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COPPER REFINING.

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My present invention relates to a new and improved process for the refining of copper, and relates particularly to methods for the production of copper which is entirely free from dissolved and occluded gas and from oxygen.

In response to industrial and technical demands, many attempts have been made to produce oxygen free copper by direct refining methods and otherwise. While it has been possible heretofore to produce oxygen free copper by means of previously proposed methods, copper so produced did not have the necessary additional qualities of high metallic copper content, high electrical conductivity, and freedom from dissolved or occluded gas which, latter, resulted in gas or "blow" holes in the solid copper. Consequently, copper produced by previously proposed methods does not possess the necessary properties and qualities to meet the general industrial and technical requirements, hence, none of such previously proposed processes have been of commercial importance.

I have discovered that by means of the hereinafter described process I can produce copper which is entirely free from dissolved or occluded gas, such as carbon monoxide, and entirely free from oxygen. Furthermore, the copper so produced contains lower percentages of various impurities, such as iron and sulphur, than copper produced by heretofore known pyrometallurgical methods, and copper produced by means of the present invention is entirely free from residual impurities resulting from reagents used in effecting complete removal of oxygen.

By reason of the combined advantageous factors—absence of dissolved or occluded gases, absence of oxygen, and high metallic copper content—copper produced by the operation of the present invention possesses higher percentage of electrical conductivity, higher tensile strength and greater reduction in area and percentage of elongation than copper refined by previously known methods.

The present process is equally adapted for the refining of cathode copper produced by electrolytic refining and the direct refining of copper bearing material which has not been refined electrolytically, such as blister copper, cement copper, scrap copper, etc. It is also adapted for use in both the production of cast shapes to be used in the production of wire, tubes, sheets and other wrought articles, and for the production of finished or semi-finished castings in sand or other molds, particularly castings having high electrical conductivity, high tensile strength and excellent machining qualities.

Before describing my invention I will give, for the purpose of comparison, an outline of the pyrometallurgical method which has heretofore been generally used for the refining of copper, and the additional operations required for the production of deoxidized copper.

Electrolytic copper in the form of cathodes has an average metallic copper content of 99.975%, and an electrical conductivity of 101% or more (Matthissen standard), and is substantially free from oxygen. However, cathode copper is not in suitable condition for rolling or other working, and must be subjected to a pyrometallurgical refining process before it can be rolled, drawn, etc.

The cathodes are melted in fuel fired reverberatory furnaces, the charges ranging from 20 to 250 tons. The major portion of the melting is accomplished by indirect dissolving, i. e., the solid copper is under the surface of the bath and not in direct contact with the fuel flames. The charging and melting operations require from 10 to 13 hours, regardless of the size of the charge, and during this time the molten copper absorbs a relatively large amount of sulphur from the fuel flames.

When the charge is molten, air is blown into the copper until the bath consists of the saturated copper-copper oxide eutectic, containing .39% oxygen, and, in addition, some free cuprous oxide, so that the bath generally contains from .45% to .55% oxygen. Oxidation in this manner removes substantially all sulphur from the bath, mainly as sulphur dioxide; and substantially all iron, and a portion of certain other impurities, such as arsenic and antimony. The latter impurities are removed from the copper as oxides which enter the slag. Following oxidation, a large proportion of the slag is removed.

Partial deoxidation of the bath is then undertaken by "poling" i. e., logs or poles of green wood are introduced under the surface of the metal, the wood being converted into charcoal which in turn reacts with the cuprous oxide of the bath. Reduction of the cuprous oxide in this manner is continued until the oxygen content of the bath is between .035% and .055%, within which range the metal is said to be "tough pitch" copper. At this stage the copper is cast into wire bars, cakes, ingots, etc.

The "poling" operation requires from 3 to 4½ hours, and from 4 to 6 hours are consumed in casting, and during these periods the copper again absorbs appreciable amounts of sulphur, as well as iron and other impurities.

In the refining of copper by the above described method it is essential that the oxygen content be maintained within the range of from .035% to .055%, as when the oxygen exceeds approximately .060% the cast copper is unsound, apparently due to the presence of a gas. Furthermore, the relatively high oxygen content reduces the percentage of reduction in area and elongation to such an extent that the copper does not possess sufficient ductility for mechanical working.

In a similar manner, when the oxygen content is reduced to less than .035% the cast copper is unsound, the metal invariably rising or "swelling" in the molds, due to the presence of carbon monoxide, and possibly other gas, and such copper, termed "over-poled", is also unsuitable for mechanical working by reason of porosity, impaired ductility, low electrical conductivity, etc.

It will be apparent, therefore, that the poling operation can not be utilized for the production of oxygen free copper having the requisite reduction in area and elongation, i. e., ductility, tensile strength, electrical conductivity and other essential or desirable physical properties.

Copper produced by the above described pyrometallurgical method, generally termed "electrolytic copper", thus contains between .035% and .060% oxygen and has a metallic copper content of between 99.900% and 99.960%. Wire of approximately .080 of an inch diameter drawn from such copper and annealed, will have an electrical conductivity of from 99.5% to 100.8%; a reduction in area of from 35% to 47%; elongation in 10 inch lengths of from 30% to 38%, and will show an average of between 38 and 44 twists in 6 inch lengths.

Therefore, the metallic copper content and the percentage of electrical conductivity of copper refined by such methods are substantially lower than the copper content and electrical conductivity of the original cathode copper. Furthermore, the presence of oxygen, in the form of cuprous oxide, in such copper renders it entirely or partially unsuitable for many industrial applications.

Many attempts have been made to produce oxygen free copper by means of a combination of the above described method and the additional operation of adding a metallic deoxidizing agent, such as phosphorus or silicon, to the "poled" copper, i. e., the copper containing between .035% and .060% oxygen.

While it is possible to produce copper which is substantially oxygen free by such methods, the cast copper is invariably unsound, due to the presence of gas in the molten metal, hence it is not suitable for rolling, drawing, or other mechanical working. Furthermore, such copper always contains impurities in the form of residual metallics of the deoxidizing agent, hence the percentage of electrical conductivity is materially reduced, being, in such cases, between 85% and 92% (Matthissen standard), so that the copper is not suitable for use in wire or other wrought forms for the transmission of electrical energy.

It will be apparent that it is not possible to produce copper, by methods heretofore available, which possesses the following combined properties: (*a*) entire freedom from oxygen; (*b*) entire freedom from dissolved or carbon monoxide or other gases; (*c*) metallic copper content of 99.970% or higher; (*d*) electrical conductivity of 100.5% (Matthissen standard) or higher.

By means of the process of the present invention I convert cathode copper into any desired shapes or forms for use in the manufacture of wrought products, or for use as finished or semi-finished castings, and the copper so produced is characterized by entire freedom from dissolved or occluded carbon monoxide and other gases; entire freedom from oxygen; a metallic copper content as high as, or higher than in the original cathode copper; a percentage of electrical conductivity as high or higher than that of the original cathode copper; high tensile strength; high percentage of reduction in area, e. g., approximately 80% in the case of annealed wrought products. Furthermore, by means of this invention I also refine copper containing material which has not been refined electrolytically, such as blister copper, cement copper and scrap copper, and convert such copper into any desired forms for use in the manufacture of wrought products, or for use in finished or semi-finished castings, and the copper so produced is characterized by; entire freedom from dissolved or occluded carbon monoxide and other gases; entire freedom from oxygen; a metallic copper content appreciably higher than in the original copper containing material; a percentage of elec-

trical conductivity higher than that of the original copper containing material; a relatively high percentage of reduction in area, e. g., 70% or more in the case of annealed wrought products.

The process of the present invention is based upon my discovery that, under certain conditions, carbon monoxide is soluble in molten copper. I have found through extensive research that carbon monoxide which is generated or formed within molten copper dissolves or is occluded in the copper.

I have further discovered that when the percentage of oxygen exceeds a definite amount, approximately .10% of the total weight of the bath, that any carbon monoxide formed within the copper is more or less simultaneously converted into carbon dioxide, which is not soluble in molten copper. On the contrary, when the percentage of oxygen in the bath is less than approximately .10%, an appreciable proportion of carbon monoxide generated or formed within the molten copper remains dissolved or occluded therein as long as the copper is molten.

It appears, therefore, that .10% is what may be termed a "critical oxygen point", i. e., when the oxygen content exceeds this amount there is evidently a mass reaction of cuprous oxide with carbon monoxide, probably according to the following:

$$Cu_2O+CO=2Cu+CO_2$$

and, as carbon dioxide is not soluble in molten copper such gas readily escapes from the bath; on the other hand, when the oxygen content is less than this amount the mass reaction of cuprous oxide and carbon monoxide does not take place, with the result that a portion or all of the carbon monoxide present within molten copper remains occluded or dissolved therein.

When molten copper containing carbon monoxide in solution, or otherwise, is cast the carbon monoxide is not released until the copper has cooled to a temperature which is relatively not much higher than the freezing point of copper, the result being that carbon monoxide is expelled shortly prior to the formation of the crystal and thus tends to become more or less concentrated along the crystal boundaries with the consequent formation of gas holes. Such gas holes are, of course, readily detected in the case of oxygen free copper. However, in the case of cast copper containing from .035% to .055% oxygen the occurrence of holes due to the presence of carbon monoxide in the copper when molten is not as readily apparent, unless the amount of carbon monoxide has been excessive. It appears that in such oxygen containing copper the copper-copper oxide eutectic, which occurs on the crystal boundaries, acts to retain a relatively large amount of carbon monoxide, and in this case the holes caused by the gas are smaller and less apparent due to dissemination of the gas.

Copper which has been partially deoxidized by the reaction of carbon with cuprous oxide, such as by "poling", introduction of charcoal, coke, etc., may, and undoubtedly usually does contain other gases, e. g., hydrogen, in addition to carbon monoxide. I have found however, that in the operation of the process of this invention the presence of additional gas or gases in molten copper may be disregarded as they are apparently entirely eliminated by the methods used to prevent the occurrence of carbon monoxide in molten copper.

The process of the present invention comprises the following essential operations:

(*a*) Partial reduction of the cuprous oxide in the molten copper by reaction with carbon.

(*b*) Stopping the reduction with carbon before the oxygen content has been reduced to the "critical oxygen point", i. e., the point at and below which there is not sufficient oxygen or cuprous oxide in the bath to react with all carbon monoxide present in the copper to convert it to carbon dioxide; this critical point being approximately .01% oxygen.

(*c*) Subsequent removal of all remaining oxygen by means of subjecting the oxygen and oxygen compounds of the bath to reaction with a metallic reducing agent, the reaction of which with oxygen or oxygen compounds does not generate carbon monoxide in appreciable amounts.

The process of my invention may be successfully carried into effect in the following manner:

Copper or copper bearing material may be melted in any furnace to which a sufficient volume of energy in the form of heat may be supplied to melt the copper, and maintain it in a thoroughly molten condition during the necessary operations. When the copper is not sufficiently oxidized coincidental with melting, and when the bath absorbs an appreciable amount of sulphur or other impurities during melting oxidation by blowing is necessary.

After the desired amount of oxidation has been effected, the bath is partially deoxidized by the introduction of carbon into the metal. This may be accomplished by "poling" in the usual manner, the introduction of charcoal, coke, or other carbonaceous materials into the copper, such as by means of immersion, agitation or otherwise. During the partial deoxidation operation samples of the copper may be taken from time to time to determine the progress of reduction of oxygen, or this operation may be timed, that is, an approximate weight of carbon

may be allowed to react with the oxygen of the bath for a predetermined length of time.

Immediately following the partial deoxidation operation, one or more metallic reducing agents are introduced into the molten metal, and allowed to react with the remaining oxygen. I have found that silicon, manganese, phosphorus and a number of boron containing reagents may be successfully used as the metallic reagents in removing all of the oxygen from the bath. The purpose for which the copper is intended will usually determine the proper reagent to employ. For example, when it is desired to produce gas free and oxygen free copper having an electrical conductivity of more than 100% it is essential to use a metallic reducing agent which will not alloy or otherwise combine with the copper to lower the electrical conductivity. In a similar manner when it is desired to produce copper billets possessing the maximum ductility for the manufacture of seamless tubes by the piercing method it is also of advantage to use a metallic reducing agent which will not combine with the copper nor result in residual impurities therein, either or both of which conditions would tend to make the piercing operation more difficult.

When all of the oxygen has been removed the copper is ready for casting into any desired commercial shape, or into sand or other molds for the production of finished or semi-finished castings.

While the process of the present invention can be successfully and satisfactorily carried into effect according to the above general outline of operations, for the purpose of further illustration I give herewith a preferred method of operation.

In this particular scheme of operation, I use a combination stack and reverberatory furnace for melting the copper, and use oil or powdered coal as the fuel for heating the furnace. The solid copper, which may be cathodes or metal which has not been refined electrolytically, is charged into the stack, and as it passes down through the stack it is preheated and finally melted. The molten metal flows out of the stack into the hearth of the reverberatory portion of the furnace. It will be apparent that the character of the combustion gases in the stack portion of the furnace may be closely regulated and controlled, thus giving advantageous melting conditions. Furthermore, by melting in this manner the molten metal does not remain in contact with the fuel flames for more than a few minutes, consequently, the metal does not absorb an appreciable amount of sulphur nor other impurities. By reason of this, together with the fact that any desired degree of oxidation can be readily obtained by regulating the atmosphere of the stack, the usual oxidation, or blowing operation of previous refining processes is wholly eliminated.

When a sufficient quantity of molten copper has accumulated in the hearth this metal is transferred to a second furnace, which is also heated by the combustion of oil or powdered coal. Coincidental with the transfer of the copper to the second, or deoxidation furnace it is separated from substantially all slag which may have accumulated thereon.

The copper is maintained in a thoroughly molten condition in the second furnace and partial removal of oxygen is accomplished by reaction of carbon with the oxygen and oxygen compounds of the bath. Such removal of oxygen is, according to my process, stopped before the cuprous oxide content is reduced to the "critical oxygen percentage". The bath is then partially or entirely covered with charcoal or other carbonaceous material for the purpose of maintaining a neutral or reducing atmosphere within the furnace; or the bath may be covered with oxygen compounds, such as lime, magnesia, etc., which are inert under the prevailing conditions. After the copper has thus been protected from possibility of oxidation by the atmosphere of the furnace, a metallic reducing agent is introduced into the copper for the purpose of removing all remaining oxygen. The metallic reducing agent employed must be capable of reacting with oxygen and oxygen compounds of copper under the physical conditions prevailing within the furnace, and it is essential that such reactions do not generate appreciable amounts of carbon monoxide. When it is desired to produce copper having an electrical conductivity of 101% or higher (Matthissen standard) it is necessary to use a metallic reducing agent which does not dissolve in or otherwise combine with, or contaminate copper. As an example of reducing agents which are suitable for this purpose I cite aluminum boride, calcium boride and silicon boride. When electrical conductivity is not an objective other metallic reducing agents, such, for example, as phosphorus, silicon or manganese may be used.

When the oxygen has been entirely removed the copper is cast into any suitable molds in the usual manner.

Copper produced by means of the process of this invention is characterized by entire freedom from dissolved or occluded carbon monoxide and entire freedom from oxygen and oxides, consequently, castings made therefrom are characterized by entire freedom from holes and other defects due to the presence of gas or oxygen in the molten metal.

A further distinctive advantage of the present invention is that the gas free and

oxygen free copper produced by means of this process possesses higher percentage of electrical conductivity, greater tensile strength and greater percentages of reduction in area and elongation than oxygen free, or oxygen containing copper which has been refined by previously known methods.

It will be apparent that in the case of copper which has been oxidized to an appreciable extent that the major portion of reduction of the oxygen of the bath is accomplished by means of carbon, which is of decided economical advantage.

The terms "critical oxygen point" and "critical oxygen percentage" used herein and in the appended claims refer specifically to the percentage of oxygen present in molten copper in the form of cuprous oxide, and such terms are used to designate the percentage point at which cuprous oxide ceases to react with carbon monoxide to oxidize the latter compound.

I have found also that copper which has been refined by means of the process of the present invention and which contains relatively small percentages of oxygen and/or dissolved or occluded carbon monoxide will possess physical properties approximating the physical properties of similarly refined copper which is entirely free from carbon monoxide and oxygen. Although the presence of even such relatively small amounts of oxygen, chiefly in the form of cuprous oxide, will render copper unsuitable or undesirable for various applications, I have found that copper refined by means of this process and which is substantially free from included carbon monoxide and oxygen can be used for certain industrial applications.

Therefore, the herein described refining process may be advantageously utilized for the production of copper which is substantially free from dissolved or occluded carbon monoxide and/or oxygen. It will be evident that such small amounts of these impurities may be allowed to remain intentionally or otherwise in the refined copper without departing from the scope of my present invention. As an example, in the operation of the process a small percentage of oxygen may be allowed to remain in the copper by the use of a quantity of metallic reducing agent which is insufficient to remove all of the oxygen in the molten metal. It will be understood, however, that the physical properties of such copper containing impurities in the form of carbon monoxide, other oxygen compounds or oxygen will not be entirely the same as the physical properties of copper which is entirely free from such impurities.

By the term "substantially free from oxygen" used herein and in the appended claims, I refer specifically to copper containing not more than .008% oxygen.

I claim:

1. The method of producing copper which is entirely free from dissolved or occluded gas and entirely free from oxygen compounds which comprises reducing the oxygen content of the copper, while molten, by reaction of carbon with the oxygen of the bath to a point above the critical oxygen percentage at, and below which carbon monoxide is retained in molten copper; subsequently removing from said molten copper all remaining oxygen by subjecting such oxygen to reaction with a metallic reducing agent, the reaction of which does not generate carbon monoxide.

2. The method of producing copper which is entirely free from included gas and entirely free from oxygen compounds which comprises reducing the oxygen content of the copper, while molten, by reaction of carbon with the oxygen of the bath to a point above the critical oxygen percentage at, and below which mass reaction of cuprous oxide with carbon monoxide does not occur; subsequently removing from said molten copper all remaining oxygen by subjecting such oxygen to reaction with a metallic reducing agent, the reaction of which does not generate carbon monoxide.

3. The process of producing copper which is entirely free from carbon monoxide and entirely free from oxygen in any form which comprises reducing the amount of cuprous oxide in molten copper by reaction with carbon to a point above the critical percentage at, and below which reaction of cuprous oxide with carbon monoxide does not proceed at the temperature prevailing in the bath; subsequently removing all remaining oxygen by subjecting such oxygen to reaction with a metallic reducing agent, the reaction of which does not generate carbon monoxide.

4. The process of producing copper which is entirely free from cuprous oxide and carbon monoxide which comprises reducing the amount of cuprous oxide in molten copper by reaction with carbon to a point higher than the critical percentage at, and below which mass reaction of cuprous oxide with carbon monoxide does not occur; subsequently removing all remaining cuprous oxide by subjecting such cuprous oxide to reaction with a metallic reducing agent, the reaction of which does not generate carbon monoxide.

5. The process of producing cast copper which is entirely free from oxygen and substantially free from gas holes and other defects due to the presence of cuprous oxide and dissolved or occluded gas which comprises reducing the amount of cuprous oxide in molten copper by reaction with carbon and carbon monoxide to a point higher than the critical percentage at, and below which

reaction of cuprous oxide with carbon monoxide does not proceed in such a manner as to remove substantially all carbon monoxide from the metal; subsequently removing all remaining oxygen by subjecting such oxygen to reaction with a metallic reducing agent, the reaction of which does not generate carbon monoxide.

6. The process of producing cast copper which is entirely free from oxygen, substantially free from gas holes and other defects caused by carbon monoxide, and which has a minimum electrical conductivity of 101% (Matthissen standard) which comprises reducing the amount of oxygen in molten copper by reaction with carbon and carbon monoxide to a point higher than the critical percentage at, and below which carbon monoxide is retained in the molten copper; subsequently treating said molten copper which contains oxygen, but is substantially free from carbon monoxide, to remove all remaining oxygen by subjecting such oxygen to reaction with a metallic reducing agent which is not soluble in molten copper and the reaction of which does not generate carbon monoxide.

7. The process of producing cast copper which is entirely free from oxygen and substantially free from holes and other defects caused by carbon monoxide, and which is further characterized by a minimum metallic copper content of 99.985%, a minimum electrical conductivity of 101% (Matthissen standard) and a minimum reduction of area, in the annealed condition, of 74%, which comprises reducing the amount of oxygen in molten copper by reaction with carbon to a point higher than the critical percentage at, and below which carbon monoxide is retained in molten copper; subsequently removing all remaining oxygen by subjecting such oxygen to reaction with a metallic reducing agent which is not soluble in molten copper, and the reaction of which does not generate carbon monoxide.

8. As a step in the process of producing copper which is entirely free of carbon monoxide and oxygen in any form by means of reducing a portion of the oxygen contained in molten copper by reaction with carbon, stopping the reduction of cuprous oxide with carbon while sufficient cuprous oxide remains in the bath to react with all carbon monoxide present in such a manner as to oxidize such carbon monoxide to carbon dioxide or other compounds which are not retained in molten copper.

9. The process of producing copper which is entirely free from dissolved or occluded carbon monoxide and from oxygen which comprises melting copper directly in heat generated by combustion of carbonaceous fuel, allowing the molten copper to flow continuously from the melting zone of the furnace to a hearth situated at a lower elevation than said melting zone; intermittently removing molten copper from said hearth, and transferring it to a second furnace in which the copper is maintained in a molten condition by the direct heat of the combustion of carbonaceous fuel; reducing the oxygen content of the molten copper in said second furnace by reaction with carbon to a point higher than the critical oxygen percentage at, and below which molten copper retains carbon monoxide; subsequently removing from said molten copper all remaining oxygen by subjecting the oxygen and oxygen compounds to reaction with a metallic reducing agent, the reaction of which does not generate carbon monoxide.

10. The process of producing copper which is entirely free from cuprous oxide and from dissolved or occluded carbon monoxide, and which is further characterized by a minimum metallic copper content of 99.985% and a minimum electrical conductivity of 101% (Matthissen standard) which comprises melting copper directly in the products of combustion of carbonaceous fuel, intermittently removing molten copper from the melting furnace and transferring it to a second furnace where said copper is maintained in a molten condition by direct exposure to the products of combustion of carbonaceous fuel; reducing the cuprous oxide content of said copper in said second furnace to an amount which is in excess of the percentage of cuprous oxide necessary to react with all carbon monoxide present and oxidize it to carbon dioxide or other compounds which are not soluble in molten copper; subsequently removing from said molten copper all remaining cuprous oxide by subjecting such cuprous oxide to reaction with a metallic reducing agent which is not soluble in, and does not alloy or otherwise combine with molten copper, and the reaction of which does not generate carbon monoxide.

11. In the process of producing copper substantially free from oxygen, which comprises removing oxygen from molten copper by reaction with carbon; the step of removing carbon monoxide which consists in stopping the removal of oxygen with carbon while sufficient oxygen remains in the bath to react with substantially all the carbon monoxide present and permitting said oxygen and carbon monoxide to react to form carbon dioxide or other compounds which are not retainable by molten copper.

12. The process of producing copper substantially free from oxygen gas holes and other defects caused by the presence of dissolved or occluded gas which comprises reducing the amount of oxygen in molten cop-

per by reaction with carbon to a point sufficiently higher than the critical percentage at and below which reaction of cuprous oxide with carbon monoxide does not proceed to remove substantially all carbon monoxide from the metal; and subsequently removing substantially all remaining oxygen by subjecting such oxygen to reaction with a metallic reducing agent, the reaction of which does not generate carbon monoxide.

Signed at New York in the county of New York and State of New York this twenty-fourth day of March, A. D. 1927.

ANTHONY G. DE GOLYER.