July 9, 1963 R. LACROIX 3,097,149

METHODS OF MANUFACTURING MICROPOROUS METALLIC MEMBRANES

Filed Aug. 18, 1959 2 Sheets-Sheet 1

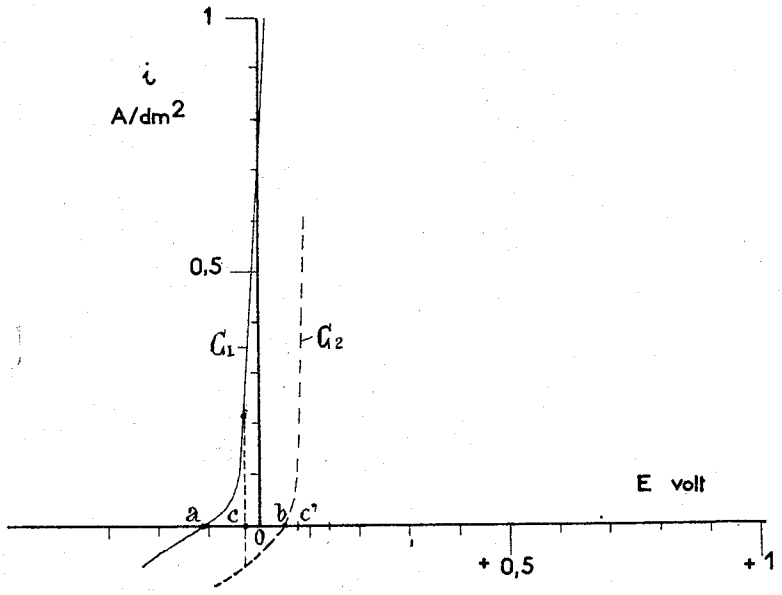


FIG.1

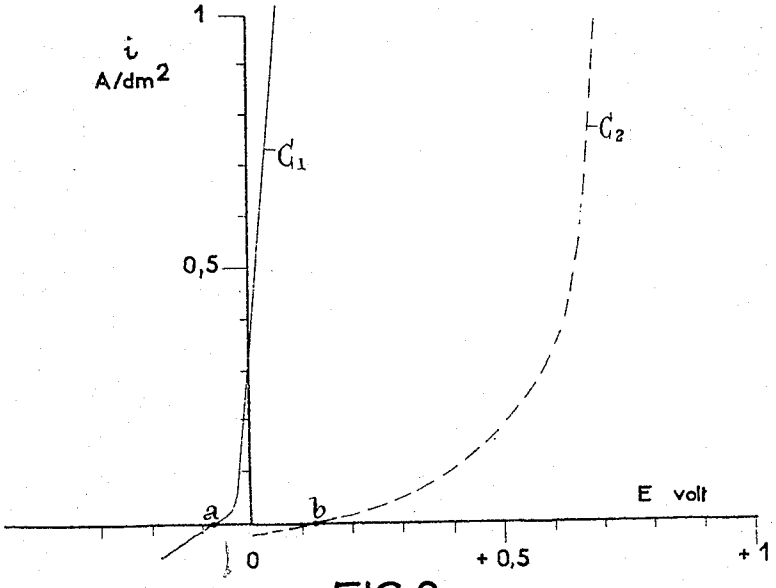


FIG.2

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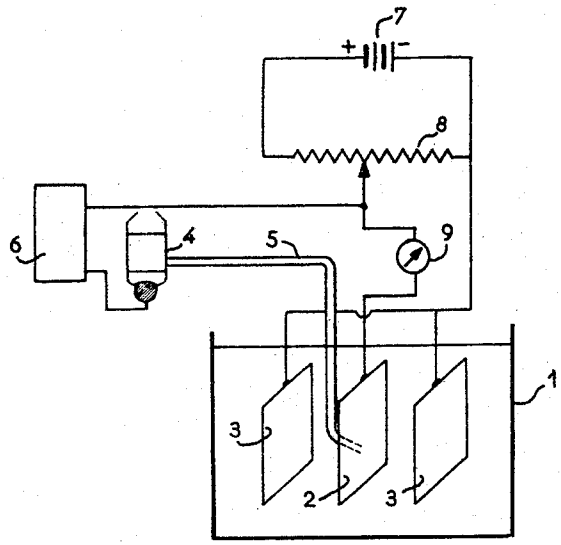


FIG.3

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METHODS OF MANUFACTURING MICROPOROUS METALLIC MEMBRANES

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There are a certain number of processes for the preparation of porous bodies. They may be classified in two groups: processes comprising the direct building up of the porous product and processes comprising removal of material from a compact body.

The first group includes powder-metallurgy and ceramic processes. The porous bodies obtained by these methods have unduly coarse pores and cannot be used for certain work requiring very thin porous membranes of the order of 1/10 mm. thickness and having pores the mean radius of which is of the order of 0.01μ for example. However, it is possible partly to fill in the cavities of a coarse-pored support by porous electrolytic deposition or dense electrolytic deposition technique.

To the second group belong all the methods of selective extraction of part of a compact body which are based on differences in volatility or speed of diffusion in the solid state, or solubility in a solvent, or corrodibility in a chemical reagent.

The compact body may be homogeneous: chemical combination or solid solution; or heterogeneous if it contains a plurality of phases, at least one of which may be partially or totally displaced by one of the said processes.

The present invention belongs to this second group of methods of preparation of porous bodies and is based on the extraction of one or more constituents of an alloy which, after their departure, leave a porous metal or alloy.

The phenomenon of selective attack or corrosion of alloys has long been known. It forms the basis for the process of refining gold by inquartation and sulphuric or nitric attack, this process being many centuries old and still used by refiners of precious metals. It has been studied by Tammann, who formulated empirical laws of limited value. It still manifests itself to specialists in combatting corrosion from the aspect of the dezincification of brasses.

Generally, when an electrolytic attack or a chemical attack (they are in fact two aspects of one and the same phenomenon, that of exchanges of electrons between electrolytic ions and atoms) affects an alloy, the various constituents dissolve simultaneously at rates differing from one another to a greater or lesser degree. The extreme cases are, on the one hand, polishing and rendering brilliant, in which all the rates of dissolution are equal, and on the other hand the perfectly selective attack in which at least one of the constituents of the alloy remains unattacked.

Silver ultrafilters have been prepared by selective dissolution of the zinc of a certain silver-zinc alloy in hydrochloric acid to which cesium chloride has been added. Yet the method used to prepare these ultrafilters could not be used to prepare ultrafilters of varying kinds.

It has been shown by the author of the present invention that the reagent to be used to effect a selective attack of the constituents of an alloy must possess a group of well defined characteristics adapted to each alloy treated and that in consequence very diverse alloys could be prepared and treated to give microporous metallic filters of varying kinds; it has finally been shown that the selective attack could be effected not only purely chemically but also electrolytically.

It is known that metals may be classified according to

their aptitude for passing into electrolytic solution; the most noble metals—gold, platinum, silver—have a high positive normal dissolution potential, while the most unstable metals have highly negative normal dissolution potentials. Similarly, reduction-oxidation solutions may be classified according to their redox potentials; those which are very oxidizing, that is to say which energetically fix electrons, have high positive redox potentials, while on the other hand the reducing solutions, that is to say those which easily give up electrons, have low redox potentials.

It is these considerations relating to the dissolution potentials of metals in the pure state or in the alloyed state which have enabled the inventor to perfect a process whereby the selective attack of the constituents of an alloy becomes possible and is effected in the best possible conditions.

The present invention relates essentially to a process for the production of microporous metallic membranes by selective attack of the constituents of an alloy, for the purpose of obtaining membranes having very fine pores, for example less than 0.05μ, comprising: forming an alloy from at least one metal of a first group and at least one metal of a second group consisting of metals distinctly more unstable than the metals of the first group, at least 40 percent of the atoms of the alloy being a metal of the second group; forming a thin membrane of such alloy; and subjecting such membrane to an electrochemical treatment which selectively causes the dissolution of the metals of the second group, by subjecting the ions of these metals to an extraction potential permitting their elimination from the alloy.

This may be achieved either purely chemically by bringing the alloy into contact with an electroyltic solution to which a reduction-oxidation reagent is added which has a redox potential greater than the dissolution potentials of the metals of the second group in the alloyed state, or electrolytically by bringing it, within the electrolytic solution, to an anode potential greater than the dissolution potentials of the metals of the second group in the alloyed state and less than the dissolution potentials of the metals of the first group.

During a preliminary operation the polarisation curves in the electrolytic solution are determined, on the one hand for the alloy in question, and on the other hand for a sample of the metal or of the metals of the membrane taken in a physical state as close as possible to the desired final state, so as to produce only alloys for which the two foregoing curves are distinctly different, the polarization curve of the alloy containing at least at its origin a zone of potentials less than those of the metals to be preserved.

When operation is effected chemically, the redox potential of the reduction-oxidation reagent added may be chosen either to be less than the dissolution potentials of the metals of the first group, in which case the end of the reaction then being awaited or the reaction is stopped after the desired quantity of the metals of the second group has been dissolved, or to be greater than the dissolution potentials of the metals of the first group, in which case the reaction is stopped when the amount of metals of the second group dissolved has reached the required value.

When the operation is effected electrolytically, the anode potential may be kept constant and the electrolysis is stopped after the desired quantity of the metals of the second group has been dissolved.

The progress of the selective dissolution may be supervised by periodically weighing the alloy or by effecting periodic determinations of the bath (the general case) or by measuring the amounts of electricity used (the case of the electrolytic method).

The metal or alloy with which it is desired to produce the microporous metallic membrane having been selected,

another metal or a plurality of other metals adapted to be alloyed with it and distinctly more unstable, that is to say with distinctly lower dissolution potentials, will be sought.

Thus, if it is desired to produce a microporous membrane of gold (normal dissolution potential of gold +1.36 v.) it is possible to produce a gold-silver alloy (normal dissolution potential of silver +0.798 v.); if it is desired to produce a microporous membrane of silver, it is possible to produce a silver-zinc alloy (normal dissolution potential of zinc: −0.762 v.) or a silver-aluminium alloy (normal dissolution potential of aluminium: −1.33 v.). The normal dissolution potentials are known from technical literature. They further correspond to the potentials, for zero current, of the polarization curves as indicated hereinafter.

If it is desired to obtain microporous membranes of constant or small thickness, it will be convenient to choose rollable alloys.

In the case of a chemical attack, the attacking reagent must be capable of reaching the atoms to be dissolved wherever they are situated in the alloy, and in the case of an electrolytic attack passivation phenomena must be avoided. After elimination of the surface atoms of the soluble metals (metals of the second group), there must not be a continuous front of atoms of the nobler metals (metals of the first group). The proportion of the metals of the second group must therefore be sufficiently high for the attack to be effected both in depth and superficially; to this end it must be at least 40 atoms percent.

It will have to be borne in mind that the dissolution potentials of the alloyed metals are different from those of these same metals in the pure state; they depend on the nature, number and arrangement of the neighboring atoms. In addition to these factors bound up with the general composition and local composition of the alloys, there are those which depend on the "topographical" structure of the alloy. It is demonstrated by thermodynamics that the solubility of a solid body increases when the radius of curvature of its surface decreases. The atoms situated at the end of "capes" are therefore more soluble than those situated on a flat region or at the bottom of a "gulf." The following points will have to be taken into consideration for the choice of the alloy to be produced:

(*a*) The dissolution potential of a pure unstable metal may be greatly less than that of the metal in the alloyed state.

(*b*) The dissolution potential of a pure noble metal may be much greater than that of the metal in the alloyed state.

(*c*) The alloy content of a certain metal being constant, the solubility of the metal in the attacking reagent may be increased if the metal is more finely distributed in the alloy.

(*d*) The atoms of noble elements situated on a peak tend to dissolve in order to become re-deposited on the parts of less curvature.

In order that the invention may be more readily understood, some supplementary explanations will now be given, especially with regard to the polarization curves, together with some specific examples, with reference to the accompanying drawings, in which:

FIGURES 1 and 2 are two diagrams relating to polarization curves for silver-zinc alloys in two different reagents.

FIGURE 3 shows diagrammatically an apparatus for performance of the process electrolytically.

The curves in FIGURES 1 and 2 illustrate in a general manner the essentials of the process according to the invention, that is to say the curves which will be taken as basis to determine the characteristics of the selective dissolution.

The left-hand curve C_1 is the polarization curve of the alloy, while the right-hand curve C_2 is the polarization curve of the metal to be preserved. These curves, which are prepared before-hand by experiment, give the density of the dissolution current i against the potentials E to which the metallic ions are subjected.

The intensity of the dissolution current due to a constituent of the alloy varies in the same manner as the speed of dissolution of this constituent; a positive intensity corresponds to an effective attack (dissolution) of the constituent and a negative intensity to its deposition on the alloy (if the bath contains the constituent at that moment).

This is shown for example in FIGURE 1, in which it will be seen that the curves C_1 and C_2 cut the x-axis at points a and b which, for a given solution, termed a normal solution, would correspond to the normal dissolution potentials. For a point c disposed, for example, between the points a and b and corresponding to a certain extraction potential characteristic of the process according to the invention, it will be seen that the ordinate of the curve C_1 is positive, while the other is negative: this means that the intensity of the dissolution current corresponding to the metal to be dissolved (zinc) is positive, while that corresponding to the metal to be preserved (silver) is negative. These are the ideal conditions for the performance of the process.

In the first place it is necessary that the two curves such as C_1 and C_2 should be sufficiently different.

In the second place it is necessary to chose an operating potential—that is to say the potential of the alloy taken as anode, in relation to the potential of a reference anode—in such a manner that it appears at c, between points such as a and b (FIGURE 1), (preferably sufficiently near b to increase the dissolution speeds) or beyond the point b to the right (at c' for example, FIGURE 1). In this latter case, the metal to be preserved might itself ultimately be attacked, so that it will be necessary to stop the reactions at a determined moment.

To obtain an operating point of the kind indicated above (at c or c') there will be available in particular the two means already specified hereinabove, namely:

The addition or selection of a solution having a suitable redox potential,

Or the application of a determined potential to the anode electrolytically.

In the case of the first arrangement, the procedure will for example be as follows:

(*a*) To the electrolytic solution there will be added in one batch or gradually a reduction-oxidation agent of a redox potential greater than the dissolution potentials of the metals of the second group in the alloyed state but less than the dissolution potentials of the metals of the first group; the end of the reaction will be awaited.

It will also be possible to stop the reaction after having dissolved only a certain amount of the metals of the second group.

(*b*) To the electrolytic solution there will be added in one batch or gradually a reduction-oxidation agent of a redox potential greater than the dissolution potentials of the metals of the first group to be preserved (which is equivalent to bringing the operating point to a point such as c' in FIGURE 1). This potential is then obviously greater than the dissolution potentials of the metals of the second group; the reaction will be stopped when the desired quantity of the metals of the second group has been dissolved.

If, in this case, the reaction were allowed to progress normally, the reagent whose redox potential is sufficiently high to be able to attack even the nobler elements of the alloy would begin to dissolve these when the metals of the second group were practically completely attacked. That is why the reaction is stopped at the desired moment in order to preserve the metals of the first group which are to constitute the microporous membrane.

During the attack, the noblest metals of the alloy may provisionally be re-dissolved, being re-precipitated where

the element having the low dissolution potential is exposed (pseudo-selective attack).

In the case of the second abovementioned arrangement (electrolysis), the alloy within the electrolytic solution is brought to a constant anode potential greater than the dissolution potential of the metals of the second group in the alloyed state and lower than the dissolution potentials of the metals of the first group.

Results substantially identical to those obtained are achieved by subjecting the same alloy to the chemical attack of a reduction-oxidation agent of a redox potential equal to the anode potential.

The electrolysis will be stopped after the desired quantity of the soluble metals has been dissolved.

To follow the progress of the chemical attack of the constituents of the alloy by the reduction-oxidation agent in the case where it is necessary to stop the same, the alloy will be periodically weighed or determination of the bath effected.

To follow the progress of the electrolytic attack of the constituents of the alloy, measurement of the amounts of electricity used will be effected in addition to the methods indicated hereinabove in the case of chemical attack.

Microporous membranes of gold may be prepared by dissolution of the silver of a gold-silver alloy, or of the copper of a gold-copper alloy; silver microporous membranes may be prepared by selective dissolution of the zinc, cadmium or aluminium of silver-zinc, silver-cadmium or silver-aluminium alloys and copper microporous membranes by selective dissolution of the zinc contained in a brass.

According to the invention microporous membranes are obtained in which the radius of the pores is less than 1μ and may be below 0.05μ; the permeability to gases is very great; in the case of air, with membranes having a thickness of 0.1 mm., it may under low pressure attain 2000 to 2500×10^{-7} mol. of air per square centimetre per minute per centimetre of mercury pressure difference between the two sides of the membrane.

These microporous membranes may be used to treat by diffusion mixtures of different gases in order to enrich them in certain of them, which operation, if repeated, may lead to very extreme separations.

They may also be used to effect isotopic enrichments and separations; they permit more especially the enrichment of natural uranium in its isotope of the mass number 235 and the separation of this isotope, by diffusion of gaseous uranium hexafluoride.

There are finally given four concrete examples of membranes obtained by the processes according to the invention.

In the various examples, the contents given are contents by weight and they all correspond to a content of unstable metal greater than 40 atoms percent.

Example I.—Preparation of Microporous Membranes of Gold

A gold alloy is prepared containing by weight 40 percent of gold and 60 percent of silver. It is then rolled in order to obtain foils of a thickness of 40μ. These foils are treated at 100° C. by an acid oxidizing medium constituted by nitric acid at 36° Bé.

After completely eliminating the silver, microporous membranes of pure gold are obtained and washed with water to eliminate any trace of silver salts and are dried.

The characteristics of these microporous membranes are:

Mean radius of pores: 0.01 to 0.06μ

Permeability to air under low pressure: 1000 to 2500×10^{-7} mol. per square centimetre per minute per centimetre mercury.

Example II.—Preparation of Microporous Membranes of Silver

A silver-zinc alloy is made with 65 percent of silver

and is rolled to obtain foils of 0.1 mm. thickness which are treated at 50° C. by a solution of hydrochloric acid to which tin(II)-tin(IV) reduction-oxidation reagent has been added having a normal redox potential equal to +0.15 v. The choice of the reagent was guided by the outline of the polarization curves of the alloy and the silver, which curves are those shown in FIGURE 1 already discussed hereinabove.

After elimination of a quantity of zinc corresponding to 30 to 35 percent of the initial weight of the foils, microporous membranes are obtained which have the following characteristics:

Mean radius of pores: 0.05 to 0.10μ

Permeability to air under low pressure: 1000 to 2500×10^{-7} mol. per square centimetre per minute per centimetre Hg

Example III.—Preparation of Microporous Membranes of Silver

A silver-zinc alloy is prepared containing 65 percent of silver. This alloy is rolled so as to obtain foils of 0.1 mm. thickness which are treated with a solution of hydrochloric acid to which has been added the uranous-uranic reduction-oxidation reagent having a normal redox potential equal to +0.26 v.

The zinc is dissolved selectively.

The microporous membranes obtained have the following characteristics:

Mean radius of pores: 0.04 to 0.12μ

Permeability to air: 1000 to 2500×10^{-7} mol. per square centimetre per minute per cm. Hg

Example IV.—Preparation of Microporous Membranes of Silver

A silver-zinc alloy is prepared containing 67 percent of silver and is subjected in a caustic soda solution to an anodic attack under constant potential lying between −0.07 v. and +0.13 v. at 50° C.

The polarisation curves of the silver and of this alloy in caustic soda show that the dissolution of the zinc is selective; these curves are shown in FIGURE 2.

The attack is effected for example in accordance with the circuit shown diagrammatically in FIGURE 3.

This figure shows the electrolysis tank **1**, the anode **2** constituted by the silver-zinc alloy, the cathodes **3**, the reference electrode **4**, which is connected by a very slender siphon **5** to the electrolysis tank **1** and which enables the anode potential to be measured, the measuring potentiometer **6**, the source of direct current **7** with the regulating resistance **8** connected as a potentiometer, and the meter **9** which indicates at each moment the amount of electricity consumed and hence the quantity of zinc extracted from the alloy.

The microporous membranes thus obtained from foils of a thickness of 0.1 mm. have the following characteristics:

Mean radius of pores: 0.01 to 0.02μ

Permeability to air under very low pressure: 100 to 200×10^{-7} mol. per square centimetre per minute per cm. Hg

Using silver-zinc alloys containing more than 33 percent of zinc, the permeability can be increased appreciably without the mean radius of the pores being substantially modified.

What I claim is:

1. A process for forming a thin microporous silver membrane comprising rolling a silver-zinc alloy containing about 65 percent by weight of silver to a foil of a thickness of about 0.1 mm. and subjecting said foil in a caustic soda solution at a temperature of about 50° C. to an anodic attack under a constant potential lying between −0.07 v. and 0.13 v. until about 30 to 35 percent by weight of the original foil have been dissolved.

2. A process for the production of microporous me-

tallic membranes by selective attack of the constituents of an alloy, for the purpose of obtaining membranes having very fine pores of less than about 0.12μ, comprising: forming a bimetallic rollable alloy with a first and a second metal, said second metal being distinctly less noble than the first metal and at least 40% of the atoms of said alloy being of the second metal; forming a thin membrane of such alloy; and subjecting said membrane to an electrochemical treatment which selectively causes the substantially complete dissolution of the second metal by subjecting the atoms of said second metal to an extraction potential permitting its removal from the alloy; said extraction potential being obtained electrolytically by bringing the membrane, while in an electrolytic solution, to an anode potential greater than the dissolution potential of the second metal in the alloyed state and less than the dissolution potential of the first metal in said electrolytic solution.

3. A process for the production of microporous metallic membranes by selective attack of the constituents of an alloy, for the purpose of obtaining membranes having very fine pores of less than about 0.12μ, comprising: forming a bimetallic rollable alloy with a first and a second metal, said second metal being distinctly less noble than the first metal and at least 40% of the atoms of said alloy being of the second metal; forming a thin membrane of such alloy; and subjecting said membrane to an electrochemical treatment which selectively causes the substantially complete dissolution of the second metal by subjecting the atoms of said second metal to an extraction potential permitting its removal from the alloy; said extraction potential being obtained electrolytically by bringing the membrane, whilst in an electrolytic solution, to an anode potential about the same as the dissolution potential of the first metal in said electrolytic solution.

4. A process for the production of microporous metallic membranes by selective attack of the constituents of an alloy, for the purpose of obtaining membranes having very fine pores of less than about 0.12μ, comprising: forming a bimetallic rollable alloy with a first and a second metal, said second metal being distinctly less noble than the first metal and at least 40% of the atoms of said alloy being of the second metal; forming a thin membrane of such alloy; and subjecting said membrane to an electrochemical treatment which selectively causes the substantially complete dissolution of the second metal by subjecting the atoms of said second metal to an extraction potential permitting its removal from the alloy; said extraction potential being obtained electrolytically by bringing the membrane, whilst in an electrolytic solution, to an anode potential between the dissolution potential of the second metal in the alloyed state and about the same as the dissolution potential of the first metal in said electrolytic solution.

5. A method of producing a microporous silver membrane having pores of less than 0.05μ which comprises rolling a silver-zinc alloy wherein at least 40 percent of the atoms are of zinc into a foil of a thickness of at most 0.1 mm. and subjecting said foil in a caustic soda solution at a temperature of about 50° C. to an anodic attack under a constant potential lying between −0.07 v. and 0.5 v. until substantially all zinc has been selectively dissolved from the foil.

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