APPARATUS AND PROCESS FOR THE GASEOUS DEOXIDATION OF ANODE COPPER

ABSTRACT: A process and apparatus for the gaseous deoxidation of molten metal in which a reformable hydrocarbon and steam is substantially simultaneously injected beneath the surface of molten metal in a furnace through water-cooled lances in which partial reforming of the hydrocarbon with the water vapor to carbon monoxide takes place in the lance prior to its introduction into and dispersion within the molten metal in the furnace.
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This is a division of application Ser. No. 627,779, filed Apr. 3, 1967 and now U.S. Pat. No. 3,545,962.

This invention relates to the treatment of molten metal and more particularly to the treatment of molten metal to dec- 
idize the same. It is of especial value in connection with the 
treatment of molten copper and copper-base alloys (herein 
generally referred to as copper-base metals) and will therefore 
be described with particular reference to that case. It is how- 
ever to be appreciated that the processes and apparatus herein 
described are of value also in the deoxidation of other molten 
metals.

The solubility of oxygen in copper increases rapidly as 10 
the copper is raised above its melting point. Accordingly it is a 
standard practice in the production of copper-base metals to 
subject the metal, while in the molten condition, to a treat- 
ment which will reduce, or even eliminate, the oxygen con- 
tent. A well-known technique which has been practiced for 
very many years is that known as "poling" and consists in im- 
mersing poles of green wood in the molten copper-base metal. 
The volatilization of gases from the green wood creates sub- 
stantial turbulance in the molten metal and the general effect 
is one of chemical reduction.

In order to simplify and decrease the cost of the deoxidizing 
operation, means have been sought to introduce into the mol- 
ten metal a gas which has reducing properties, either directly 
or by generation from an introduced solid substance.

One method which has been proposed in Canadian Pat. No. 
668,598 granted to Phelps Dodge Corp. on Aug. 13th 1963, 
consists in injecting into a molten metal a gaseous mixture 
containing carbon monoxide and hydrogen, both of them 
reducing gases. Such a gaseous mixture may be obtained by 
subjecting a hydrocarbon to partial oxidation, the carbon 
being converted to carbon monoxide and the hydrogen being 
released as molecular hydrogen. Provision is made for such 
oxidation to be effected as an operation separate from the 
metal-treating operation itself. Gases are commonly injected 
into molten metals by the use of lances or tuyeres and in 
the method just referred to the gas brought to the lance or tuyeres 
is already a gaseous mixture containing carbon monoxide and 
hydrogen.

It is an object of one aspect of the present invention to pro- 
vide a process for the deoxidation of molten metals, and par- 
ticularly such processes which make use of hydrocarbons 
starting materials but avoids the necessity for a separate 
unit for the partial oxidation or reforming with water vapor of 
the hydrocarbon prior to its introduction into the furnace. It 
is based on the discovery that hydrocarbons may be readily 
reformed to carbon monoxide and hydrogen by premixing 
water vapor with the hydrocarbon so that the mixture of the 
reducing gases can be produced either within the injection 
lance or as the hydrocarbon-water vapor mixture dispersed 
within the liquid bath.

Therefore, the process for the deoxidation of molten copper 
of the present invention involves producing and bubbling 
reducing gas mixtures through the melt with an injection 
lance, which lance is disclosed and referred to herein for a 
clear understanding of the process of the present invention. A 
feature of the present process is that the reducing gases are 
obtained by chemical reaction within the lance structure, and 
also in the melt, and at the same time the formation of exces- 
sive carbon either inside the lance or later after the gases have 
been bubbled through the melt is clearly inhibited if not 
prevented. It is a known fact that without the process 
described herein hydrocarbons such as propane and butane 
 injected into a copper melt, produce an excessive amount of 
carbon by thermal decomposition at the high temperature ex- 
perienced in normal copper refining. This carbon may build 
up in the lance and results in partial or complete blockage and 
also pollutes the atmosphere around the furnace with thick, 
black smoke which constitutes a health and safety hazard.

A further feature of the present process is that the heat 
required for the chemical reaction within the lance, and also 
the heat required to heat the gases to the reaction tempera- 
ture, maintains the lance cooler than the melt so that a lance 
material may be used which could not otherwise withstand the 
high temperatures experienced in the deoxidation processes.

The raw feed materials which may be used in the present 
process are water vapor (steam) mixed with the appropriate 
proportion of hydrocarbons such as methane, propane, buta- 
tane, naphtha.

According to the present invention there is provided a 
process for the deoxidation of molten metal which comprises 
substantially simultaneously injecting into a bath of said mol- 
ten metal below the upper surface of said bath a reformable 
hydrocarbon and steam whereby to achieve partial reforming 
thereof in situ to a reducing-gas mixture containing carbon 
monoxide and hydrogen, said simultaneous injection being ef- 
fected through injection means.

In the drawings:

FIG. 1 is a side view of a typical rotary furnace with cutaway 
section showing a lance depending into the melt;

FIG. 2 is a section of a reverberatory furnace with a lance 
extending through a side port thereof into the melt; and

FIG. 3 is a cutaway section of the lance which is associated 
with the process of the present invention and illustrates the 
flow of the water-gas mixture therein.

In a particularly preferred form of the said process the melt 
is a copper-based metal.

While it is not desired to be limited to any particular theory, 
it is believed that the gas issuing from the injection lance 
below the surface of the metal melt is caused to disintegrate 
into a plurality of small bubbles a short distance from the noz- 
kle or orifice of the injection lance. The high interfacial area 
results in very high rates of reaction. Consequently gas 
utilization efficiencies of 70 percent or higher are obtainable 
depending on the depth of immersion of the injection lance 
and the gas-flow rate. The depth of the lance is generally 
between 1 foot and the maximum depth of the liquid bath. The 
reducing gas-flow rates range from Reynolds 
number 2,100-1,000,000.

In a preferred process as aforesaid the mixture of hydrocar- 
bon and steam is introduced into the molten metal via the 
lance illustrated in the drawings herein so that interaction 
between the hydrocarbon and the steam may be effected as 
the gases move through the lance (itself heated by the sur- 
rounding molten metal) and the gaseous mixture emerging 
from the lance into the body of molten metal comprises a sub- 
stantial proportion of carbon monoxide and hydrogen.

The efficiency of the deoxidation of the molten metal will 
depend inter alia on the establishment of a considerable con- 
tact area between the injected gas and the molten metal. For 
this reason the design of the lance and the velocity of supply of 
the gas should preferably be such that the gas issuing from the 
lance breaks up to form a mass of small bubbles (rather than a 
relatively few large bubbles) at a few inches away from the 
lance orifice. This condition is attained when the Reynolds 
number of the gas flow through the orifice at the top of the 
lance is greater than 2,100.

While it is generally preferred that the hydrocarbon used 
should be gaseous at ordinary temperatures, e.g., it may be 
methane, ethane, propane, butane or isobutane, hydrocarbons 
which are liquid at ordinary temperatures, e.g., naphtha 
or light oils may also be used.

The preferred hydrocarbons for use are methane, ethane, 
propane and butane.

The proportion of steam flow to hydrocarbon flow used may 
be adjusted to be equal to or less than the stoichiometric 
amount sufficient to reform the hydrocarbon to carbon 
monoxide and hydrogen. If the rate of travel of the mixture 
through the lance is higher, so that the mixture does not heat 
up sufficiently to promote the interaction of the hydrocarbon 
and the steam to a sufficient extent, there may be included 
in the mixture a proportion of oxygen, to facilitate 
the oxidation of the hydrocarbon. Such added oxygen will nor- 
mally react exothermically thus adding heat to the flowing
mixture. However, care must obviously be taken to avoid the addition of so much oxygen that any important proportion of it reaches the molten metal unchanged as that would defeat, or tend to defeat, the object of the deoxidation process. It will be appreciated that added oxygen may be provided in the form of air and that if desired the injected gas stream may contain other, generally inert, gases such as nitrogen or argon. It is also possible to include in the injected gas stream other agents known per se to have a desirable conditioning effect on the molten metal.

The process of the present invention may be applied, for example, to the deoxidizing of molten copper which is intended for use as electrical anode copper or for the production of wire-bars, in reverberatory furnaces of conventional design, or in cylindrical tilting anode furnaces such as are normally used with the poling technique referred to above, without any important modification of the furnaces. Thus for example, any of the following procedures may be used:

a. A battery of lances having the structure disclosed herein e.g., 4–6) may be used for injecting gas to the metal over a period of time comparable to the normal poling period (2–3 hours). At the end of the injection period the metal can be cast.

b. A battery of lances (e.g., 2–3) can be used for reducing the metal near the tapping hole for a period of 30–45 minutes, following which the metal is cast while continuing the reduction during the whole casting period. Thus, metal flowing toward the taphole must pass through and mix with the highly reduced metal in the tapping zone. This method is in some respects preferable to (a) above, since it decreases the overall time of treatment in the furnace and requires less apparatus.

c. A variation of the above processes requires a small (e.g., 5-ton) holding furnace interposed between the reverberatory furnace and the casting machine. Lances, orifices, or tuyeres then introduce the reducing gas in this holding furnace during the entire casting period. This alternative is of particular value as an element of new furnace installations.

It has been found that the use of this invention is highly efficient, the proportion of hydrocarbon converted to carbon monoxide and hydrogen being often as high as 70 to 75 percent. The residual gases as they have the molten metal may be collected and, since they are combustible, may be burnt to provide auxiliary heat to the furnace, thereby reducing the fuel requirements of the burner used to fire the furnace, or may be used to promote heat elsewhere.

A form of apparatus for carrying out the process of the invention is illustrated in the accompanying drawing.

FIG. 1 shows a typical rotary furnace A as used in copper refining. This type of furnace is supported on rollers 21 and may be rotated by a suitable motor connected to a wing gear 22. Steam is brought to the furnace via a pipe 1 and is controlled by a pressure regulator 2 which keeps the steam in the loader pipe 4 at a constant pressure. Steam feed to each lance is controlled by individual valves 3 and is connected to the lance with a flexible hose 5. A hydrocarbon, such as propane or butane, is brought to the furnace via pipe 7 and controlled by a main valve 8. The feed to each lance from a common loader pipe 10 is also controlled by individual valves 9 and connected to the lance by flexible hose 11. The lance assembly consists of a mixing tee 6 into which the steam and hydrocarbon is introduced, lance hanger 15, lance bushing 12 and lance 14. The lance slip-bushing 12 allows the lance to be manually or mechanically rotated periodically through 180° in order to compensate for upward bending of the lance tip. The lance hanger is designed to suspend the lance at the proper angle for maximum depth of lance orifice 17 under the melt surface 19. The whole assembly is suspended to a suitable support by a hook 16 and cable or rope 24.

The lances in FIG. 1 are shown introduced through openings 18 in the end walls 13 of the furnace. However, it also understood that the lance may be introduced through any openings in the furnace that are found suitable, such as openings around the cylindrical shell of the furnace 23. It is further understood that this process may also be applied to other types of furnace such as a reverberatory furnace, a section of which is shown in FIG. 2, with a lance introduced through a sideport 18 in the wall 25 of the furnace. One or more of these lances may be introduced into a reverberatory furnace through suitable ports along one of the long sides of the furnace. For example it has been found that when using propane and steam, 3 or 4 such lances are required for treating a 200–300 ton charge of copper in a reverberatory furnace within a period of two to three hours.

The reaction between steam and hydrocarbon to form various reducing gases (commonly known as reforming reaction) takes place partially in the lance 14 and partially in the melt 20. Thus the gases emerging from the lance orifice 17 may not be completely reacted but will simultaneously continue to react to form reducing gases such as H₂ and CO which at the same time, react with oxygen in the copper as the gas mixture rises through the melt to the surface 19 to form CO₂ and H₂O. In addition to the benefit achieved by the production of reducing gases within the lance and in the melt, by the addition of steam, carbon is prevented from forming which would otherwise be deposited against the inner wall of the lance creating complete blockage and could also form a thick cloud of smoke at the vent opening of the furnace, both of which conditions are undesirable in the deoxidation process. Steam may be added in any proportion to the amount of hydrocarbon as seen fit by the personnel operating the furnace, or as established by special tests. However, the proportion of steam to hydrocarbon must be equal or less than the stoichiometric requirement for stoichiometric reforming reaction. For instance, in the case of propane the stoichiometric H₂O/propane ratio is 3:1 and therefore, the proportion of steam to propane must be kept to less than 3:1 ratio.

The following reactions are shown for the introduction of steam in the hydrocarbon flow through the lance or tuyere to achieve the partial reforming of the hydrocarbon to hydrogen and carbon monoxide:

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} & \rightarrow \text{CO} + 3\text{H}_2 \\
\text{C}_3\text{H}_8 + \text{H}_2\text{O} & \rightarrow 3\text{CO} + 7\text{H}_2 \\
\text{C}_3\text{H}_8 + 4\text{H}_2\text{O} & \rightarrow 4\text{CO} + 9\text{H}_2 \text{ for butane flow}
\end{align*}
\]

FIG. 3 is a section of the lance of the present invention, as it is introduced into a metal melt 20. Water or other liquid such as naphtha is delivered through an inlet tube 34 and end adapter 35 to a mixing and atomizing nozzle 36 and into the lance 14 through an orifice 37. The gas to be introduced into the molten metal is delivered to the lance 14 through an opening 33 in a mixing tee 6 and passes through the atomizing and mixing nozzle 36 into the lance 14 through orifice 38. The orifices 38 are so shaped and dimensioned that water enters the lance 14 in the form of a fine spray. As the mixture of water droplets and gases pass through the lance 14, in the process of copper deoxidation, the water is vaporized and reacts with the hydrocarbon gases in the lower hot section of the lance.

**EXAMPLES**

Using apparatus as shown in the accompanying drawing three of the pilot scale tests were carried out using propane as the hydrocarbon and "anode" copper as the metal under treatment. The following table sets out the conditions of the tests and the results obtained:

<table>
<thead>
<tr>
<th>Run no.</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper charge, lb.</td>
<td>4,850</td>
<td>4,850</td>
<td>4,410</td>
</tr>
<tr>
<td>Lances, internal diameter, inches</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Lances immersion in liquid bath, inches</td>
<td>7</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Propane rate, cubic feet per minute</td>
<td>2.3</td>
<td>3.0</td>
<td>4</td>
</tr>
<tr>
<td>Steam rate cubic feet per hour</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
These examples were conducted in a pilot reverberatory furnace on a 2½-ton metal blister copper which had previously been oxidized. Each reduction run was followed by a reoxidation period. The reduction gas, namely a propane-steam mixture, was introduced into the melt through a lance made of 310 stainless steel lowered vertically in the bath through the furnace roof. The depth of immersion of the lance was about 7 inches and the total depth of the molten bath at that location was 12 inches. Lances of ½ inches, ¾ inches, and 1 inches internal diameter were used.

The course of the reaction was followed by visual inspection of button samples and immersion and the examination of polished sections. The furnace gases were also analyzed chromatographically for carbon monoxide and carbon dioxide content during the run at 3-minute intervals. The samples were subsequently analyzed for oxygen content and the results appear on the above table.

In reference to the figures given for utilization efficiency it is pointed out that the efficiency involves two elements:

a. the efficiency of the propane-steam reactions:

$$\text{C}_3\text{H}_8 + 3\text{H}_2\text{O} \rightarrow 3\text{CO} + 7\text{H}_2 \rightarrow 1.$$  

b. the efficiency of utilization of the hydrogen and carbon monoxide produced by reaction (1) in reducing oxidized anode copper:

$$\text{Cu}_2\text{O} + \text{H}_2 \rightarrow 2\text{Cu} + \text{H}_2\text{O} \rightarrow 2.$$

In practice, it is difficult to distinguish between the yields of reaction (1) and reactions (2) and (3). In this specification, the term "percent utilization efficiency" indicates the combined yield of reactions (1), (2), and (3). Therefore, at the ideal situation of 100 percent gas utilization efficiency, the propane would be completely converted to hydrogen and carbon monoxide and these gases would be fully utilized according to equations (2) and (3).

It will be observed from the foregoing table that under the best conditions a gas utilization efficiency of the order of 70 percent is achieved.

It will be seen that the process of the present invention includes the advantages that it eliminates the need for a reforming plant and it eliminates the generation of any significant amounts of carbon soot. It also enables reforming within the body of the injection lance and the melt by introducing a mixture of gas-steam into the lance. The special lance construction used in the process allows for periodic rotation of 180°. It is apparent that the process herein described represents a significant advance in the field of gaseous deoxidation of molten metal.

We claim:

1. In combination with a reverberatory anode furnace, injection means adapted to inject a reformable hydrocarbon and steam below the surface of a molten metal therein, said injection means having cooling means associated therewith said cooling means comprising a lance having, (a) a feed chamber adapted to allow the flow of a gaseous treating medium therethrough, (b) a gas inlet in one wall of the feed chamber, (c) a coolant-liquid-transmitting conduit extending axially through said chamber and terminating in a liquid outlet in a second wall of the feed chamber, (d) at least one gas outlet in said second wall angled and positioned such that the flow of gaseous treating medium therethrough causes coolant liquid flowing through the liquid outlet of the transmitting conduit to disperse into liquid droplets, and (e) an elongated body defining a flow passage extending axially through said body, said passage being adapted to receive the mixture of liquid droplets and gaseous treating medium and having one end terminating at the second wall of the said chamber and a second end terminating in a discharge outlet, said elongated body being adapted to be at least partially submerged in molten material and to be cooled internally by the impingement of liquid droplets on the walls of the flow passage.

2. In combination with a cylindrical tilting anode furnace, injection means adapted to inject a reformable hydrocarbon and steam below the surface of a molten metal therein, said injection means having cooling means associated therewith, said cooling means comprising a lance having (a) a feed chamber adapted to allow the flow of a gaseous treating medium therethrough, (b) a gas inlet in one wall of the feed chamber, (c) a coolant-liquid-transmitting conduit extending axially through said chamber and terminating in a liquid outlet in a second wall of the feed chamber, (d) at least one gas outlet in said second wall angled and positioned such that the flow of gaseous treating medium therethrough causes coolant liquid flowing through the liquid outlet of the transmitting conduit to disperse into liquid droplets, and (e) an elongated body defining a flow passage extending axially through said body, said passage being adapted to receive the mixture of liquid droplets and gaseous treating medium and having one end terminating at the second wall of the said chamber and a second end terminating in a discharge outlet, said elongated body being adapted to be at least partially submerged in molten material and to be cooled internally by the impingement of liquid droplets on the walls of the flow passage.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,604,698
Dated September 14, 1971

Inventor(s) Nicholas J. Themelis et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 4, line 43, the reaction should read "C₃H₈ + 3 H₂O → 3 CO + 7 H₂"

Col. 4, in the Table at the bottom thereof under Runs 2 and 3, the values of the variable "Lance, internal diameter, inches" should read, for each "3/4"; under Runs 1 and 2, the variable should read "Propane rate, cubic feet per minute" and the values, for each said run, should read "2.3" and "3.0", respectively under their respective columns.

Col. 5, in the Table, the value of the variable "Rate of oxygen removed, lb./min" for Run No. 1 should be 0.65 under its respective column.

Col. 5, line 35, the reaction should read "C₃H₈ + 3 H₂O → 3 CO + 7 H₂ (1)"

Col. 5, line 39, the reaction should read "Cu₂O + H₂ → 2 Cu + H₂O (2)"

Col. 5, line 40, the reaction should read "Cu₂O + CO → 2 Cu + CO₂ (3)"

Col. 6, line 18, after "terminating in" delete "in".

Signed and sealed this 13th day of June 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents