oxygen + ammonia.	(a) NiO, Pt or Pa.
Bright hardening	(a) C_1 to C_{10} hydrocarbon − oxygen.	(a) NiO, Pt, or Pa.

When used as a coating on the wall of the furnace the catalyst should be applied thereto so as to provide an adherent, continuous active catalyst layer. The manner of applying the catalyst is not important as long as the continuity and adherence of the catalyst is not disturbed during the operation of the furnace. The inner wall may be ceramic, or other materials.

The following examples are merely illustrative of the scope of the present invention and are not intended as a limitation thereof.

EXAMPLE 1

Gas carbonitriding of gear wheels for automobiles.	
Working temperature	870° C.
Required depths of hardness	0.5 mm. (HV 525)
Carbon content	0.8% C
Heating to a temperature of about 870° C.	about 60 min. with a CO_2 value of about 0.6% in a mixture of propane and air in a ratio of 1:9
Time of carbonitriding	about 90 min. with a CO_2 value of about 0.3%

During the carbonitriding process the aforementioned gas-air mixture is kept and an additional amount of 100 l NH_3 passed into the mixture. Subsequently, the workpieces are quenched in oil.

The preheating of the air, e.g., to 800° C. can be employed with the process of example 1.

The following example further illustrates the preferred form of the invention wherein the air is preheated.

EXAMPLE 2

Gas carburizing of gear wheels for automobiles	
Working temperature	900° C.
Required depth of hardness	0.8 mm. (HV 525)
Carbon content	0.8% C
Heating to a temperature of about 900° C.	about 60 min. with a CO_2 value of about 0.5% in a mixture of propane and preheated air (600° C.) in a ratio of 1:9
Time of carburizing	about 180 min. with a CO_2 value of about 0.22%

During the carburizing process the aforementioned gas-air mixture is kept and an additional amount of 50 l C_3H_8 per hour passed into the mixture. Subsequently, the workpieces are quenched in oil.

What is claimed is:

1. In an apparatus including an annealing furnace adapted for the treatment therein of workpieces in an atmosphere of a protective or carrier gas, the improvement comprising an inner surface of said furnace with a layer of catalyst adapted to catalyze the formation of said gas in said furnace during said treatment, means for introducing fuel gas into said furnace, means for preheating an oxygen-containing gas, means for mixing said preheated oxygen-containing gas and said fuel gas to partially react them prior to contact with said catalytic surface and means for introducing said mixture into said furnace whereby said protective or carrier gas is formed from said fuel gas and said oxygen-containing gas.

2. An apparatus according to claim 1 wherein said mixing means comprises a nozzle.

3. In a process for treating a workpiece in an annealing furnace in an atmosphere of a protective or carrier gas, the improvement comprising forming the gas for said treatment in said furnace by preheating oxygen mixing the preheated oxygen with fuel and combusting the mixture of fuel and oxygen while contacting the mixture with a catalyst adapted to catalyze the formation of said gas.

4. A process according to claim 3 in which said catalyst is present at least in part as a coating on an inner surface of said furnace and said fuel includes hydrocarbon.

5. A process according to claim 4 wherein the preheating is to a temperature of 600° to 1,600° C.

6. A process according to claim 5 wherein the preheating is to a temperature of 800° C.

7. A process according to claim 4 wherein the catalyst is selected from the group consisting of nickel, nickel oxide, platinum and palladium.

8. A process according to claim 7 wherein the gas is selected from the group consisting of a carburizing gas, a carbonitriding gas and a bright hardening gas.

9. A process according to claim 8 wherein the fuel and preheated oxygen are partially combusted before contacting the catalyst in the furnace.

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