METHODS OF MANUFACTURING POROUS MEMBRANES

George Chadron, Paris, Michel Caron, Sevres, and Georges Cano, Paris, France, assignors to Commissariat a l'Energie Atomique, Paris, France, a state administration of France

No. 928,019. Filed Sept. 29, 1958, Ser. No. 764,021

Claims priority, application France Oct. 2, 1957

8 Claims. (Cl. 75—63)

The present invention relates to methods of manufacturing porous membranes by evaporation under a vacuum of zinc from brass or German silver plates.

Micrographic sections of brass membranes have shown us that zinc diffuses preferentially through the joints between grains. It therefore seemed necessary, for the production of membranes, to start from brass having fine and regular grains and to keep the grains very stable during the zinc evaporation operation.

It is known that pure brass grains are of big size. We have found that these grains keep growing in size during the evaporation operation and that the membrane simultaneously undergoes a shrinkage which reduces the spaces between grains where pores had formed. It therefore seemed necessary to accelerate zinc diffusion and evaporation and to prevent growth of the grains.

We further found that the incorporation into brass of pentavalent phosphorus (phosphorus, arsenic, antimony) accelerates zinc diffusion and evaporation and.

On the other hand, that the introduction of some elements (phosphorus and nickel in particular) makes the alloy grains finer. Furthermore, as nickel is not volatile like phosphorus, it permits of keeping the grain fineness and stability during the zinc evaporation operation.

The present invention is essentially concerned with a method of preparing porous membranes by evaporation under a vacuum of zinc from brass or German silver and its essential characteristic feature consists in making use of the property of certain elements such as phosphorus, arsenic and antimony to accelerate zinc diffusion and evaporation. Preferably, advantage is also taken of the property of nickel to make brass grains finer.

Furthermore, after incorporating at least two of these elements into the alloy intended to be used for preparing these membranes, it will be necessary to subject the preliminarily rolled alloy strips or bands to a succession of thermal treatments which facilitate segregation of the pentavalent additional elements in the joints between grains, after which said bands, or membranes cut therefrom, will be subjected to a heating under a vacuum to ensure zinc evaporation.

In a general manner, the brass that is used contains from 30 to 40% of zinc, preferably 35%.

The method according to the present invention may in particular include the following operations:

(a) The alloy is bottom poured at a temperature ranging from 900 to 1,100°C, preferably at 1,000°C, in the case of brass and from 950 to 1,150°C, preferably at 1,050°C, in the case of German silver.

(b) The ingots thus obtained are subjected to a cold rolling including several successive operations separated by heatings at temperatures ranging from 500 to 700°C, preferably at 600°C.

(c) The bands or strips thus obtained are annealed in a nitrogen atmosphere, first at temperatures ranging from 200 to 300°C, preferably at 250°C, then at temperatures ranging from 300 to 500°C, preferably at 400°C.

(d) Finally, after degreasing and scouring, the bands or strips are placed, for a time ranging from 10 to 20 minutes, preferably for 15 minutes, in a furnace where the temperature is kept at values ranging from 600 to 700°C, preferably at 650°C, and where a vacuum averaging 10⁻⁴ mm. mercury is maintained. This furnace includes cooled portions where zinc condenses.

We will now describe in detail the successive operations which must be carried out with the utmost care to permit of manufacturing porous membranes adapted to be used for instance for isotopic separation by gaseous diffusion.

As already pointed out, it is advantageous to start from a copper and zinc alloy containing about 35% of zinc. The rate of diffusion of zinc is in fact higher in the case of a brass which is rich in zinc and it is necessary to work from an alpha brass. The initial melting is effected in such manner that the zinc losses by evaporation are as reduced as possible. We melt in a high frequency furnace ingots of copper, zinc and nickel alloys and small ingots either of copper and phosphorus alloys containing about 2% of phosphorus or of copper and antimony alloys containing about 25% of antimony.

The following compositions are given by way of example:

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>61.8</td>
<td>56.6</td>
<td>50.95</td>
</tr>
<tr>
<td>Zn</td>
<td>38.2</td>
<td>43.4</td>
<td>49.05</td>
</tr>
<tr>
<td>Ni</td>
<td>3</td>
<td>5</td>
<td>18</td>
</tr>
<tr>
<td>As</td>
<td>0.16</td>
<td>0.72</td>
<td>0.3</td>
</tr>
<tr>
<td>P</td>
<td>0.04</td>
<td>0.06</td>
<td>0.75</td>
</tr>
</tbody>
</table>

The alloy is bottom poured into an ingot mould made of iron lined with alumina. Brass alloys such as I and II are poured at 1000°C, whereas brasses containing a higher amount of nickel, that is to say German silver alloys (III) are poured at 1050°C into the ingot mould preliminarily heated to 800°C.

The parallelepiped-shaped ingots thus obtained are forged.

Their thickness is reduced from 2.5 cm. to 2 cm. They are then annealed for 24 hours at 700°C for homogenizing purposes.

The ingots are then cold rolled in several successive operations. Intermediate annealings are effected at 600°C for alloy I and at 650°C for alloys II and III. We thus obtain strips 0.2 mm. thick in a roughing mill. The strips are then passed through a finishing mill. For instance, for alloy I, after annealing for 10 minutes at 600°C, the band is rolled down to a thickness of 0.1 mm. It is then annealed for 5 minutes at 600°C and rolled down to 0.05 mm. It is again annealed for 5 minutes at 600°C and rolled down to a thickness of 0.02 mm. The band is finally annealed at 600°C and quenched in water.

The brass strip is then annealed in an atmosphere of nitrogen for 2 hours at 250°C and for 2 hours at 400°C. This treatment which is one of the most important features of the method according to our invention is intended to eliminate stresses and chiefly to facilitate segregation of the pentavalent additional material in the joints between the grains. This treatment must be carried out under very accurate conditions so as to avoid too great an impoverishment of the crystals.

The brass strips thus prepared are degreased for instance by means of a sulfonated detergent, washed with a great amount of water, weighed with alcohol and subjected to anodic scouring for 20—30 seconds on both faces thereof.

They are then placed in a furnace where the temperature is kept at 650°C and where a vacuum averaging 10⁻⁴ mm. mercury is maintained. The capacity of the vacuum pump must be sufficient to permit quick evacuation of zinc vapors in the vicinity of the brass strip. This furnace includes portions cooled by water circula-
tion and upon which zinc deposits. For a brass of the type of alloy I (taken by way of example), the time of treatment under vacuum is 15 minutes at 600° C. for a membrane 0.015 mm. thick. In these conditions, brass loses about 85% of the weight of zinc it contained initially. The radii of the pores that are obtained range from 100 to 500 angstroms. The flow rate of air passing through the membrane ranges from 70 to 140×10⁻³ gram molecule of air per sq. cm. and per minute for a difference of pressure of 1 cm. of mercury between the two sides of the membrane.

As already indicated, all these operations must be performed very carefully and in particular both for casting and for cooling it is necessary to comply with the conditions which permit of obtaining strips of high grade brass similar to the best brass manufactured for clockwork construction. The metal used to constitute the initial alloy must be very pure. For instance, the copper that is used is of the so-called "high-conductivity type" and free from oxygen. The purity of zinc must correspond to 99.99% and the nickel that is used is the so-called "Mond" nickel. Traces of impurities may prevent the attainment of the desired result.

Melting and casting must be performed very carefully, the temperatures being checked up accurately.

The rolling operation must be carried out in precision rolling mills since the thickness of the strip must remain constant over the whole area of the membrane.

The metal must keep a perfectly homogeneous composition and structure during all the thermal operations. After the final annealing, we obtain a brass strip having regular and fine grains (about 10 microns).

What we claim is:

1. A method of preparing a porous membrane which comprises making a solid metal alloy containing copper, zinc, at least two pentavalent elements of the group consisting of phosphorus, arsenic, and antimony, and as a grain refiner nickel, the percentages of copper and zinc in said alloy being within the range corresponding to brass and German silver alloys containing about 30 to 40 percent of zinc, forming this alloy to the shape of a thin membrane, annealing said membrane in a neutral atmosphere, first at a temperature ranging from 200 to 300° C., then at a temperature ranging from 300 to 500° C., to cause said pentavalent elements to segregate in the joints between the grains of the alloy, and subsequently heating said membrane in a vacuum to cause zinc to evaporate therefrom, said pentavalent elements accelerating zinc diffusion and evaporation.

References Cited in the file of this patent

UNITED STATES PATENTS

2,070,101 Weston et al. 1937
2,157,596 Davis 1939
2,236,452 Rogers 1941
2,307,051 Litton et al. 1943
2,369,813 Wilkins 1945
2,462,045 Wulf 1949
2,792,302 Mott 1957

OTHER REFERENCES