United States Patent Office 3,501,292 Patented Mar. 17, 1970

3,501,292

PURIFICATION OF ELECTROLYTIC COPPER

Thomas Gordon Hart, San Francisco, Calif., assignor to Phelps Dodge Corporation, New York, N.Y., a corporation of Delaware

Filed Apr. 26, 1966, Ser. No. 551,828
Int. Cl. C22b 15/00, 9/02
U.S. Cl. 75—72 12 Claims

ABSTRACT OF THE DISCLOSURE

Copper cathode plates are suspended and heated in a hydrogen atmosphere for such purposes as oxygen removal. The hot plates are melted in a vacuum to remove volatile and gaseous impurities by progressively melting with radiant heat the lower region of the suspended plates to create a thin molten film which drips off the plate.

This invention relates to the purification of copper and particularly to the purification of electrolytically refined copper by a process involving both hydrogen treatment and vacuum treatment.

The present invention is concerned with means for treating copper so as mainly to remove oxygen, sulphur and volatile impurities such as lead, bismuth and tellurium, Optimum purification is achieved according to this invention by turning to advantage certain peculiarities in the configuration, the structure and the impurity distribution of electrolytic cathode-plate copper so as to remove oxygen, sulphur and volatile impurities from this copper in optimum fashion.

The impurity distribution of electrolytic cathode-plate copper, hereinafter called "cathode copper," is peculiar in that the oxygen and sulphur impurities are largely confined to the surfaces. Further, cathode copper being in the form of flat plates, affords an unusually large surface area in relation to volume. Moreover, cathode copper has a fine crystalline structure which permits progressive melting without tendency to melt off in lumps as is the case with the coarse crystalline structure of cast copper.

According to the invention, advantage is taken of the confinement to the surfaces of the oxygen and sulphur impurities in cathode copper by the use of surface treatments to remove these impurities. Surface treatment of copper, particularly gaseous surface treatment, for removing oxygen and sulphur from the copper, has been discussed in my copending patent application Ser. No. 478,612, filed Aug. 10, 1965. That application concerns a novel method of combining hydrogen treatment with vacuum treatment so as to remove oxygen, sulphur and volatile impurities from any type of copper and makes particular note of the fact that oxygen and sulphur removal from cathode copper is most expeditiously accomplished before the cathode copper is melted because the oxygen and sulphur are then most accessible and because the by-product gases produced as a consequence of the hydrogen action can then most easily escape. The present invention supplements the teaching of application Ser. No. 478,612 by teaching how, in addition to making use of the surface confinement of impurities of cathode copper, as by hydrogen treating prior to melting, effective use can also be made of the high surface area to volume ratio and the smooth melting characteristics of cathode copper for efficiently further removing impurities therefrom.

The broad purpose of the present invention is accordingly to provide an optimum method for removing oxygen, sulphur and volatile impurities such as lead, bismuth and tellurium from cathode copper. Somewhat narrower purposes are as follows:

First, to provide for heating cathode copper in controlled atmosphere so as to substantially remove oxygen and sulphur, at least from the surfaces;

Second, to provide for heating cathode copper, from which oxygen has been substantially removed, in an atmosphere containing hydrogen so as to dissolve hydrogen in the copper;

Third, to provide for melting cathode copper in an atmosphere containing hydrogen so as to dissolve hydrogen in the copper; and

Fourth, to provide for melting cathode copper in an atmosphere having very low pressure compared to atmospheric pressure so as to remove dissolved gasses and volatile impurities.

Toward the above purposes, the following factors have particular importance:

Insofar as is concerned the efficiency of hydrogen treatment of cathode copper in removing sulphur and oxygen, an important factor is, as explained at some length in my copending patent application 478,612 that this treatment be accomplished while the oxygen and sulphur are still largely confined to the surfaces which is to say before the cathode copper is melted. Also of importance is that whereas the extent of oxygen removal from the solid cathode copper by prolonged hydrogen treatment is largely independent of the amount of sulphur present, the extent of sulphur removal by this treatment may depend heavily on the amount of oxygen present. This is to say sulphur is not invariably removed from the surfaces of solid cathode copper by prolonged heating in an atmosphere containing hydrogen if oxygen is absent, depending on such things as the nature of the compounds which contain the sulphur and upon the presence of constituents such as water vapour in the hydrogen bearing atmosphere. This is further to say that generally sulphur removal by hydrogen treatment is facilitated by the presence of an amount of oxygen in the copper somewhat in excess of the amount normally found in fresh cathode copper. Hence the purpose will be understood of slightly further oxidising the cathode copper surfaces, as by heating in air, for example at 600° C. for five minutes, before hydrogen treatment.

Insofar as is concerned the efficiency of the hydrogen treatment of solid cathode copper in dissolving hydrogen in the copper, so as thereby to facilitate the removal of volatile impurities by causing agitation during the subsequent vacuum treatment as disclosed in patent application 478,612, an important factor is that as much as possible of the solid copper surface be freely exposed to the hydrogen bearing atmosphere. This is because the rate at which hydrogen dissolves into the solid cathode copper, at a particular temperature and with a particular proportion of hydrogen in the atmosphere, is proportional to the copper surface area exposed to the atmosphere. Hence the disadvantage will be understood, in terms of length of time required, for example, to saturate the solid cathode copper with hydrogen, of bundling the cathode copper together so as to be treated.

Insofar as is concerned the efficiency of the vacuum treatment of the molten cathode copper in removing dissolved gasses such as hydrogen and volatile impurities such as lead, an important factor is again that a maximum copper surface area be exposed to the treatment. This is because the rates at which dissolved gasses and volatile impurities are removed from molten copper, at a particular temperature and environmental gas pressure in a particular vacuum treatment apparatus, are proportional to the molten copper surface area exposed to the vacuum treatment. Hence the disadvantage will be understood, in terms of length of time required to, for example, substantially remove the lead from a batch of molten copper,