FIG. 2
ATMOSPHERE CONTROL IN DIP-FORMING PROCESS
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ABSTRACT OF THE DISCLOSURE

In the dip-forming process for acereting copper onto a core member passed upwardly through a crucible containing a molten bath of copper, a melt of molten copper is supplied to the crucible from a melting furnace. A reducing atmosphere comprising hydrogen, carbon monoxide, carbon dioxide, and an inert diluent in controlled amounts is supplied above the melt in the melting furnace, whereby the oxygen content in the melt is reduced to less than about 20 parts per million.

The dip-forming process, such as used in casting metal, is now well known in the art. According to this process, an elongated body such as a metal rod is typically pre-treated by passing it through a straightener, a surface cleaning apparatus, and then through a vacuum entrance chamber positioned below or at the bottom of a crucible containing a bath of molten metal. A continuous elongated core or body is passed upwardly through the molten bath, which bath may have the same chemical composition as that of the core or a different composition. The molten material in the crucible accumulates or deposits upon the outer surface of the core thereby increasing its cross-sectional area appreciably. After emerging from the crucible, the resulting cast member is cooled as by a water spray from one or more jet nozzles at least sufficiently so that the cast member can be rolled or worked. From there, the cast member may be passed through a suitable roll mechanism where it is reduced in cross-sectional area and then passed to a suitable receiving means such as a take-up reel.

The quality of the copper rod cast by the dip-forming process is influenced to a large extent by the gases dissolved in the molten copper, which are dependent upon the composition of the atmosphere in contact with the molten metal. In casting copper, gas evolution results from the presence of excessive oxygen and/or hydrogen in the melt. The problem of gas contamination in the dip-forming process has been previously recognized, and in one aspect formed the basis of U.S. Patent No. 3,060,053 to Carreker and Parke and assigned to the assignee of this invention.

Under the conditions employed in the dip-forming process, oxygen and hydrogen present in the atmosphere above the molten metal can be dissolved by and/or react with the molten material. Oxygen may cause the formation of undesirable oxides. It is recognized that copper having an oxygen content greater than approximately 20 parts per million results in progressive deterioration in casting quality. Also, the presence of hydrogen alone, or hydrogen and oxygen concurrently, in molten metal in sufficient amounts will cause formation of gas bubbles upon solidification of the accreted material on the cast member. The formation of oxides, gas bubbles and/or voids not only adversely affect the quality of the product, but also deleteriously affects the uniform accretion of molten material onto the core by creating regions of relatively poor thermal conductivity within a mass of relatively good thermal conductivity. Thus, the effect of oxygen and hydrogen is not confined to the oxide phases and bubbles they create, but is magnified due to the irregularities in heat transfer they produce, causing substantial non-uniformity in the external contour of the accreted coating. Bubbles, voids, oxide phases, internal discontinuities, and irregular accretion are all undesirable in that they promote or cause the formation of cracks and fissures when stresses are imposed, as by bending, rolling, drawing or the like. A product manifesting such defects is generally not acceptable.

According to U.S. Patent 3,060,053, referred to above, the oxygen content in the molten metal is reduced to a very low amount by utilizing graphite or comparable reducing means which will unite with the oxygen in the molten metal to form a gaseous product which escapes from the molten copper. In addition, an inert atmosphere such as nitrogen is maintained above the surface of the melt to protect the melt from the air. Such a furnace system will produce satisfactorily low oxygen content copper for use with dip-forming, if the furnace system is free of substantial air leaks and is allowed to come to substantial equilibrium. However, air leaks may be expected in a large industrial furnace, particularly under charging conditions, and long residence times for equilibration are not realized. Experience has demonstrated that graphite furnace linings and graphite heating elements are rapidly consumed by oxygen from unsealed air leaks. Ceramic furnace linings and silicon carbide electrical resistance heating elements are not harmed by such air leaks. However, oxygen from the air may react with the molten copper to form copper oxide slag, which will attack or erode the silicon carbide furnace parts. Use of a reducing atmosphere, rather than a neutral or inert atmosphere such as nitrogen, is desirable. Hydrogen is a reducing gas, but as explained above, this gas is readily absorbed by the molten copper with can result in the formation of gas bubbles, thereby causing porosity and interfering with uniform heat transfer. Carbon monoxide is another reducing gas, but it is insoluble in molten copper and can react with the melt only at its surface. Therefore, carbon monoxide is relatively slow in reducing the oxygen content in a relatively deep melt. Further, strongly reducing atmospheres harmfully affect silicon carbide heating elements in that such atmospheres cause the formation of volatile silicon monoxide, which results in the eventual disintegration of the heating element.

The purpose of this invention is to provide a controlled reducing atmosphere above the molten copper which is sufficiently reducing to maintain the oxygen in the molten copper at less than approximately 20 parts per million, yet sufficiently oxidizing to avoid substantial erosion or attack of silicon carbide furnace elements employed in the system, and sufficiently low in hydrogen to avoid evolution of hydrogen bubbles during solidification in the dip-forming process.

According to the present invention, molten copper from a melting furnace is supplied to a crucible through which a continuous, elongated core rod is passed, which molten metal deposits or accretes to the rod. A reducing atmosphere comprising 1 to 10 percent by volume hydrogen, 1 to 10 percent carbon monoxide, carbon dioxide, the ratio of carbon dioxide to carbon monoxide being from about 2:1 to 1:20, and the balance being an inert diluent such as nitrogen is maintained above the melt. By reason of the reducing atmosphere maintained above the melt, the oxygen content in the molten metal is reduced to less than 20 parts per million. By limiting the maximum percentage of hydrogen, the formation of gas bubbles due to the solution of hydrogen in molten copper is minimized or substantially eliminated, and further the erosion of the silicon carbide heating elements is substantially avoided. By requiring the presence of appreciable hydrogen, the time required to achieve equilibria-
tion between the atmosphere and the melt at low oxygen contents is reduced.

Reference is now had to the following detailed specification and to the accompanying drawings illustrating a preferred embodiment of the invention.

FIGURE 1 is a perspective view partially in section of an apparatus for practicing the present invention.

FIGURE 2 is a graph showing the solubility of hydrogen in copper.

Referring to FIGURE 1, core rod 10 is supplied to a drawing apparatus 12 located adjacent a suitable shoving apparatus 14 which shaves a thin layer of metal from the periphery of the rod to remove the oxide coating and other surface contaminants therefrom. If desired, other cleaning means such as chemical cleaning means, may be utilized for removing the oxide coating and cleaning the surface of the rod. The rod is passed through a suitable drive mechanism, including capstan 15 and drive rolls 16 contained in housing 18, and from there into tube 20. Members 12, 14, 18 and 20 are sealed and interconnected to a suitable passageway, and tube 20 has connected thereto exhaust tube 22 and evacuating pump 24 to maintain a vacuum in the passageway. Entry port member or nozzle 26 is mounted in the upper end of tube 20 and extends into crucible 28 which is maintained at the desired elevated temperature by suitable heating means such as electric induction heater 30. Core rod 10 is fed through nozzle 26 and into crucible 28 where the rod comes in contact with the molten copper which accretes to the rod, as described hereinafter in greater detail.

Molten copper is supplied to crucible 28 from melting furnace indicated generally by the numeral 32, which is heated by a plurality of silicon carbide electric radiant heaters 34. Cathode copper plates 35, or other suitable feed material of low oxygen content, is supplied to the furnace 32 by any suitable means such as a mechanical drive means (not shown). Desirably the furnace is provided with a sloping or inclined section 36 and an integral horizontal section 38. The cathode copper plates are charged to section 36 of the furnace through a slipper-type door (not shown) and melted gradually on the incline as they pass to the horizontal section 38 where a pool of molten metal collects. The molten metal flows by displacement over a weir 40 into a level control section 42 of the furnace. A suitable liquid level sensing control, indicated generally by the reference numeral 44, which is commonly employed in the art, controls subsurface flow through passageway 45 into the crucible 28. An electric probe 46 in the crucible senses the bath level and automatically regulates the level sensing control to maintain a constant level in the crucible.

Copper supplied to the furnace may contain an undesirably high oxygen content, or air may leak to the furnace such as through the entranceway to the furnace through which the copper is charged. For this reason, it is necessary to maintain a controlled reducing atmosphere above the molten metal. The reducing atmosphere is supplied to the furnace through line 48 from a suitable source (not shown). The reducing atmosphere lowers the oxygen content of the copper to less than 20 parts per million and maintains this low level. As a result, the molten copper fed to the crucible having this low oxygen content, and further does not contain sufficient hydrogen to cause bubble formation to a significant degree. Desirably, an atmosphere of an inert gas such as nitrogen is maintained above the molten metal in the crucible which may be supplied to the crucible through line 49 from source 50. As the core rod 10 passes through the molten bath of metal in the crucible, copper accretes progressively thereto forming a rod of increased diameter with molten metal substantially bonded to the core rod.

An elongated tube 52 extends upwardly from crucible 28, and the resulting cast rod having copper accreted thereto is passed out of the crucible to the extension tube.

The cast rod emerging from the crucible and extension tube is at a relatively high temperature and is cooled somewhat by cooling means 54, such as a water spray nozzle, before the rod is passed through direction changing rolls 56. From there the cast rod is directed to a suitable rope dropper mill and copper apparatus (not shown) and to a storage area as desired.

In practicing this invention, the reducing atmosphere supplied to the furnace comprises about 1 to 10 percent by volume hydrogen, 1 to 10 percent by volume carbon monoxide, carbon dioxide, the ratio of carbon dioxide to carbon monoxide being from about 2:1 to 1:20, and the balance being nitrogen or another suitable inert diluent. As mentioned above, the reducing gases of the atmosphere, that is, the hydrogen and carbon monoxide, react with the oxygen present in the molten metal thereby reducing the oxygen content to less than 20 parts per million. The oxidizing tendency of the atmosphere at a given temperature is specified by the ratio of carbon dioxide to carbon monoxide or by the ratio of water vapor to hydrogen; specifying either one of these ratios specifies the other, at equilibrium, according to the chemical Equation 1.

$$\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$$  

The oxygen content of the molten copper, at equilibrium is governed by Equation 2.

$$\frac{1}{2}\text{O}_2 = \text{O} \quad (\text{in copper})$$  

which is related, through Equation 2, to the CO/CO ratio by Equations 3 and 4.

$$\frac{1}{2}\text{O}_2 + \text{CO} = \text{CO}_2$$  

(3)

$$O \quad (\text{in copper}) = \frac{\text{K}_1\text{CO}_2}{\text{CO}}$$  

(4)

$$\text{O}_2 \quad \frac{1}{2} = \text{K}_1 \text{CO}_2$$  

(5)

where $\text{O}_2$ is the oxygen in the molten copper in parts per million; $\text{O}_2$, $\text{CO}_2$, and $\text{CO}$ are the volume fractions of the respective gases in the atmosphere; and $\text{K}_1$ and $\text{K}_2$ are the equilibrium constants for Equations 2 and 3 respectively. The constants $\text{K}_1$ and $\text{K}_2$ are temperature dependent. At 1200° C., $\text{K}_2$ is approximately $4.2 \times 10^6$ and $\text{K}_2$ is approximately $3.3 \times 10^{-4}$. Thus, at equilibrium at 1200° C., the oxygen in the copper in parts per million is related to the ratio of $\text{CO}_2$ to $\text{CO}$ in the atmosphere by Equation 6.

$$O = \text{K}_1\text{K}_2 \cdot \frac{\text{CO}_2}{\text{K}_2} = 14 \cdot \frac{\text{CO}_2}{\text{CO}}$$  

(6)

The constant $\text{K}_1\text{K}_2$ is approximately 7, 14 and 16 at 1100°, 1200°, and 1300° C., respectively. Thus, as a useful first approximation, the oxygen content of the molten copper in parts per million may be said to be about ten times the ratio of per cent carbon dioxide to percent carbon monoxide in the atmosphere, at equilibrium.

The presence of hydrogen offers more complete assurance against oxidation. Hydrogen is soluble in molten copper, and the amount dissolved is related to the hydrogen content in the atmosphere above the molten metal and to the temperature. Solid copper at its melting point of 1083° C. can retain up to 1.7 parts per million of hydrogen in solid solution in equilibrium with a hydrogen pressure of 1.0 atmosphere. If the melt contains more than 1.7 parts per million of hydrogen, hydrogen gas will be rejected as bubbles during cooling or solidification, thereby causing porosity in the solidified metal. In order to avoid the formation of hydrogen bubbles, the hydrogen content in the furnace atmosphere above the melt is such that the molten metal can absorb no more than the solid solubility of about 1.7 parts per million. In this manner there will be no rejection of hydrogen during solidification and therefore no hydrogen bubble formation.

In typical dip-forming operations, the ambient temperature in the furnace may range from about the melting point of copper (1083° C.) to about 1300° C., and
more preferably from about 1125° C. to 1175° C. FIGURE 2 illustrates graphically the quantitative relationship between percent hydrogen in the atmosphere and the amount which can be dissolved in liquid copper at several temperatures. In the graph, the dissolved hydrogen in parts per million is plotted as the abscissa and the percent hydrogen in the atmosphere as the ordinate. From the graph, it can be seen that the percent hydrogen in the atmosphere should not exceed about 10 percent by volume at the melting temperature of 1083° C., or about 7 percent at 1200° C., in order to avoid formation of hydrogen bubbles. In the preferred operating conditions, the hydrogen content in the atmosphere above the melt should range from about 2 to 5 percent.

It will be observed that the combination of hydrogen and carbon monoxide in the atmosphere in controlled amounts offers the desired reduction in oxygen content and further avoids any adverse results where only one gas is used. Generally, the carbon monoxide content will range from about 1 to 10 percent by volume, and a ratio of carbon dioxide to carbon monoxide is from 2:1 to 1:20. In the preferred embodiment the carbon monoxide content is from about 4 to 8 percent by volume, and the ratio of carbon dioxide to carbon monoxide is from about 1:2 to 1:10. However, carbon monoxide does not penetrate the melt and therefore reacts with the oxygen at or near the surface of the melt only. On the other hand, hydrogen dissolves readily in the molten copper and will react with the oxygen deep in the bath. Also, carbon monoxide alone will attack the silicon carbide heating elements, and to avoid this a controlled amount of carbon dioxide is included in the atmosphere. For these reasons, the ratio of carbon monoxide to carbon dioxide is particularly important. If the ratio is too low (i.e., too much carbon monoxide), the atmosphere will not be sufficiently reducing to decarburize the copper. If, on the other hand, the ratio is too high, the excessive reducing atmosphere will attack the silicon carbide heating elements.

To further illustrate the invention, copper rod was formed by passing a copper core rod having a diameter of 0.38 inch through a molten bath of copper contained in a crucible. The molten copper was supplied to the crucible through an integrally connected spout extending from a refractory-lined melting furnace which was heated by a plurality of silicon carbide electric radiant heaters, as described above. A reducing atmosphere was maintained over the molten copper in the furnace which comprised 5 percent hydrogen, 7 percent carbon monoxide, 0.7 percent carbon dioxide and the balance nitrogen, all percentages being by volume. Also, a protective atmosphere of nitrogen was maintained above the molten copper in the crucible. The resulting cast rod exhibited high quality being substantially free from irregularities and contamination, and upon analysis showed an oxygen content of about 5 parts per million. In a second run, the reducing atmosphere maintained above the molten copper in the furnace comprised 13 percent hydrogen, 10 percent carbon monoxide, 1 percent carbon dioxide and the balance nitrogen, all percentages being by volume. The resulting cast rod from this second run had a low oxygen content of 3 parts per million, but nevertheless was a poor quality exhibiting high porosity resulting from hydrogen evolution.

I claim:

1. In a method of accreting copper onto a core rod comprising supplying to a crucible a melt of molten copper from a melting furnace, passing said core rod through the molten copper contained in said crucible to accrete copper thereon and removing the resulting cast rod from said crucible, the improvement comprising: maintaining above said melt in the melting furnace an atmosphere comprising from about 1 to 10 percent by volume hydrogen, about 1 to 10 percent by volume carbon monoxide, carbon dioxide, the ratio of carbon dioxide to carbon monoxide being from about 2:1 to 1:20, and the balance being an inert diluent, whereby the oxygen content in said melt is maintained at less than approximately 20 parts per million.

2. A method according to claim 1 wherein the hydrogen content is from about 2 to 5 percent.

3. A method according to claim 1 wherein the carbon monoxide content is from about 4 to 8 percent.

4. A method according to claim 1 wherein the ratio of carbon dioxide to carbon monoxide is from about 1:2 to 1:10.

5. In a method of accreting copper onto a core rod comprising supplying to a crucible a melt of molten copper from a melting furnace, passing said core rod through the molten copper contained in said crucible to accrete copper thereon and removing the resulting larger cast rod from said crucible, the improvement comprising: maintaining above said melt in the melting furnace an atmosphere comprising from about 2 to 5 percent by volume hydrogen, about 4 to 8 percent by volume carbon monoxide, carbon dioxide, the ratio of carbon dioxide to carbon monoxide being from about 1:2 to 10:1, and the balance being nitrogen, whereby the oxygen content in said melt is maintained at less than approximately 20 parts per million.

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