

Jan. 20, 1970

J. E. DORE ET AL

3,490,897

PROCESS FOR PRODUCING LOW OXYGEN, HIGH CONDUCTIVITY COPPER

Filed Oct. 27, 1967

4 Sheets-Sheet 1

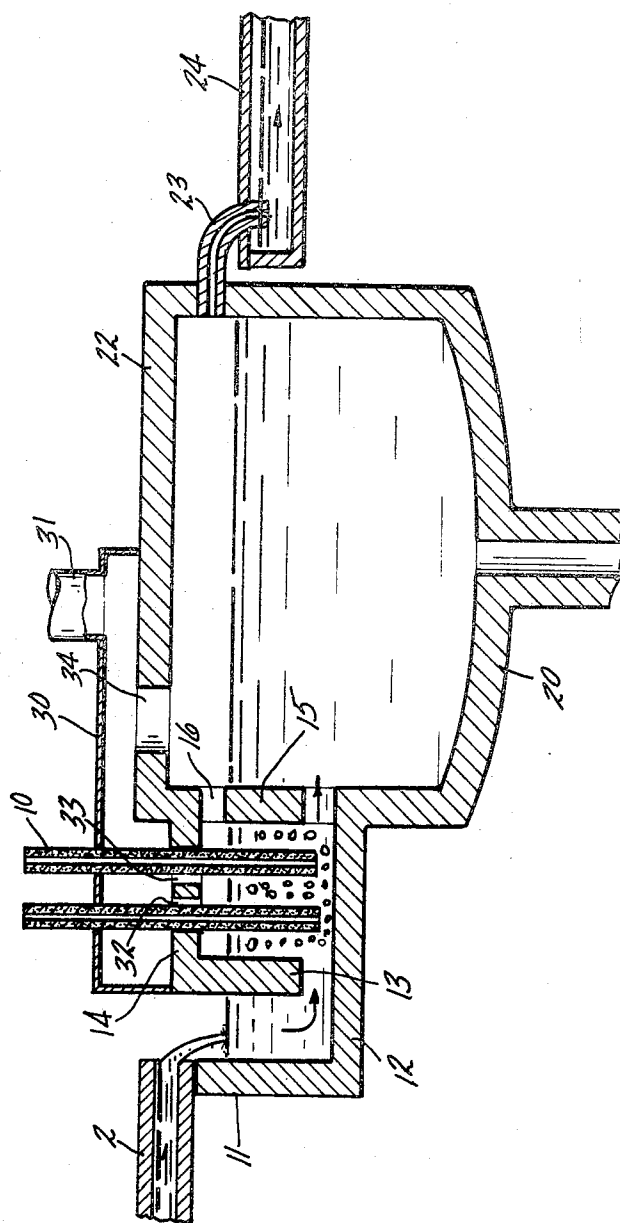


FIG-1

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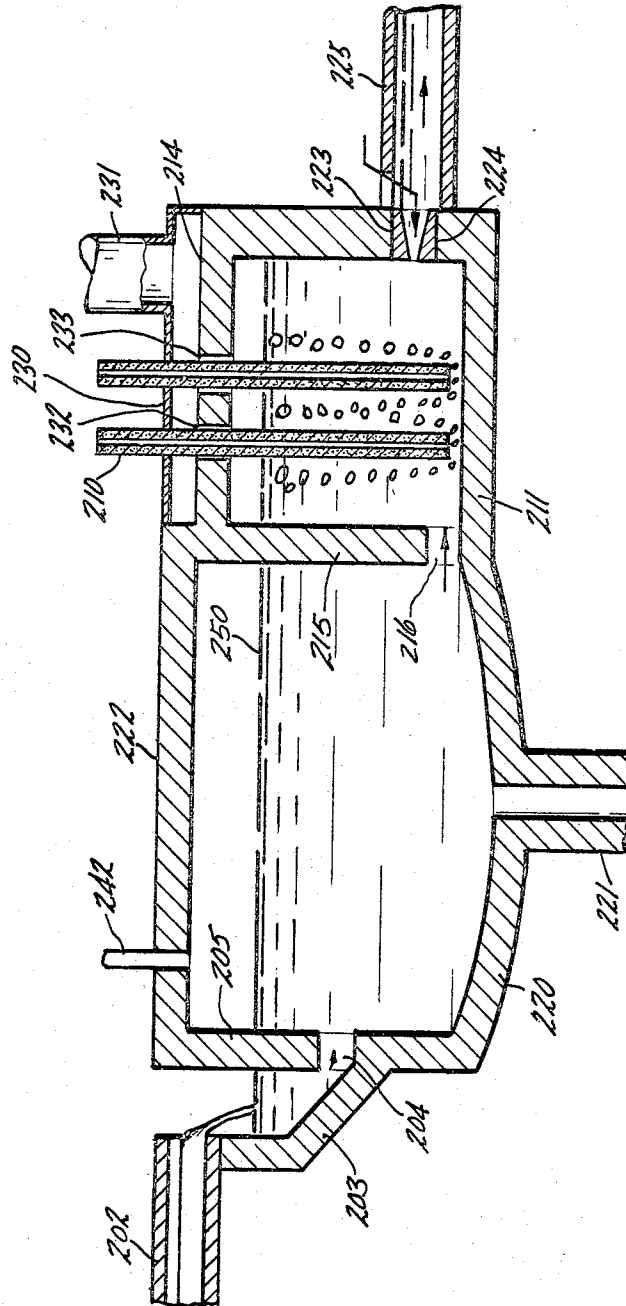
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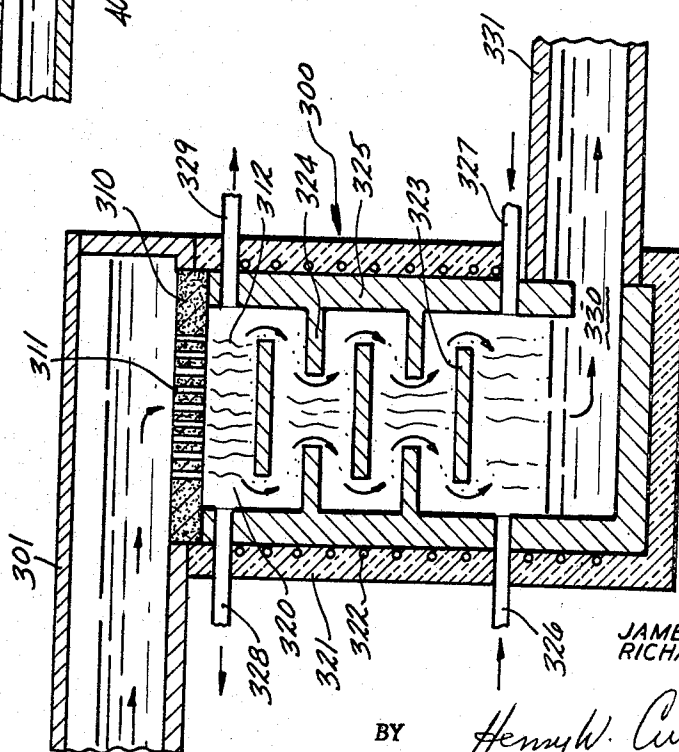
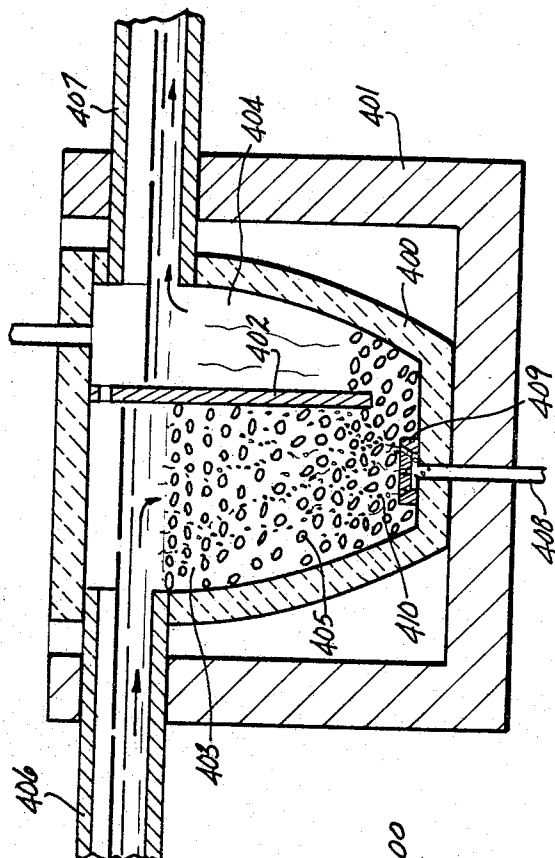
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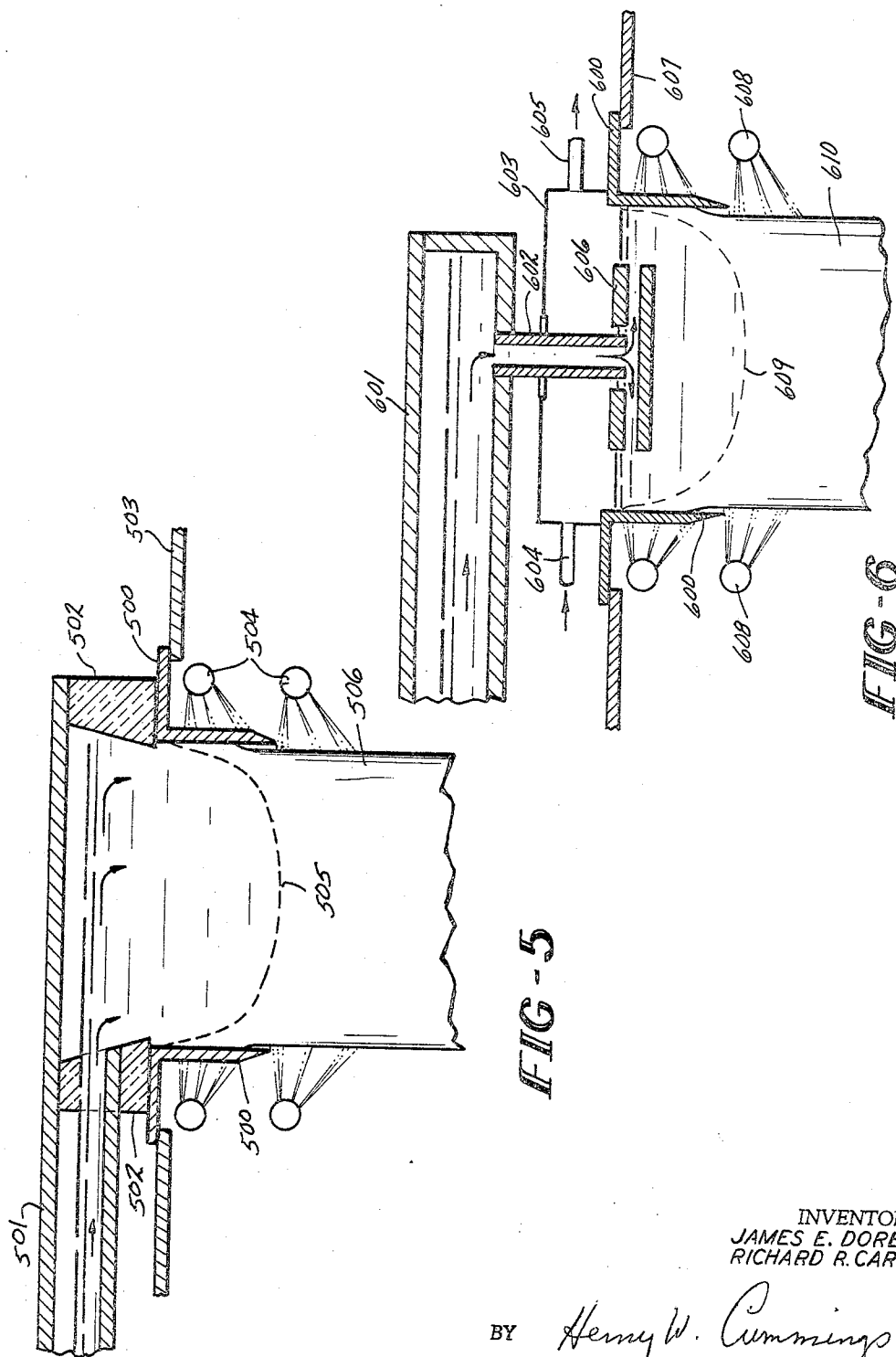


FIG-5

FIG-6

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PROCESS FOR PRODUCING LOW OXYGEN, HIGH CONDUCTIVITY COPPER

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Continuation-in-part of application Ser. No. 554,988, June 3, 1966. This application Oct. 27, 1967, Ser. No. 678,755

Int. Cl. C22b 15/00, 9/12

U.S. Cl. 75—76

15 Claims

ABSTRACT OF THE DISCLOSURE

An improved process is described for producing low oxygen high conductivity copper ingot for fabrication into wrought semi-finished products comprising: melting the copper base alloy in a furnace, covering the molten metal with a layer of a carbonaceous material selected from the group consisting of graphite and charcoal, bubbling a halogen containing compound through said molten metal, transferring said molten metal to a casting station under a protective atmosphere, and casting said molten metal into ingots. Prior to applying the carbonaceous layer, any reducing elements present in the molten copper may be removed by oxidation or by treatment with a monomeric, halogen containing, lower aliphatic hydrocarbon containing at least one fluorine atom.

This application is a continuation-in-part of S.N. 554,988, filed June 3, 1966 and now U.S. Patent No. 3,434,825, which issued Mar. 25, 1969.

This invention relates to a new and improved method for producing low oxygen content, high purity copper process ingot suitable for fabrication into wrought semi-finished products. Strip produced from such ingots is preferred for a large number of applications, because of low susceptibility to hydrogen embrittlement, good weldability, and high electrical conductivity (in excess of 100% IACS).

Low oxygen copper is manufactured in the U.S. under the trade name of OFHC copper (oxygen free, high conductivity copper). OFHC copper commands a very high price in ingot form. The reason for this is largely due to the demanding and complex nature of presently known manufacturing procedures.

According to these prior art methods, high purity select grade cathode copper is used as the starting material. Melting is carried out in a special two hearth electric furnace under a protective atmosphere (believed to be a mixture of N_2 and CO) to prevent oxygen infiltration. After melting, the metal is transferred through a closed launder to a holding furnace from which it is cast into process billet or ingot. Protective atmospheres of N_2 -CO must also be maintained during the transfer, holding, and casting operations to insure freedom from oxygen.

Thus, these prior art methods of manufacturing OFHC copper have the following limitations:

(1) Premium grade cathode copper extremely low in oxygen, sulfur and other impurities must be used as starting material;

(2) Melting and casting operations are geared to maintain this purity level. No steps are or can be taken to remove oxygen, or any other impurities from the system. As a consequence, raw material requirements are very rigid and the melting and casting processes must be carefully controlled.

The present invention overcomes these limitations. Any high purity copper free of non-reducing elements such as Sb, As, Ag, Bi, Ni, etc., that cannot be removed by oxida-

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tion or treatment with a monomeric, halogen containing, lower aliphatic hydrocarbon containing at least one fluorine atom can be used as a charge material. Moreover, positive means are provided for controlling and reducing the oxygen and other impurities including Zn, Fe, Cr, Al, Si, B, Pb, and Sn in the melt.

Suitable copper charge material (free of elements that cannot be removed by oxidation or by treatment with a monomeric, halogen containing, lower aliphatic hydrocarbon containing at least one fluorine atom) is melted down in a conventional induction furnace, such as an Ajax-Tama-Wyatt induction melting furnace or any other suitable melting furnace. Depending on the grade of raw material used, the melt is either (a) immediately covered with a layer of graphite or charcoal, or (b) oxidized with dry air to remove reducing elements such as, carbon, sulfur, phosphorous, etc., and then covered with a layer of graphite or charcoal. This treatment reduces the residual oxygen level to about 0.10% to 0.05%.

The melt is then transferred to a suitable holding furnace (such as an induction heating holding furnace) and treated with a halogen compound, for example, $AlCl_3$, $AlBr_3$, $TiCl_4$, C_2Cl_6 , CCl_4 , and/or CBr_4 or with a monomeric halogen containing, lower aliphatic hydrocarbon, for example, CCl_2F_2 , C_2ClF_5 , C_4F_8 , and/or C_2ClF_3 , which will remove oxidizable impurity elements including Zn, Fe, Cr, Al, Si, B, Pb, and Sn, as well as oxygen and/or hydrogen.

For a batch treatment the selected reagent is introduced into the melt using either a phosphorizer or fluxing wand. In order to insure good coverage of the melt and efficient use of the treating agents, the phosphorizer or wand is held several inches above the hearth floor and may be moved slowly back and forth. Percolation of the gaseous reagent through the melt reduces the oxygen content to less than 0.001%, and also removes dissolved hydrogen to below 0.5 part per million.

After treatment is complete, an N_2 , N_2 -CO, or argon preferably containing a halogenated gas, for example 0.1 to 10% hereafter termed a "protective atmosphere," may be introduced in the furnace if excessively long holding times are necessary before casting or subsequent treatment before casting. Also for added protection against oxygen infiltration, a second graphite or charcoal cover may be used in the holding furnace during and after treatment.

Up to this point, the process has been considered as a batch-type operation wherein, an individual heat of metal is treated in the holding furnace and thus made ready for casting. It is possible, however, to continuously treat the melt with the selected treatment reagents either as it enters (as shown in FIGURE 1) or leaves (FIGURE 2), the holding furnace by using the treatment chamber apparatus of the type shown in FIGURES 1 and 2.

As shown in FIGURES 1 and 2, the treatment agent is introduced into the melt in gaseous form by means of graphite tubes which are located just above the floor of the treatment chamber to insure good coverage of the melt as it enters or leaves the furnace. Both the treatment chamber and furnace are designed to operate under a slightly positive pressure.

As can be seen from FIGURE 1, molten melt from a melting furnace is passed into a launder 2. From the launder molten metal passes into a treatment chamber 11. The treatment chamber has a bottom 12 together with a weir 13 and a roof section 14. Ports 32 and 33 are formed in the roof section through which pass tubes 10 which, for example, may be made of graphite. The halogen containing gas is introduced through these tubes. A gas rate, for example, of from 5 to 60 cubic feet per hour per tube may be used. The ports 32 and 33 allow the products of reaction to

pass into the hood and out through the exhaust system 31 during treatment of the molten copper. A second weir 15 having an opening 16 provides the divider between the treatment chamber 11 and the holding furnace 20 which, for example, may be heated by electrical induction coils. Thus, the furnace 20 has a lower portion 21 which is surrounded by heating coils (not shown) which heat the molten metal. Other heating means could be used however provided. The furnace also has a roof 22 which has a port 34 therein to allow the escape of reaction products which came not only from furnace 20, but also from treatment chamber 11 through opening 16, into the hood 30 and out through the exhaust system 31. The furnace also has an outlet 23 into transfer launder 24 which may convey the molten metal to a casting station (not shown). After the holding furnace is full and the melt has been treated a protective atmosphere may be introduced into the furnace and/or treatment chamber if excessively long holding time is necessary before subsequent treatment and/or transfer.

The embodiment shown in FIGURE 2 differs from that shown in FIGURE 1 in that the treatment operation and the treatment chamber are provided after the metal passes through the holding furnace. Thus, the molten metal enters in the launder 202 and passes into a trough 203. The molten metal then passes through opening 204 into a holding furnace 220. Again the holding furnace has a lower portion 221 for heating the metal by induction heating. However, it is to be emphasized that other types of heating could be utilized other than induction heating, provided that none of the materials used in the heating contact the molten metal. The furnace has a wall 205 containing the previously mentioned opening 204. The furnace also has a roof 222 through which a tube 242 passes which may be used to introduce a "protective atmosphere."

The furnace 220 is provided with a weir 215 which has an opening 216 through which the molten metal passes into the treatment chamber 211. The treatment chamber 211 has a roof 214 containing openings 232 and 233 through which halogenation tubes 210 may pass. However, as what the case in regard to FIGURE 1, clearance is provided between the tubes 210 and the roof 214 so that vapors resulting from the treatment operation may pass through the openings 232 and 233 and into the exhaust system 231 through the hood 230.

The treatment chamber also has an opening 223 containing a tap block 224. When the molten metal is tapped from the treatment chamber, it passes into the launder 225 and on to a casting station, not shown.

In both FIGURES 1 and 2, the holding furnaces are fitted with special hoods 30 and 230, and exhaust systems 31 and 231 respectively. The lids are sealed tightly against the furnace shell to prevent infiltration of air. Ports 32, 33, and 34, 232 and 233 are provided for the escape of fumes. The fumes are picked up by the exhaust system as they exit the holding furnace and are disposed of in a conventional fashion. The entire assembly is designed so that the furnace and treatment chamber will operate under positive pressure during the treatment operation. In this manner, an atmosphere of reaction products and excess treating reagent is generated which prevents infiltration of oxygen. As an alternate, the previously defined "protective atmosphere" may be used.

The following alternate processing routes may be followed after leaving the holding furnace.

The melt can be transferred directly to the casting station in a covered launder or trough such as 24 in FIGURE 1 or 225 in FIGURE 2 in which a "protective atmosphere" is maintained, and cast directly into process billet or ingot. In this instance, the final ingot material contains below 0.001% oxygen and below 0.5 part per million hydrogen and has an electrical conductivity approximating 100% IACS.

In some instances it is preferred to give the melt only

a rough "cleaning-up" in the batch treatment or in the continuous treatment. If this is the case, then additional processes must be carried out to obtain the previously mentioned low levels of oxygen and hydrogen.

As shown in FIGURE 3, the melt during transit to the casting station can be passed through a scrubbing device. This device breaks up the melt into fine streams, greatly increasing melt surface area in contact with the N_2 -CO gas, which is introduced near the bottom. As a result, oxygen remaining in the melt is removed efficiently with only relatively small quantities of the gas (for example, between 1 and 30 cubic feet per hour).

The scrubbing device, for example, shown in FIGURE 3 operates as follows. Molten metal from a holding furnace such as those illustrated in FIGURES 1 and 2 enters through the launder 301 which may be provided with a "protective atmosphere." It then passes through the plate 310 which contains openings 311. The plate may be of graphite or of other suitable refractory material. The openings 311 divide the molten metal into small streams 312. The molten metal then passes into the scrubbing tower 320. The scrubbing tower is provided with insulation 321 and heating elements which, for example, may be induction coils 322. The scrubbing tower contains a plurality of baffles 323, together with additional baffles 324 which are a part of the refractory 325. The particular baffle design shown is preferred, but it will be apparent that those skilled in the art can readily provide modifications within the scope of the invention. Circumferential gas inlet ports 326 and 327, which may be of any convenient number, are provided, together with gas exit ports 328 and 329, so that a mixture of nitrogen and carbon monoxide can be passed upwardly and countercurrently with respect to the molten metal. The molten metal, in the form of small streams, contacts the rising gas streams very effectively in the arrangement as it passes downwardly and tortuously over and around the baffles 323 and 324 resulting on very effective degassing.

During this operation, the oxygen content of the molten metal can be lowered to below 0.001%. Furthermore, dissolved hydrogen is removed to a level below 0.5 part per million. After being so treated, the molten metal passes through the opening 330 and into launder 331, which may be provided with a "protective atmosphere," and on to the casting operation.

As indicated, the scrubbing device may be located midway in the transfer system between the holding furnace and casting station as shown in FIGURE 3. Preferably, however, it may be positioned directly over the DC (Direct Chill) mold in the casting station. The latter innovation offers several important advantages. First, metal is treated just before it enters the mold, thus minimizing the chance of oxygen and hydrogen infiltration. Second, the scrubber serves as a "hot top" for the mold, thus providing for good distribution of molten metal in the mold and improving casting operations.

As an additional alternative, as shown in FIGURE 4, the molten metal may be passed through an aggregate bed in transit from the holding furnace to the casting station. In addition to reducing the oxygen content of the melt to below 0.001%, and removing additional dissolved hydrogen to below 0.5 part per million, this device also filters out entrained oxide particles and foreign material.

The aggregate bed illustrated in FIGURE 4 is relatively simple in construction. Essentially, it consists of a crucible 400 of suitable material mounted in a gas-fired or electrically heated furnace 401. A wall or weir 402 divides the crucible into two chambers 403 and 404. The inlet chamber 403 is filled with sized refractory aggregate 405, which has a bulk density greater than that of molten copper, for example, dense, sintered, stabilized zirconia. Metal introduced into the crucible from a covered launder 406 flows through the filter bed 405, under the

weir 402, and into a launder 407 to the casting station. Gravity is the driving force.

As the metal percolates through the aggregate bed, a mixture of N_2 -CO gas is introduced through the tube 408 and into sparger 409 at the bottom of the crucible and flows as small bubbles 410 up through the filter bed counter to the direction of metal flow providing for very effective metal-gas content. The combined action of the filter bed and N_2 -CO gas removes suspended particulate from the melt, as well as dissolved oxygen and hydrogen. Oxygen and hydrogen removal is very efficient, and only requires small quantities of gas, for example, between 1 and 30 cubic feet per hour due to the large contact area between the gas and liquid metal.

After final treatment of the melt as described above, the metal is transferred to the casting station in a closed launder 407 and cast into ingot or billet. Transfer to the casting station is carried out under a "protective atmosphere" to prevent infiltration of oxygen or hydrogen.

Semi-continuous or continuous direct chill casting is the preferred casting process and will assure a high quality process ingot. Either copper, copper alloy, or graphite mold liner may be employed. Several alternate methods for introducing molten metal into the mold which avoid oxygen and hydrogen pickup are shown in FIGURES 5 and 6.

In FIGURE 5, from either a holding furnace, scrubber, or aggregate bed, the molten metal enters through launder 501, through which a "protective atmosphere" may be maintained. Between the launder and the mold 500, there is placed an insulated hot top 502. If desired, this hot top may be electrically heated. However, this is not essential. The mold 500 is preferably made of copper or other suitable copper alloy and is supported by the table top 503. Sources for a cooling fluid, such as water, are provided such as manifolds 504. However, it is apparent that these manifolds are shown schematically and that many other means for applying the cooling fluid to the mold and casting may be provided by those skilled in the art. The resulting casting has a crater profile 505 and upon solidification, an ingot 506 is obtained.

In the embodiment shown in FIGURE 6, again the molten metal enters through a launder 601 from either a holding furnace, a scrubber or an aggregate bed. The launder is provided with a pouring spout 602 through which the molten metal passes to the distributor 606 through the hood 603. The hood is provided with an inlet 604 and an outlet 605 for the passage of gas, preferably the previously defined "protective atmosphere." Obviously, any desired number of such inlets and outlets may be provided. The distributor 606 directs the molten metal radially outward towards the mold 600 through a plurality of radial passageways. The mold is supported, for example, by way of a table top 607. Provisions for cooling the mold and the casting are shown schematically as cooling water manifolds at 608, but it is to be understood that those skilled in the art may provide other appropriate cooling apparatus for cooling the mold and the casting. The solidifying casting has a crater profile 609 and results in an ingot 610.

Thus, it is seen that the improved process for producing low oxygen containing copper described herein has a number of major advantages over presently used commercial processes.

Positive control can be exercised over the oxygen content of the melt. Oxygen can be introduced during the melting cycle to burn out undesirable oxidizable elements such as C, S, P, etc., and then reduced to below 0.001% by one of several methods prior to casting. Also, the melt may be treated with a monomeric, halogen containing, lower aliphatic hydrocarbon containing at least one fluorine atom to remove Zn, Fe, Cr, Al, Si, B, Pb, and Sn in the melt.

A wide variety of starting materials including scrap can be used. The only prerequisite is that the charge

material must be free of elements that cannot be removed by oxidation or treatment with a monomeric, halogen containing, lower aliphatic hydrocarbon containing at least one fluorine atom.

By comparison, existing processes require exclusive use of high purity, low oxygen, copper as a charge material because they are only geared to prevent reentry of oxygen, not removal of it.

Hydrogen and certain metallic impurities and suspended particulate are removed from the melt, as well as oxygen. The treatment chamber and scrubber provide effective means for removing dissolved hydrogen in the melt down to a level below .5 part per million. The aggregate bed is equally effective for hydrogen and also removes suspended oxides and inclusions.

Conventional melting and casting equipment can be employed with only minor modification. The special melt treatment devices, treatment chamber, aggregate bed and/or scrubber can be added in the metal flow stream with relative ease.

It should also be noted that use of the process described here is not confined to the production of low oxygen or oxygen free high conductivity copper. It is equally suitable to produce copper alloys which are susceptible to oxidation, exemplary being alloys including Cu-Ag, Cu-Zr, Cu-Cr, Cu-Ni, Cu-Be, etc., and more complicated systems can be treated as well. Also, the entire process or portions thereof (particularly the treatment steps) can be employed to advantage in the production of a wide variety of copper alloys including cartridge brass, commercial bronze, leaded brass, phosphour bronzes, aluminum bronze, silicon bronze, nickel silver, and cupronickels.

It is to be understood that the invention is not limited to the illustrations described and shown herein, which are deemed to be merely illustrative of the best modes of carrying out the invention, and which are susceptible of modifications of form, size, arrangement of parts and detail of operation. The invention rather is intended to encompass all such modifications which are within the spirit and scope of the invention as set forth in the appended claims.

What is claimed is:

1. A process for producing copper base ingots containing a very low oxygen content comprising melting the copper base alloy in a furnace, covering the molten metal with a layer of a carbonaceous material selected from the group consisting of graphite and charcoal, bubbling a halogen containing gaseous compound through said molten metal, transferring said molten metal to a casting station under a controlled atmosphere, and casting said molten metal into ingots.

2. A process according to claim 1 in which the melted copper is treated to remove impurity elements.

3. A process according to claim 2 in which the melt is oxidized with dry air to remove said elements prior to covering the melt with a layer of carbonaceous material.

4. A process according to claim 2 in which said elements are removed by treatment with a monomeric, halogen containing, lower aliphatic hydrocarbon containing at least one fluorine atom.

5. A process according to claim 1 in which said controlled atmosphere is a protective atmosphere.

6. A process according to claim 1 in which after the molten metal is treated with a halogen containing material, it is treated counter-currently with a mixture of nitrogen and carbon monoxide gas.

7. A process according to claim 6 in which the molten metal moves vertically downward and in which the nitrogen-carbon monoxide gas moves vertically upward.

8. A process according to claim 7 in which in the region where the molten metal is treated with nitrogen-carbon monoxide gas, the molten metal is passed through a chamber containing sized refractory aggregate.

9. A process according to claim 7 in which the molten

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metal is passed through a refractory plate which divides the molten metal into small streams above the chamber where the nitrogen-carbon monoxide gas is introduced.

10. A process according to claim 9 in which the molten metal, after passing through the refractory plate, is passed over a plurality of baffles which provides for improved contact of the molten metal with the nitrogen-carbon monoxide gas.

11. A process according to claim 10 in which the refractory plate and baffles are placed directly above the casting station so that impurity pick-up is minimized.

12. A process according to claim 5 in which the protective atmosphere is a CO—N₂ mixture.

13. A process according to claim 5 in which the protective atmosphere is argon containing a halogenated gas.

14. A process according to claim 1 in which the process is a batch process.

15. A process according to claim 1 which is carried out continuously.

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