

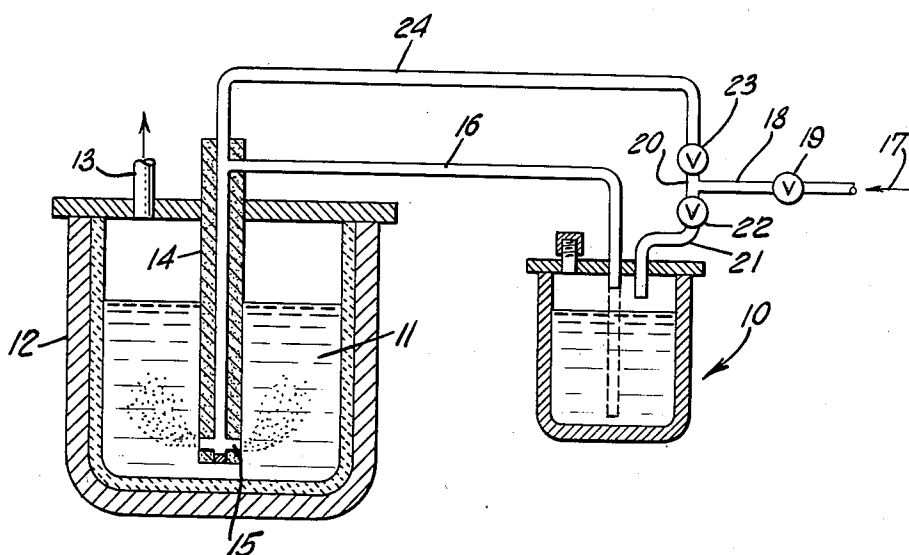
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METHOD OF PRODUCING COPPER-SULFUR ALLOYS

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1

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METHOD OF PRODUCING COPPER-SULFUR ALLOYS

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This invention relates to a new and novel method of preparing copper-sulfur alloys and relates more particularly to a method of producing copper-sulfur alloys that are not susceptible to hydrogen disease.

An object of our invention is to provide a method of alloying copper directly with sulfur using reactants and reaction conditions which eliminate the condition in the resulting alloy known as hydrogen disease.

Another object of our invention is to provide a method of alloying copper with sulfur wherein the utilization of sulfur is made more efficient and economical and improved copper-sulfur alloys result.

Alloys of copper and sulfur commonly used for alloying purposes and referred to as master alloys are conventionally made by mixing copper powder with sulfur and igniting the mixture in the presence of air to form the desired composition, Cu_2S . This relatively simple process suffers from the drawback that the reaction is difficult to control and appreciable sulfur losses generally occur. Then too, oxide formation cannot be avoided in the course of the reaction, the result being that the copper-sulfur alloy product inevitably contains a rather substantial amount of oxidic contaminant. This oxidic material imparts susceptibility to hydrogen disease in varying degrees to other metals or alloys in which such material is incorporated as an alloying ingredient.

In producing copper-sulfur alloys of a high degree of purity, initially oxygen-free copper has heretofore been used in making the alloy, the procedure generally consisting of adding the aforesaid master alloy in pieces to molten copper maintained in a protective atmosphere. Notwithstanding the precautions taken to preclude the occurrence of oxidation during the alloying procedure, the condition known as hydrogen disease is encountered from time to time even with such specially prepared material. This is attributable to the use of a master alloy containing oxidic contaminants as previously mentioned. In addition to this difficulty, the piecemeal addition of the master alloy generally results in poor mixing and also involves appreciable losses of sulfur so that precise control of the desired composition is difficult to maintain.

We have now discovered an improved method whereby sulfur is alloyed directly with oxygen-free copper thereby dispensing with the need for using a master alloy in making copper-sulfur alloys of any desired sulfur content. In accordance with the invention, the sulfur in molten form or as a vapor is pumped together with a neutral or reducing gas into a bath of molten copper, said copper being essentially oxygen-free. The introduction of the protectant gas together with sulfur at a position near the bottom of the molten copper bath agitates the molten metal thereby effecting thorough mixing of the ingredients. The protectant gas is also utilized to enable transfer of the sulfur in fluid form into the body of molten copper and further provides an effective means of controlling the sulfur addition rate as desired. Additionally, the protectant gas provides a protective atmosphere in the entire system whereby oxidation of the reactants or the resulting product does not occur during the alloying operation. This method of making copper-sulfur alloy has been found to be advantageous not only with respect to more efficient sulfur utilization in the alloying operation and in the pro-

2

duction of alloys of improved homogeneity but, with the use of oxygen-free copper, the resulting copper-sulfur product has been found to be entirely free of hydrogen disease. The method of this invention can be used for the making of copper-sulfur alloys of any desired sulfur composition.

In the drawing which represents simplified apparatus suitable for carrying out the alloying method of the present invention, there is shown a covered crucible 10 in which the sulfur is heated preferably by the use of steam to its liquefaction temperature or higher to vaporize the same if desired. The cover of said crucible is provided with an opening through which sulfur may be added to the crucible, said opening also serving as a vent for the crucible for purging the same with non-reactive gas while melting the sulfur in preparation for alloying. Otherwise this opening remains closed as shown during the actual alloying operation. The copper melt 11 to which the sulfur addition is to be made is contained in covered crucible 12 equipped with a vent 13 and with any suitable heating means (not shown). A hollow addition tube 14 preferably made of refractory material such as silicon carbide, graphite or the like is provided with perforations 15 for discharge of sulfur and diluent gas therethrough near the bottom end of said tube and suitably positioned in melt 11 in crucible 12 so that said perforations shown in the illustrated embodiment in the sides of the addition tube are as close to the bottom of the copper melt as possible. An addition line 16 consisting suitably of metal tubing equipped with heating means (not shown) provides a conduit for the passage of molten sulfur or sulfur vapor from crucible 10 to the molten copper in crucible 12, one end of said addition line being sealably connected with the longitudinal bore in the refractory tube near the upper extremity thereof and the other end terminating above the molten sulfur level in crucible 10. If it is desired to utilize liquid sulfur instead of sulfur vapor in the alloying process, the end of addition line 16 terminating in crucible 10 above the liquid sulfur level is projected downwardly toward the bottom of said crucible as shown by the broken line extension thereof which is immersed in the molten sulfur.

A source of high pressure gas indicated at 17 consisting of either an inert gas such as argon, nitrogen, etc. or a reducing gas other than hydrogen such as carbon monoxide, producer gas or mixtures thereof is made available for use in the system as a diluent for the sulfur during the sulfur addition step and also for providing the required protectant atmosphere. The gas flow is appropriately regulated in gas duct 18 by means of pressure regulating valve 19. Gas duct 18 provided with an arrangement such as the T-connection shown at 20 enables passage of the gas to either or both the crucible 10 through gas line 21 of said gas duct by way of valve 22 and also to the molten copper contained in crucible 11 by passage of the gas through valve 23 and thence through the gas line 24 of said gas duct shown in the drawing as being sealably connected to the longitudinal bore of refractory addition tube 14. The valves 22 and 23 may be independently operated along with valve 19 to provide the necessary gas flow to either or both of the crucibles as required in the course of making the alloy as will be hereinafter described.

In operation, the oxygen-free copper may be charged either in molten form to crucible 12 or it may be melted therein in which event the protective atmosphere therefor may be provided, if desired, by opening valve 23 to permit the flow of sufficient protectant gas through line 24 and out of perforations 15 near the bottom of the addition tube to overcome the hydrostatic head in said crucible. The sulfur is rendered molten in crucible 10 after appropriately purging the unit with protectant gas admitted

by opening valve 22 after which said valve and the opening in the cover of said crucible is closed.

When the copper is ready for alloying, a known quantity of sulfur in crucible 10 now in molten form is gradually passed into the copper by opening valve 22 to the extent required for the alloying to occur at a satisfactory rate as will be evidenced by the intensity of the flame emitted at vent 13. The necessary adjustment of valves 22 and 23 to effect the desired degree of dilution of the sulfur whereby the sulfur may be properly taken up by the copper involves a reduction to some degree of the amount of gas flow through line 24 upon gradually opening valve 22 to cause passage of sulfur through addition line 16. The adjustment of said valves conducive to satisfactory operation of the alloying process is quickly ascertainable by those skilled in the art with little or no difficulty after preliminary adjustments thereof on a trial and error basis. It is important, however, that a positive pressure be maintained within the addition tube at all times to preclude the backing up of molten metal or alloy therein. It is also important that the sulfur be sufficiently diluted with the protective gas not only to provide the necessary protective atmosphere but to also enable proper control of the rate of sulfur addition to insure take-up by the copper of substantially all of the added sulfur.

When the predetermined amount of sulfur has been taken up by the copper as will be apparent by the weight loss of crucible 10, valve 22 is closed and valve 23 is adjusted accordingly to maintain the needed protective atmosphere in crucible 12 until the alloy has cooled somewhat. Before excessive cooling of the alloy occurs, however, crucible 12 is lowered or, alternatively, addition tube 14 is raised sufficiently to preclude contact of perforations 15 with the mass of alloyed material to prevent any siphoning of the molten alloy therethrough. After the alloy, still under a protective atmosphere, has been allowed to settle usually for about 15 minutes, it is then removed from the crucible and cast in accordance with conventional practices using a protective atmosphere during such casting of the material.

It will be readily apparent that the use of molten sulfur or sulfur vapor is immaterial with respect to the end result, it being noted that by the time the sulfur in addition line 16 reaches the molten copper mass it becomes vaporized anyway. The use of molten sulfur as such, however, is preferred since this method of sulfur addition utilizing the extended end of the addition line (shown by the broken line immersed in the sulfur) lends itself to simplified control of the operation with all of the diluent and protective gas required by the operation being supplied primarily through gas line 24 under such an arrangement. With the use of sulfur vapor, the gas flow through the addition tube must be controlled between lines 16 and 24 respectively which operation requires somewhat more manipulation for effective control during the alloying operation.

The method of alloying herein described provides excellent results with respect to making not only alloys containing relatively small amounts of sulfur as from 0.1 to 0.5% by weight but also copper-sulfur alloys containing much higher and practically any desired sulfur content as, for example, may be required in making master alloys of as much as 20% sulfur content. The copper-sulfur alloys made in accordance with this invention containing about 0.3% sulfur were found to be entirely free of hydrogen disease as were the alloys made with oxygen-free copper using the master alloy prepared as herein described.

The copper suitable for use in accordance with the present invention referred to herein as "oxygen-free copper" is readily recognizable by those skilled in the art as meaning a high purity copper which has been substantially freed of its oxygen content by any of the known methods employed for the purpose. Although copper

which has been produced in a reducing atmosphere such as OFHC brand copper provides excellent results, copper prepared in an inert atmosphere, in a vacuum or electrolytic copper may also be used as well as chemically deoxidized copper.

Specific embodiments of the invention are illustrated in the following examples:

Example I

Copper-sulfur alloys containing 0.3% sulfur were made utilizing direct addition of molten sulfur to oxygen-free copper with argon gas being used to control the reaction rate and to provide the protective cover over the melt. The average sulfur utilization over a series of such preparations amounted to better than 80%, the overall sulfur losses accordingly being less than 20%. A comparison series of tests again using oxygen-free copper but employing a 20% sulfur master alloy for the preparation of 0.3% sulfur alloys showed sulfur utilization to the extent of 86%, but after taking into account a previous sulfur loss of close to 20% in making the master alloy, thereby utilizing less than 70% of the added sulfur, it will be readily seen that the direct sulfur addition method is highly advantageous compared to using the master alloy for making the copper-sulfur alloys of relatively low sulfur content.

Example II

Master alloys having a 20% sulfur content and made by the direct addition of molten sulfur to oxygen-free copper using nitrogen as the protectant gas and as the diluent for the sulfur during the course of the alloying showed an overall sulfur utilization by the copper of 94% as opposed to about 80% sulfur recovery which is typical of the prior art processes wherein copper powder is mixed with sulfur and ignited to form the alloy. More important, the alloying results obtained with the use of each master alloy in the making of 0.3% sulfur content copper alloys under comparable conditions of operation in all respects excepting the use of different master alloys showed a marked improvement in respect to freedom from hydrogen disease in favor of the alloys made with the master alloy prepared in accordance with the present invention. This is attributable to the avoidance of oxidic contaminants throughout the entire method of alloying herein described.

Example III

Copper-sulfur alloy (0.3% S) made in accordance with the present invention and processed into 0.081 inch diameter wire, upon annealing in hydrogen at 850° C. for 30 minutes possessed an electrical conductivity of 98% I.A.C.S. The bend number (180° bends) for such material ranged from 10 to 14. Copper-sulfur alloy of the same sulfur content made using the master alloy prepared with oxygen-bearing copper similarly processed into 0.081 inch diameter wire and subsequently annealed in hydrogen at 850° C. for 30 minutes possessed the same electrical conductivity but the bend number therefor varied from only 1/2 to 8 showing the adverse effect of hydrogen embrittlement.

It is apparent that many differing embodiments of this invention may be made without departing from the spirit and scope thereof and it is not intended to be limited except as indicated in the appended claims.

What is claimed is:

1. In a process in which molten copper is contacted with sulfur for alloying therewith, the improvement providing a copper-sulfur alloy of reduced susceptibility to hydrogen embrittlement which comprises pumping into a molten mass of essentially oxygen-free copper protected by a cover of non-oxidizing gas a predetermined quantity of sulfur in fluid form said sulfur being in admixture with a non-oxidizing gas providing sufficient pressure to overcome the hydrostatic pressure exerted by said molten copper thereagainst, said gas further effect-

5

ing dilution of the sulfur being pumped into the copper mass, adjusting the flow rate of said gas relative to the flow rate of the sulfur being pumped into the copper mass to limit the sulfur made available to the copper during the alloying commensurate with the ability of the copper to take up the same and thereafter cooling and casting the resulting alloy while maintaining said cover of non-oxidizing gas thereover.

2. In a process in which molten copper is contacted with sulfur for alloying therewith, the improvement providing a copper-sulfur alloy of reduced susceptibility to hydrogen embrittlement which comprises providing a supply of essentially oxygen-free copper in one zone and molten sulfur in a separate zone, each reactant being under a non-oxidizing protectant gas, controllably transferring the sulfur in admixture with additional protectant gas as a diluent therefor to within the mass of said molten copper at a rate commensurate with the ability of said copper to absorb such added sulfur, said sulfur transfer being continued until a predetermined amount of sulfur has been consumed by the copper and cooling the resulting alloy while maintaining the protectant gas cover thereover.

3. In a process in which molten copper is contacted with sulfur for alloying therewith, the improvement providing a copper-sulfur alloy of reduced susceptibility to hydrogen embrittlement which comprises providing a mass

6

of essentially oxygen-free copper in molten form protected by a non-oxidizing gas cover, gradually feeding to said oxygen-free copper in the proximity of the bottom thereof a controlled stream of sulfur fluid diluted with said non-oxidizing gas and together providing a positive pressure sufficient to overcome the hydrostatic pressure of said molten copper mass, adjusting the flow rate of the gas relative to that of the sulfur thereby regulating the sulfur content of said stream to avoid any appreciable excess with respect to the amount of sulfur effectively taken up by the copper during the resulting alloying, continuing said alloying until a predetermined amount of sulfur is consumed by the copper and thereafter cooling and casting the resulting alloy under a protective non-oxidizing atmosphere.

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