GAS POLING OF COPPER
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Filed Nov. 21, 1967, Ser. No. 684,745
Int. Cl. C22B 9/08, 19/00, 12/14
U.S. Cl. 75—76
4 Claims

ABSTRACT OF THE DISCLOSURE

This application is concerned with a procedure for poling copper with natural gas. A pool of molten oxygen-bearing copper ready for poling is established in a substantially closed tilting furnace and the natural gas is injected into the pool beneath the molten surface of the metal at a rate which is sufficient to provide a positive pressure and at least about 2% methane, by volume on the dry basis, in the furnace atmosphere; such injection of the natural gas being continued until the oxygen content of the copper is reduced to a desired amount.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention relates to poling copper; and, more particularly it relates to poling oxygen-bearing copper with natural gas.

(2) Description of the prior art

In the art of fire refining of copper, "poling" is practiced to remove unwanted oxygen from molten copper containing such oxygen. As is known in the art, the molten copper, after having been subjected to the oxidation step of the fire-refining procedure (such step sometimes being referred to in the art as "blowing"), is subjected to poling to remove the oxygen introduced into the copper by the blowing step. As is also known in the art, fire refining is practiced to refine molten copper produced by the blowing of copper matte in a copper converter; such fire refining being conventionally conducted in a so-called anode furnace which, in turn, is usually a conventional tilting furnace. Generally the fire refined copper is cast into anodes which are further refined electrolytically; the copper cathodes from the electrolytic refining being melted and cast into semi-finished products such as, for example, wire bars, billets, rods, cokes and ingots. When such cathodes are melted in a conventional reverberatory melting furnace, it is necessary to fire refine the copper again by blowing and poling before casting the copper into the semi-finished shapes; such further fire refining usually being conducted in the reverberatory melting furnace. In some instances in the industry, the semi-finished shapes are cast directly from fire refined copper which has not been electrolytically refined.

In fire refining, the copper which is ready for poling after the blowing step, usually contains more than about 0.5% oxygen by weight; and, during the poling step, the oxygen content of the copper is usually reduced to less than about 0.2% oxygen by weight, as desired. Generally in producing fire-refined copper for casting into anodes, the oxygen content of the blown copper is reduced during the poling step to an oxygen content of about 0.5% to 0.1% oxygen by weight. On the other hand, when the fire-refined copper is to be cast into semi-finished shapes, the oxygen content of the copper during the poling step is reduced to a value below 0.05% oxygen by weight, usually in the range 0.015 to 0.04% oxygen by weight and often in the range .015 to .02% oxygen by weight. It will be understood, of course, that the art resorts to poling whenever it wishes to remove unwanted oxygen from copper whenever such oxygen becomes incorporated therein while handling the molten metal.

In commercial practice, it is often essential, because of work and casting schedules, that the duration of the poling step be as short as practicable and less than about six hours. Generally it is desirable to complete the poling in less than five hours and usually it is more convenient to have the poling procedure completed in about 2½ to 4 hours. In poling copper in the past, trees or poles of green timber were employed; the poles or trees being held below the surface of the molten metal until the oxygen content of the copper was reduced to a desired amount. Poling with trees or poles is still in general use although it is both an expensive and hazardous procedure. Therefore, although many substitutes for the trees or poles have been proposed in the patent and technical literature, no one has, so far as we are aware, taught poling copper with natural gas. In fact, the art believed prior to the present invention that, if natural gas had any capacity as a poling agent when passed directly into the molten metal, the reducing effect would be small and intolerably slow.

We have found that natural gas can be used to pole copper. One of the advantages of the invention is that it permits natural gas to be used to pole copper at poling rates which are commercially acceptable. Another advantage of the invention is that it affords a relatively simple as well as a relatively cheap and safe procedure for poling copper. These and other advantages will become apparent from the following description of the invention.

SUMMARY OF THE INVENTION

Broadly, the invention comprehends a method of poling copper which comprises establishing a pool of molten oxygen-bearing copper in a furnace and reducing the oxygen content of the copper by injecting natural gas into the pool below its surface at a rate sufficient to provide at least about 2% methane, by volume on the dry basis, in the furnace atmosphere above the pool of the molten metal. Preferably such atmosphere contains at least about 4% and more preferably at least about 6% methane, by volume on the dry basis.

Unpreheated gas or gas which has been preheated to any desired degree may be injected into the pool. The gas injected into the pool may be natural gas per se, preferably at ambient temperature, or a mixture of natural gas with other gases may be injected so that the proportion of the gas or gases admixed with the natural gas is such that the mixture provides the instant atmosphere in the furnace. When a mixture is used, the gas or gases
mixed with the natural gas may be an oxidizing, inert or a reducing gas or mixtures thereof. Of these latter gases, air or steam or both are preferred. It will be understood that when air or other oxidizing gas is admixed with the natural gas, the proportions are such that the oxidizing gas will be in amounts less than the stoichiometrical amounts required to completely burn the natural gas. In the most preferred procedure natural gas per se and at ambient temperature is injected into the molten pool. Natural gas such as is commercially available in the United States is preferred. Such natural gas, as is known, is predominantly methane and is substantially free of sulphur values.

The temperature of the molten bath is preferably at least 2050° F., preferably in the range 2050–2300° F. and more preferably in the range 2100–2200° F. When the temperature of the molten metal in the pool at the start of the poling is within these preferred ranges, and especially when it is within the more preferred range, the poling can be conducted on a commercial scale without adding heat to the molten pool during the poling step.

The present process is preferably and most efficiently conducted in a substantially closed furnace. Thus, for example, in employing a tilting or reverberatory furnace the various openings for charging, discharging, shimming or other access openings with which the furnace is provided, are closed before the poling step is conducted so as to prevent, insofar as is practically possible, the entry of air into the furnace atmosphere. Preferably, the gas injected into the pool is introduced therein at a rate sufficient to provide a positive pressure in the furnace atmosphere. Where the furnace is provided with a flue having a damper, the damper preferably is closed to assist in providing positive pressure in the furnace. Preferably also, the rate of injection of the gas is such that the methane content in the furnace atmosphere is less than 50%, and more preferably less than 25%, methane by volume on the dry basis.

The gas may be injected below the surface of the pool through one or more lances (blow pipes) or tuyeres having their outlets submerged below the surface of the pool. Preferably a tilting furnace provided with at least two tuyeres is employed. Determination of the reduction of the oxygen in the copper during the poling step may be made by the conventional procedures available to the art. Thus, for example, small samples of the molten copper may be taken from the bath from time to time and allowed to cool and solidify. Such samples may be chemically analyzed or their oxygen content estimated from the character of the surface (i.e., the "set"). Usually the copper is poled until the surface of a sample displays a flat or slightly convexed surface or set. Sampling of the furnace atmosphere may be carried out in any conventional manner. Generally it is most convenient to take the samples inside the furnace adjacent the flue or in the flue at or adjacent the inlet to the flue from the furnace. Preferably a conventional water-cooled probe is employed to take such gas samples. The poled copper resulting from the practice of the present process has the characteristics required for casting and is at least equal in quality to that produced by the conventional procedures heretofore practiced in the art.

The invention is further illustrated in the accompanying drawings and in the following examples. It should be understood, however, that the drawings and examples are given for purposes of illustration and that the invention in its broader aspects is not limited thereto.

**BRIEF DESCRIPTION OF THE DRAWINGS**

In the drawings:

FIG. 1 is a view diagrammatic in nature, showing the preferred furnace for practicing the invention.

FIG. 2 is an end view of the furnace; and

FIG. 3 is a broken-away enlarged sectional view of a tuyere.

**DESCRIPTION OF THE PREFERRED EMBODIMENTS**

In the drawings like reference characters refer to like parts. Referring now to the drawings, the furnace 1 is a conventional furnace provided with a pair of tuyeres 2, burner 3, flue 4 having conventionally mounted damper 5, pouring spout 7, skim port 8 and charge port 9. The furnace is conventionally mounted on rollers by means of collars 10 and rollers 11 and is provided with conventional drive means (not shown) so that the furnace can be rotated. Thus, for example, the furnace can be rotated from its normal operating position shown in FIG. 1 to a position to pour metal through the pouring spout 7 or it can be rotated to elevate the outlets of the tuyeres to a position above the level of the metal in the furnace. Likewise it can be rotated to move ports 8 and 9 into more convenient positions.

Any number of tuyeres may be provided for the furnace; the number provided being dependent on the rate at which the gas is to be injected into the furnace. The furnace as shown is provided with two tuyeres disposed at a distance from the center of the furnace equal to one-third the length of the furnace. Where additional tuyeres are used, the tuyeres preferably are mounted to be spaced uniformly along the length of the furnace.

As shown in FIG. 3, the tuyeres 2 comprise a tuyere pipe 15 extending through plate 16 and furnace lining 17. Plate 16 is suitably secured, as by bolts 18, to the brick shell 19 of the furnace. T 21 is threaded onto tuyere pipe 15. Threaded into one end of T 21 is pipe 22 provided with valve 23. Flexible air hose 24 is attached to pipe 22 for delivering air through the tuyere into the furnace. Pipe 30, provided with valve 31, is threaded into the other end of the T. The end of pipe 30 away from the T is connected to flexible conduit 32 for feeding natural gas (from a source not shown) through the tuyere into the furnace. As will be seen from FIGS. 2 and 3, the top, bottom, side and end walls of the furnace are conventionally lined with lining 17 which is comprised of an innermost layer of magnesite brick 35 and a layer of suitable insulating material 36, between the brick and shell 19. T's 21 may also be provided with a conventional tuyere punching opening aligned with pipe 15 for insertion of a conventional tuyere punching tool.

In conducting poling in a furnace containing oxygen-bearing copper which is ready for poling, the furnace is rotated to elevate the outlets from tuyere pipes 15 above the level of the pool of molten metal 40, spout 7 having been previously suitably plugged with clay. While passing natural gas through the tuyeres, ports 8 and 9 are suitably closed with a suitable refractory material, for example fire clay, or by door members which may be sealed about their edges with the refractory material. If no heat is to be added during the poling step, the inlet for the burner may be closed with the refractory material and the damper 5 may also be closed. With the furnace thus readied, it is rotated to submerge the outlets of tuyeres pipes 15 and the natural gas is introduced at a pressure sufficient to provide the furnace atmosphere of the invention. Preferably the furnace is rotated to lower the outlets of the tuyere pipes to a position 6 to 20 inches, more preferably about 18 inches, below the level of the molten metal in the furnace. Preferably also the charge of molten metal in the furnace is sufficient to fill the furnace to a level below but adjacent to the longitudinal axis of the furnace.

**EXAMPLE 1**

A charge of 181 tons of copper from a conventional copper converter was charged into a tilting furnace of the type illustrated in FIGS. 1 through 3; the pouring spout 7 having been plugged with clay before charging the metal. The level of the charged metal with the furnace in
its normal operating position shown in FIG. 1 was just below the center of the furnace. The copper was blown in the conventional manner by passing air through the tuyeres while the outlets of the tuyere pipes 15 were sub-
merged 18 inches below the surface of the molten metal. After the copper had been fully injected into the furnace beneath the surface of the pool of molten metal and the furnace was rotated to raise the outlets of the tuyeres above the level of the bath while still continuing to feed air through the tuyeres. The temperature of the molten metal at this point was 2180°F. While the outlets of the tuyeres were in position above the metal in the bath, the valves 23 were closed and valves 31 were opened to deliver to the tuyeres unpreheated natural gas at a temperature of 60°F. With natural gas passing through the tuyeres, ports 8 and 9 and the inlet to the furnace for burner 3 were closed with a refractory material; the burner inlet was closed since no heat was to be added to the metal during the poling. Damper 5 also was closed. At this point, the temperature of the molten metal was still 2180°F and the copper contained 0.60% oxygen by weight. The furnace was then rotated to the position shown in FIG. 1; the outlets to the tuyere 15 being submerged 18 inches below the surface of the molten metal. Natural gas at the rate of 261 cubic feet per minute (measured at standard conditions, i.e. 60°F and a pressure of 30 inches of mercury) was de-
levered through the two tuyeres 2. At this rate of introduc-
tion of the gas, a positive pressure was provided in the furnace atmosphere. Injection of the gas at this rate was continued and samples of the molten copper were taken from time to time. Samples of the furnace atmosphere were also taken from time to time with a conventional water-cooled probe 41, inserted into the flue with the inlet to the probe at the approximate center of the furnace outlet 42 to the flue 4. It was found that after introduc-
ing the gas in this manner for 143 minutes, the oxygen content of the copper was reduced to 0.03% oxygen by weight and that the methane content in the furnace atmos-
phere during such introduction was 7% methane (CH₄), by volume, on the dry basis. At the end of the 143-minute period, pouring spout 7 was unplugged and the molten metal which was at a temperature of 2080°F, was cast into anodes for electrolytic refining; natural gas being passed through the tuyeres while the copper was being cast. During the 143-minute poling period a total of 37,900 cubic feet of natural gas (corresponding to 206 cubic feet per ton of copper in the charge), measured at standard conditions, were injected into the furnace beneath the surface of the molten metal. The anodes were found to be at least as good as anodes produced by the prior con-
ventional practice.

EXAMPLE 2

Example 1 was repeated but in this instance only one tuyere was employed in furnace 1. The charge of metal to the furnace was 165 tons of copper, the temperature of the metal at the beginning of the poling period was 2160°F. Preheated natural gas at a temperature in the range of 730 to 780°F was employed for the poling. The oxygen content of the copper before poling was begun was 0.86% oxygen by weight. During the poling the pre-
heated natural gas was injected into the molten metal at the rate 227 cubic feet per minute measured at standard conditions. After injecting the gas in this manner for 188-
minute period the oxygen content in the copper was reduced to 0.13% oxygen by weight. The methane content of the furnace atmosphere was found to be 5% methane by volume on the dry basis. The temperature of the metal at the end of the 188-minute poling period was 2190°F. and during that period a total of 42,700 cubic feet of natural gas (corresponding to 228 cubic feet per ton of copper charge), measured at standard conditions, were in-
jected into the furnace beneath the surface of the pool of molten metal. At the end of the poling period the molten metal was cast into anodes and the latter were found to be the equal in quality to anodes cast from metal which had been pole by the conventional procedure of the prior art. Similar results are obtained when air or steam or both are admitted with the natural gas in proportionate amounts to provide the required atmosphere; such proportionates of air, of course, being less than that of the stoichiometric amount required to burn the natural gas.

Example 3

A charge of 168 tons of molten copper from a copper converter was charged into a furnace of the type illustrated in FIG. 1 to provide in the furnace a pool of metal with its surface just below the center of the furnace. The thus charged copper metal was blown with air in the manner described in Example 1. The oxygen content of the copper upon commencement of the poling step was 0.75% oxygen by weight. Natural gas was injected into the pool of molten metal at a rate sufficient to provide 2.2% methane, by volume on the dry basis, in the furnace atmosphere. After injecting natural gas at this rate for about 20 minutes, the oxygen content of the copper was reduced to 0.52% oxygen by weight. Natural gas was then injected into the molten metal at a rate to provide 0.2% methane by volume on the dry basis, in the furnace atmosphere. After injecting natural gas at this rate for a period of two hours, the oxygen content of the copper was reduced to 0.50% oxygen by weight. Natural gas was then injected into the furnace to provide 4.7% methane, by volume on the dry basis, in the furnace atmosphere. After injecting natural gas at this rate for two hours, the oxygen content of the copper was reduced to 0.28% oxygen by weight. It will be seen from the foregoing that the present in-
vention affords a simple and a relatively cheap and safe method for poling copper with natural gas at poling rates which are commercially acceptable. In practicing the in-
vention, various modifications may be made in the process without departing from the essential principles of the in-
vention, which is intended to be limited only by the scope of the appended claims.

What is claimed is:

1. In a method of poling oxygen containing copper in a horizontal furnace provided with at least one side wall tuyere for introducing gas beneath the surface of a pool of molten copper contained in the furnace, the improve-
ment which comprises establishing in said furnace a pool of molten oxygen containing copper to be pole, poling the copper contained in the pool by injecting natural gas through said side wall tuyeres into the molten pool below the pool surface at a rate of 2% methane, by volume on the dry basis in the furnace atmosphere above the pool of molten metal, and con-
tinuing such injection of natural gas until the oxygen con-
tent of the copper is reduced to a desired amount.

2. A method according to claim 1 in which said furnace is a tilting furnace and is provided with at least two tuyeres, the molten pool of metal is at a temperature in the range 2050–2300°F, and unpreheated natural gas alone is injected through the tuyeres to provide said atmos-
phere in the furnace.

3. A method according to claim 2 in which the inlet and outlet openings to the furnace are closed prior to injecting the natural gas into the molten pool, and the natural gas is injected at a rate to provide a positive pressure and at least 4% methane, by volume on a dry basis, in the furnace atmosphere.

4. A method according to claim 3 in which molten copper is blown by injecting air through said tuyeres into the molten pool beneath the pool surface until the copper contains more than 0.5% oxygen by weight and slag is skimmed from the molten pool prior to poling the copper, said natural gas is introduced at a rate to provide at least 6% methane, by volume on the dry basis in the furnace atmosphere above the molten pool, the outlets from said tuyeres are disposed 6 to 20 inches beneath the surface of
said molten pool during the poling and the introduction of the natural gas is continued until the oxygen content of the copper is reduced to a value which is less than about 0.2% oxygen by weight in less than six hours.

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U.S. Cl. X.R.

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