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METHOD OF MAKING DEOXIDIZED COPPER AND COPPER ALLOYS

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This invention relates to the manufacture and treatment of copper to be used in various forms, and to copper alloys and method of making them, and has for an object the production of deoxidized copper and improved copper alloys and an improved method whereby such deoxidized copper and improved alloys may be readily produced in large quantities and with uniformity in the mill.

It is also an object of the invention to provide an improved method of deoxidizing copper to be used in various forms such as electrical conductor wire, bars, and so forth, to secure a conductor of high electrical conductivity and which is able to withstand repeated bending without breaking after being annealed in hydrogen.

Another object of the invention is to provide a method of deoxidizing copper whereby a uniform product may be produced commercially and one having definite characteristics which may be secured with certainty.

This application is in part a continuation of each of our prior applications Serial No. 616,096 filed June 8, 1932 for Method of making deoxidized copper, and Serial No. 690,764 filed September 23, 1933 for Method of making deoxidized copper.

The improved method of making the copper alloys consists broadly in first the removal of the greater proportion of the gases in the copper which readily come out, that is, give the gases an opportunity to escape, to then completely deoxidize the copper with a deoxidizer which does not form a reaction product which is gaseous at room temperature upon combining with the oxygen of the copper, and then adding one or more alloying elements. The deoxidizer is preferably used in amounts in excess of that required to completely deoxidize the copper so that there is an excess or a residual amount of the deoxidizer in the copper when the alloying element or elements is or are added, and this deoxidizer may form one of the elements of the alloy produced.

There are several different methods of procedure by which the copper may be treated. Broadly, as disclosed in our prior application Serial Number 690,764 above mentioned the copper is melted in a suitable container and brought to an oxygen content of not more than 0.090 percent, preferably considerably less than this, probably never over 0.040 percent, and generally less than 0.025 percent, by treatment with carbonaceous or other reducing materials, then allowing the greater proportion of the gases to escape, and then the copper is completely deoxidized by the addition of a deoxidizing agent which does not form a reaction product which is gaseous at room temperature upon combining with the oxygen of the copper and therefore will prevent swelling of the copper on freezing. The final deoxidizer may or may not be a metallic deoxidizer depending upon for what the copper is to be used or upon the alloy it is desired to produce, and when the copper is to be used for alloys the deoxidizer is preferably added in sufficient amount so that there is a residual amount of the deoxidizer remaining in the copper when the alloying element or elements are added. That is, it is preferred that somewhat more of the deoxidizer be added than is required merely to deoxidize the copper to insure that the copper is completely deoxidized, and furthermore, this excess of deoxidizer may be one of the alloying elements of the finished alloy. It is, however, not necessary that the final deoxidizer be used in excess of that required to deoxidize the copper, as we have developed methods of deoxidizing the copper whereby very little, if any, final deoxidizer remains in the copper.

The procedure in our method of making deoxidized copper and copper alloys may vary considerably. Thus, for example, the copper when melted in the container may be melted under any type of cover or under no cover at all and the melted copper treated with carbonaceous or other reducing material until practically deoxidized. We prefer to use charcoal as this reducing material and may melt the copper under a layer of this charcoal until the proper temperature is secured, which we estimate to be in the neighborhood of 1200° C., or if preferred the charcoal may be stirred into the melted copper. At this time the copper contains gases. If the copper has been melted under reducing conditions as for example under a layer of charcoal, if oxygen is present it is only in minute amounts. If the copper is treated by stirring carbonaceous material into it we prefer to use partially burned or calcined charcoal or other carbonaceous material similar in composition to said partially burned or calcined charcoal. The charcoal which has been used as a cover in melting down the copper is very satisfactory for this purpose. The copper is then exposed to oxidizing conditions, preferably to the air, to permit the gases to get out. These gases apparently are those which readily react with the air when they come in contact with it and other gases which may be in the metal and escape when the metal is exposed, and during this time the copper may or may not be stirred with a graphite

rod or any suitable type of rod. It is not necessary to this process that all of the gases escape, but it is preferred that the larger proportion of them do so, or that those that come out readily be permitted to do so. During this exposure of the copper to the air or other oxidizing conditions there is come oxidation of the copper, but it never exceeds 0.090 percent and it is generally considerably less than this, probably never over 0.040 percent and generally less than 0.025 percent. The copper may then be covered with carbonaceous material to prevent further oxidation if desired, but this, however, is not necessary unless possibly the copper is to be exposed for an unusual length of time.

The copper is then deoxidized with non-carbonaceous material which is capable of preventing the swelling of the copper on freezing. That is, the copper is deoxidized with the addition of a deoxidizing agent or agents which does not form a reaction product which is gaseous at room temperature upon combining with the oxygen of the copper. We prefer to use a metallic deoxidizer for this purpose although we are not necessarily limited thereto. Thus for example we may use aluminum, manganese, lithium, calcium, or other suitable metallic deoxidizers, or we may use suitable non-metallic deoxidizers, such for example as boron, silicon, or phosphorus, or we may use such deoxidizers as metallic borides, metallic silicides, metallic phosphides or other suitable deoxidizers. In making alloys we preferably add sufficient of the deoxidizer so that there is a residual amount of this deoxidizer remaining in the finished metal. This insures that the copper is completely deoxidized, and more or less of the deoxidizer may be desirable in the finished metal. Thus, for example, in making a phosphor-bronze, phosphorus may be used as the final deoxidizer and in amount not only sufficient to deoxidize the copper but a sufficient excess is used to provide the amount of phosphorus desired in the finished phosphor-bronze alloy. Then the desired amount of tin is added to complete the alloy.

The amount of deoxidizer required to complete the deoxidation of the copper may be determined by taking samples of the copper and adding deoxidizer until the metal does not swell on freezing and then adding sufficient surplus to insure that there is some residual deoxidizer in the finished copper. As the oxygen content never goes over 0.090 percent and generally is much less than this, for a given weight of copper the amount of deoxidizer required to insure complete deoxidation can be readily determined. If borides and similar deoxidizers are used there may not be any of the deoxidizer remaining in the alloy after casting. We may use one metallic or non-metallic deoxidizer for deoxidizing the copper, such for example as aluminum, manganese, calcium, boron, silicon, and phosphorus, or we may use two or more of the deoxidizers if it is so desired.

The deoxidizer may be added as a free element or if a more fine control is desired it may be added in the form of an alloy with copper. Thus for example if aluminum is the deoxidizer it may be added as a metallic aluminum in small pieces or it may be added as a copper aluminum alloy. Such alloy may contain 75 percent copper and 25 percent aluminum, or any other known or suitable proportion may be used without affecting the principle of operation. As stated above we may use combinations of two or more different deoxidizers. Thus, for example we may partially deoxidize copper with the aluminum or another metal and then complete the deoxidation by the addition of a different and another metal, such for example as manganese where the first metal is aluminum. The second metal may be added either as free metal or as an alloy with copper.

After the copper is deoxidized with the final deoxidizer an alloy element or elements is or are added to produce the desired alloy. These, for example, may be such elements as cadmium, tin, zinc, aluminum, nickel, or any other suitable element or combination of elements to produce such alloys as for example phosphor-bronze, cadmium-bronze, nickel-silver, cupro-nickel, brass, or any other copper alloy. The alloy may then be poured into suitable molds and may be used for the purpose intended.

A slightly modified procedure is to melt the copper in a suitable container under oxidizing conditions. The copper is then treated with carbonaceous or other reducing materials, such for example as the calcined or partially burned charcoal, until the oxygen content is reduced to 0.090 per cent or less. Ordinarily it would be much less than this amount. The copper is then exposed to oxidizing conditions to allow the greater proportion of the gases to escape. Then the metal is deoxidized with non-carbonaceous material by adding predetermined amounts of metallic or other deoxidizers capable of preventing swelling of the metal on freezing, that is by use of deoxidizers which do not form a reaction product which is gaseous at room temperature upon combining with the oxygen of the copper. If metallic deoxidizers or such non-metallic deoxidizers as phosphorus or silicon are used they may be added in sufficient amount to produce a residual amount of deoxidizer in the copper as indicated above. If borides and similar deoxidizers are used there may not be any of the deoxidizer remaining in the copper after deoxidizing. In other words the copper is finally deoxidized after treating with carbonaceous or other reducing materials to bring it to an oxygen content of less than 0.090 per cent in the same manner as is indicated in the first procedure. If an alloy is desired then one or more alloying elements are added in the proper amounts to produce the alloy desired. The metal may then be cast and worked as desired.

Another somewhat modified procedure is to melt the copper in a suitable container under any type of cover or under no cover at all. The molten copper is then poured into a ladle or other suitable and portable container which may or may not have a source of heat for raising or maintaining the temperature of the copper therein. Such containers may be in the form of electric furnaces, gas fired furnaces, or oil fired furnaces. When a furnace is substituted for a ladle in this operation we prefer some form of an electric furnace. The melted copper is then treated with carbonaceous or other reducing material until substantially deoxidized. We prefer to use partially burned or calcined charcoal. The copper is then exposed to the air to permit the larger proportion of the gases to escape, and there is some oxidation of the copper, but never to an oxygen content of over 0.090 percent and ordinarily much less than this as indicated in the first procedure described above. The copper may then be covered with carbonaceous material to prevent further oxidation if desired, but this ordinarily is not necessary. The copper is then finally deoxidized with non-carbonaceous material capable of preventing swelling of the metal

on freezing. As indicated above the deoxidizer used preferably is added in sufficient amount to produce a residual deoxidizer in the copper. If borides or similar deoxidizers are used there may not be any deoxidizer remaining in the copper. One or more alloying elements are then added to the copper to produce the alloy desired. This alloy may then be cast and worked as desired.

Still another somewhat modified procedure may be used in which the copper is melted in a suitable container under oxidizing conditions. The molten copper is poured into a ladle or other suitable and portable container, which may or may not have a source of heat for raising or maintaining the temperature of the copper therein. Such container may be in the form of an electric furnace, gas fired furnace, or oil fired furnace. When a furnace is substituted for a ladle in this operation we prefer some form of an electric furnace. The melted coper is then treated with carbonaceous or other reducing materials until the oxygen content in the copper is reduced to not more than 0.090 percent and preferably considerably less than this as above indicated, and then exposed to oxidizing conditions to allow the larger proportion of the gases to escape. The copper is then finally deoxidized by non-carbonaceous materials, such as metallic or other deoxidizers capable of preventing swelling of the metal on freezing as described in connection with the other procedures as above noted, and preferably with a surplus of deoxidizer so that there is a residual amount of deoxidizer in the copper, and then one or more alloying elements are added to produce the alloy desired.

It will be noted from the above that we can reduce the oxygen content of melted copper to 0.090 percent or less with suitable reducing agents, particularly carbonaceous material, such as charcoal, and can produce completely deoxidized copper before adding the alloying element or elements by treating the copper from this point with non-carbonaceous material which does not form a gaseous reaction product upon combining with the oxygen of the copper and is therefore capable of preventing swelling of the metal on freezing. After the metal has been treated with the carbonaceous material the oxygen content is never more than 0.090 percent and is ordinarily much less than this, probably never over 0.040 percent, and the indications are it is less than 0.025 per cent.

It has not been generally realized that the melted copper is saturated with gases, probably some combustible and some non-combustible, and we have found that if these are allowed to escape and the oxygen content is not over 0.090 percent, although preferably much less than this amount, then the final deoxidizer added, and then the alloying element or elements added much better alloys and castings of these alloys which are preferably sound can be obtained. With a little testing we can soon find out how much of the final deoxidizer to add under given conditions so as to secure a residual amount of the deoxidizer in the copper and still deoxidize it. We have discovered that there is never an oxygen content of over 0.090 percent when the gases have been allowed to escape, and as a matter of fact ordinarily much less than this. With a little practice one can tell from the general appearance of the copper when the gases have escaped sufficiently from the metal to permit adding the final deoxidizer safely, one indication being that the absence of a fine copper spray is very noticeable. Also that the molten copper gradually takes on a bluish or greenish cast and boils quite violently.

Where a more accurate control of the final deoxidizer and a more accurate and uniform control of the characteristics of the metal is desired we use a somewhat different procedure, as disclosed in our prior application Serial Number 616,096, above mentioned.

It has been difficult to produce deoxidized copper with a high electrical conductivity and which will stand the desired amount of bending without breaking, after annealing in hydrogen, and especially it has been difficult to secure a uniform product. We have discovered a method of deoxidizing copper by which we can secure an electrical conductivity of at least 99.5 per cent at 20° C. in terms of the International Annealed Copper Standard, and it can also withstand a minimum of ten bends after a thirty minute anneal in a hydrogen atmosphere at 850° C. Furthermore we can produce this copper on a commercial scale and with a uniformity which will maintain at least these standards. In the bending test the copper is bent around a radius 2.5 times the thickness or diameter of the copper rod, wire, or whatever the shape happens to be, the copper being first bent 90° in one direction and then back to the original position. This constitutes one bend. The second bend is in the opposite direction around the same radius 90° and then back to the original position. The third bend is the same as the first, and so on.

Metals have been used for many years to deoxidize copper but never before has such a copper passed the above tests. In order for the copper to pass such tests there must be only minute amounts of the deoxidizer remaining in the finished copper, as only small amounts will materially reduce the electrical-conductivity of the copper. On the other hand if sufficient amounts of the deoxidizer are not added to the copper to completely deoxidize it then the copper can not withstand the bending test as above noted. It will be evident that as it is difficult to determine under ordinary operations the exact amount of the oxygen in the copper and therefore to determine the exact amount of deoxidizer required to completely deoxidize the copper and still not have a surplus of the deoxidizer to remain in the copper and decrease the electrical conductivity, it was practically impossible to produce deoxidized copper commercially which could meet the above standards.

We have discovered that with certain treatments of the copper we can bring it to a definite end point or condition where it has a definite oxygen content. and we therefore know the exact amount of deoxidizer which should be added to completely deoxidize the copper and still have a minimum amount of deoxidizer remain in the copper, and we can keep the content of the deoxidizer sufficiently low so that the electrical conductivity is 99.5 per cent or higher at 20° C. in terms of the International Annealed Copper Standard.

In carrying out this method or procedure the copper may first be melted in any suitable furnace but, we prefer a high frequency electric furnace as in such a furnace the operation may be more easily controlled. The copper is preferably melted under a cover of charcoal but other covers may be used and in fact it may be melted

with no cover at all, but we prefer charcoal as this gives us less work and more definite control in another part of the method.

When the copper is melted and the proper temperature attained which we estimate to be in the neighborhood of 1200° C. the charcoal or other cover is removed. The copper at this point contains gas, and if oxygen is present it is only in minute amounts. The copper is agitated with a suitable stir rod such for example as graphite, or it may be agitated with a furnace current, until it shows a boiling action. This action tends to throw off the gases in the copper and particularly the easily combustible gases or those which readily react with the air when they come in contact with it. This boiling action of the copper exposed to the air also causes some oxidation of the copper. After the copper has boiled in this way, say for example for a few minutes, the charcoal is placed on the metal and stirred into it with a rod. It is preferable to use the old and partially burned charcoal which was used as a cover in melting the metal. In other words it is preferable to use partially burned or calcined charcoal, or some carbonaceous material which has a composition similar to partially burned or calcined charcoal. This heating and partial burning of the charcoal appears to drive off the moisture and gases from the charcoal. Also as the charcoal has been partially burned part of the carbon has been burned and it has a relatively high ash content. Its combustibility is therefore reduced and it is less active as a reducing agent thus permitting much more accurate control of the deoxidizing operation and a more accurate determination of the end point. A somewhat similar effect can be secured by calcining the charcoal by roasting or by baking in an oven. If desired, the furnace current may be applied at times to help this stirring operation and the deoxidizing of the copper by the charcoal. This operation of stirring the charcoal into the molten copper is continued until all signs of boiling in the copper have just disappeared. This is a definite end point and shows that the copper has been brought to a condition of a definite oxygen content. This point is very definite and positive for a given temperature.

After this point is reached we add definite amounts of deoxidizer to completely deoxidize the copper, and as the oxygen content of the copper has been brought to a definite amount we can, if desired, use just the amount of deoxidizer required so that only minute amounts of the deoxidizers remain in the copper. The final deoxidizer or deoxidizers used are those which do not form a reaction product which is gaseous at room temperature upon combining with the oxygen of the copper and are therefore capable of preventing swelling of the metal on freezing. This end point therefore gives us a definite condition from which the exact amount of deoxidizer required to give a complete deoxidation of the copper can be definitely determined, and we can definitely determine the exact amount of deoxidizer required to give a complete deoxidation of the copper without a great surplus of deoxidizer remaining in the copper, and we can therefore of course also definitely determine the exact amount of additional deoxidizer to add when we desire a given surplus of deoxidizer in the copper as desired for forming certain alloys. The exact amount of deoxidizer required to be added after this end point is reached is determined by testing. If after adding some deoxidizer it is insufficient in amount a bar cast from this metal will swell on freezing and will be unsound. If more deoxidizer is added than is required to deoxidize the copper the electrical conductivity would be under 99.5 percent. Therefore by observing the behavior of the metal on freezing and making the conductivity test the amount of deoxidizer required will be readily determined. These tests can be made for each deoxidizer it is desired to use, and after once determined for each deoxidizer can be depended upon to give uniform results. We have found that our end point is very definite and by introducing definite amounts of deoxidizer after the end point was reached our metal invariably met the conductivity and hydrogen tests. Therefore when this definite end point is reached we add the deoxidizer. If a metallic deoxidizer is used, such for example as aluminum, this may be added either as metallic aluminum in small pieces, or, in order to secure very fine control of the aluminum content, it may be added in the form of a copper aluminum alloy. Such alloy may contain for example 75 percent copper, and 25 percent aluminum, or any other known proportion may be used without affecting the principle of operation. It is also possible to use other metals than aluminum as the deoxidizers, such for example as lithium, manganese, calcium, or any other suitable metallic or non-metallic deoxidizer such as boron, phosphorus, and silicon, or such deoxidizers as calcium-boride, metallic phosphides metallic silicides, or other suitable deoxidizers as pointed out in the procedures above described. If sufficient of the deoxidizer is used to provide a surplus in the copper the deoxidizer chosen will depend on the alloy which it is desired to produce as the final product.

We are not confined of course to the use of a single deoxidizer as we may use combinations of different deoxidizers or we may partially deoxidize with one deoxidizer and complete the deoxidation with another deoxidizer. Thus for example we may partially deoxidize the copper with aluminum and then complete the deoxidation by the addition of manganese, preferably in the form of an alloy of copper and manganese as this will permit a more delicate regulation or adjustment of the manganese content in the copper. The other alloying element or elements may then be added to complete the alloy desired and the molten metal poured into suitable molds and worked and used for the purpose intended.

As a definite example of this method and operation 645 pounds of N. E. C. ingot copper (comprising approximately 99.9 percent pure copper) were melted under a heavy layer of charcoal in a high frequency electric furnace. The charcoal was used very freely as the copper was melted down, no attempt being made to use the charcoal sparingly. This melting operation usually requires about 1 hour and 25 minutes, although, of course, variations from this time are to be expected.

When the copper was melted and the proper heat attained, which we estimate to be in the neighborhood of 1200° C., the charcoal was completely skimmed off. The current may then again be applied, and the application of the current agitates the copper, and in the absence of the cover probably most of the contained gases are driven off or removed, or at least the greater proportion of the easily oxidizable gases are oxidized out. Also some oxidation of the copper takes place as the copper is exposed to the air.

This will oxidize the copper to a degree to give an oxygen content considerably greater than the minute amounts which may already be in the copper but it is never more than 0.090 percent and generally very much less than this, probably less than 0.025 percent. From the time the charcoal is removed until the current is again shut off there is a time interval of only a few minutes. During this time the metal may also, if desired, be stirred with a graphite or other suitable rod. At the end of this period the copper is somewhat active and has the appearance of boiling. After this stirring and agitating period is over some of the old or partially burned charcoal, which had previously been removed, was placed on the copper and the copper stirred rather vigorously with a graphite rod to stir in this charcoal. The partially burned or calcined charcoal is preferred as it permits more definite and delicate control of the operation. After stirring in this charcoal for a minute or two the current may again be placed on the furnace and allowed to run for a short time. The copper is then inspected very carefully both in the middle of its top surface and around its edges next to the container to see if it is quiet or still agitated, or that is, has a boiling appearance. If the metal is not quiet this indicates that the end point has not been reached, and more charcoal is stirred in and the current placed on the furnace for a short time. The metal is then again inspected and if not quiet these operations are continued until the metal is quiet both around the sides of the top surface and in the center. This is a very definite end point and indicates that the deoxidation by means of charcoal has been carried to a definite point, and therefore this end point is very fine and positive and indicates that the copper has been brought to a condition of definite oxygen content, which is to the best of our knowledge less than 0.015 percent. This end point therefore gives us a definite and positive condition of the copper from which the the exact amount of deoxidizer required to completely deoxidize the copper may be determined. This end point also indicates the proper time for adding this deoxidizer.

If the copper was melted under oxidizing conditions, or that is, without the cover, it is treated with charcoal and then the greater proportion of the gases allowed to escape before the partially burned or calcined charcoal is stirred into the metal. As the charcoal is stirred into the metal it may cause a boiling action due to the escape of the gases formed by combining of the carbon of the charcoal with the oxygen of the copper. The charcoal is stirred in until the boiling action ceases and the metal becomes quiet, that is, until there is no more boiling action. This also gives the definite end point of definite oxygen content from which the final deoxidizer may be added as above described. Also, as indicated above, after the proper and desired amount of the final deoxidizer has been added the desired amount or amounts of one or more alloying elements may be added to the copper to produce the desired alloy the same as in the procedures described above.

We have discovered and worked out still another procedure which may be used for producing our improved alloy with deoxidized copper. It is a modified procedure employing certain treatments to bring the copper to a definite end point or condition where it has a definite oxygen content, and we therefore can determine the exact amount of the deoxidizer which should be added to the copper before adding the final alloying element or elements to secure the desired results and produce a uniform product having the characteristics desired. With this method we can determine the exact amount of the deoxidizer which should be added to deoxidize the copper and still have a minimum amount of the deoxidizer remain in the copper, and we therefore can also accurately determine how much additional deoxidizer to add to secure a desired amount of residual deoxidizer in the copper for any particular alloy we wish to produce.

In carrying out our method the copper may first be melted in any suitable furnace, but we prefer the electric furnace known in the trade as an induction furnace as the operations can more easily be controlled. However, we are not limited to the use of such furnace but may use other types of furnaces for melting the copper, such for example as what is known in the trade as the high frequency furnace. The latter or high frequency furnace is preferred for use in our procedure above described where an end point is used which is indicated by the metal becoming quiet as the result of stirring in charcoal after boiling when exposed to the air.

In our present method or procedure the copper is preferably melted under reducing conditions and preferably under a cover of charcoal, but other covers may be used. We prefer the charcoal as this gives us less work and more definite control in another part of the method. When the copper is melted and a suitable temperature attained, preferably a temperature suitable for pouring, which is in the neighborhood of 1200° C., the charcoal or other cover is removed. The copper at this point contains gas, and if oxygen is present it is only in minute amounts. The copper may be melted without the cover but in this case after melting it should be subjected to reducing conditions until it is substantially deoxidized. After the charcoal is removed we may place electric current on the furnace and stir with a graphite or other suitable rod and expose the copper to the air in this way. This stirring action while exposed to the air removes most of the gas from the copper, although it is not necessary to remove all of it. As the copper was melted under reducing conditions, although it may contain gases the oxygen content, if any, is very small. It will therefore be evident that if we expose the copper to the air after removing the charcoal cover for a given definite time this exposure and stirring action removes gas from the copper or allows it to escape, probably most of the gas in the copper, and the copper is brought to a definite oxygen content or end point by partial oxidation of the copper, and if successive charges of approximately the same weight of copper are exposed for the same length of time they will be brought to this same end point or condition. During this time the copper may or may not be stirred continuously, and the current may or may not be on the furnace all of the time. At the end of this definite period of time as described the old or partially burned charcoal used as a cover in melting the copper down, or other carbon in a form having a similar composition to partially burned or calcined charcoal, is placed on the copper and is then stirred into the copper for a definite length of time. The current may be on for all or for a part only of this last stirring period or operation. At the end of this last stirring period we add the final deoxidizer

the same as in the procedures above described to deoxidize the copper. We may use a metal for deoxidizing the copper, such for example as aluminum, manganese, calcium, lithium, and other deoxidizers, or we may use non-metallic deoxidizers, such for example as boron, phosphorus, silicon, or we may use metallic borides, metallic silicides, metallic phosphides, or we may use two or more of these deoxidizers depending on the final alloy which it is desired to produce. At the end of this second definite stirring period the copper has a definite oxygen content and the amount of deoxidizer required to completely deoxidize the copper or to produce a finished metal having given characteristics can readily be determined. If it is desired that only a minimum of the deoxidizer remain in the copper only sufficient of the deoxidizer is added to completely deoxidize the copper, while if it is desired that a surplus or a residual amount of the deoxidizer remain in the copper, such for example as in using phosphorus preparatory to making a phosphor-bronze, then the amount of additional deoxidizer that may be added to produce this surplus may be accurately determined. The end point at the end of the definite stirring time with charcoal gives us a definite condition from which the exact amount of deoxidizer required, depending upon the characteristics desired in the finished alloy, can be definitely determined, although it is not necessary to know what the oxygen content is at this point.

The exact amount of deoxidizer to be added after this end point is reached or at the end of this definite period is determined by testing. If after adding some deoxidizer it is insufficient in amount a bar cast from this metal will swell on freezing and will be unsound. If more than the necessary amount of deoxidizer is added to completely deoxidize the copper the electrical conductivity will be below 99.5 per cent at 20° C. in terms of the International Annealed Copper Standard. Therefore upon observing the behavior of the metal on freezing and making the conductivity test the amount of deoxidizer required can be readily determined. These tests can be made for each deoxidizer it is desired to use, and after once determined for each deoxidizer and for the two definite periods of exposure to the air and stirring in of the charcoal, can be depended upon to give uniform results if the same conditions are observed in treating subsequent charges of copper. We find that this end point is very definite and by introducing definite amounts of deoxidizer after the end point is reached for these conditions our finished metal invariably has the same characteristics.

As in the other procedures described the final deoxidizer, such for example as metallic aluminum, may be added either as a metallic aluminum in small pieces or in order to secure very fine control of the aluminum it may be added in the form of a copper-aluminum alloy. Whatever the deoxidizer or deoxidizers used they may be the same and added in the same manner as described in connection with the other procedures above noted and then one or more alloying elements may be added to the deoxidized copper to produce the final alloys as above described.

As a definite example of this method 645 pounds of N. E. C. ingot copper were melted under a heavy layer of charcoal in an electric induction furnace. The charcoal was used very freely as the copper was melted down no attempt being made to use the charcoal sparingly. This melting operation usually requires about 1 hour and 25 minutes, although, of course, variations of this time are to be expected.

When the copper was melted and the proper heat attained, which we estimate to be in the neighborhood of 1200° C., the charcoal was completely skimmed off. After skimming the charcoal the current was applied, and during this time the copper may be stirred with a graphite rod or other suitable rod. The application of the current agitates the copper considerably which is also assisted by stirring with the rod, and in the absence of the cover probably most of the contained gases are driven off or removed, and as the copper is exposed to the air some oxidation of the copper takes place. In the present example this exposure to the air was for a definite period of time, in the present case three minutes, although this time may be varied as will be presently indicated. During this time the copper may or may not be stirred continuously and the current may or may not be on the furnace all of the time. This exposure to the air will oxidize the copper to a degree to give an oxygen content greater than the minute amounts which may already be in the copper. After exposure for the above length of time the oxygen content was less than 0.025 percent.

At the end of this three minute period the partially burned charcoal used in melting the copper down was again placed on the copper and this charcoal was stirred into the metal for a definite period, in the present example for two minutes. No attempt was made to weigh or use a predetermined amount of carbon in the form of partially burned charcoal. We merely shoveled partially burned charcoal back on to the copper regardless of the amount of charcoal skimmed off before the stirring of the copper in contact with air. The electric current may be on the furnace for all or a part only of this last stirring period as desired. This brings the metal to a definite end point or oxygen content and at the end of this last stirring period we added the final deoxidizer. As above noted we may use one metal for deoxidizing the copper, such for example as aluminum, manganese, or calcium, or we may use other deoxidizers as above described, or we may use two or more deoxidizers the same as in the procedures above described.

In the specific example above described we found that after stirring the copper in the presence of air our oxygen content was less than 0.025 percent and that after the period of stirring the charcoal into the copper the oxygen content was less than 0.01 percent. In other words when the final deoxidizer was added there was less than 0.01 percent oxygen present in the copper. It will be evident that these amounts of oxygen in the copper at the ends of the periods of the exposure to air and the stirring in of charcoal will vary depending on the length of time of the periods, which may vary considerably as we are not limited to the two and three minute periods given in the specific example described. It is preferred that the maximum content of oxygen be not over approximately 0.05 percent and probably would never go over 0.09 percent. Ordinarily it is not over 0.03 percent. Thus the lengths of these periods may be varied without affecting the final results, and for example we might stir the copper for five, six or ten minutes when the copper is exposed to the air and then stir with charcoal for a given suitable length of time, which in this case would preferably be

more than the two minutes mentioned. We wish to point out our method involves the stirring of the copper when exposed to the air for a definite length of time and then stirring in the presence of the charcoal for a definite length of time, all before adding the final deoxidizer. By following this method a definite oxygen content is attained and the final deoxidizer can be controlled very nicely. Thus if it is determined that with stirring for a given length of time in contact with air and stirring in contact with charcoal for a given definite time prior to adding the given amount of deoxidizer secures the desired results, if successive charges of copper are stirred for the same lengths of time in contact with air and in contact with charcoal and the same amount of the deoxidizer added, and then one or more alloying elements are added depending upon the alloy to be produced, metal will be secured having the same characteristics as the first charge. Although for certain results we prefer to start with copper of a purity of 99.5 percent or better, it is not required that we use high purity copper.

Thus with the above described methods and procedures we have found we can produce in commercial quantities alloys of uniform characteristics and we can definitely produce alloys having these characteristics and repeat as often as desired. This is possible because by these methods before adding the final deoxidizer the melted copper is brought to a definite point having a definite condition, or that is a definite oxygen content, and this condition is the same for separate charges of copper which are treated in the same manner, and we have found that by these methods improved alloys may be readily produced in large quantities and with uniformity in the mill.

We wish it distinctly understood that while describing the different procedures above of making alloys we have referred to melting copper, permitting the gases to escape, deoxidizing, and so forth, we are not limited to the use of new copper or copper alone. We have used the term copper in describing the charge for simplicity and convenience, and although the charge may be entirely of new copper, ordinarily it contains some scrap and may even be all scrap. In the manufacture and use of alloys there is always some scrap which must be used in subsequent charges. Thus for example in making phosphor bronze as described above, we use a certain percent of phosphor bronze scrap and melt this scrap down with the copper. After the gases have been allowed to escape by one of the methods described we then treat the metal by any of the procedures above outlined. In other words we have used the term copper in the specification and claims in a generic sense as describing a charge which may be all copper, or copper plus some scrap, or even all scrap if desired. The final steps would be to deoxidize the metal and add an alloying element or elements as described.

Having thus set forth the nature of our invention, what we claim is:

1. A method of making copper alloys comprising melting copper under reducing conditions, exposing the melted copper to air to permit escape of gases and to partially oxidize the copper but to an oxygen content less than 0.090 percent, adding non-carbonaceous deoxidizer which does not form a reaction product which is gaseous at room temperature upon combining with the oxygen of the copper and sufficient in amount to deoxidize the copper, and then adding one or more alloying elements.

2. A method of making copper alloys comprising melting copper under reducing conditions, exposing the melted copper to the air to permit easily oxidizable gases to escape, adding deoxidizer which does not form a reaction product which is gaseous at room temperature upon combining with the oxygen of the copper and sufficient in amount to deoxidize the copper, and then adding one or more alloying elements.

3. A method of making copper alloys comprising melting the copper under charcoal, removing the charcoal and exposing the melted copper to the air to permit easily oxidizable gases to escape and partial oxidation of the copper not in excess of 0.090 percent oxygen, adding deoxidizer which does not form a reaction product which is gaseous at room temperature upon combining with the oxygen of the copper and sufficient in amount to deoxidize the copper, and then adding one or more alloying elements.

4. A method of making copper alloys comprising melting copper under reducing conditions, exposing the melted copper to the air to permit easily oxidizable gases to escape, adding deoxidizer which does not form a reaction product which is gaseous at room temperature upon combining with the oxygen of the copper and in excess of the amount required to deoxidize the copper, and then adding one or more alloying elements.

5. A method of making copper alloys comprising melting copper under reducing conditions, agitating the copper under oxidizing conditions until it shows a boiling action, stirring carbonaceous material similar in composition to partly burned or calcined charcoal into the copper until the metal becomes quiet, adding deoxidizer which does not form a reaction product which is gaseous at room temperature upon combining with the oxygen of the copper and at least sufficient in amount to deoxidize the copper, and then adding one or more allowing elements.

6. A method of making copper alloys comprising melting copper under reducing conditions, agitating the melted copper under oxidizing conditions until it shows a boiling action, stirring partly burned or calcined charcoal into the metal until it becomes quiet, then adding deoxidizer which does not form a reaction product which is gaseous at room temperature upon combining with the oxygen of the copper and at least sufficient in amount to deoxidize the copper, and then adding one or more alloying elements.

7. A method of making copper alloys comprising melting the copper and exposing to reducing conditions for a sufficient time to substantially deoxide the copper, exposing the melted copper to the air until the metal becomes active by escape of gases, stirring carbonaceous material similar in composition to partly burned or calcined charcoal into the copper until it becomes quiet, adding deoxidizer which does not form a reaction product which is gaseous at room temperature upon combining with the oxygen of the copper and at least sufficient in amount to deoxidize the copper, and then adding one or more alloying elements.

8. A method of making copper alloys comprising melting copper under charcoal, exposing the metal to the air until the metal becomes active by escape of gases, stirring partly burned or calcined charcoal into the active metal until it becomes quiet, adding deoxidizer which does not

form a reaction product which is gaseous at room temperature upon combining with the oxygen of the copper and at least sufficient in amount to deoxidize the copper, and adding one or more alloying elements.

9. A method of making deoxidized copper comprising melting the copper and treating with carbonaceous material to bring it to an oxygen content of less than 0.090%, then exposing to the air to permit gases to escape and partial oxidation of the copper not in excess of 0.090% oxygen, and adding deoxidizer which does not form a reaction product which is gaseous at room temperature upon combining with the oxygen of the copper and sufficient in amount to deoxidize the copper.

10. A method of making deoxidized copper comprising melting the copper and subjecting to reducing conditions until it is substantially deoxidized, exposing the copper to the air to permit gases to escape and partial oxidation of the copper not in excess of 0.090% oxygen, and adding deoxidizer which does not form a reaction product which is gaseous at room temperature upon combining with the oxygen of the copper and sufficient in amount to deoxidize the copper.

11. A method of making deoxidized copper comprising melting copper under reducing conditions, exposing the melted copper to air to permit escape of gases and to partially oxidize the copper but to an oxygen content less than 0.090%, and adding non-carbonaceous deoxidizer which does not form a reaction product which is gaseous at room temperature upon combining with the oxygen of the copper and sufficient in amount to produce a residual amount of the deoxidizer in the copper.

12. A method of making deoxidized copper comprising melting copper and subjecting to reducing conditions, exposing the melted copper to air to permit gases to escape and oxidizing to a content of less than 0.090% oxygen, then adding deoxidizer which does not form a reaction product which is gaseous at room temperature upon combining with the oxygen of the copper and sufficient in amount to deoxidize the copper.

13. A method of making deoxidized copper comprising melting the copper and subjecting to reducing conditions for a sufficient time to bring it to an oxygen content of less than 0.09%, exposing the melted copper to the air to permit gases to escape and oxidation to an oxygen content of not more than 0.09%, and adding metallic deoxidizer in excess of the amount required to deoxidize the copper.

14. A method of making deoxidized copper comprising melting the copper under reducing conditions, exposing the melted copper to the air to permit easily oxidizable gases to escape, and adding metallic deoxidizer in excess of the amount required to deoxidize the copper.

15. A method of deoxidizing copper comprising melting copper under reducing conditions and exposing the melted copper to air to permit easily oxidizable gases to escape and a partial oxidation of the copper not in excess of 0.090% oxygen, and adding metallic deoxidizer in excess of the amount required to deoxidize the copper.

16. A method of deoxidizing copper comprising melting the copper under charcoal, removing the charcoal and exposing the melted copper to the air to permit easily oxidizable gases to escape and partial oxidation of the copper not in excess of 0.090% oxygen, and adding deoxidizer which does not form a reaction product which is gaseous at room temperature upon combining with the oxygen of the copper and sufficient in amount to deoxidize the copper.

17. A method of deoxidizing copper comprising melting the copper under charcoal, removing the charcoal and exposing the melted copper to the air to permit easily oxidizable gases to escape and partial oxidation of the copper not in excess of 0.090% oxygen, and adding metallic deoxidizer in excess of the amount required to deoxidize the copper.

18. A method of making deoxidized copper comprising melting copper under reducing conditions, agitating the melted copper under oxidizing conditions until it shows a boiling action, stirring carbonaceous material similar in composition to partly burned or calcined charcoal into the copper until the metal becomes quiet, and adding deoxidizer which does not form a reaction product which is gaseous at room temperature upon combining with the oxygen of the copper and sufficient in amount to deoxidize the copper.

19. A method of making deoxidized copper comprising melting the copper under reducing conditions, exposing the melted copper to the air and agitating until it shows a boiling action, treating with carbonaceous material similar in composition to partly burned or calcined charcoal until the metal becomes quiet, and then deoxidizing by adding non-carbonaceous deoxidizer which does not form a reaction product which is gaseous at room temperature upon combining with the oxygen of the copper.

20. A method of making deoxidized copper comprising melting copper under reducing conditions, agitating the melted copper under oxidizing conditions until it shows a boiling action, stirring partly burned or calcined charcoal into the metal until it becomes quiet, and then adding sufficient metallic deoxidizer to prevent swelling of the metal on cooling.

21. A method of making deoxidized copper comprising melting the copper under charcoal, exposing the copper to the air and at the same time agitating it until it shows a boiling action, then stirring partly burned or calcined charcoal into the metal until it becomes quiet, and adding sufficient metallic deoxidizer to prevent swelling of the metal on cooling.

22. A method of making deoxidized copper comprising melting the copper and bringing it to a substantially deoxidized condition, oxidizing the copper sufficiently to cause a boiling action in the copper, stirring carbonaceous material similar in composition to partially burned or calcined charcoal into the copper until it becomes quiet, and then adding deoxidizer which does not form a reaction product which is gaseous at room temperature upon combining with the oxygen of the copper and sufficient in amount to deoxidize the copper.

23. A method of making deoxidized copper comprising stirring a carbonaceous material similar in composition to partly burned or calcined charcoal into partially oxidized melted copper until the copper becomes quiet, and then deoxidizing the copper with a metallic reducing agent.

24. A method of making deoxidized copper comprising melting copper in a suitable container and exposing it to the atmosphere until the metal becomes active by escape of gases, stirring partly burned or calcined charcoal into the metal until it becomes quiet, and then adding deox-

idizer which does not form a reaction product which is gaseous at room temperature upon combining with the oxygen of the copper and sufficient in amount to deoxidize the copper.

25. A method of making deoxidized copper comprising melting the copper under charcoal, exposing the metal to the air until the metal becomes active by escape of gases, stirring partly burned or calcined charcoal into the active metal until it becomes quiet, and then adding sufficient metallic deoxidizer to prevent swelling of the copper on cooling.

26. A method of making deoxidized copper comprising melting the copper and exposing to reducing conditions for a sufficient time to substantially deoxidize the copper, exposing the melted copper to the air until the metal becomes active by escape of gases, stirring carbonaceous material similar in composition to partly burned or calcined charcoal into the copper until it becomes quiet, and then deoxidizing the copper by adding a sufficient amount of non-carbonaceous deoxidizer which does not form a reaction product which is gaseous at room temperature upon combining with the oxygen of the copper.

27. A method of making deoxidized copper comprising melting the copper, agitating the melted copper while exposed to the air to permit escape of gases, stirring partially burned or calcined charcoal into the copper until signs of activity in the copper have disappeared, and then adding sufficient metallic deoxidizer to prevent swelling of the metal on cooling.

28. A method of making deoxidized copper comprising melting the copper, agitating the copper while exposed to the air to permit escape of gases, stirring partially burned or calcined charcoal into the metal until signs of activity in the metal have disappeared, adding sufficient amount of metallic deoxidizer other than manganese to partially deoxidize the copper, and adding a sufficient amount of manganese to prevent swelling of the metal on cooling.

29. A method of making deoxidized copper comprising melting copper under reducing conditions, agitating the melted copper under oxidizing conditions until it shows a boiling action, stirring carbonaceous material similar in composition to partly burned or calcined charcoal into the copper until the metal becomes quiet, adding sufficient of metallic deoxidizer other than manganese to partially deoxidize the copper, and then adding sufficient manganese to prevent swelling of the metal on cooling.

30. A method of making deoxidized copper comprising melting the copper under charcoal, exposing the metal to the air until the metal becomes active by escape of gases, stirring partly burned or calcined charcoal into the active metal until it becomes quiet, adding sufficient of metallic deoxizer other than manganese to partially deoxidize the copper, and then adding a sufficient amount of manganese to completely deoxidize the copper.

31. A method of making deoxidized copper comprising stirring carbonaceous material similar in composition to partly burned or calcined charcoal into partially oxidized melted copper until the copper becomes quiet, and then adding deoxidizer which does not form a reaction product which is gaseous at room temperature upon combining with the oxygen of the copper and sufficient in amount to deoxidize the copper.

32. A method of making deoxidized copper comprising melting the copper, exposing the melted copper to the air to permit escape of gases, stirring partially burned or calcined charcoal into the copper until signs of activity in the copper have disappeared, and then adding deoxidizer which does not form a reaction product which is gaseous at room temperature upon combining with the oxygen of the copper and sufficient in amount to deoxidize the copper.

33. A method of making deoxidized copper comprising melting the copper under reducing conditions, exposing the copper to the air to permit gases to escape, stirring carbonaceous material similar in composition to partly burned or calcined charcoal into the copper for a period of time sufficient to reduce the oxygen content of the melt to a definite amount, and then adding deoxidizer which does not form a reaction product which is gaseous at room temperature upon combining with the oxygen of the copper and sufficient in amount to deoxidize the copper.

34. A method of making deoxidized copper comprising melting the copper under reducing conditions, agitating the melted copper under oxidizing conditions to permit gases to escape, stirring partially burned or calcined charcoal into the copper for a period of time sufficient to reduce the oxygen content of the melt to a definite amount, and then adding deoxidizer which does not form a reaction product which is gaseous at room temperature upon combining with the oxygen of the copper and sufficient in amount to deoxidize the copper.

35. In the art of making deoxidized copper the method comprising melting the copper under reducing conditions, exposing the copper to the air and agitating to permit gases to escape, and stirring partially burned or calcined charcoal into the copper for a period of time sufficient to reduce the oxygen content to a definite amount.

36. In the art of making deoxidized copper, the method which comprises melting copper under reducing conditions, agitating the copper under oxidizing conditions until it shows a boiling action, and deoxidizing the copper by stirring in partly burned or calcined charcoal.

37. In the art of making deoxidized copper, the method which comprises melting copper under charcoal, exposing the copper to the air and agitating to permit gases to escape, and stirring partly burned or calcined charcoal into the copper to deoxidize it.

38. In the art of making deoxidized copper, the method which comprises melting copper under reducing conditions, exposing the melted copper to oxidizing conditions and agitating to permit gases to escape, and then stirring carbonaceous material similar in composition to partly burned or calcined charcoal into the copper to deoxidize it.

39. A method of making deoxidized copper comprising melting the copper and bringing it to a substantially deoxidized condition, exposing the melted copper to the air until the metal becomes active by escape of gases, stirring carbonaceous material similar in composition to partly burned or calcined charcoal into the metal for a period of time sufficient to reduce the oxygen content of the melt to a definite amount, and then adding deoxidizer which does not form a gaseous reaction product upon combining with the oxygen of the copper which will remain in the metal on solidification thereof and sufficient in amount to deoxidize the copper.

40. A method of making deoxidized copper comprising melting the copper under charcoal, ex-

posing the copper to the air and agitating to permit gases to escape, stirring partly burned or calcined charcoal into the metal for a period of time sufficient to reduce the oxygen content of the melt to a definite amount, and then adding deoxidizer which does not form a gaseous reaction product upon combining with the oxygen of the copper which will remain in the copper on solidification thereof and sufficient in amount to deoxidize the copper.

41. A method of making copper alloys comprising melting copper and treating with carbonaceous material to bring it to an oxygen content of less than 0.090 percent, then exposing to the air to permit gases to escape and partial oxidation of the copper not in excess of 0.090 percent oxygen, adding deoxidizer which does not form a reaction product which is gaseous at room temperature upon combining with the oxygen of the copper and sufficient in amount to deoxidize the copper, and then adding the alloy metal or metals.

42. A method of making copper alloys comprising melting the copper and subjecting to reducing conditions until it is substantially deoxidized, exposing the copper to the air to permit gases to escape and partial oxidization of the copper not in excess of 0.090% oxygen, adding deoxidizer which does not form a reaction product which is gaseous at room temperature upon combining with the oxygen of the copper and sufficient in amount to deoxidize the copper, and then adding an alloying metal or metals.

43. A method of making copper alloys comprising melting copper and subjecting to reducing conditions to bring it to an oxygen content of less than 0.090%, exposing the melted copper to air to permit gases to escape and oxidizing to a content of less than 0.090% oxygen, adding deoxidizer which does not form a reaction product which is gaseous at room temperature upon combining with the oxygen of the copper and sufficient in amount to deoxidize the copper, and then adding one or more alloying elements.

44. A method of making copper alloys comprising melting the copper and subjecting to reducing conditions for a sufficient time to bring it to an oxygen content of less than 0.09%, exposing the melted copper to the air to permit gases to escape and oxidation to an oxygen content of not more than 0.09%, adding metallic deoxidizer in excess of the amount required to deoxidize the copper, and then adding one or more alloying elements.

45. A method of making copper alloys comprising melting the copper under reducing conditions, exposing the melted copper to the air to permit easily oxidizable gases to escape, adding metallic deoxidizer in excess of the amount required to deoxidize the copper, and then adding one or more alloying elements.

46. A method of making copper alloys comprising melting the copper under reducing conditions, exposing the copper to the air to permit gases to escape, stirring carbonaceous material similar in composition to partly burned or calcined charcoal into the copper for a period of time sufficient to reduce the oxygen content of the melt to a definite amount, then adding deoxidizer which does not form a reaction product which is gaseous at room temperature upon combining with the oxygen of the copper and sufficient in amount to deoxidize the copper, and then adding one or more alloying elements.

47. A method of making copper alloys comprising melting copper under reducing conditions, agitating the melted copper under oxidizing conditions until it shows a boiling action, stirring carbonaceous material similar in composition to partly burned or calcined charcoal into the copper until the metal becomes quiet, adding deoxidizer which does not form a reaction product which is gaseous at room temperature upon combining with the oxygen of the copper and sufficient in amount to deoxidize the copper, and then adding one or more alloying elements.

48. A method of making copper alloys comprising melting the copper under reducing conditions, exposing the melted copper to the air until it shows a boiling action, treating with carbonaceous material similar in composition to partly burned or calcined charcoal until the metal becomes quiet, then deoxidizing by adding non-carbonaceous deoxidizer which does not form a reaction product which is gaseous at room temperature upon combining with the oxygen of the copper, and then adding one or more alloying elements.

49. A method of making copper alloys comprising melting the copper under charcoal, exposing the copper to the air until it shows a boiling action, then stirring partly burned or calcined charcoal into the metal until it becomes quiet, adding sufficient metallic deoxidizer to prevent swelling of the metal on cooling, and then adding one or more alloying elements.

50. In the art of making deoxidized copper the method comprising melting the copper and treating with carbonaceous material to bring it to an oxygen content of less than 0.090%, exposing the copper to the air to permit gases to escape, and deoxidizing the copper by stirring in partly burned or calcined charcoal.

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