Aug. 7, 1956 J. F. JORDAN 2,758,022

CONTINUOUS COPPER REFINING

Filed May 20, 1953 2 Sheets-Sheet 1

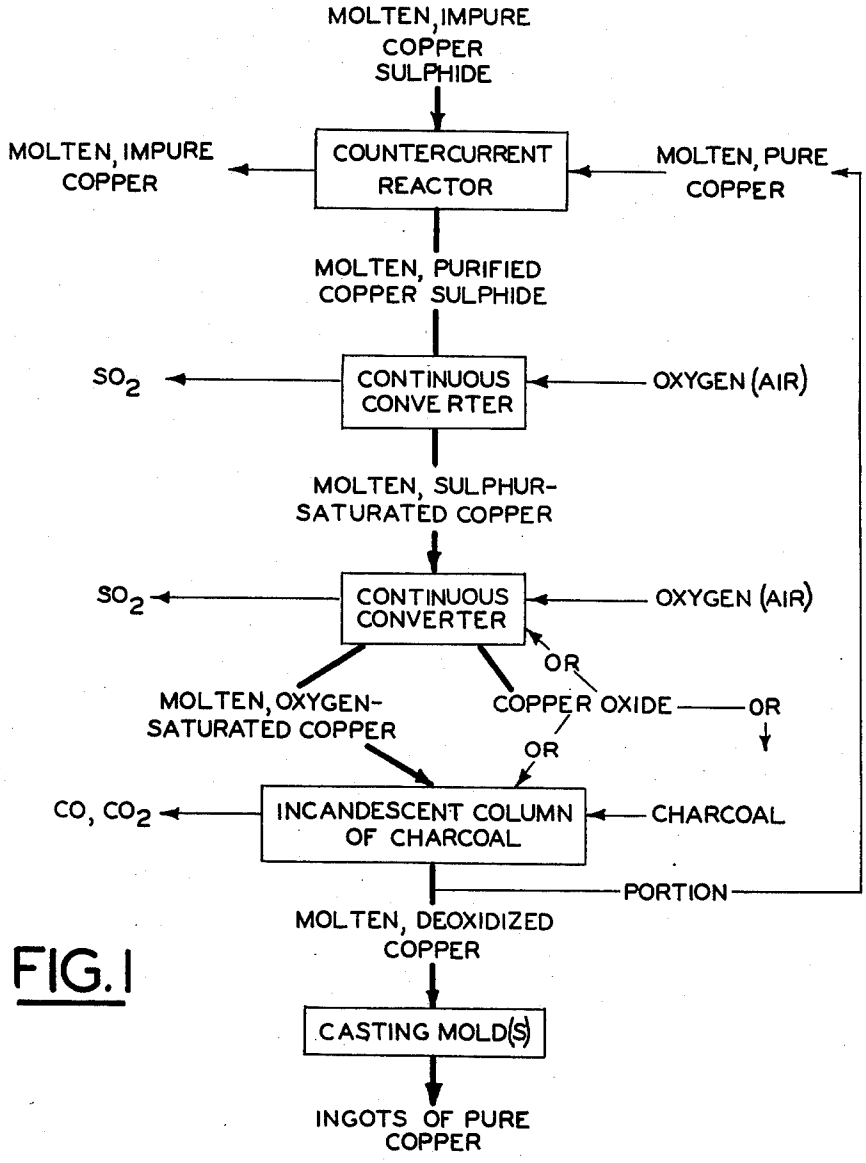


FIG. 1

INVENTOR:-

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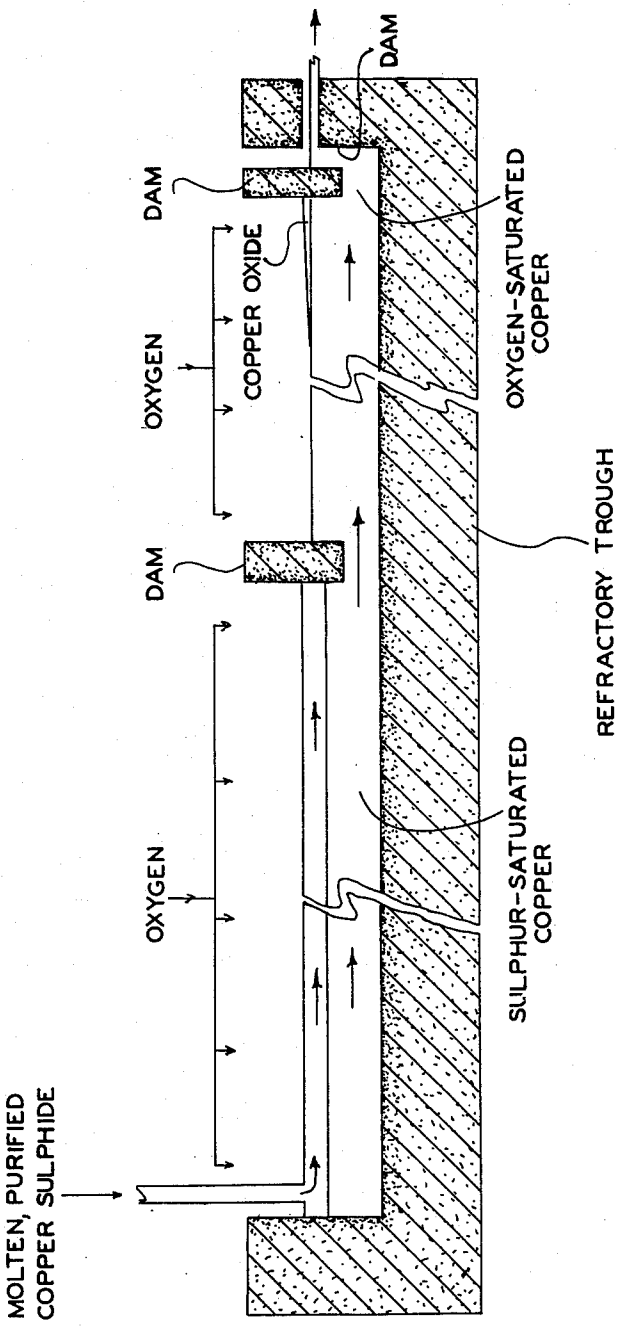


FIG. 2

INVENTOR:-

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2,758,022

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Application May 20, 1953, Serial No. 356,197

10 Claims. (Cl. 75—76)

My invention relates to metallurgy wherein copper sulphide is to be converted into copper.

Pyrometallurgical methods never having shown an ability to refine copper to electrical standards, present-day refining procedures consist of a combination of pyrometallurgical methods and the electrolytic process. Such combinations, while yielding the desired purity, do so at the expenditure of large amounts of capital and at high cost, for the overall operation is metallurgically awkward. When the cost of producing the common metals is high, whether for metallurgical or other reasons, all business suffers. The cost of producing copper is high, and it is clear that a correction of this must be found in the metallurgical phase of the industry, for there is small chance that any dramatic improvement will be made in the present-day mining and concentration procedures.

I have found a pyrometallurgical refining procedure that yields copper of electrical purity without the electrolytic step.

Practically-all copper smelters arrive at a pool of molten white metal at some stage of their operations, either as a result of melting an iron-free, sulphide ore or concentrate or as the result of a converting operation wherein air has been employed to oxidize the iron sulphide content of a molten matte. It is at this white metal stage that my process begins.

In the usual case, the pool of molten white metal contains, in addition to the gold and silver, objectionable amounts of iron, arsenic, antimony, lead, selenium/tellurium and nickel. I remove substantially-all of the gold and silver from the white metal, and lower each of the listed objectionable metals to below about 0.002%, by treating said molten white metal with the reagent, copper. This I do by contacting a small stream of white metal with a countercurrent stream of molten copper.

While the old "bottoms" process never showed an ability to produce a metal that met the critical conductivity test, I have found that the "bottoms" reactions will yield the required purity if my critical steps are employed in carrying out said reactions. In general, these critical steps involve: (1) a countercurrent flow of the reactants, and (2) the maintenance of something approaching equilibrium between the reactants all along the contact therebetween. While there are few problems involved in entertaining a contra-flow of molten copper and molten white metal, the second critical factor requires the most careful consideration respecting the design of the vessel wherein the contact is maintained and the most careful operating procedure.

The countercurrent refining vessel disclosed in my patent, U. S. No. 2,572,489, is highly suited for treating a molten white metal with molten copper. 2,572,489 should be consulted for details regarding this refining vessel, the shelf arrangement shown in Figures 4 and 5 of said patent being particularly recommended. It will be understood that the "waste slag" of Figure 1 in 2,572,489 is the refined white metal of the present invention.

While the molten white metal being passed to my first refining step will ordinarily come from a converter or from a holding vessel into which white metal from converters is poured until needed, the molten copper employed as the refining agent will ordinarily come from a later step in the process. I recommend that both the white metal and the refining copper be at about 1200° C. when they are brought into countercurrent contact, however, slightly lower or much higher temperatures may be employed.

The removal of elements such as iron, arsenic, antimony and nickel from the white metal by the copper involves simple reduction reactions, while the removal of elements such as selenium and tellurium involves extraction processes. It has been observed that the amount of copper required to refine a given white metal depends upon the extraction processes rather than the reduction processes. The amount of copper required to extract the selenium and/or tellurium from a given white metal depends upon the distribution coefficient of copper selenide between the molten white metal and the molten copper at the copper-exit end of the refining process. The most important factor in this distribution coefficient seems to be the purity of the copper, and this purity depends of course on the purity of the molten white metal. It has been observed that, in any given case, the amount of copper required is inversely proportional to the distribution coefficient of copper selenide at said copper-exit end of the extraction process, and it has observed that, if the selenium is being removed from the molten white metal, elements such as iron, arsenic, antimony, nickel, silver and gold are being removed also.

The desired white metal purity is only achieved when the molten white metal has been brought into substantial equilibrium with a molten copper that is essentially-free from all of these impurities, silver and gold being exceptions to this rule. This is a critical point, a point overlooked by the Welsh and bottoms processes. As mentioned, silver and gold seem to be exceptions to this rule, for a copper reagent containing silver and gold still exhibits an excellent ability to remove essentially all silver and gold from a molten white metal. As an illustration of the results obtained from gaining equilibrium between an impure white metal and a pure copper reagent: in one test that I carried out on a white metal containing 0.09% As, 0.11% Sb, 0.05% Fe, 0.02% Ni, 11.5 oz/ton Ag and 2.1 oz/ton Au, brought into substantial equilibrium with a copper of electrical purity, I obtained a white metal containing only traces of silver and gold, 0.0004% As, 0.0010% Sb, 0.0015% Fe and 0.002% Ni. The amount of copper employed in this test was 5% of the white metal, by weight.

In view of the fact that the molten white metal and molten copper being fed to this process will ordinarily vary little insofar as the impurity levels are concerned, seeking and establishing the optimum refining rate and relative rates of reactant flow into the process is simple. With the molten white metal flowing thru the refining vessel at a selected rate and in flowing contact with a stream of molten copper, so that the overall process is not producing white metal of the desired purity, the rate of flow of copper into the process is increased in steps until the desired purity is obtained in the white metal product, or, alternately, the rate of flow of the raw white metal into the process is decreased in steps until the desired white metal purity is being obtained, or both. When the desired white metal product is being obtained, the flow of copper into the process should be increased by some preselected amount, so as to afford protection against the variables which are inherent with such a process.

The copper extraction yields a pure molten white metal and an impure copper. The impure copper is best cast into anodes and purified electrolytically, thereby recov-

ering the valuable impurities concentrated therein. The pure white metal is flowed to the next step of my process, the desulphurizing step.

Desulphurization

The next step of my process involves the continuous conversion of the molten, pure white metal into a sulphur-saturated copper metal. This I carry out within a refractory-lined refining trough into which I permit the pure white metal from the extraction process to flow, the conversion being carried out by means of a series of air jets which are spread out along said trough so that said jets impinge into the molten copper sulphide, preferably from a position that lies above the surface of the stream of molten sulphide within said trough. The molten, sulphur-saturated copper arising from the reaction between the copper sulphide and the oxygen accumulates as a stream that flows along underneath the molten copper sulphide, said sulphur-saturated copper leaving said molten copper sulphide by underflowing a dam positioned across the trough downstream from the position whereat the molten sulphide is entering said trough. Figure 2 pictures this first stage of my desulphurizing process.

Air may be employed in the jets of the first stage of my desulphurizing step if the mass of sulphide/copper is sufficiently large and if the trough is well insulated, however, I prefer to use oxygen or air enriched with oxygen, due to the increased refining capacity achieved thereby and due to the favorable temperature build-up that accompanies the substitution of oxygen for nitrogen.

The sulphur-saturated copper from my first desulphurizing phase flows immediately into the second, final desulphurizing phase wherein the sulphr content of the metal stream is substantially eliminated by saturating said metal stream with oxygen, said saturation with oxygen being achieved by means of a series of impinging air jets. Figure 2 shows a combination of the first and second phases of my desulphurizing step in one refining vessel. The two phases of the desulphurization step may be carried out in two separate troughs, if desired.

As the molten, sulphur-bearing copper metal flows along under the impinging air jets, the sulphur content of the metal stream rapidly falls. In view of the fact that the end point of this desulphurization is difficult to detect without taking samples of the flowing stream—a procedure that is not practical in a continous-flow process, I prefer to operate this second phase so that a substantial amount of copper oxide separates as a separate phase to float on the molten copper at the metal-exit end of the second phase of this desulphurizing step. The formation of this separate, copper oxide phase assures the completion of the desulphurizing step, for it indicates that the metal is saturated with oxygen. This separate, copper oxide phase may be passed with the oxygen-saturated copper to the next, deoxidizing step, or it may be blocked from leaving the vessel with the oxygen-saturated copper, thus causing the molten copper oxide to flow back over sulphur-bearing copper within the second desulphurizing step.

The separate, copper oxide phase formed in this second phase will contain a portion of the impurities left in the metal after the copper extraction step. Such impurities will of course reenter the metal unless steps are taken to separate the separate, copper oxide phase from the oxygen-saturated metal. Generally speaking, the amount of such impurities will be very small if the copper extraction step was properly carried out, however, if desired, such impurities as may be held in the separate, copper oxide phase may be removed by simply skimming off the floating copper oxide phase, either within the vessel or after the metal plus molten oxide have left said vessel. If the separate, copper oxide phase is to be separated from the oxygen-saturated copper, I prefer to carry out the operation after the immiscible liquids have left the vessel. A simple underflow/overflow dam arrangement may be employed to accomplish this.

Deoxidation

The metal leaving the second phase of my desulphurizing step is saturated with oxygen. As the next step in my process, I remove essentially all of said oxygen from said metal by reacting said oxygen with incandescent charcoal, by flowing the oxygen-bearing copper thru a column of said charcoal, much in the manner that OFHC copper is produced. I prefer to maintain the charcoal column at temperature by means of the molten copper flowing therethru, by operating the desulphurizing steps so that the molten copper entering the deoxidizing unit contains sufficient heat to maintain the charcoal column at temperature. This I do by enriching the air employed in the desulphurizing step sufficiently with oxygen to yield the required temperature build-up.

The deoxidizing step of my process always produces an oxygen-free copper, whether the final product is to be an oxygen-free copper or a tough-pitch copper.

Casting

The preferred embodiment of my process involves the continuous casting of the fully-deoxidized copper leaving the deoxidizing step. By continuous casting, I mean in a water-jacket mold such as is conventional in the continuous casting art, not a continuous series of ingots or castings. The metal requirements of a continuous casting mold are admirably met by the continuous flow of deoxidized copper from my process. Of course, if desired, the metal of my process may be fed to one of the casting machines conventional to the copper refinery. If it is desired to form tough-pitch copper, then the deoxidized copper from my process should be flowed along a refractory trough under a circulating, controlled flow of an oxidizing gas; for, at a given temperature, the oxygen pick-up by the flowing metal stream will vary as the interval of contact. Another simple method of lifting the oxygen content of the copper to tough-pitch levels involves feeding copper oxide into a flowing copper stream, the rate of feed being in accordance with the rate of copper flow. Copper oxide for this purpose may be obtained from the second phase of the desulphurizing step, preferably by cooling the oxide, crushing it to a powder and then feeding it into the copper stream with a reagent feeder.

Figure 1 pictures the flow pattern of my process.

The refractories employable in the various refining vessels of my process are those conventional in the present art. While the refractories in contact with the molten liquids of my process may be the same as those in contact with the same liquids within conventional procedures, it is important to remember that the small amount of such liquids in action, at any given moment, makes the use of insulation necessary. Such insulation, and the judicious use of oxygen in place of all or part of the refining air, makes feasible the maintenance of the required temperature levels in the flowing streams of my process.

In any given continuous-flow process, such as this, the trick is to arrange the reaction sequence so that the controls lie within the process itself, for only then is it possible to envision automatic control. It is not practical to employ the control laboratory in a continuous-flow process in the same manner that such a laboratory is employed in the batch-type processes. My present invention admirably meets all control problems. In the first, copper extraction step, the required automatic control is gained by employing an excess of the reagent, copper, over that required to remove the average impurities, and this excess may be related to the maximum expectancy with respect to the swing of the impurities over this norm. Control in the first phase of the desulphurizing step is fully automatic, for the copper flows out of the phase as soon as it is formed, and control over the second phase is also

automatic, once the oxygen input has been regulated to the end that a substantial excess of copper oxide is being produced at the metal-exit end of said second phase. All that is needed in this second phase is an occasional check to assure that the process is continuing to produce substantial amounts of copper oxide. The final, deoxidizing step is fully automatic in that the molten copper is brought into contact with much more carbon than that required to attain the desired degree of deoxidation.

The reagent in the air jets of my process is always oxygen. Such oxygen may be derived from air, oxygen gas or air enriched with oxygen gas. I therefore employ the term, oxygen, to refer to air, oxygen gas or air enriched with oxygen gas throughout my claims.

I claim as my invention:

1. The method of converting a stream of molten white metal into a stream of essentially sulphur-free, oxygen-saturated, molten copper, which comprises: pouring said molten white metal into one end of an elongated reaction zone to form a stream of molten white metal within said reaction zone; directing a series of oxygen jets into reacting contact with and along said flowing white metal stream within said reaction zone to form molten copper that settles through said molten white metal stream to form a stream of sulphur-saturated, molten copper upon which said molten white metal stream is floating; flowing said sulphur-saturated, molten copper stream into one end of an elongated refining zone while blocking the flow of said molten white metal thereinto; directing a series of oxygen jets into reacting contact with and along said sulphur-saturated, molten copper stream within said refining zone as said copper stream flows through said refining zone, sufficient oxygen being fed into reacting contact with said copper stream within said refining zone by means of said oxygen jets to form a separated layer of molten copper oxide floating on said copper stream within said refining zone; and thereupon flowing said copper stream out of said refining zone.

2. The method according to claim 1 in which said layer of molten copper oxide separates from said copper stream near the copper exit end of said elongated refining zone.

3. The method according to claim 1 in which said molten white metal is refined before being poured into said reaction zone by contacting and reacting said molten white metal with an essentially pure, molten copper solvent, said solvent being separated from the refined molten white metal before said white metal is poured into said reaction zone.

4. The process according to claim 1 in which said molten, separated copper oxide is flowed back over said stream of sulphur-saturated copper.

5. The process according to claim 1 in which said molten, separated copper oxide flows into a deoxidizing process with the oxygen-saturated copper.

6. The process according to claim 1 in which the oxygen-saturated copper is flowed through and in intimate contact with a loosely-packed column of incandescent charcoal until said copper is essentially deoxidized.

7. The process according to claim 6 in which said oxygen-saturated copper is accompanied by a molten slag consisting of copper oxide.

8. The process according to claim 6 in which said deoxidized copper is flowed into a continuous, water-jacket mold.

9. The process according to claim 6 in which said deoxidized copper is poured into a series of individual molds.

10. The process according to claim 9 in which oxygen is added to said deoxidized copper before said copper is poured into said molds.

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