

Oct. 13, 1970

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3,533,863

PROCESS FOR PRODUCING APERTURED BODY COMPRISING CASTING AN
ALLOY, PLASTICALLY DEFORMING THE CAST ALLOY, AND ETCHING
TO REMOVE ONE OF ALLOYS, AND BODY PRODUCED THEREBY
Filed Dec. 30, 1968

Fig. 1.

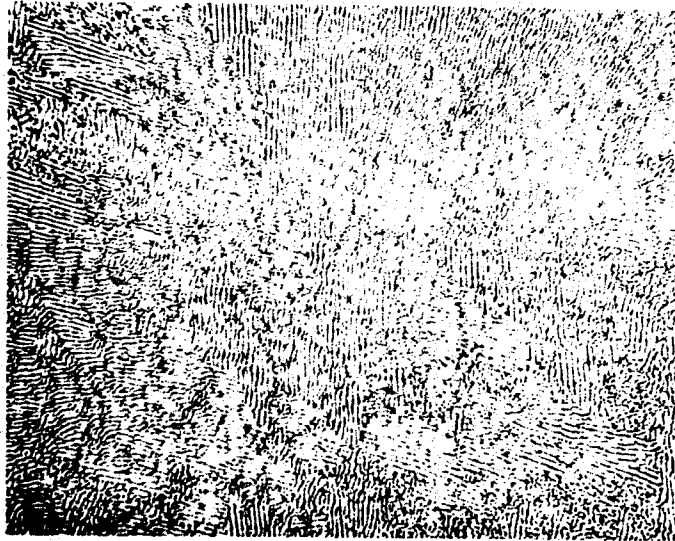
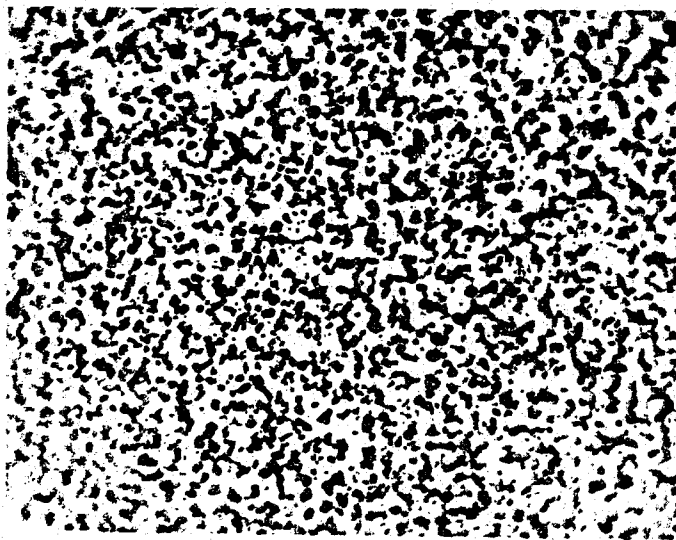


Fig. 2.



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**PROCESS FOR PRODUCING APERTURED BODY
COMPRISING CASTING AN ALLOY, PLASTI-
CALLY DEFORMING THE CAST ALLOY, AND
ETCHING TO REMOVE ONE OF ALLOYS, AND
BODY PRODUCED THEREBY**

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Filed Dec. 30, 1968, Ser. No. 787,751

Int. Cl. C23f 1/02

U.S. Cl. 156—18

11 Claims

ABSTRACT OF THE DISCLOSURE

A process for preparing a body with apertures of small cross-section useful as a filter. An alloy is cast which in the solid state is comprised of at least two phases which are substantially lamellar in form. The cast alloy is plastically deformed to convert the lamellar phase structure to a substantially equiaxed structure. The resulting alloy is etched to remove at least part of one of the equiaxed phases to produce apertures or, if desired, recesses.

The present invention relates generally to the art of producing articles having openings or apertures of uniquely small cross-sectional dimension.

It has long been recognized that a thin sheet-like body having openings of extremely small size would have a number of potentially important uses. In the past, metal filters have been made by weaving wires to form fine screens but the resulting holes are coarse. In another method, a fine metal powder is mixed with another powder which may be metal, and the mixture is sintered to form a dense mass which is then etched to remove one of the powders. The pores of the resulting product, however, are not regular in size or shape. Porous bodies such as expanded Vycor tubing and certain filter papers have holes of minimum cross-sectional dimension, but they cannot be used for a number of applications where high tensile strength, or electrical or metallic properties are desired. Although filters having holes of small cross-section have also been prepared by irradiating a sheet of plastic and etching away the radiation tracks, this method cannot be used on metals.

By virtue of the present invention, openings or apertures can be formed in thin sheets of an alloy to produce articles for uses not met by prior art porous bodies.

Further, in accordance with this invention, apertures or recesses or substantially uniform size can be produced. In addition, by partially or completely filling these apertures or recesses, as the case may be, with selected materials, composite bodies for a wide variety of special purposes and uses can be made.

Those skilled in the art will gain a further and better understanding of the present invention from the detailed description set forth below, considered in conjunction with the figures accompanying and forming a part of the specification, in which:

FIG. 1 is a cross-sectional view magnified 1000 times of a silver-copper ingot of eutectic composition cast as disclosed in Example 1 of the present application, showing the fine two-phase substantially lamellar structure of the cast alloy.

FIG. 2 is a cross-sectional view magnified 1500 times of a silver-copper disc showing the equiaxed structure produced by hot swaging the ingot of FIG. 1 and compressing a transverse slice of the ingot as disclosed in Example 1 of the present application.

Described broadly and generally, an article of this invention is a solid body which has a plurality of re-

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cesses or apertures of minimum cross-sectional dimensions. As used herein, by the terms "pore," "aperture" or "hole" is meant a hole extending from one surface of the etched sample through the opposite surface. On the other hand, by the term "recess" is meant a hole extending from one surface of the etched sample and ending within the etched sample. In addition, the word "phase" defines a quantity of matter having substantially the same properties such as crystal structure and composition.

Briefly stated, the process of the present invention comprises casting an alloy which in the solid state is comprised of at least two phases in lamellar form, as for example platelike or rodlike form, that are substantially alternately disposed. The cast alloy is plastically deformed to convert the lamellar structure of the phases to phases of a substantially equiaxed structure. The resulting alloy is etched to selectively remove at least part of one equiaxed phase to form apertures, or if desired, recesses.

The alloy of the present invention is one which in its cast solid state is comprised of a mixture of at least two lamellar substantially alternately disposed phases. Specifically, there are three types of alloys which have such a characteristic lamellar or banded phase structure in the solid state, namely eutectic alloys, eutectoid alloys and monotectic alloys.

A eutectic alloy is one which freezes or solidifies from the liquid alloy solution to a mixture of two solid phases. Representative of such alloys are Ag_3Al-Al , $Ag-Cu$, $Ag-Ge$, $Ag-Pb$, $Al-Be$, $CuAl_2-Al$, $Al-Ge$, $Mg_{17}Al_{12}-Mg$, $Al-Al_3Ni$, $Al-Si$, $Al-Zn$, $Cu-Cu_3As$, $Fe-Fe_2As$, $InAs-As$, $Mn-Mn_3As$, $Ni-Ni_5As_2$, $As-Pb$, $SnAs-As$, Au_2Bi-Bi , $AuCd_3-Cd$, $Au-CeAu_3$, $Au-Ge$, $Au-AuSb_2$, $Au-Si$, $Au-Tl$, $Au-AuZn$, $Ti-Ti_2B$, $Be-Be_{21}Co_5$, $Cr-Be_2Cr$, $Ni-BeNi$, $Mg-Mg_3Bi_2$, $Bi-Sn$, $TiBi_2Bi$, $Fe-C$, $Mg-Mg_3Ca$, $Ca-Ca_3Pb$, $Mg-CaTi$, $Cu-In$, $Cd-Pb$, $Cd-Cd_3Sb_2$, $Cd-Sn$, $Cd-Ti$, $Cd-Zn$, $CeCu-Ce$, $Co-CoSn$, $CoTiCo_2$, $Cr-ZrCr_2$

$Cu-MgCu_2$

Cu_2Sb-Sb , $Te-CuTe$, $Fe-TaFe_2$, $Fe-TiFe_2$, $FeZrFe_2$, $Ga-In$, $Ge-Mn_3Ge_2$

$Sb-Ge$, $In-Zn$, $La-LaZn$, $Li-LiZn$, Mg_2Sr-Sr , $Ti-TiMin$, $Zr-ZrMo_2$, $Nb-Th$, ZrO_2-Zr , $Pb-Sb$, $Pb-Sn$, $PtSi-Si$, $Sb-Sb_2Te_3$, $Sb-ZnSb$, $Ti-Ti_5Si_3$, $Tl-Sn$, $Zn-Sn$, and $Th-Ti$. Typical of the non-metallic eutectic alloys are $NaF-LiF$, $LiF-NaCl$, $NaF-NaCl$ and $NaF-NaBr$.

A eutectoid alloy is one which is a mixture of two solid phases formed during cooling from a simple solid phase. Representative of such alloys are Ag_3Al-Al , $Ag-Cu$, $C-Fe_3C$, $MgCe-Ce$, $Cr-Ni$, $Ti-TiCr_2$, $Cr-Zr$, $Fe-Cu$, $Zr-Cu$, $Mn-Mn_3In$, $Ti-Mn$, $Zr-ZrMo_2$, and $Zr-Th$.

In the monotectic type of alloy, the liquid alloy forms a solid phase during cooling and also a liquid phase of different composition which, with additional cooling, solidifies to form the second solid phase. Representative of this type of alloy are $Cu-Pb$, $BiU-U$, $Zn-Bi$, $Ca-Na$, $Cr-Cu$, $Cu-Cu_2Te$, $Ti-Ti_2Cu$, $Cu-Tl$, $Tl-P$, and $Zn-Pb$.

The composition of the alloy of the present invention is one which upon being cast cools to a solid which is comprised of at least two solid lamellar substantially alternately disposed phases. For the eutectic alloy, this would be the eutectic composition or a composition close thereto. For the eutectoid type of alloy, this would be the eutectoid composition or a composition close thereto. Likewise, for the monotectic alloy, this would be the monotectic composition or a composition close thereto. In each instance, the range that the composition may vary from the eutectic, eutectoid or monotectic compositions is determinable empirically for the specific alloy. For a majority of alloys, such range varies generally up to about 10% by weight from the eutectic, eutectoid or monotectic compositions.

Generally, in carrying out the instant process, the alloy components are melted together to obtain as uni-

form a molten sample as possible. The molten sample is then cast by a conventional method to the desired size.

The specific form of the lamellar phases produced in the cast solid alloy depends upon the specific composition of the alloy and the temperature gradient at which it is cooled. The temperature gradient may vary widely and depends largely on the size of the lamellae desired to be produced in a specific alloy. The greater the temperature gradient, the faster is the rate of cooling, and the finer and closer are the lamellae. Conversely, as the temperature gradient is reduced, the rate of cooling is slowed and fewer lamellae are formed but these lamellae will be, substantially, correspondingly thicker.

The cast alloy is plastically deformed to convert the lamellar phase structure to a substantially equiaxed structure. A number of conventional methods can be used to carry out such deformation. For example, the alloy can be worked while hot and plastic by methods such as extrusion, rolling, compression or swaging. The specific temperature at which the alloy is hot worked depends largely on its malleability at such temperature. The alloy can also be cold worked, i.e., worked at room temperature, by methods such as rolling and swaging. The size of the equiaxed grains initially produced in the worked alloy depends largely on the size of the lamellae formed upon casting the alloy. Additional working, i.e. deformation, of the alloy refines the equiaxed grains to an even finer equiaxed structure. On the other hand, heating the worked alloy, preferably in an inert atmosphere for those alloys which have a tendency to interact with gases such as oxygen, nitrogen or hydrogen, will enlarge the equiaxed grains to the desired size.

Generally, prior to etching, the alloy is cut in a direction transverse to the oriented phases to a size desired for etching. Any conventional cutting means such as a moving saw, cut-off wheel or spark cutting can be used. For example, for the preparation of a filter, it is sliced transversely to a thickness depending largely on the strength of the alloy and alloy ductility in relation to the thickness desired in the final etched product. The slice of alloy can be etched directly, or preferably, it is mechanically polished prior to etching to remove the distorted surface layer generated during mechanical slicing. Such polishing is also useful to reduce the slice to a desired thickness, such as, for example, a foil.

The particular etchant used depends largely upon the specific composition of the phase to be removed as well as the remainder of the workpiece. Such compositions are known from phase diagrams in the literature. If the phase diagram is not available, the compositions are easily determinable by standard metallographic procedure and x-ray analysis. The etchant used should selectively etch the phase desired to be removed and should not significantly affect the remainder of the workpiece.

The etching can be carried out in a number of conventional ways. For example, the alloy article can be immersed in a solution of the etchant until the equiaxed phase to be removed is etched sufficiently to form holes. However, if recesses rather than holes are desired, only one surface of the workpiece should be contacted with the etchant until the phase to be removed is etched to form recesses of the desired depth. In some instances, especially when the workpiece is as thin as a foil, electrolytic etching is preferred because it can be carried out at a fast but easily controlled rate. Upon completion of the etching, the workpiece is preferably rinsed with water or neutralizer to stop further etching action.

The etching procedure, whether by simple contact of the etchant with the workpiece or other etching method, can be manipulated to obtain holes of the desired size. Specifically, the etched holes can be as large as the grain size of the phase to be removed. However, holes having a size finer than the grain size can be produced by proper control of workpiece thickness and/or rate of chemical attack. In this respect, an important factor is the relative

electrochemical nature of the phases, specifically their reactivity with etchants which are also electrolytes. For example, in a copper-silver alloy, the copper phase is more active than the silver phase as shown by its position in the electromotive series. The copper atoms, therefore, have a greater tendency to go into solution as ions leaving electrons on the remaining copper thus making it negative and resulting in a galvanic effect. In the process of etching of the alloy sample of the present invention, there appears to be a concentration of this galvanic effect at the central portion of each grain being etched resulting in that area of the grain being preferentially attacked by etching proceeds from the center to the periphery or boundary of the grain. This galvanic effect can be increased by increasing the rate of etching by the use of a proper electrolyte. Advantage of this effect can be taken in thicker samples, especially thicker foil samples, to produce fine holes since, in such instance, the etching can be stopped once the hole is formed and before the etching proceeds toward the phase boundary. On the other hand, in thinner foil samples, the etchant etches through the central portion of the grain at a rate too rapid to stop before it proceeds toward the grain boundary, and therefore, produces larger holes. In addition, the faster the rate of chemical attack, i.e. the faster the grain is dissolved by the etchant, the more difficult the control of the etched hole size. Therefore, the rate of attack by an etchant preferably should be made directly proportional to the thickness of the foil being etched. This rate may be controlled by proper selection of the type or reactivity of the etchant and/or method of etching.

In the present invention, the specific thickness of the workpiece can vary widely and will depend somewhat on its final use. As a minimum, it need only be thick enough to form a continuous film, generally about 1000 angstroms, depending on the particular alloy used. Its minimum as well as maximum thickness is limited by the etchability of the phase which serves as matrix as well as the phase to be removed. The etched holes or recesses are of substantially uniform cross-sectional size. Their cross-sectional area, i.e. diameter, depends largely on the final use of the product and may be as low as about 50 angstroms or lower. There is no limit on the maximum cross-sectional area since, prior to etching, the worked alloy can be heated to enlarge the equiaxed grains to the desired size. The present invention is especially useful for producing porous foils.

All parts proportions or amounts used herein are by weight unless otherwise noted.

The invention is further illustrated by the following examples.

EXAMPLE 1

An eutectic silver-copper alloy was prepared by melting 71.9 percent by weight of silver and 28.1 percent by weight of copper, each of which was about 99.999 percent pure, under argon in a graphite crucible. The molten alloy was chill cast in a vertical aluminum oxide mold which was 1¼ inches in diameter and 5 inches long and which had a copper plate at the bottom. The copper plate was maintained at room temperature. The resulting cast cylindrical rod was about 1¼ inches in diameter and 1½ inches in height.

Metallographic examination of both ends and along the length of the rod showed two lamellar alternatively disposed phases in the direction of solidification, i.e. the phases were substantially perpendicular to the planes of both ends of the rod. The lamellar structure is illustrated in FIG. 1. The rod was cold worked, i.e. rolled at room temperature, until it had a diameter of 0.40 inch.

The worked rod was cut transversely, i.e. in a direction transverse to the oriented phases, by a cut-off machine to produce a sample ⅜ inch in diameter and ⅜ inch long. This sample was heated in a resistance-type furnace having a helium atmosphere to a temperature of 675° C. and held at this temperature for 10 minutes. At the end

of this time, while still at a temperature of 675° C., it was compressed by means of platens to a thickness of about $\frac{1}{16}$ inch.

The compressed specimen looked like a disc. It was examined metallographically and found to have a two phase structure with each phase being comprised of substantially equiaxed grains approximately one micron in size, a micrograph of which is shown in FIG. 2.

The thickness of the disc was reduced by grinding to about 0.002 inch thickness. The resulting foil was polished by Al_2O_3 abrasives, and finally polished by a mechanical-chemical method with a Cr_2O_3 abrasives slurry in 5% aqueous CrO_3 solution to a thickness of about 3 microns. The polishing also produced mirror smooth surfaces.

The foil was immersed in an etching solution at room temperature for about 15 seconds to etch out the copper phase. The silver phase was reduced slightly in thickness to approximately 2 microns. The etchant was comprised of 100 ml. concentrated (38%) hydrochloric acid containing one gram of chromtrioxide. The etched foil was rinsed with water and examined.

Transmission electron micrographs of the foil showed that the copper phase had been partially etched away to produce holes. The remainder of the foil was not substantially affected except that the foil now had a thickness of about 2 microns. About 50% of the holes had a diameter of about 200 angstroms. Some of the remaining holes appeared to be finer in diameter, i.e. as high as about 500 angstroms. The holes passed substantially straight through the foil and were substantially parallel.

The etched foil was strong and flexible. It appeared to be useful as a selective membrane or filter for specific applications where metallic properties are desirable.

EXAMPLE 2

A magnesium-aluminum eutectic alloy was prepared by melting 67.7 percent by weight magnesium and 32.3 percent by weight of aluminum, each of which was about 99.999 percent pure, under argon in a graphite crucible. The molten alloy was chill cast in a vertical aluminum oxide mold which had a copper plate at the bottom. The copper plate was maintained at room temperature. The resulting ingot was 8 inches long and $2\frac{1}{2}$ inches in diameter. It was cut to produce cylinders $2\frac{3}{8}$ inches long and $2\frac{1}{8}$ inches in diameter.

Metallographic examination of both ends and along the length of the cylinders showed two lamellar substantially alternately disposed phases which were substantially perpendicular to the planes of both ends of each cylinder.

Each such cylinder was extruded at 300° C. to a rod having a diameter of $\frac{1}{2}$ inch. The extrusion was carried out in a copper container with $\frac{1}{16}$ inch walls to minimize surface tearing problems.

A thin transverse slice, approximately 0.50 inch thick, was cut from the magnesium-aluminum rod by means of an abrasive cut-off wheel and then ground and polished with Al_2O_3 abrasives on both faces to produce a foil .002 inch thick which was substantially free of disturbed or worked metal. The foil showed a two phase structure with each phase being comprised of substantially equiaxed grains approximately one micron in size.

The foil was thinned, i.e. etched and further polished electrolytically. Specifically, the foil was made the anode in a D.C. cell at a potential of 20 v. D.C. to a stainless steel cathode in an electrolyte solution comprised of 20 ml. (70%) perchloric acid and 80 ml. glacial acetic acid. The electrolyte was cooled to slightly below room temperature but maintained above the freezing point of the glacial acetic acid and agitated. After 5 seconds, the foil was removed, washed in ethanol and dried. Its thickness had been reduced to approximately 3 microns, and the magnesium phase was substantially removed, leaving holes in the thin foil.

Examination of the etched foil by transmission electron microscopy and electron micrographs of it showed that

the magnesium phase had been substantially removed and that the holes were approximately 1 micron in diameter. The holes passed substantially straight through and were substantially parallel and uniform in size.

EXAMPLE 3

Additional foils of the magnesium-aluminum eutectic alloy were prepared as disclosed in Example 2. These foils were electrothinned, i.e. etched and further polished electrolytically, as disclosed in Example 2 except that the final thickness of each etched specimen was approximately 5 microns.

Examination of the etched foils in the same manner as disclosed in Example 2 showed that the magnesium phase had been partially removed resulting in substantially uniform holes having an average diameter less than 0.5 micron. This indicates that control of the size of the holes can be achieved by varying the thickness of the foil. The etched foils appeared to be suitable for use as filters.

Since the porous etched solid of the present invention can be produced in thin foil form having high tensile strength, it is especially useful as a filter for the separation of very fine materials, as for example in the purification of water. Such a filter allows good fluid flow since its thinness offers little drag or resistance for fluid to pass through. In addition, its high tensile strength would allow pressure to be applied to the fluid to still further increase flow.

If desired, composites can be formed for a wide variety of special applications by filling the holes or recesses of the etched material of the present invention with a foreign material, i.e. a material different from that of the etched material. For example, they can be filled with superconductive material or with iron particles to produce oriented, single-domain ferromagnetic sheets.

It will be apparent to those skilled in the art that a number of variations are possible without departing from the scope of the invention.

Additional methods of treating alloys to produce a solid two phase structure wherein one phase is distributed in a fine form in a matrix comprised of the second or other phases and wherein said finely distributed phase is selectively removed by etching and/or articles formed therefrom are disclosed and claimed in the following co-pending applications:

U.S. patent application Ser. No. 787,838 (Docket RD-2813) filed of even date herewith in the name of Daeyong Lee and assigned to the assignee hereof is directed to the treatment of an alloy having the characteristic of being comprised of at least two phases in the solid state to produce at least one phase in a fine form distributed in a matrix comprised of the second or other phases. The resulting treated article is etched to remove the finely distributed phase to produce apertures, or if desired, recesses.

U.S. patent application Ser. No. 787,802 (Docket RD-1589) filed of even date herewith in the name of Harvey E. Cline, Robert R. Russell and Warren DeSorbo, and assigned to the assignee hereof is directed to the directional solidification of a eutectic alloy to produce a structure wherein one of the phases is present as a plurality of substantially parallel rods passing through the second or other phases which serve as the matrix. The directionally solidified structure is etched to selectively remove the rod-like phase to form straight through apertures or, if desired, recesses.

U.S. patent application Ser. No. 787,837 (Docket RD-1749) filed of even date herewith in the name of Harvey E. Cline, Robert R. Russell, and Warren DeSorbo, and assigned to the assignee hereof is directed to the preparation of thin porous metallic film with substantially parallel and uniform apertures by means of a replication technique. The etched article produced in the aforementioned U.S. patent application Ser. No. 787,802

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(Docket RD-1589) is used as a master from which a negative replica is formed. The negative replica is then used as a substrate on which there is deposited metal which is then recovered from the substrate as a porous film.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. A method for preparing an article with apertures or recesses which comprises providing a cast alloy body which in the cast solid state is comprised of at least two phases having a substantially lamellar structure, plastically deforming said cast alloy body to convert said lamellar phase structure to a substantially equiaxed structure, and etching the resulting alloy article to selectively remove at least part of one phase to form recesses or holes in the article.

2. A method according to claim 1 wherein said cast alloy of the body is a eutectic type alloy.

3. A method according to claim 2 wherein said alloy body is formed from silver and copper.

4. A method according to claim 2 wherein said alloy body is formed from magnesium and aluminum.

5. A method according to claim 1 wherein said alloy body is of a eutectoid type alloy.

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6. A method according to claim 1 wherein said alloy body is of a monotectic type alloy.

7. A method according to claim 1 wherein said alloy body is reduced to a foil prior to etching.

8. The product produced by the method of claim 1.

9. The product produced by the method of claim 2.

10. The product of claim 8 wherein said recesses or holes contain a foreign material.

11. The product produced by the method of claim 1 in which the apertures are of substantially uniform diameter less than about one micron throughout their lengths.

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U.S. Cl. X.R.

29—424, 527.6, 527.7; 72—700; 75—147, 153, 173