Oct. 8, 1929. H. S. LUKENS ET AL 1,730,775

METHOD OF FREEING COPPER FROM COPPER OXIDE

Filed Dec. 29, 1924 3 Sheets-Sheet 1

Fig. 1.

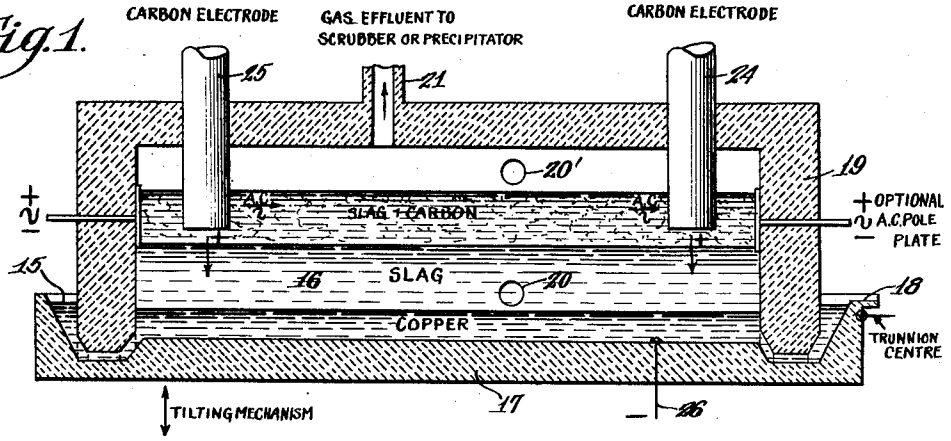


Fig. 2.

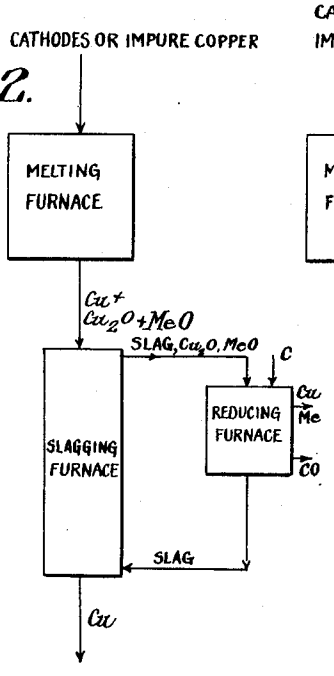
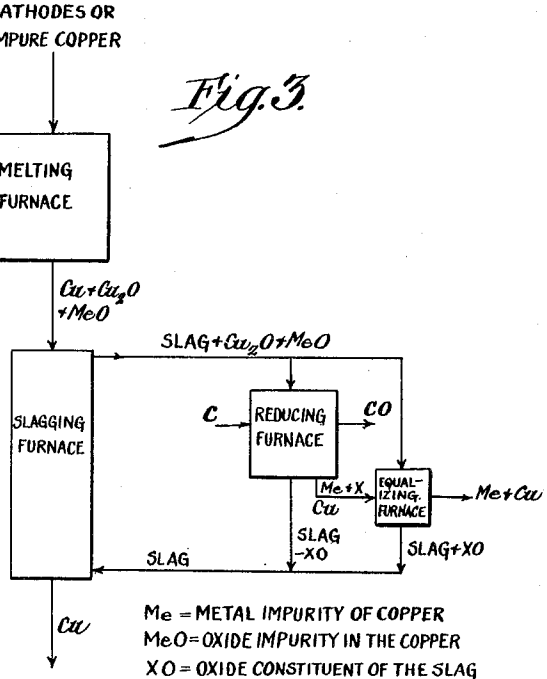


Fig. 3.



Me = METAL IMPURITY OF COPPER
MeO = OXIDE IMPURITY IN THE COPPER
XO = OXIDE CONSTITUENT OF THE SLAG
X = ABOVE CONSTITUENT AFTER REDUCTION
C = CARBON REDUCING AGENTS
CO = OXIDE OF ABOVE

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Fig. 4.

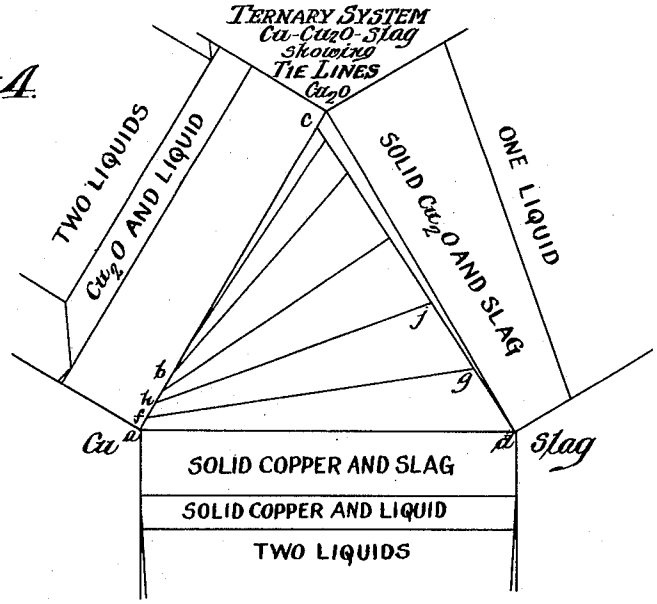


Fig. 5.

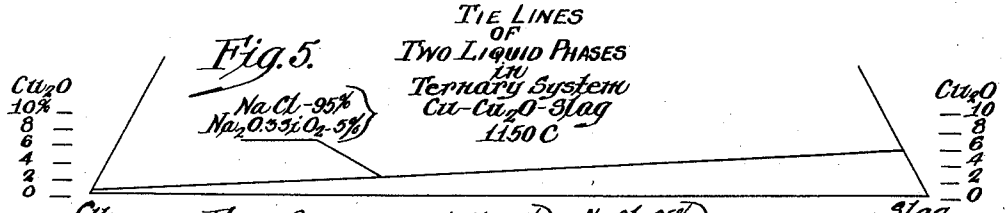


Fig. 6.

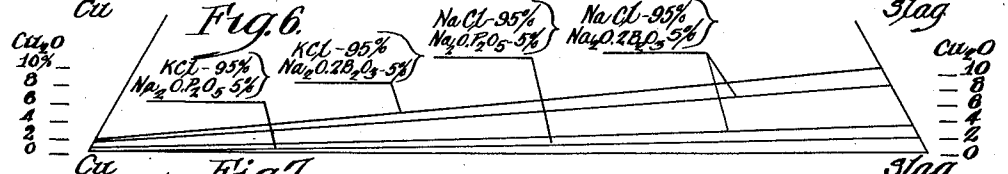


Fig. 7.

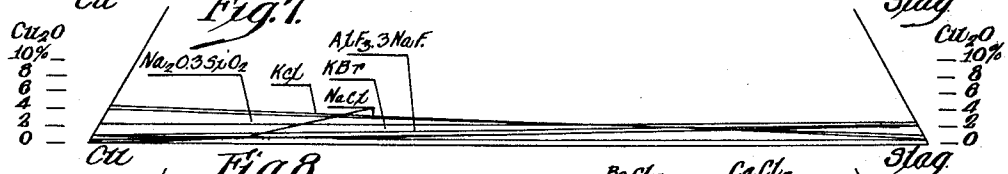
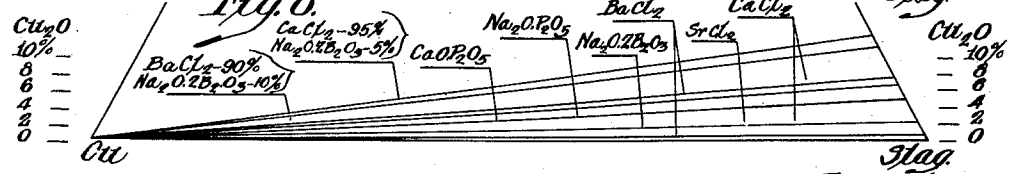


Fig. 8.



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Fig. 9.

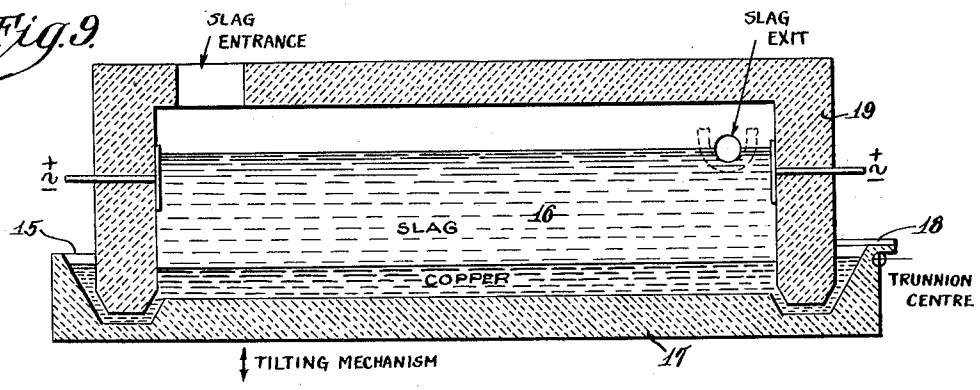


Fig. 10.

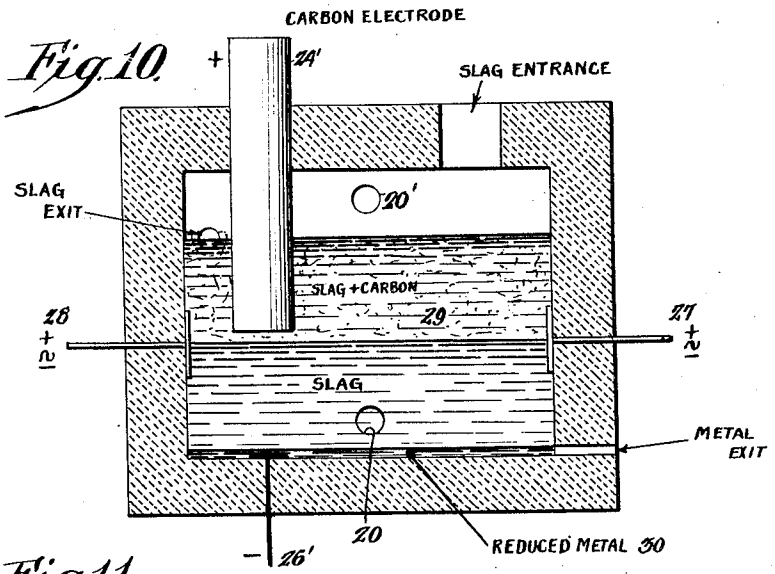
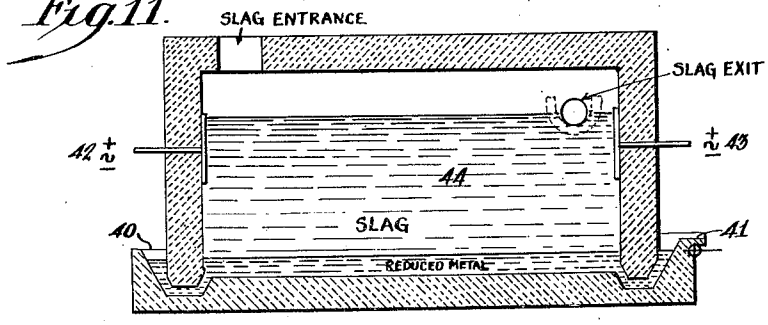


Fig. 11.



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UNITED STATES PATENT OFFICE

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METHOD OF FREEING COPPER FROM COPPER OXIDE

Application filed December 29, 1924. Serial No. 758,723.

Our invention relates to the deoxidation of copper.

Our main purpose is to deoxidize molten copper by slag and to use the slag over and over, reducing the oxide taken up by the slag either between the deoxidizing uses of the slag or continuously during the deoxidizing use of the slag.

A further purpose is to pass molten copper intermittently or continuously through a bath in which its oxide content is withdrawn by a slag and to remove the oxide from the slag while it is free from the presence of the bath.

A further purpose is to provide a slag above the molten metal and immiscible to the metal, into which the copper oxide within the metal may diffuse and to remove the slag for reduction of its oxide content chemically or electrically or otherwise so that the slag may be used repeatedly.

A further purpose is to provide for intermittent or progressive removal of portions of the slag for treatment to reduce its copper oxide content with corresponding substitution of fresh slag low in copper oxide for that removed.

Further purposes will appear in the specification and in the claims.

Our invention relates both to the methods or processes involved and to apparatus by which these methods or processes may be carried out.

This application is a continuation as to most of its subject matter of our co-pending application for method of removing copper oxide from copper, Serial Number 703,122, filed March 31, 1924.

Figure 1 is a vertical section of diagrammatic apparatus using our invention.

Figures 2 and 3 show, diagrammatically, desirable arrangements of or schemes for operation, somewhat different in the two figures to accommodate differences in the operating characteristics of different slags.

Figure 4 is a ternary diagram for the ternary system of copper, copper-oxide and a hypothetical slag, showing the tie-lines at one temperature.

Figures 5, 6, 7 and 8 are each representative of different experimental tests, showing the experimentally determined tie-lines of the two liquid phases with different slags.

Figures 9, 10 and 11 are vertical sections partly diagrammatic of apparatus using our invention.

Commercial copper has been subject to the disadvantage of containing a small percentage of copper oxide in spite of many efforts of different kinds to remove the copper oxide. This percentage in the best copper available has approximated ½ of 1%. Though small in quantity, this oxide has seriously affected the copper in altering its physical properties and, more particularly, in increasing its electric resistance.

Efforts have been made to improve the copper by laboratory use of slags to remove the oxide of copper from the copper, but this has never been capable of extensive use because of its laboratory character and primarily because the slags have never been freed from the absorbed copper oxide, the copper has not been improved greatly and the operation has never been made a continuous one.

Electrolytic copper might at first glance seem to avoid this objection by being wholly free from copper oxide. However, it is not possible to use the electrolytic copper in the form deposited without recasting. In this recasting process, copper oxide forms and dissolves within the molten copper. To correct this, carbon, hydrocarbons, etc., have been introduced within and upon the molten copper, whereby the oxide content is reduced to about ½ of 1% copper oxide. This amount however remains in commercial copper and its ill-effect has been well recognized. Efforts have been made to further remove it by car-

bon, hydrocarbons, etc., but if the reduction be continued the copper liberates a gas whilst cooling in the molds and the castings are unsuited for use. These gases seem to gain access to the copper with the direct contact of copper and oxide reducing agents.

By our invention we deoxidize molten copper by floating upon its surface a suitable slag. Deoxidization results from the transfer of copper oxide to this slag. The mechanism of such transfer is evident from consideration of the phase rule relations governing the distribution of one component, copper oxide between two liquid phases, a slag-rich phase and a copper-rich phase.

When molten copper containing copper oxide comes into contact with an oxide-free slag the partial free energy of copper oxide in the copper is contrasted with the zero partial free energy of copper oxide in the slag. Copper oxide moves into the slag from the copper to an extent determined by its partial free energies in the copper and in the slag, respectively, flow of copper oxide from the copper into the slag ceasing when the rising partial free energy of copper oxide in the slag and the falling partial free energy of copper oxide in the copper reach the same level.

At the same level of partial free energy, different slags may have very different concentrations of copper oxide, which accounts for their corresponding different effectivenesses for the removal of copper oxide from the molten copper.

Whatever the slag there will at equilibrium be a definite concentration of copper-oxide in the slag for each concentration (no matter how small) in the copper, so that any one of many different slags may be used, but with very different effectivenesses. We suggest a number which we have tried but without any thought that the list is complete nor that it includes all of the more highly effective slags.

The slag is treated to remove copper oxide so that the slag may be used again. By electrolysis or other means the concentration of copper-oxide in the slag may be reduced practically to zero, and it follows that the copper phase in equilibrium when in contact with such slag will approximate zero content of copper-oxide.

We remove the copper-oxide from the molten copper by bringing the latter into contact with a slag and treat this slag to keep its copper-oxide content at or below a required amount.

While any slag which is effectively immiscible with molten copper and miscible with molten copper-oxide will serve the purpose, not all operative slags work equally well. Properties, such as melting-point, viscosity, vapor pressure, stability, etc., will favor certain slags. Other factors that may determine or affect the choice of a slag will be local conditions, rapidity and effectiveness in functioning and lack of corrosiveness to furnace linings.

The equilibrium distribution of copper-oxide between the copper and the slag will be better understood by a brief discussion of this subject from the standpoint of binary and ternary component relations in the molten two component system, copper-oxide and copper, and the molten three component system copper-oxide, copper and slag, as follows:—

Our slag deoxidation puts to useful application these phenomena which occur when a molten, two-component system—copper and copper-oxide—is brought into contact with a third component—a slag, immiscible with molten copper and miscible with molten copper-oxide. The construction of a ternary diagram—Cu, Cu_2O, slag—will show the resultant equilibria.

For a perfectly general treatment, we assume any slag, and develop the two binary equilibrium diagrams—Cu plus slag and Cu_2O plus slag for temperatures exceeding the liquidus curves. To these can be added the binary diagram Cu plus Cu_2O, as determined by Slade and Farrow, (Proc. Roy. Soc'y 1912 LXXXVII, page 524).

Since copper shows such limited liquid miscibility with both slag and oxide, most concentrations on the ternary diagram will show two liquids in equilibrium—one, in general, rich in slag, the other rich in copper; the total Cu_2O present being divided between these two liquid phases. (See diagram, Figure 4).

The composition of the liquid phase or phases present in the three-component system, copper, copper-oxide and slag, at a given temperature is graphically indicated in the ternary equilibrium diagram of Figure 4, which is constructed with a hypothetical slag miscible when molten with molten copper-oxide and immiscible with molten copper.

This diagram shows that within the area *abcd* two immiscible liquids coexist for every ratio of the three components of the system. The composition of the one liquid (being molten slag containing dissolved copper oxide and some copper) will vary along *dc* with the simultaneous variation of the conjugate liquid (molten copper containing dissolved copper-oxide and, theoretically, some slag) along *ab*. For any given composition on *ab* (showing the copper-oxide content of the copper), only one composition on *cd* (showing the copper-oxide content of the slag) can be maintained in equilibrium. The tie lines, such as *fg*, *hj*, etc., illustrate this relationship; compositions *f* and *h* of the impure copper require compositions *g* and *j* respectively of the impure slag.

We have experimentally determined the

compositions of the coexisting liquids (impure copper and impure slag) for the lower portion of the ternary diagram for quite a number of different slags, with the results that are plotted in Figures 5, 6, 7 and 8 with an assumption (substantially true) of negligible solution of slag into the copper and of negligible solution of copper into the slag.

These tie-lines are self-explanatory, the composition of the slag used being noted upon each tie-line. From these figures it will be noted that there is a wide divergence in the effectivenesses of the slags used. Among the better slags are seen to be the chlorides of calcium or barium mixed with a little sodium borate, and the chlorides of sodium or potassium mixed with a little sodium silicate, phosphate or borate. Sodium silicate alone and the chloride of potassium or sodium alone are seen to be less effective.

Figure 1 illustrates apparatus well adapted to reduce a slag chemically or electrolytically simultaneously with its use to remove dissolved oxide from molten copper, a mode of operation illustrating the broad invention of the parent application and specifically claimed therein. It is also capable of use when it is the intention to remove the slag for deoxidizing treatment in a special furnace, e. g., Figure 10.

In the apparatus of Figure 1, molten copper is introduced at 15 into the body 16 of the deoxidizing furnace 17. A trunnion and tilting mechanism is indicated diagrammatically for periodic pouring after the copper has been deoxidized or, if desired, the discharge may be by overflow (intermittent or continuous) at a spout 18. The refractory 19 seals the slag from the copper inlet and outlet and keeps the heat in the furnace. Above the slag which covers the molten copper may be advantageously floated a layer of carbon to help deoxidize the slag, or (and) a reducing gas or hydrocarbon might be introduced into the slag or above the slag as at 20, 20', respectively, for the same purpose. Liberated carbon monoxide or other gas effluent escapes from the furnace at 21.

Positive electrodes 24 and 25 are provided above the slag for electrolytic deposition of the copper of the Cu_2O diffused from the metal bath into the slag. The molten copper of the bath forms the negative electrode, electric connection being made from it, as indicated diagrammatically at 26, to the source of direct current, not shown.

Normally the electric resistance of the slag and carbon above the slag will be considerably less than the resistance of the slag proper, with the result that the slag-carbon mixture above the slag acts as a continuous positive electrode covering the whole slag bath. The electrolytic deposition of the copper is upon the copper of the bath. It will be obvious that the oxide of the slag is continuously reduced by both the electrolytic action of the current and by the carbon floating upon the slag and that if desired either may be used without the other.

If it be desired to supply additional heat to this reducing furnace, an alternating voltage may be impressed across the two carbon electrodes shown or across any other suitable electrodes (such as the pole pieces shown), the slag and metal bath being thereby used as a resistor for heating purposes.

This mode of operation, in which the slag is continuously reduced in place while it is operating to remove copper oxide from molten copper, has many advantages and was selected as the main form of the parent application. It does however, also have disadvantages, notably in a tendency to reduce to metal other oxides which accompany copper, with a resultant tendency toward contaminating the molten copper bath with impurities.

For this reason, when the melt of impure copper contains in solution other metallic oxides which accompany the copper oxide into the slag, it is advantageous to reduce these oxides in a separate reduction furnace, to prevent the return of the reduced metals to the copper. The same treatment can be applied also when copper oxide only is to be reduced but for any other reason it be desired to conduct the operation away from the slagging furnace.

Figure 2 indicates an advantageous scheme for carrying out this process whether the raw material requiring purification be substantially free from other metals or metallic oxides than of copper or not. The raw material is charged in the melting furnace, and the molten product containing copper oxide with or without oxides of other metals as impurity is delivered continuously or intermittently to the slagging furnace which may advantageously be as shown in Figure 1 or Figure 9. Complete reduction could take place in Figure 1, or partial reduction there and the remainder in Figure 10; or the form of Figure 9 be used, without any reduction in it and with entire reduction in some such furnace as in Figure 10.

It is quite desirable to perform the melting at sufficient distance from the deoxidizing furnace or container or under such conditions as to free the latter from the deteriorating effect upon the slag of the gases attending fuel combustion, so as to permit selection of slags independently of this factor and thus permit the use of cheap fuel heating. Where complete reduction is not effected in the slagging furnace (whether partial or no reduction take place there) the slag is then removed continuously or intermittently to a reducing furnace of which one example is given in Figure 10, where the ox-

ide is reduced chemically and (or) electrolytically using the electrodes 24′ and 26′.

With strong reducing agents there may be slight disadvantageous reduction of a portion of the original slag. Phosphate bearing slag reduced with carbon is one example of this. Such partial reduction is advantageously corrected, as shown in Figure 3, by treating the reduction product from the reducing furnace with a suitable small portion of the unreduced slag which reoxidizes the reduced portion of the slag for return with the slag product from the reducing furnace to the slagging furnace as indicated.

It is obvious that the forms of furnaces used in the diagrammatic cycles of Figures 2 and 3 are subject to very wide variation without departing from the invention. One form each of the slagging furnace, reducing furnace and equalizing furnace, intended to be conventional, for use in the cycles of Figures 2 and 3 is shown respectively in Figures 9, 10 and 11.

The slagging furnace shown in Figure 9 is substantially similar to that of Figure 1 except that no provision is shown for reducing the slag in place, portions of the slag being transferred periodically or continuously to a reducing furnace, as through a pouring spout 18.

One form of reducing furnace is illustrated in Figure 10. The reducing furnace is shown provided with substantially the same means as in Figure 1 for slag reduction. The slag bath is provided with A. C. heating electrodes 27 and 28 and is covered with a floating layer of carbon 29. Optional means are shown for electrolytic reduction of the slag, the positive pole 24′ dipping into the slag and the negative pole 26′ lying in the bed 30 of reduced metal. The direct current for electrolysis can be used for heating, both in Figure 1 and in Figure 10, and in either figure hydrocarbons or reducing gas may be introduced at 20 below the slag surface.

The equalizing furnace illustrated in Figure 11 is generally similar to the furnace of Figure 1 but much smaller and without provision for electrolytic or chemical reduction. Its function is that of a mixing chamber facilitating reaction between untreated slag and reduced metal from Figure 10.

As distinguishing between Figures 9 and 11, in Figure 9 all of the copper being treated passes through the furnace of Figure 9 whereas in the furnace of Figure 11 the only metal present is that which has been reduced from the slag in some such furnace as that of Figure 10.

Obviously there may be very wide variation in the details of our process according to the whim or particular need of the user and we claim all such in so far as they fall within the reasonable spirit and scope of our invention.

Having thus described our invention, what we claim as new and desire to secure by Letters Patent is:—

1. The process of removing copper oxide from molten copper continuously, which consists in covering the molten copper bath with slag capable of dissolving the copper oxide from the copper, using the slag to dissolve the copper oxide, removing a portion of the slag with its content of copper oxide and supplying fresh slag to maintain the activity of the slag.

2. The process of removing copper oxide from molten copper continuously which consists in dissolving the copper oxide from the molten copper bath in a slag floated upon the surface of the bath and in reducing the oxide in the slag to copper away from the bath.

3. In the art of removing copper oxide from molten copper by means of a slag, the invention which consists in slagging preliminarily melted copper with a material in which copper oxide has low partial free energy as compared to its partial free energy in the same concentration in the molten copper, in removing and revivifying portions of the slag, and in replacing the removed portions of slag with revivified slag.

4. In the art of removing copper oxide from molten copper by means of a slag, the step which consists in slagging the molten copper with a slag having lower partial free energy of copper oxide than the partial free energy of copper oxide in the copper, in removing and revivifying portions of the slag and in replacing the removed portions of slag with revivified slag.

5. The process of freeing molten copper from the copper oxide dissolved in it, which consists in providing a medium into which the oxide will diffuse, in applying the medium to the surface of the molten copper to permit diffusion of copper oxide out of the copper into the medium, in maintaining freedom of the copper oxide to diffuse out of the copper by progressively replacing used medium with fresh medium, and in maintaining a supply of fresh medium by removing copper oxide from the used medium.

6. The process of freeing molten copper from the copper oxide dissolved in it, which consists in providing a pool of molten copper, in supplying molten copper with dissolved copper-oxide in it to the pool at one point and withdrawing molten copper from the pool at another point while removing the oxide from the metal of the pool by permitting it to diffuse into a slag, in maintaining the freedom of the oxide to diffuse out of the pool by replacing used slag with fresh slag, and in maintaining a supply of fresh slag by removing the copper oxide from the used slag.

7. The process of freeing molten copper from the copper oxide dissolved in it, which

consists in melting copper at one point, transferring it molten to another point where it is free from the conditions surrounding the melting, removing the oxide from the copper in the second position by permitting it to diffuse into a slag which would be deteriorated by the gases attending fuel combustion, in maintaining the freedom of the oxide to diffuse out of the copper by progressively replacing used slag with fresh slag, and in maintaining a supply of fresh slag by revivifying treatment of the used slag.

8. The process of removing copper oxide from molten copper continuously, which consists in covering the molten copper with slag capable of dissolving the oxide to lower the copper oxide content in the molten copper, in progressively replacing used slag with fresh slag and in maintaining a supply of fresh slag by revivifying the used slag.

9. The process of removing copper oxide from molten copper continuously, which consists in covering the molten copper with slag capable of dissolving the oxide to lower the oxide content of the molten copper, in progressively replacing used slag with fresh slag, and in maintaining a supply of fresh slag by revivifying the used slag by reducing the oxide in the slag.

10. The process of removing copper oxide from molten copper continuously, which consists in covering the molten copper with slag capable of dissolving the oxide to lower the oxide content of the molten copper, in progressively replacing used slag with fresh slag, and in maintaining a supply of fresh slag by revivifying the used slag by reducing the oxide in the slag with carbon.

11. The process of removing copper oxide from molten copper continuously, which consists in covering the molten copper with slag capable of dissolving the oxide to lower the oxide content of the molten copper, in progressively replacing used slag with fresh slag, and in maintaining a supply of fresh slag by revivifying the used slag by reducing the oxide in the slag with hydrocarbons.

12. The process of removing copper oxide from molten copper continuously, which consists in covering the molten copper with slag capable of dissolving the oxide to lower the oxide content of the molten copper, in progressively replacing used slag with fresh slag, and in maintaining a supply of fresh slag by revivifying the used slag by reducing the oxide in the slag electrolytically.

13. The process of removing copper oxide from molten copper continuously, which consists in continuously protecting the upper surface of the molten copper from contact with the air by slag capable of receiving copper oxide from the molten copper and in continuously reducing the copper oxide in the slag to restore the copper thereof as copper to the molten copper.

14. The process of freeing molten copper from the copper oxide dissolved in it, which consists in providing a cover for the molten copper to protect it from the air, which cover has a lower partial free energy of copper oxide than that of the copper oxide in the molten copper and in maintaining the partial free energy of copper oxide in the cover well below the partial free energy of copper oxide in the molten copper.

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