Method for removing carbonaceous deposits from heat treating furnace.

A process for removing carbonaceous deposits (e.g. soot) from a heat-treating furnace by passing a burn out gas containing from, by volume, 10 to 100% carbon dioxide, 0 to 20% water vapor balance nitrogen, air, or mixtures thereof through the furnace at a temperature of at least 1500°F.
METHOD FOR REMOVING CARBONACEOUS DEPOSITS FROM HEAT TREATING FURNACES

TECHNICAL FIELD

This invention pertains to the removal of carbonaceous deposits such as soot from heat-treating furnaces used to heat treat ferrous metals under an atmosphere containing reactive carbon.

BACKGROUND OF THE PRIOR ART

The metallurgical industry employs heat-treating furnaces for a variety of purposes. Under certain heat-treating conditions deposits of carbon may form in the furnace. For example, in gas carburization an atmosphere containing carbon donating (reactive carbon) constituents is employed to transfer carbon to the surface of steel, thereby causing a high carbon surface layer to be formed which increases the surface hardness of the part after rapid cooling (e.g. quenching). The presence of these carbon donors in the atmosphere may
also lead to unwanted deposits of elemental carbon being formed at various points in the furnace.

Powder metallurgy involves the sintering of objects produced by compression of powdered metals. To insure the development of adequate density, and release of the object from the mold, these powders contain a lubricant which is usually a carbon-containing solid, such as a metal soap. During heating in the furnace, the lubricant decomposes releasing volatile materials which form sooty deposits in the furnace.

Deposition of soot or other carbonaceous material in the furnace is undesirable. It may obstruct the flow of gases through the furnace, interfere with effective heat transfer, and in some cases, may react with high temperature alloy components of the furnace reducing their strength and durability. It is necessary periodically to remove carbon from heat-treating furnaces. An effective way to achieve this end is to burn the carbon out with air or with air diluted with an inert gas such as nitrogen.

However, since the reaction of oxygen with carbon to form carbon dioxide is highly exothermic (96,000 calories (96 kcal) per gram mole at 1700°F.) great care must be exercised to avoid overheating which can cause severe damage to the furnace or its internal components. The effects of sooting and of the catastrophic melting of an alloy radiant heating tube during soot burnout is shown and discussed in an article entitled, "Understanding Conditions that Affect Performance of Heat Resisting Alloys", Parts I and II appearing in the March and April 1979 editions of Industrial Heating, Vol. XLVI, No. 3, pp. 8-11 and Vol. XLVI, No. 4, pp. 44-47. It is customary to control the rate of carbon burnout by lowering the furnace temperature, and by using a gas containing only a low concentration of
oxygen so the heat may be removed as it is produced. However, this slow process may require many hours for completion, and during this time the furnace is not available for useful work.

**BRIEF SUMMARY OF THE INVENTION**

We have discovered means which rapidly remove carbon deposits by reaction with a gaseous cleaning agent (burnout gas) without creating excessive temperatures (hot spots) at any point in the furnace. It has been found that if the furnace is maintained at the temperature normally employed for heat-treating, e.g., from about 1500°F. to about 1900°F. (816°C to 1038°C), an atmosphere containing substantial quantities of carbon dioxide will rapidly and completely convert any deposits of carbon to gaseous carbon monoxide. Further, since the reaction of carbon and carbon dioxide to form carbon monoxide is endothermic, (40 kcal being absorbed per gram mole of carbon removed), the region in which carbon removal takes place is actually cooler than the remainder of the furnace, and heat must be supplied. Upon completion of the carbon removal, which may be monitored by observing the concentration of carbon monoxide in the exit gases, the furnace may be put back on stream in a short time simply by flushing with the normal heat-treating atmosphere to which a small amount of a carbon dioxide scavenger, such as natural gas, has been added.

Water may also be employed for safe removal of carbon since it too reacts rapidly with carbon in a process which requires 32 kcal per gram mole of carbon removed. Water is more difficult to remove from a furnace than is carbon dioxide, and, therefore, additional time will be lost before the furnace is completely prepared to go back into heat-treating service. Furthermore, when water is employed as a cleaning agent, it usually must be diluted with an inert carrier gas such
as nitrogen to avoid condensation in cooler parts of the system such as inlet ducts, vent lines and stacks.

Carbon dioxide may be employed in admixture with an inert carrier, or if desired, may be used undiluted, in which case the most rapid clean out of the furnace will be attained.

DETAILED DESCRIPTION OF THE INVENTION

Normally furnaces containing heavy deposits of carbonaceous material (e.g. soot) are burned out with air or diluted air, for example, 10% air in nitrogen. The reason for this is the generation of hot spots when substantial amounts of soot are deposited on the radiant tubes. Oxygen reacts with carbon to form either carbon monoxide or carbon dioxide depending on the relative amounts of oxygen and carbon. This reaction is exothermic, by generating one gram mole of carbon monoxide at 1700°F about 28 kcal would be produced; by generating one gram mole of carbon dioxide at 1700°F about 95 kcal would be produced. On the other hand, the reaction between carbon dioxide and carbon consumes 39 kcal per gram mole and hot spots simply cannot occur. Therefore, it was reasoned that pure carbon dioxide could be used for removing the soot and a much faster operation would result.

The following example illustrates the furnace cleaning process of the present invention.

Example 1

A heat-treating furnace having a volume of 7.5 cu. ft. was intentionally sooted by passing a mixture of nitrogen and propane through it for a period of 17 hrs. at a temperature of 1700°F (927°C). The flow rate of nitrogen was 100 standard cubic feet per hour (SCFH) and of propane was 2.5 SCFH. A total of about four pounds of soot was deposited in the furnace. The nitrogen propane mixture was then replaced by a stream
of carbon dioxide at a rate of 100 SCFH whereupon the
temperature of the furnace dropped about 60°F (33.3°C),
an indication of an endothermic process. The furnace
atmosphere was sampled and analyzed at periodic intervals
with the results as shown in the following Table I:

<table>
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<tr>
<th>Time Minute</th>
<th>Furnace Atmosphere (By Volume)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>% H₂</td>
</tr>
<tr>
<td>10</td>
<td>5.49</td>
</tr>
<tr>
<td>13</td>
<td>2.05</td>
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<tr>
<td>20</td>
<td>0.92</td>
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<td>15</td>
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<tr>
<td>41</td>
<td>0.11</td>
</tr>
<tr>
<td>47</td>
<td>0.07</td>
</tr>
<tr>
<td>60</td>
<td>0.05</td>
</tr>
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</table>

The concentration of hydrogen, which resulted from
cracking of the propane, drops rapidly as carbon dioxide
sweeps through the furnace. However, only a low concen-
tration of the latter appears at the exit of the furnace,
most of it being converted to carbon monoxide by reaction
with soot. This process occurs for about 40 minutes,
at which time an abrupt rise in carbon dioxide concen-
tration and a corresponding decline in carbon monoxide
is observed as complete burnout is approached.

From these data it is estimated that approximately
three pounds of carbon has been removed in a period of
about 60 minutes without production of a hot spot in
the furnace.

To remove the same quantity of carbon with 100
SCFH flow of pure air requires 2.2 hours, and would
result in generation of localized high temperatures at the points where the soot burns. If the normal mixture of 10% air and 90% nitrogen were employed at a flow rate of 100 SCFH, 22 hours would be required to achieve the same result.

The carbon dioxide level in the burnout mixture is preferentially 100% but could be varied between 10 and 100%. The flow of burnout gas can be as high as 300 SCFH or 40 volume changes. Since the gas volume is doubled upon combining with carbon, a considerable increase in gas pressure occurs in the furnace. The upper limit of the carbon dioxide flow is determined by the maximum flow the furnace is designed for. The preferred carbon dioxide flow is between 10 and 40 volume changes. At smaller flows, carbon dioxide would be completely converted but the burnout would last longer. The burnout temperature is limited to the normal carburizing temperatures and will preferentially be between 1500 and 1700°F (816°C and 927°C). At lower temperatures burn out will be slower and less efficient. Higher temperatures will not be a problem. The upper limit is given by the maximum operating temperature of the furnace.

In order to prepare the furnace for normal operation and reduce the carbon dioxide level a mixture of 100 SCFH nitrogen and 20 SCFH natural gas was fed to the furnace. After 10 minutes the furnace atmosphere contained 20% hydrogen, 0.05% carbon dioxide, 1.6% methane and 12% carbon monoxide. This may be considered a perfect atmosphere to start any nitrogen based carburizing system.

The results indicate that the proposed method of burning out a furnace results in production time savings of 1.2 up to 21 hours. At the same time the risk of tube burnout is completely eliminated.

Water vapor can be used as a component of the burnout gas since water vapor has a heat consumption of 32 kcal/gram mole of carbon. The water in a nitrogen gas
mixture should be present in an amount from, by volume, 0% to 20%. However, water in the liquid form complicates metering it into the furnace and the furnace will have a high dew point. Thus it requires at least several hours at temperature after cessation of water injection to dry out the furnace.

Having thus described our invention, what is desired to be secured by Letters Patent of the United States is set out in the appended claims.
I Claim:

1. A method for removing carbonaceous deposits from a furnace utilized for heat-treating ferrous metals under an atmosphere containing reactive carbon without creating hot spots in interior parts of said furnace comprising the steps of:

   heating said furnace to a temperature of at least 1500°F;
   injecting a burnout gas into said furnace said burnout gas consisting essentially of from 10 to 100% by volume carbon dioxide, 0 to 20% water or mixtures thereof, balance nitrogen; and continuing flow of said burnout gas into said furnace until between 10 and 40 volume changes of carbon dioxide in said furnace have occurred.

2. A method according to Claim 1 wherein 100% by volume carbon dioxide is injected into said furnace.

3. A method according to Claim 1 wherein after said burnout gas injection is completed said furnace is conditioned for normal operation by flowing a conditioning gas mixture through said furnace for a minimum of ten minutes.

4. A method according to Claim 3 wherein said conditioning gas mixture contains by volume 40% nitrogen and 10% natural gas.

5. A method according to Claim 1 wherein said flow of burnout gas containing carbon dioxide is continued while monitoring the furnace atmosphere until said furnace atmosphere passes a point at which the residual carbon dioxide has reached its lowest level.
## DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document with indication, where appropriate, of relevant passages</th>
<th>Relevant to claim</th>
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<td>A</td>
<td>DE - A - 2 841 626 (BROWN BOVERIE &amp; CIE.) * claims 1-4 *</td>
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<td>A</td>
<td>GB - A - 604 538 (GENERAL ELECTRIC) * claims 1-3 *</td>
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<td>A</td>
<td>DE - A - 2 155 897 (RIVENAES) * page 3, lines 23-28; page 4, line 1 *</td>
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### CLASSIFICATION OF THE APPLICATION (Int. Cl.)

| C 23 C 11/10 | C 21 D 1/76 |

### TECHNICAL FIELDS SEARCHED (Int. Cl.)

| C 23 C | C 21 D | F 23 J | F 28 G |

### CATEGORY OF CITED DOCUMENTS

- X: particularly relevant
- A: technological background
- O: non-written disclosure
- P: intermediate document
- T: theory or principle underlying the invention
- E: conflicting application
- D: document cited in the application
- L: citation for other reasons

### The present search report has been drawn up for all claims

- A: member of the same patent family, corresponding document

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**Place of search:** The Hague  
**Date of completion of the search:** 16.11.1981  
**Examiner:** RIES