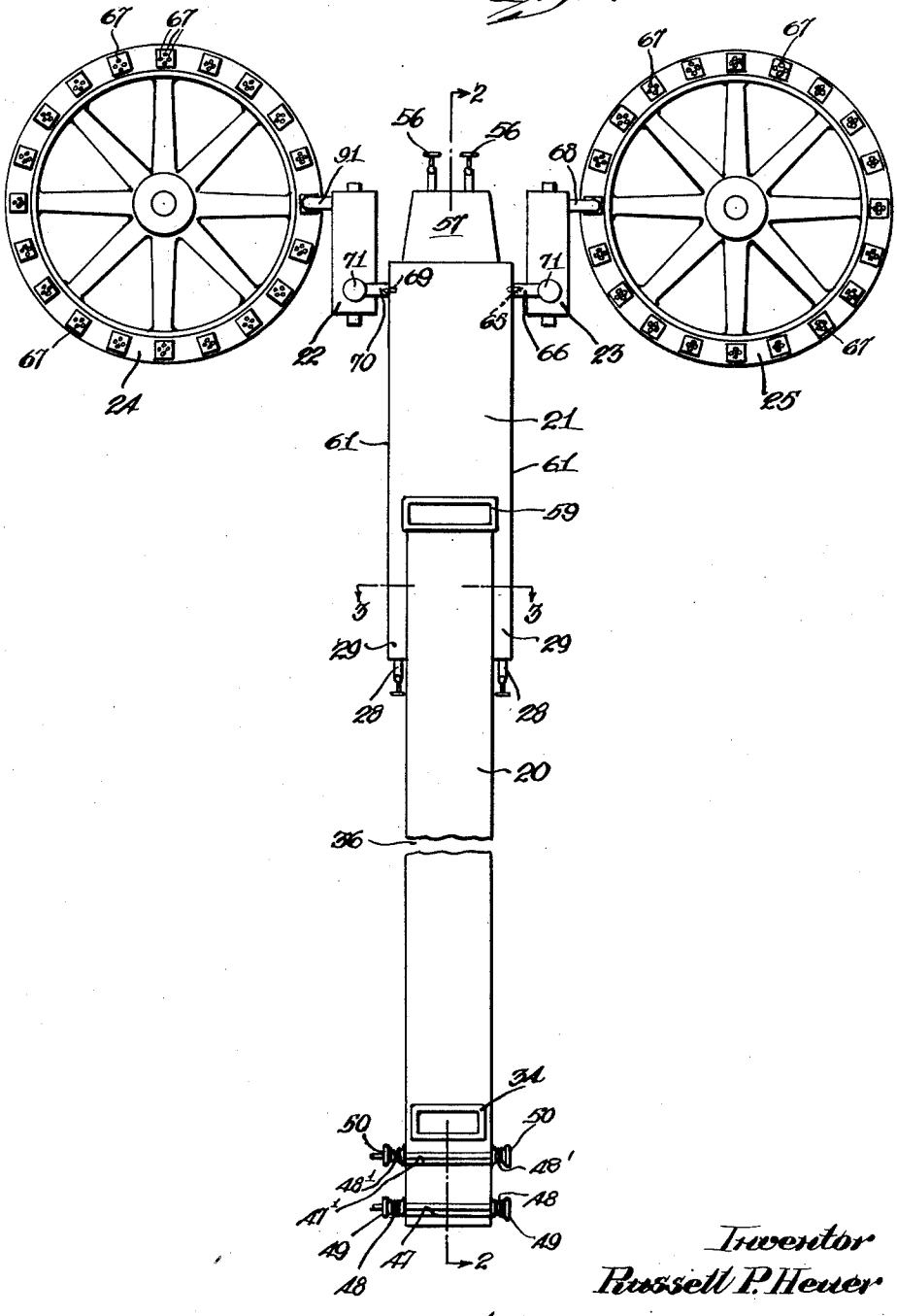
July 18, 1939. R. P. HEUER 2,166,354

COPPER REFINING PROCESS

Filed Nov. 7, 1936 3 Sheets-Sheet 1

Fig. 1.



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July 18, 1939. R. P. HEUER 2,166,354

COPPER REFINING PROCESS

Filed Nov. 7, 1936 3 Sheets-Sheet 2

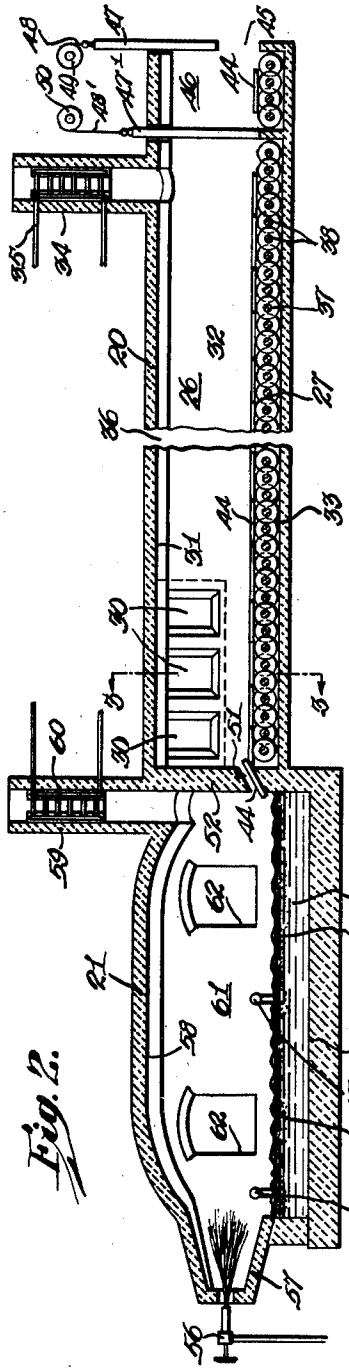


Fig. 2.

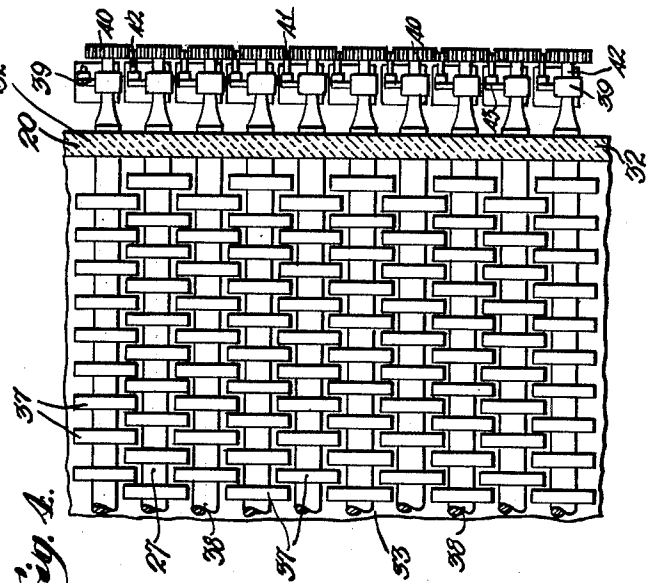


Fig. 4.

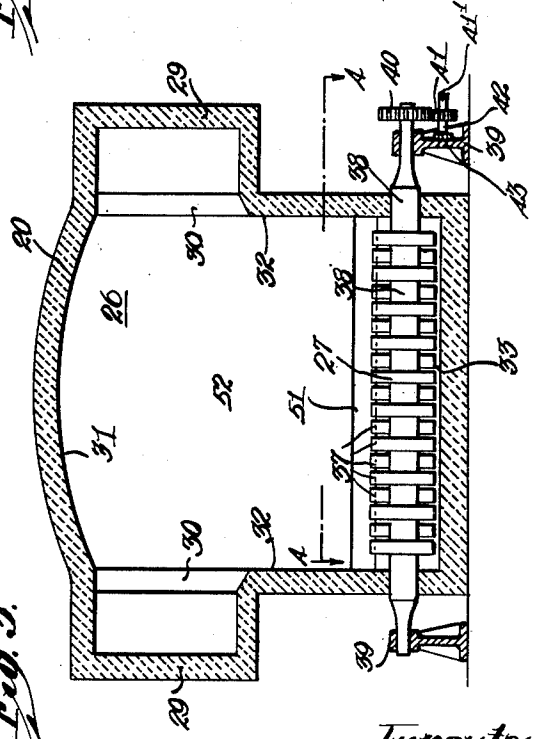


Fig. 5.

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COPPER REFINING PROCESS

Filed Nov. 7, 1936 3 Sheets-Sheet 3

Fig. 5.

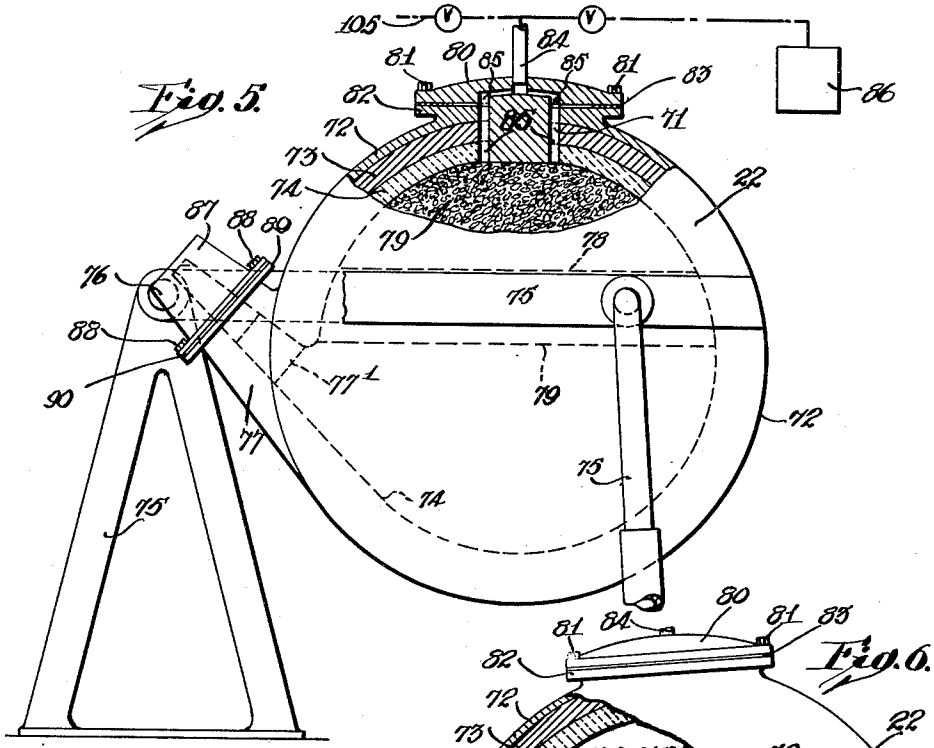
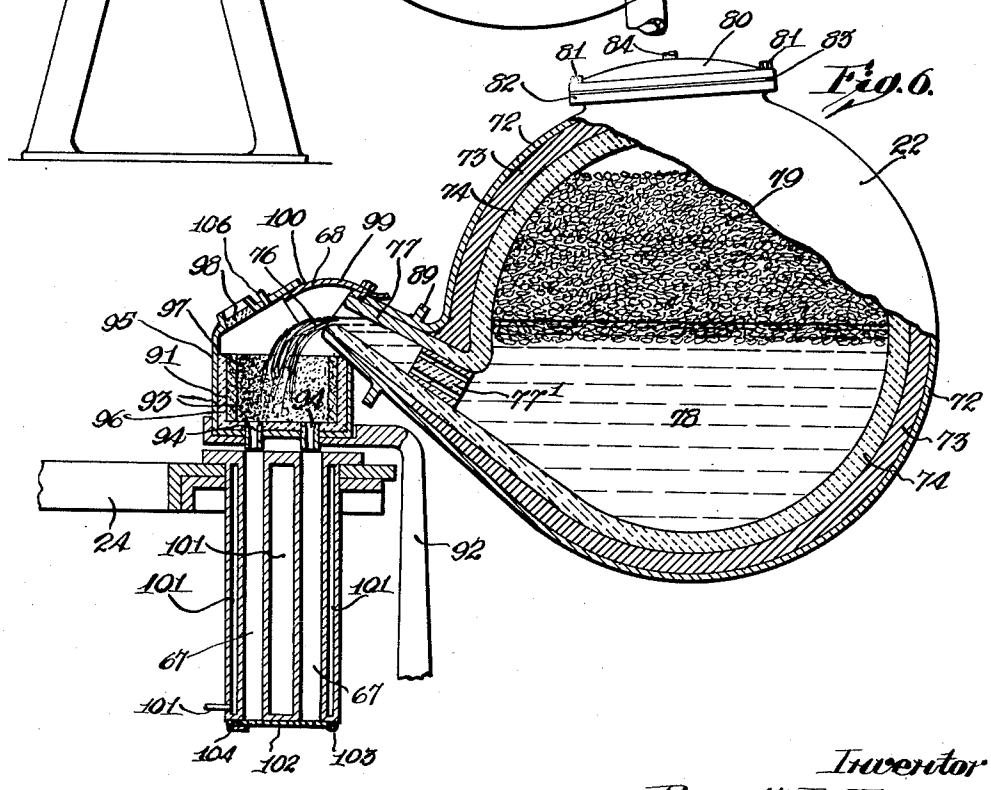


Fig. 6.



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Patented July 18, 1939

2,166,354

UNITED STATES PATENT OFFICE

2,166,354

COPPER REFINING PROCESS

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Application November 7, 1936, Serial No. 109,781

25 Claims. (Cl. 75—76)

The present invention relates to methods for producing copper shapes of the desired quality from refined copper such as electrolytically refined cathodes. This application is a continuation in part of my United States Patents No. 2,060,073, granted November 10, 1936, for Copper refining methods, and No. 2,060,074, granted November 10, 1936, for Copper refining apparatus.

A purpose of the invention is to obtain dense oxygen-free copper castings notwithstanding contact of the copper with air during casting.

A further purpose is to expose molten oxygen-free copper during casting to a volume of air not more than a few times the volume displaced by the casting, preferably rendering the air less oxidizing by a reducing vapor from a mold dressing or the like.

A further purpose is to increase the convenience of casting oxygen-free copper by dispensing with the use of carbon monoxide at the point of casting.

A further purpose is to lower the total oxygen content of molten copper substantially free from metallic impurities by treatment with solid carbon, to a value sufficiently below that at which a distinct phase of cuprous oxide appears in the castings and also sufficiently below that at which excessive gas cavities appear in the castings, so as to allow for a limited pick-up of oxygen during casting without causing excessive gas cavities or the appearance of a distinct phase of cuprous oxide in the castings, and then to cast the copper with not more than that exposure to air which will cause the limited pick-up of oxygen.

A further purpose is to obtain the very low total oxygen content of the molten copper necessary to permit casting dense oxygen-free castings in air, by deoxidizing the molten copper with solid carbon in a closed vessel at a pressure substantially below atmospheric pressure.

A further purpose is to facilitate and accelerate the deoxidation of molten copper by solid carbon through the use of reduced pressure, thus assisting the reaction between carbon dioxide and carbon in molten copper, so as to obtain dense oxygen-free copper more easily.

A further purpose is to deoxidize molten copper by solid carbon in a closed vessel under reduced pressure and to cast the deoxidized copper in a protecting atmosphere consisting primarily as an active ingredient of carbon monoxide.

A further purpose is to make "tough-pitch" copper and oxygen-free copper using the same melting furnace, so that, with increased demand for one product, more of that product and less of the other product can be made, and in case one of the casting plants must be shut down, the melting furnace may continue to operate.

A further purpose is to preheat and desirably concurrently oxidize solid copper masses by fuel combustion and subsequently to melt the copper masses, desirably submerged in molten copper, by fuel combustion, the fuel combustion used in preheating being separate and separately controlled from the fuel combustion used in melting.

Further purposes appear in the specification and in the claims.

The invention relates to the processes involved.

The drawings show diagrammatically apparatus which may be used in accordance with the invention. No effort has been made to show the structural details which are within the routine skill of those working in the art nor to illustrate the various changes which may be made in the structures without departing from the invention. The illustrations have been chosen primarily with a view to convenient explanation of the principles involved.

Figure 1 is a top plan of the preheating and oxidizing furnace, the melting furnace, the deoxidizing vessels and the casting plants.

Figure 2 is a broken vertical section along the line 2—2 of Figure 1.

Figure 3 is a transverse section of the preheating and oxidizing furnace on the line 3—3 of Figures 1 and 2.

Figure 4 is a fragmentary section on the line 4—4 of Figure 3, showing in top plan the continuous hearth used in the preheating and oxidizing furnace.

Figure 5 is a partly broken side elevation of one of the deoxidizing vessels during deoxidation.

Figure 6 is a sectional elevation corresponding to Figure 5 but showing the deoxidizing vessel during pouring.

In the drawings like numerals refer to like parts.

In common practice, refined copper masses such as cathodes produced by electrolytic copper refining are changed into the copper castings used in fabrication, such as ingots, wire bars, cakes, billets, etc., by melting in large reverberatory furnaces, some of which hold as much as 300 tons (270 metric tons) and then casting in air. The conventional mode of operation in such re-

verberatory furnaces is as follows: (1) charging, (2) melting, (3) blowing, (4) skimming, (5) poling, (6) coking, (7) casting. Ordinarily each such reverberatory furnace treats one charge every twenty-four hours.

Copper masses such as copper cathodes commonly carry sulphur as an impurity picked up during the electrolytic refining and not susceptible of complete removal by ordinary washing. This sulphur, as well as sulphur from the gases of combustion, forms an impurity in the molten copper bath in the reverberatory furnace. The blowing operation is therefore used to remove the sulphur by forming cuprous oxide in the bath to react with the sulphur and form volatile sulphur dioxide. Blowing removes sulphur, but it increases the oxygen content of the bath to approximately 0.9% (in some cases the oxygen content is not carried so high). After blowing, the oxygen is ordinarily removed by poling, through the reducing action of carbon, hydrocarbons and hydrogen present in green poles, which reduce the oxygen to volatile compounds such as carbon monoxide, carbon dioxide and water vapor. Coking protects the surface of the bath somewhat during casting.

It has long been a phenomenon of copper metallurgy that the poling operation cannot be carried to the extent of complete removal of oxygen without causing the copper castings to be filled with blow-holes or gas cavities. It is commonly considered bad practice to reduce the oxygen content by poling much below the point (about 0.033% oxygen) which corresponds to a cuprous oxide content of 0.3%.

As explained in my United States Patent No. 2,060,073, above referred to, the reduction of cuprous oxide under the conditions of poling involves the following reactions:

$$Cu_2O+C=2Cu+CO \quad (1)$$

$$Cu_2O+CO=2Cu+CO_2 \quad (2)$$

$$Cu_2O+H_2=2Cu+H_2O \quad (3)$$

From Reaction (1) we may derive the expression:

$$-\Delta F_0=RT\ In\ \frac{(A.Cu)^2(A.CO)}{(A.Cu_2O)(A.C)} \quad (4)$$

ΔF_0 = standard free energy change

R = gas constant

T = absolute temperature

In = logarithm to the base e

(A.Cu) = activity of copper

(A.CO) = activity of carbon monoxide

$(A.Cu_2O)$ = activity of cuprous oxide

(A.C) = activity of carbon

In Reaction (1) equilibrium is never reached during poling.

Using the same nomenclature, the following expression can be derived from Reaction (2):

$$-\Delta F_0=RT\ In\ \frac{(A.Cu)^2(A.CO_2)}{(A.Cu_2O)(A.CO)} \quad (5)$$

$(A.CO_2)$ = activity of carbon dioxide

It is probable that the bath will become saturated with carbon dioxide during the poling operation, so that $(A.CO_2)$ will be constant and, of course, (A.Cu) is constant as the bath is practicaly pure copper. Then Equation (5) becomes:

$$-\Delta F_0=RT\ In\ \frac{K}{(A.Cu_2O)(A.CO)} \quad (6)$$

where K is a constant for the particular conditions. At constant temperature this expression becomes:

$$(A.Cu_2O)(A.CO)=K_1 \quad (7)$$

K_1 = proper constant

It will of course be evident from Equation (7) that decrease in cuprous oxide activity will result in increase in carbon monoxide activity.

Using the same symbols, the expression for Reaction (3) is:

$$-\Delta F_0=RT\ In\ \frac{(A.Cu)^2(A.H_2O)}{(A.Cu_2O)(A.H_2)} \quad (8)$$

$(A.H_2O)$ = activity of water

$(A.H_2)$ = activity of hydrogen

If we assume the activities of copper and of water to be constant, this equation becomes at constant temperature:

$$(A.Cu_2O)(A.H_2)=K_2 \quad (9)$$

K_2 = proper constant

From Equation (9) it will be evident that decrease in the activity of cuprous oxide will result in increase in the activity of hydrogen.

Since the activity of any component is a function of the concentrations, it will be evident that the concentration of carbon monoxide and hydrogen will be low when the concentration of cuprous oxide is high (say above 0.3%), but that the concentrations of carbon monoxide and hydrogen will increase rapidly with lowering of the cuprous oxide concentration below about 0.3%.

Large quantities of carbon monoxide and hydrogen present during solidification may cause gas cavities by virtue of their reactions with cuprous oxide whose concentration increases in the supernatant liquid during solidification due to preferential crystallization of pure copper. Reaction (1) can ordinarily not take place during solidification due to the absence of carbon, but Reactions (2) and (3) can occur where both carbon monoxide and hydrogen are present. The condition of excessive gas cavities in the copper castings known as "over-poling" is thus due just as much to the presence of cuprous oxide as to the presence of carbon monoxide and/or hydrogen, as the cuprous oxide on the one hand and the carbon monoxide and/or hydrogen on the other hand contribute to the liberation of carbon dioxide and/or water vapor during solidification of the copper castings.

In my United States Patents Nos. 2,060,073 and 2,060,074, above referred to, the production of cast copper having an oxygen content far below that of "tough-pitch" copper and nevertheless of high density is described. This product is obtained from copper melted under fuel-fired conditions by special deoxidation procedure and avoidance of or minimal exposure to air during casting. Where reference is made herein to casting it is intended to include the conventional process of teeming into molds, as well as special forms of castings, for example continuous solidifying, whether or not accompanied by mechanical working such as extrusion.

As the deoxidation of copper melted in contact with gases of combustion continues below the oxygen content of "tough-pitch" copper, a point is eventually reached at which the distinct phase

of cuprous oxide, previously visible under the microscope in the solidified castings, is no longer visible. Such solid copper which contains no distinct phase of cuprous oxide visible under the microscope may be said to be oxygen-free, notwithstanding that it may contain a relatively minute quantity of oxygen as cuprous oxide or some other oxide in solid solution. Molten copper of the proper oxygen content to produce such solid copper may likewise be said to be oxygen-free. The maximum oxygen content which such oxygen-free copper may contain has not been accurately determined, but it would appear to be about 0.007% according to the determination of Rhines and Mathewson, "Solubility of Oxygen in Solid Copper", American Institute of Mining and Metallurgical Engineers, Technical Publication No. 534–E 162, paper delivered February, 1934.

Such oxygen-free copper may or may not be free from excessive gas cavities. In order to obtain oxygen-free copper which is free from excessive gas cavities, having a bulk specific gravity in excess of 8.8, deoxidation should be continued below the point at which a distinct phase of cuprous oxide ceases to be visible in the castings, thereby changing over carbon dioxide present in the copper to carbon monoxide according to the reaction:

$$CO_2+C=2CO \qquad (10)$$

The oxygen content of oxygen-free copper which is free from excessive gas cavities is difficult to determine.

Analyses have been made under the direction of Dr. Hiram S. Lukens by igniting copper in a silica tube at 1472° F. (800° C.) whilst simultaneously passing a stream of purified, water free hydrogen over the copper. The hydrogen reacted with the oxygen present in the copper in the form of cuprous oxide as well as other oxides including carbon dioxide, to form water vapor. The exit gases were passed through an absorption tube containing anhydrone (anhydrous magnesium perchlorate). The gain in weight after subtraction for a blank to compensate for possible impurities in the hydrogen was considered to be the oxygen content of the copper. Every precaution was taken in preparing the copper sample to avoid surface contamination with oxygen, and prior to the ignition in hydrogen at 1472° F. (800° C.) the sample was heated in hydrogen to 572° F. (300° C.) to remove surface contamination. Wherever oxygen content is referred to herein it is intended to indicate the oxygen content as determined in the foregoing manner. Such analyses indicate that a total oxygen content of 0.002% is permissible in dense oxygen-free copper.

In my United States Patent No. 2,060,073, above referred to, reference is made to casting the deoxidized molten copper in a protecting atmosphere such as carbon monoxide so as to procure dense oxygen-free copper castings. While the use of a protecting atmosphere containing carbon monoxide at the point of casting is highly desirable from the standpoint of obtaining a high grade product, uniformity of casting conditions, and minimal deoxidizing efficiency for satisfactory results, there are certain concomitant disadvantages.

The structural enclosure often found desirable to economize on the atmosphere at the point of casting may be expensive, require maintenance and cause delay in manipulation of the casting. The generation of the protecting atmosphere adds to the expense.

An important feature of the present invention is the casting of dense oxygen-free copper castings in air.

Of course a certain amount of reoxidation is inevitable when the copper is cast in contact with air. The maximum exposure to air which is permissible in casting dense oxygen-free copper is a question of the particular casting installation, especially the rate of pouring, the dimensions of the parts and the rate of cooling of the castings. In any case, however, there should not be sufficient air exposure to cause a distinct phase of cuprous oxide to appear in the castings or to produce excessive gas cavities in the castings. From the determination of Rhines and Mathewson above referred to, it can be stated that an oxygen pick-up of about 0.007% is too much even assuming that the oxygen content of the molten copper before casting is practically zero. If the total oxygen content of the molten copper before casting reaches practically zero, the Lukens analyses above referred to indicate that an oxygen pick-up of 0.002% during casting is not objectionable.

Assuming that the air in the mold is at 20° C. and under a pressure of 760 millimeters of mercury, that the copper is exposed only to the volume of air in the mold actually displaced by the copper casting and that the copper absorbs all of the oxygen present in that volume of air, the oxygen pick-up of the copper casting would be about 0.003%. Other conditions remaining the same, if the air in the mold were heated to 165° C., the oxygen pick-up of the casting would be about 0.002%. Even though the volume of air in contact with the copper is several times the volume of air displaced by the casting, dense oxygen-free copper may nevertheless be cast if the pouring and solidifying rates, and the surface exposed to the air during pouring, are such that the casting does not absorb all of the oxygen present in the air to which it is exposed. Likewise, if the air in the mold and around the pouring stream is diluted by a harmless or preferably reducing ingredient, for example a vapor given off from a mold dressing, it may still be possible to cast dense oxygen-free copper in contact with a volume of diluted air several times the volume of the casting.

To render such casting in air feasible as a commercial matter, it is preferable to strictly limit the volume of air which can come in contact with the casting stream by structurally enclosing the stream and the top of the mold. The casting shield used need not, however, be nearly so elaborate as that intended for casting in gas at superatmospheric pressure or for casting in vacuum. The joints need not be absolutely tight nor need the shield be entirely closed, since there is preferably no appreciable pressure differential between the interior of the shield and the outer atmosphere.

The inventor has succeeded in casting dense oxygen-free copper in air by treating the molten copper with solid carbon until the oxygen content of the copper is well below that necessary and commonly used when dense oxygen-free copper castings are to be cast in a protecting atmosphere consisting for example of carbon monoxide. It is possible to obtain the very low oxygen content required where copper is to be cast in air into dense oxygen-free castings, by sufficiently long exposure at atmospheric pressure to solid

carbon in contact with the molten copper and preferably submerged beneath its surface, in the absence of objectionable contamination with hydrogen-containing gases or oxidizing gases of combustion. The exposure to carbon should be effective to lower the oxygen content: (1) below that at which a distinct phase of cuprous oxide would appear in castings which solidify without oxygen pick-up (below about 0.007% oxygen), (2) far enough below the oxygen content required by step (1) to change carbon dioxide to carbon monoxide until insufficient carbon dioxide remains to cause objectionable gas cavities in castings which solidify without oxygen pick-up; and (3) far enough below the oxygen content required by step (2) so that the oxygen pick-up during casting in air will not cause the oxygen content of the castings to exceed the value required by step (2). This necessitates an extremely low oxygen content in the molten copper before casting in air, so low in fact that the total oxygen percentage will be small or negligible in the third decimal place.

The present invention is applicable to copper substantially free from metallic impurities, such as iron, silicon and arsenic, and having a purity above about 99.95% or better. The presence of any substantial quantity of metallic impurities, especially iron, changes the problem as far as casting in air is concerned, because such metallic impurities, present in any substantial quantity in high quality commercial copper, are themselves oxidizable by air.

The inventor has furthermore discovered that the reduction of carbon dioxide to carbon monoxide in molten copper by contact with carbon, as well as the reduction of cuprous oxide, are greatly facilitated by maintaining reduced pressure on the system.

Scott United States Patent No. 1,948,316, granted February 20, 1934, for Process of refining copper, proposes to deoxidize copper by carbon under reduced pressure but does not propose to deoxidize carbon dioxide in copper by this means, or to exclude contamination with oxidizing gases of combustion and hydrogen-containing substances. Deoxidation of carbon dioxide can readily be done by confining the molten copper and the carbon in a closed vessel connected with a vacuum pump. The use of a pressure substantially below atmospheric pressure not only renders the reduction of carbon dioxide much more rapid, but decreases the extent of exposure to carbon necessary and makes it possible to obtain a much lower total oxygen content including a lower content of carbon dioxide. Experiments indicate that halving the pressure substantially more than doubles the reaction velocity; in other words, the reaction velocity increases at a rate substantially greater than inverse proportion to the pressure. While any reduction in pressure below atmospheric pressure is desirable, and it is preferred to use a pressure of about 35 millimeters of mercury, or below, excellent results are obtained with pressures below about 300 millimeters of mercury.

An important feature of the deoxidation with carbon at reduced pressure is that the reaction is so accelerated that low total oxygen contents are obtained in the molten copper in a fraction of the time necessary when reducing under atmospheric pressure. A charge of substantial size may be deoxidized in 10 or 15 minutes. It is therefore possible to apply deoxidation of copper by carbon under reduced pressure advantageously to installations in which dense oxygen-free copper is cast in a protecting atmosphere. A serious limitation upon the production capacity of a plant producing dense oxygen-free copper castings is the time and extent of exposure to carbon necessary for sufficiently complete deoxidation of the molten copper. When, however, the exposure to carbon takes place under reduced pressure, the time of exposure is cut down or the completeness of the deoxidation in a given time is much increased so that higher production by the deoxidizing vessel is possible.

In the prior art, deoxidized copper has been degasified under reduced pressure in a carbon vessel, but advantage has not been taken of reduced pressure to deoxidize copper containing substantial quantities of oxygen, say 0.03%, or even as little as is necessary to produce a distinct phase of cuprous oxide in the copper castings, to an extent sufficient to change over carbon dioxide to carbon monoxide as well as eliminate any distinct phase of cuprous oxide, in the absence of contamination with oxidizing gases of combustion and hydrogen-containing substances.

As the production requirements for oxygen-free copper and "touch-pitch" copper vary from time to time, it is quite desirable to obtain both "tough-pitch" copper and oxygen-free copper from a given installation which is flexible enough to produce at any time entirely "tough-pitch" copper, entirely oxygen-free copper or quantities of each as required.

The copper masses such as cathodes are preferably first preheated and oxidized to remove sulphur. This is best accomplished by conducting the cathodes through a preheating and oxidizing furnace in which they are exposed to gases of combustion which roast the copper masses to remove sulphur and at the same time preheat the copper masses. For certain aspects of the invention, the preheating furnace may be that shown in Lukens and Heuer United States Patent No. 1,733,419, granted October 29, 1929, for Continuous copper melting furnace, or Heuer United States Patent No. 1,914,716, granted June 20, 1933, for Copper melting furnace.

The preheater illustrated in the drawings of the present application offers the distinct advantage over the above preheaters for the present purpose because it is heated by gases of combustion which are separate and separately controlled from those employed in the melting furnace. This makes it possible to oxidize the solid copper masses to approximately the proper extent required to give to the molten copper in the melting furnace the oxygen content required for "tough-pitch" copper (say 0.03% to 0.05% oxygen). This is a real economy as it not only avoids blowing but it also avoids or greatly shortens the necessary poling for "tough-pitch" copper. The correct oxidation in the preheater could not be reliably obtained if the gases of combustion from the melting furnace were used in the preheater, because the oxidizing character of the gases of combustion in the preheater would not be subject to independent control.

The independence of the fuel heating means in the preheater from that in the melting furnace not only simplifies the production of "tough-pitch" copper, but also makes possible the production of oxygen-free copper using "tough-pitch" copper as an intermediate product. Considerable economy is possible because the

fuel used in preheating need not be so closely controlled as to sulphur content as the fuel used in the melting furnace.

The preheated copper masses are conducted to a fuel-fired melting furnace, which preferably melts the copper masses while submerged in a bath of molten copper. In making oxygen-free copper, the molten copper from the melting furnace is withdrawn to a separate deoxidizing vessel where it is exposed to contact with carbon, preferably at reduced pressure, until the copper is sufficiently deoxidized. The deoxidized molten copper may either be cast in air or in a protecting atmosphere consisting predominately as an active ingredient of carbon monoxide at subatmospheric, atmospheric or superatmospheric pressure. A duplicate deoxidizing and casting installation is provided which may also be used to produce oxygen-free copper from the same melting furnace. On the other hand, where "touch-pitch" copper is desired, the duplicate deoxidizing and casting installation may be used to produce "tough-pitch" copper or both installations may be used for making "tough-pitch" copper, the only important changes being the omission of carbon or marked decrease in the quantity of carbon and the omission of the protecting vapor when "tough-pitch" copper is being cast.

The apparatus employed in carrying out the processes of the invention may desirably consist of a preheater 20 operatively connected to a melting furnace 21. When the entire production is oxygen-free copper, molten copper will be withdrawn from the melting furnace 21 to deoxidizing vessels 22 and 23 which supply casting plants 24 and 25. In case "tough-pitch" copper is being produced, one or both of the deoxidizing vessels 22 or 23 will be used as a pouring ladle. In order to simplify the explanation it will be assumed that deoxidizing vessel 22 and casting plant 24 are producing oxygen-free copper while pouring ladle 23 and casting plant 25 are producing "tough-pitch" copper.

The preheater 20 desirably comprises a substantially horizontal flue 26 containing a suitable movable hearth 27 and supplied with heat by fuel burners 28 in doghouses 29 connected to flue 26 by inlet ports 30. The amount of fuel supplied to the burners 28, as well as the mixture of air and fuel burned which determines the oxidizing character of the gases of combustion, are subject to the control of the operator in any well-known manner, the detail of which is not shown. The gases of combustion from the inlet ports 30 pass through the flue beneath the roof 31, between the side walls 32 and above the floor 33, for substantially the full length of the preheater, to a preheater stack 34. An economizer 35 in the preheater stack 34 may if desired be employed in heating the inlet air to the preheater.

The length of the preheater will, of course, depend upon the desired rate of preheating and the melting capacity of the furnace, but it will ordinarily be substantially longer in proportion to the melting furnace than the flue illustrated in the drawings, in order that the bulk of the sensible heat in the preheater gases may be absorbed by the copper masses. This fact is shown by breaking the preheater at 36. A length as great as 100 feet (30 meters) may in some cases be desirable. The preheater need not of course be straight. Where a straight preheater is used, it is preferred to employ a roller hearth consisting of interlocking rollers 37 on shafts 38 supported in bearings 39. The shafts 38 carry gears 40 which are interconnected by gears 41 on stub-shafts 42 in bearings 43. One of the gears 41 may be suitably driven as at 41'.

The hearth is charged with copper masses, suitably cathodes 44, at the charging end 45, which is desirably equipped with a vestibule 46 having doors 47 and 47' operated through flexible connections 48 and 48' passing around motor driven drums 49 and 50. Copper masses, such as copper cathodes 44, can thus be conveniently placed on the movable hearth at 45 when the door 47 is open and then the door 47 can be closed until the time for supplying the next charge.

Where refined products such as wire bars, cakes, billets and the like are being manufactured, the copper masses will advantageously be electrolytic cathodes. Such cathodes will usually be contaminated with slight surface impurities in the form of sulphur from the electrolytic tanks and negligible amounts of injurious metallic impurities, such as antimony, arsenic, bismuth, etc. The copper masses may also consist of scrap or secondary copper such as used wire, used copper tubing, rods, bus bars, copper clippings and other salvaged products, which will preferably be consolidated into blocks or bales before charging.

In operation of the preferred preheater, the copper masses are progressed through the preheater and are discharged into the melting furnace at 51 when they reach the end of the movable hearth. The preheater is preferably heated to a maximum temperature of about 1800° F. (about 980° C.) by means of oil, natural or manufactured gas, powdered coal (less desirable on account of the ash) or other suitable fuel applied at the burners 28. The combustion gases pass through the preheater in a direction countercurrent to the direction of the movement of the copper masses. The time of preheating will vary with the installation, but in a typical case it may be about one hour. The copper masses are efficiently preheated to a temperature approximating 1600° F. (870° C.). This temperature is close enough to the melting temperature so that the melting furnace need supply little heat except the latent heat of fusion, and is low enough so that there is little danger of melting in the preheater, which would be undesirable not only because it would prevent the movable hearth from functioning, but also because molten copper readily absorbs sulphur from the combustion gases while solid copper does not. Molten copper dissolves cuprous oxide and cuprous sulphide, reducing the thermodynamic activity and preventing the quantitative elimination of sulphur.

It is preferable to control the atmosphere of the preheater so that slight oxidation of the copper occurs during preheating. This oxidation serves to remove as sulphur dioxide gas the sulphur adhering to the surfaces of the copper masses. Other volatile impurities may be removed to some extent. In the case of scrap copper charges, adhering organic substances are burned, and superficial impurities such as lead and tin are oxidized so as to facilitate their removal.

During preheating the copper masses are desirably oxidized to an extent such that the molten copper in furnace 21 will have a suitable oxygen content for "tough-pitch" copper without either blowing or poling. The oxygen content of the molten copper after melting should preferably fall within the range of about 0.03% to 0.05% oxygen, and desirably at or about 0.03% oxygen. In any case, it is very desirable that the oxygen

content of the molten copper after melting be between about 0.03% and 0.10% oxygen, so that only a little poling will be required to reduce the oxygen content to that of "tough-pitch" copper, if poling be required at all. The use of separate fuel heating means for the preheater, separately controlled, makes possible accurate adjustment of the extent of oxidation in the preheater, as well as of the preheater temperature, and it is with these ends in view that dependence is no longer placed upon preheating with the waste gases from the melting furnace as in United States Patents Nos. 1,914,716 and 1,733,419, aforesaid.

The melting furnace is separated from the preheater by a wall 52 in which the opening 51 occurs. Preheated copper masses are plunged at periodic intervals through the opening 51 and into a bath 53 of molten copper covered with a slag 54 and resting on the hearth 55 of the melting furnace 21. The masses are melted while submerged in molten copper, thus reducing contamination from exposure to combustion gases during melting and permitting solution melting, that is, dissolving of solid copper in already molten copper.

The melting furnace 21 is provided with burners 56 for oil, natural or manufactured gas, powdered coal or other suitable fuel combustion means, in a burner box 57. Coal firing may be substituted, in which case the burners 56 and burner box 57 will be replaced by a suitable coal-burning grate. The gases of combustion from the melting furnace pass beneath the furnace roof 58 to a stack 59. An economizer 60 in the stack 59 may be used to heat the inlet air to the burners 56. The side walls 61 of the melting furnace 21 are provided with suitable doors 62 to permit access to the furnace interior, particularly for the purpose of poling if this be necessary, and a tap hole 63 is provided to remove the slag 54, which is desirably the slag normally forming on molten copper due to oxidation.

The molten copper is maintained at a suitable temperature for the treating and casting operations which follow. To prevent excessive oxidation, it may be covered with a layer of charcoal or coke 64 which of course is not effective to completely deoxidize the copper because of the presence of oxidizing combustion gases.

The copper bath 53 preferably has an oxygen content suitable for casting "tough-pitch" copper. This oxygen content is preferably maintained by regulating the oxidation in the preheater, and without blowing or poling, at least to any great extent. It is possible to avoid excessive blowing, such as to an oxygen content of 0.9% as in the prior art, because the sulphur content of the copper masses is substantially removed during preheating. On the other hand, it is desirable to avoid excessive oxidation during preheating, as this would necessitate considerable poling. Where the oxygen content of the bath 53 becomes excessive, green poles may be introduced beneath the copper bath through the doors 62.

Assuming that it is desired to cast "tough-pitch" copper in the casting plant 25, the molten copper from the bath 53 may simply be withdrawn through a tap opening 65 and runner 66 to the pouring ladle 23. The pouring ladle 23 (called at other points deoxidizing vessel 23, when it is used to make dense oxygen-free castings) is identical with the deoxidizing vessel 22, except that it of course should not contain submerged carbon. Should the oxygen content of the "tough-pitch" copper withdrawn from melting furnace 21 to pouring ladle 23 be improper, it may be adjusted in pouring ladle 23 by blowing or poling. If any substantial deoxidation of the "tough-pitch" copper is desired, this may be accomplished with carbon in the pouring ladle 23 in the manner explained later in connection with deoxidizing furnace 22, although the operation will be stopped of course before the oxygen content reaches the low value attained in the deoxidizing furnace 22.

The main function of pouring ladle 23 when operating on "tough-pitch" copper is that of pouring into molds 67. Although the casting shield 68 is unnecessary in casting "tough-pitch" copper, it will preferably be retained, as it is desired to make the same casting plant serve whether "tough-pitch" or oxygen-free copper castings are being made. In all important respects the casting plant 25 is similar to the casting plant 24 which will be described more in detail below, except that no carbon nor protecting vapor at the point of casting should be present in pouring "tough-pitch" copper.

In certain cases it may be desirable to use the pouring ladle 23 for the complete adjustment of the oxygen content of the "tough-pitch" copper. In this case the preheater and melting furnace may be operated without regard to the oxygen content of the copper bath 53 and the molten copper in the pouring ladle 23 may have its oxygen content adjusted by blowing, or poling with green poles, charcoal, coke, etc.

The production of oxygen-free copper has been described in my United States Patents Nos. 2,060,073 and 2,060,074, aforesaid.

It has been discovered that molten copper which contains oxygen and other gases in the amounts present in "tough-pitch" copper can be used in accordance with the present invention as a source of copper for the production of oxygen-free copper. Molten copper from the copper bath 53 is withdrawn through the tap hole 69 and runner 70 into the charging opening 71 of the deoxidizing vessel 22. The deoxidizing vessel 22 comprises a completely closed vacuum-tight outside casing 72 lined with heat insulation 73 and then a refractory lining 74. The vessel is tiltably supported on structure 75 preferably having the axis of tilting at 76 near the end of the pouring spout 77, so that accurate control may be had of the pouring from the vessel. The tilting mechanism may also be used to a limited extent to agitate the contents of the deoxidizing vessel.

The deoxidizing vessel contains molten copper 78 and solid carbon 79 in contact with the molten copper and desirably submerged beneath its surface. The carbon bed should preferably extend 12 inches (30 centimeters) or more below the surface of the molten copper. The carbon may be charcoal or coke, substantially free from hydrogen, hydrocarbons and water. The carbon will preferably be introduced before a charge of molten copper is placed in the deoxidizing vessel, and will be replenished from time to time as it becomes exhausted. A suitable strainer 77' in the pouring spout, having a plurality of openings of about 0.5 inch (1.3 centimeters) diameter, prevents carbon from being poured out of the deoxidizing vessel with the molten copper.

It is preferred to have no heating means associated with the deoxidizing vessel. The metal charged into the deoxidizing vessel should have sufficient superheat to remain molten for the

time of treatment. The heat insulation 73 will assist in preventing heat losses. In case heating means are to be used, to control the pouring temperature, prevent freezing of metal in the deoxidizing vessel, etc., the heating means will preferably be electric arc or induction, or other noncontaminating heating means. Of course the copper could be transferred from the deoxidizing vessel to a pouring furnace for temperature control if desired.

Closure of the charging opening 71 of the deoxidizing vessel is accomplished by a door 80 which is bolted at 81 to a flange 82 on the furnace casing 72. The joint at the door is made vacuum tight by a gasket 83. The door is preferably provided with a vacuum connection at 84 which communicates through passages 85 to the interior of the deoxidizing vessel 22. The vacuum connection 84 is suitably connected with a vacuum pump 86. The opening of the pouring spout 77 may be made vacuum tight by a cap 87 which is bolted at 88 to a flange 89 on the casing 72, the joint being rendered vacuum tight by a gasket 90. When it is desired to pour oxygen-free copper from the deoxidizing vessel 22, the cap 87 is removed. As an alternative, a barometric molten copper seal protected at the exposed end from oxygen and hydrogen contamination might be used.

It is possible to pour dense oxygen-free copper castings without use of a shield by pouring into a vertical mold from a position as close to the mold as possible. It is much preferable however to pour through a casting shield which will cut down the introduction of air from the outside atmosphere into the vicinity of the pouring stream. The casting shield 91 is detachably mounted on the support 92 adjacent the pouring spout 77 after the cap 87 is removed from the pouring spout. The casting shield 91 includes a strainer 93 having openings 94 communicating with a plurality (usually four) vertical molds 67 which are simultaneously positioned below the strainer on the casting wheel 24. The strainer casing 95 contains refractory lining 96 and an inner carbon lining 97. A silica window 98 enables the operator to observe the stream. The pouring spout 77 is articulated at 99 to the casting shield 91 by an arcuate member 100 removably secured to the pouring spout and continuously engaging the casting shield as the deoxidizing vessel swings about its axis 76.

The molds 67 are desirably steel molds, of the vertical type disclosed in Eppensteiner United States Patent No. 1,779,534, although they may permissibly be of some other type. Steel molds have produced sound castings where castings obtained from molds made of another material were unsound. The molds are suitably water cooled as at 101 and their bottoms are closed by a door 102 hinged at 103 and latched at 104. When the castings have solidified they are allowed to drop out of the molds by releasing the latch 104. It will of course be evident that the molds could be arranged for casting one at a time or several at a time as desired.

In the preferred deoxidation procedure, the copper in the deoxidizing vessel is subjected to intimate contact with carbon under a reduced pressure of say 35 millimeters of mercury. This greatly accelerates the deoxidation, so that copper having the oxygen content of "tough-pitch" copper can in a short time be deoxidized so completely that it not only will not produce castings containing a distinct phase of cuprous oxide visible under the microscope, nor containing excessive gas cavities when cast under a protecting atmosphere, but it will even yield dense oxygen-free castings when cast with limited exposure to air within the molds and the shield.

Under best conditions the bulk specific gravity of the castings should reach 8.87 and in general bulk specific gravities in excess of 8.8 should be obtained. To reach such high specific gravities, particularly when casting in air, the deoxidation must be managed carefully.

The reactions taking place in the deoxidizing vessel appear to be:

$$Cu_2O+C=2Cu+CO \quad (1)$$
$$Cu_2O+CO=2Cu+CO_2 \quad (2)$$
$$CO_2+C=2CO \quad (10)$$

Carbon monoxide from Reaction (1) between cuprous oxide and carbon will dissolve in the molten copper and tend to saturate the copper at a particular pressure, while Reaction (2) between cuprous oxide and carbon monoxide will remove some carbon monoxide from the molten copper and tend to saturate the copper with carbon dioxide at the particular pressure. Carbon dioxide is to be kept at a minimum because it is formed by reactions between cuprous oxide and carbon monoxide during solidification of the copper, but carbon monoxide is not subject to this difficulty. Therefore, by prolonged deoxidation with carbon, the content of carbon dioxide is lowered to such a value by Reaction (10) that it does not cause objectionable gas cavities when the copper solidifies.

Lowering the pressure in the deoxidizing vessel below atmospheric pressure reduces the carbon monoxide activity in Equation (4) for Reaction (1), and so lowers the activity of cuprous oxide, the activities of copper and carbon remaining unchanged. In Reaction (2) the lowering of the pressure in the deoxidizing vessel below atmospheric pressure to reduce the carbon monoxide activity and the simultaneous lowering of the activity of cuprous oxide yield a lower activity of carbon dioxide. According to Reaction (10) equilibrium requires at constant temperature that:

$$\frac{(A.CO)^2}{(A.CO_2)(A.C)}=K_3 \quad (11)$$

K_3 = proper constant

Since the activity of the carbon is constant, the lowering of the pressure in the deoxidizing vessel lowers the carbon monoxide activity and the carbon dioxide activity in such a way that the reduced activity of the carbon dioxide remains proportional to the square of the reduced activity of carbon monoxide. Thus the activity of carbon dioxide is reduced rapidly by reducing the pressure.

The quantity of carbon dioxide which will remain dissolved in the copper under reduced pressure is substantially lower than that which will remain dissolved under atmospheric pressure, so that the copper deoxidized under reduced pressure is likely to be lower in carbon dioxide than copper deoxidized under atmospheric pressure, thus allowing for a certain oxygen pick-up without producing excessive carbon dioxide during pouring.

During the deoxidation there is always a relation between carbon dioxide and carbon monoxide present in the molten copper, depending upon the oxygen content, temperature, pressure and approach to equilibrium conditions. The effect of

the reduced pressure is therefore to establish a lower ratio between the carbon dioxide and carbon monoxide present in the molten copper. After the deoxidation is finished in the deoxidizing vessel and atmospheric pressure is restored, the molten copper will be unsaturated with carbon dioxide not only because of the effect of Reaction (10) but also because of the much greater solubility of carbon dioxide at atmospheric pressure than at the reduced pressure.

It would appear to be impossible to determine the small oxygen content of the molten copper remaining after deoxidation in the deoxidizing vessel **22**. The oxygen content in the molten copper should be small or negligible in the third decimal place, and preferably below about 0.002%. To the operator skilled in the art, the attainment of the desired oxygen content is not difficult, as castings are poured and the deoxidation time varied until the absence of a distinct phase of cuprous oxide in the castings as viewed under the microscope shows that they are oxygen-free and the bulk specific gravity in excess of 8.8 (preferably in excess of 8.87) shows that they contain insufficient gas forming substances present in the molten copper to produce gas cavities which would interfere with the mechanical working of the copper.

The deoxidation under reduced pressure appears to be advantageous from the standpoint of removal of other contaminating gases which may be present in "tough-pitch" copper. Water vapor and the like are successfully removed under the reduced pressure. It will, of course, be evident that the deoxidizing vessel should be kept from contact with hydrogen-containing substances to prevent objectionable hydrogen contamination of the molten copper. Contamination with oxidizing gases of combustion is of course not possible during the deoxidation.

The deoxidizing vessel is completely sealed when the reduced pressure is maintained in it. In restoring the atmospheric pressure prior to casting, it is preferable to introduce into the deoxidizing vessel through a valved connection **105**, a noncontaminating reducing gas such as carbon monoxide or the gas recommended below as a protected casting atmosphere, at a pressure at least as high as atmospheric pressure.

The functions of the single deoxidizing vessel may, of course, be divided among several vessels which can be unheated or heated as desired.

As already explained, the molds and the casting shield **91** may permissibly contain air when oxygen-free copper is cast. The volume of air in the molds and casting shield should preferably be not more than about four times the volume of the molds. The air will desirably, however, be diluted by a non-oxidizing or, better, reducing gas or vapor. In casting oxygen-free copper, the interiors of the molds are preferably coated with a mold dressing, consisting for example of a film-forming substance such as lard oil or a petroleum distillate or hydrocarbon mixed with carbon in the form of powdered graphite or lamp black. The molds before use are preferably warmed to about 187° F. (86° C.) and they become filled with vapor from the oil which lowers the oxygen content of the air and exerts some reducing action. The presence of hydrogen in the vapor of the oil does not appear to be objectionable because of the short time of exposure, and the slight contact, which is not sufficient to cause gas cavities. The vapor from the mold dressing is more convenient than the use of a protecting gas because the vapor is heavier than air and stays in the molds, it is not necesasry to sweep air out of the molds, and the molds and shield need not be constructed and maintained absolutely gas tight.

In making oxygen-free copper, the use of vertical molds reduces the area of the "set" surface of the casting. By pouring from a point as near as possible to the top of the molds, the length of the pouring stream is cut down, so that the exposure to air in contact with the pouring stream is at a minimum. By making the shield as small as possible, the volume of air additional to that in the mold which can come in contact with the copper is kept at a minimum and the air is rendered less oxidizing by the vapor from the mold dressing. If the deoxidation has carried the oxygen content of the copper far below the point at which excessive gas cavities or a distinct phase of cuprous oxide form in the solidifying copper, the limited pick-up of oxygen during casting is not effective to prevent the casting from being dense and oxygen-free.

The deoxidation of copper containing a substantial amount (say 0.04% or even 0.01%) of oxygen by carbon under reduced pressure as already explained is advantageous notwithstanding that casting is to take place in a protecting gaseous atmosphere at reduced pressure, atmospheric pressure or superatmospheric pressure, because the reduced pressure accelerates and facilitates the deoxidation and makes it possible to maintain the total oxygen content, and particularly the content of dissolved carbon dioxide, at a lower value.

If a protecting atmosphere is to be used, it may be introduced into the shield **91** through the connection **106** and allowed to sweep out the molds before the door **102** at the bottom is closed. If superatmospheric pressure is employed, the noncontaminating reducing gas will escape through any leaks in the shield or at the point of connection between the molds and the shield. Carbon monoxide is a desirable protecting gas as the copper contains substantial quantities of carbon monoxide when it comes from a deoxidizing vessel in any case, and the carbon monoxide does not therefore additionally contaminate the copper. Carbon monoxide dissolved in the copper in fact exerts a slight protecting action by reacting with oxidizing gases. Carbon monoxide also has the desirable property of burning when it comes in contact with the atmosphere.

A gas containing carbon monoxide as an active ingredient, for example producer gas made from charcoal or coke, may be used. Typical analyses of such a gas are:

Gas No. 1

	Per cent
CO	21.1
CO_2	7.5
O_2	0.1
N_2	Balance

Gas No. 2

	Per cent
CO	28 to 29
CO_2, less than	0.5
O_2, within accuracy of customary Orsat apparatus	0
N_2	Balance

Gas No. 2 is of course preferable to gas No. 1. In some cases it is desirable to have the protecting atmosphere low in hydrogen to prevent excessive gas cavities caused by hydrogen, where-

upon the air and charcoal used in making the charcoal producer gas should be first freed from water vapor.

If the casting wheel is to be removed to the next position before the tops of the castings have solidified, it is desirable to protect the tops of the castings by placing powdered carbon such as charcoal on them as the wheel is moved. The carbon should be so finely divided that it will behave as a fluid.

Although it is preferred to carry out the deoxidation under reduced pressure, the deoxidation may nevertheless be conducted at atmospheric pressure and the castings can still be cast in air providing the deoxidation is sufficiently prolonged. If the deoxidation is to be carried on under atmospheric pressure, the connection **84** to the vacuum pump **86** can simply be removed and the small opening used as a vent for gases.

By the process explained herein, it is possible to obtain dense oxygen-free copper castings by casting in air. It is also possible to facilitate and accelerate the deoxidation of copper whether it is to be cast in a protecting atmosphere or in air.

It will be evident that a distinct advantage of the present invention is the use of the same equipment to produce "tough-pitch" copper and oxygen-free copper, so that within a considerable range of flexibility, increased demand for one product may be met by increased supply of that product and correspondingly decreased supply of the other product.

It will further be evident that the deoxidation under reduced pressure in the deoxidizing vessel, while explained herein as an intermittent process, can if desired be made continuous by equipping the inlet and outlet of the deoxidizing vessel with barometric molten copper column seals.

In view of my invention and disclosure variations and modifications to meet individual whim or particular need will doubtless become evident to others skilled in the art, to obtain all or part of the benefits of my invention without copying the process shown, and I, therefore, claim all such in so far as they fall within the reasonable spirit and scope of my invention.

Having thus described my invention, what I claim as new and desire to secure by Letters Patent is:

1. In the art of producing dense oxygen-free copper castings, the process which comprises deoxidizing molten copper substantially free from metallic impurities by a carbon-containing reducing agent until the copper has an oxygen content substantially lower than that necessary to obtain dense oxygen-free copper castings when casting without oxygen pick-up, conducting the deoxidation in the absence of contamination with hydrogen-containing substances, and casting the deoxidized molten copper in contact with air under conditions in which the oxygen pick-up is insufficient to cause a distinct phase of cuprous oxide and insufficient to cause excessive gas cavities in the castings.

2. In the art of producing dense oxygen-free copper castings, the process which comprises lowering the total oxygen content of molten copper substantially free from metallic impurities by treatment with solid carbon, to a value sufficiently below that at which a distinct phase of cuprous oxide appears in the castings and also sufficiently below that at which excessive gas cavities appear in the castings, so as to allow for a limited pick-up of oxygen during casting without causing the appearance of a distinct phase of cuprous oxide and without causing excessive gas cavities in the castings and then casting the deoxidized molten copper with exposure to air and with not more than that exposure to air which will cause the limited pick-up of oxygen.

3. In the art of producing dense oxygen-free copper castings, the process which comprises deoxidizing oxygen-bearing molten copper substantially free from metallic impurities by solid carbon in contact with the molten copper until it has an oxygen content substantially lower than that necessary to obtain dense oxygen-free copper castings when casting without oxygen pick-up, conducting the deoxidation in the absence of contamination with hydrogen-containing substances, and casting the deoxidized molten copper with air exposure so limited that the oxygen pick-up does not cause a distinct phase of cuprous oxide in the castings and does not cause a bulk specific gravity of the castings below 8.8.

4. In the art of producing dense oxygen-free copper castings, the process which comprises deoxidizing oxygen-bearing molten copper substantially free from metallic impurities with carbon until the oxygen content is substantially below that necessary to produce dense oxygen-free copper castings when casting without oxygen pick-up, conducting the deoxidation in the absence of contamination with hydrogen-containing substances, and casting the deoxidized molten copper with exposure to air in a casting shield which so limits the oxygen pick-up that it is insufficient to cause a distinct phase of cuprous oxide and insufficient to cause excessive gas cavities in the castings.

5. In the art of producing dense oxygen-free copper castings, the process which comprises deoxidizing oxygen-bearing molten copper substantially free from metallic impurities with carbon until the oxygen content is substantially below that necessary to produce dense oxygen-free copper castings when casting without oxygen pick-up, conducting the deoxidation in the absence of contamination with hydrogen-containing substances, and casting the deoxidized molten copper with exposure to a mixture of air and oil vapor under conditions in which the oxygen pick-up is insufficient to cause a distinct phase of cuprous oxide and insufficient to cause excessive gas cavities in the copper castings.

6. In the art of producing dense oxygen-free copper castings, the process which comprises deoxidizing oxygen-bearing molten copper substantially free from metallic impurities with carbon until the oxygen content is small or negligible in the third decimal place, and casting the deoxidized molten copper under a casting shield with exposure to a mixture of air and reducing vapor from a mold dressing under conditions in which the oxygen pick-up is insufficient to cause the appearance of a distinct phase of cuprous oxide in the castings and insufficient to lower the bulk specific gravity of the castings below 8.8.

7. In the art of producing dense oxygen-free copper castings, the process which comprises producing molten "tough-pitch" copper, withdrawing the molten "tough-pitch" copper to a deoxidizing vessel and there treating it with carbon until the oxygen content is substantially lower than that necessary to produce dense oxygen-free copper castings when casting without oxygen pick-up and casting the deoxidized molten copper with exposure to air under conditions in which the oxygen pick-up is insufficient to cause a distinct phase of cuprous oxide and insufficient to

cause excessive gas cavities in the copper castings.

8. In the art of producing dense oxygen-free copper castings, the process which comprises deoxidizing oxygen-bearing molten copper by carbon in a closed vessel at a pressure below atmospheric pressure until the oxygen content is below that necessary to obtain dense oxygen-free copper castings when casting without oxygen pick-up and casting the copper with exposure to air under conditions in which the oxygen pick-up is insufficient to cause a distinct phase of cuprous oxide and insufficient to cause excessive gas cavites in the copper castings.

9. In the art of producing dense oxygen-free copper castings, the process which comprises lowering the total oxygen content of molten copper substantially free from metallic impurities containing at least 0.01% oxygen by treatment with solid carbon at a pressure below atmospheric pressure, to a value sufficiently below that at which a distinct phase of cuprous oxide appears in the castings and also sufficiently below that at which excessive gas cavities appear in the castings, so as to allow for a limited pick-up of oxygen during casting without causing excessive gas cavities or the appearance of a distinct phase of cuprous oxide in the castings and then casting the deoxidized molten copper with exposure to air and with not more than that exposure to air which will cause the limited pick-up of oxygen.

10. In the art of producing dense oxygen-free copper castings, the process which comprises deoxidizing oxygen-bearing molten copper substantially free from metallic impurities by solid carbon in contact with the molten copper at a pressure substantially below atmospheric pressure until the molten copper has an oxygen content substantially lower than that necessary to obtain dense oxygen-free copper castings when casting without oxygen pick-up, conducting the deoxidation in the absence of contamination with hydrogen-containing substances, and casting the deoxidized molten copper with air exposure so limited that the oxygen pick-up does not cause a distinct phase of cuprous oxide in the castings and does not cause a bulk specific gravity of the castings below 8.8.

11. In the art of producing dense oxygen-free copper castings, the process which comprises deoxidizing oxygen-bearing molten copper substantially free from metallic impurities with carbon at a pressure substantially below atmospheric pressure until the oxygen content is substantially below that necessary to produce dense oxygen-free copper castings when casting without oxygen pick-up, conducting the deoxidation in the absence of contamination with hydrogen-containing substances, and casting the deoxidized molten copper with exposure to air in a casting shield which so limits the oxygen pick-up that it is insufficient to cause a distinct phase of cuprous oxide and insufficient to cause excessive gas cavities in the castings.

12. In the art of producing dense oxygen-free copper castings, the process which comprises deoxidizing oxygen-bearing molten copper substantially free from metallic impurities with carbon at a pressure substantially below atmospheric pressure until the oxygen content is substantially below that necessary to produce dense oxygen-free copper castings when casting without oxygen pick-up, conducting the deoxidation in the absence of contamination with hydrogen-containing substances, and casting the deoxidized molten copper with exposure to a mixture of air and oil vapor under conditions in which the oxygen pick-up is insufficient to cause a distinct phase of cuprous oxide and insufficient to cause excessive gas cavities in the copper castings.

13. In the art of producing dense oxygen-free copper castings, the process which comprises deoxidizing oxygen-bearing molten copper substantially free from metallic impurities with carbon at a pressure substantially below atmospheric pressure until the oxygen content is small or negligible in the third decimal place and casting the deoxidized molten copper under a casting shield with exposure to a mixture of air and reducing vapor from a mold dressing under conditions in which the oxygen pick-up is insufficient to cause the appearance of a distinct phase of cuprous oxide in the castings and insufficient to lower the bulk specific gravity of the castings below 8.8.

14. In the art of producing dense oxygen-free copper castings, the process which comprises melting copper under fuel-fired conditions in which the gases of combustion are in contact with the molten copper, producing molten copper having an oxygen content of at least 0.03%, deoxidizing the oxygen-bearing molten copper by carbon at a pressure below 300 millimeters of mercury until the oxygen content of the molten copper is substantially below that necessary to produce dense oxygen-free copper castings when casting without oxygen pick-up and concurrently removing objectionable gases due to the combustion melting, and casting the deoxidized molten copper with air exposure so limited that the castings are free from a distinct phase of cuprous oxide and have bulk specific gravities in excess of 8.8.

15. In the art of producing dense oxygen-free copper castings, the process which comprises oxidizing solid copper masses, melting the copper masses under fuel-fired conditions in which the molten copper is exposed to gases of combustion to produce molten copper having an oxygen content in excess of 0.03%, deoxidizing the molten copper by carbon at a pressure of 35 millimeters of mercury or below until the oxygen content is substantially below that necessary to produce dense oxygen-free copper castings when casting without oxygen pick-up and concurrently removing objectionable gases of combustion from the melting, and casting the deoxidized molten copper with exposure to air under conditions in which the oxygen pick-up is insufficient to cause a distinct phase of cuprous oxide and insufficient to cause excessive gas cavities in the castings.

16. In the art of producing dense oxygen-free copper castings, the process which comprises producing molten "tough-pitch" copper, withdrawing the molten "tough-pitch" copper to a deoxidizing vessel and there deoxidizing it by carbon under a pressure substantially below atmospheric pressure until the oxygen content is too low to produce a distinct phase of cuprous oxide and too low to produce excessive gas cavities in the copper castings and casting the copper with exposure to air but without sufficient oxygen pick-up during casting to cause a distinct phase of cuprous oxide in the castings and without sufficient oxygen pick-up during casting to lower the bulk specific gravities of the casting below 8.8.

17. In the art of preparing copper castings from copper masses, the process which comprises continuously preheating the copper masses by fuel combustion and concurrently oxidizing the copper masses, controlling the oxidation by regulat-

ing the fuel combustion used for preheating separately from heating used in subsequent melting, subsequently continuously melting the copper masses, while the masses are submerged in molten copper and finally casting the molten copper.

18. In the art of preparing copper to make castings from copper masses, the process which comprises continuously preheating and concurrently oxidizing the copper masses by fuel combustion, controlling the oxidation by regulating the fuel combustion used for preheating, subsequently continuously melting the copper masses by separate fuel combustion, separately controlled, while the masses are submerged in molten copper and adjusting the oxygen content of the molten copper to that required for "tough-pitch" copper by reducing with a carbonaceous reducing agent.

19. The process of producing "tough-pitch" copper castings having an oxygen content of from 0.03% to 0.05%, which comprises oxidizing copper masses in solid condition in a preheating furnace to an extent sufficient to give, when molten, an oxygen content in the molten copper of from 0.03% to 0.10%, thereby oxidizing sulphur present as an impurity at the surface, melting the copper masses in a separate melting furnace to produce molten copper containing from 0.03% to 0.10% of oxygen, regulating the oxygen content of the molten copper to between 0.03% and 0.05% while always maintaining the oxygen content below 0.10%, and casting the molten copper to produce castings containing from 0.03% to 0.05% oxygen.

20. The process of producing "tough-pitch" copper, which comprises preheating and concurrently oxidizing copper masses by fuel combustion, melting the masses to form molten copper by separate fuel combustion, separately controlled, transferring the molten copper to a separate vessel and there adjusting its oxygen content to that required for "tough-pitch" copper and casting the molten copper as "tough-pitch" copper.

21. In the art of preparing copper castings from copper masses, the process which comprises continuously preheating the copper masses by fuel combustion and concurrently oxidizing the copper masses, controlling the oxidation by regulating the fuel combustion used for preheating, subsequently continuously melting the copper masses by separate heating means, separately controlled, while the masses are submerged in molten copper, completely deoxidizing the molten copper with carbon and finally casting the molten copper.

22. In the art of preparing copper to make castings from copper masses, the process which comprises continuously preheating and concurrently oxidizing the copper masses by fuel combustion, subsequently continuously melting the copper masses by separate fuel combustion, separately controlled, while the masses are submerged in molten copper, adjusting the oxygen content of the molten copper to that required for "tough-pitch" copper by reducing with a carbonaceous reducing agent and completely deoxidizing the molten copper with carbon.

23. In the art of preparing copper castings from copper masses, the process which comprises continuously preheating the copper masses by fuel combustion and concurrently oxidizing the copper masses, subsequently continuously melting the copper masses by separate heating means, separately controlled, while the masses are submerged in molten copper, completely deoxidizing the molten copper with carbon and finally casting the molten copper while protecting it from the uncontrolled oxidizing influence of the atmosphere.

24. The process of producing copper castings of high density and low oxygen content, which comprises preheating and concurrently oxidizing copper masses by fuel combustion, melting the copper masses by separate fuel combustion, separately controlled, deoxidizing the molten copper by carbon in the absence of contamination with hydrogen and oxidizing gases until there are insufficient oxygen in the molten copper to form a distinct phase of cuprous oxide in the copper castings and insufficient gas-forming substances in the molten copper to produce a bulk specific gravity of the copper castings below 8.8 and casting the molten copper while concurrently protecting it from the uncontrolled action of the atmosphere.

25. In the art of preparing copper castings from copper masses, the process which comprises continuously preheating and concurrently oxidizing the copper masses by fuel combustion, subsequently continuously melting the copper masses by separate fuel combustion, separately controlled, while the masses are submerged in molten copper, adjusting the oxygen content of the molten copper to that required for "tough-pitch" copper by reducing with a carbonaceous reducing agent, completely deoxidizing the molten copper with carbon, and finally casting the molten copper while protecting it from the uncontrolled oxidizing influence of the atmosphere.

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