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CAST POROUS METAL

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This invention relates to porous metallic structures and more particularly to metal shapes perforated by a plurality of random interconnecting passageways; and to the process for their production.

The production of porous metal bodies from powdered metals is well known. In carrying out the processes of the prior art it is commonly the practice to prepare the desired metal in finely divided form, and then to compact the powdered metal, with or without a binder, into a relatively weak intermediate structure of the desired shape and of such dimensions that after sintering to the desired extent, the resulting product will be of the proper size. The intermediate structure is commonly relatively fragile and difficult to handle, especially if the final shape is to be very porous, i.e. to contain a relatively large free space. It is thus often not practical to carry out machining operations which may stress either the intermediate or final structures, particularly in the case of highly porous metals, the final size and shape of which is difficult to control because of the possibility of variable degrees of shrinkage. The latter becomes an increasingly greater problem as the dimensions of the structures increase.

It is an object of this invention to provide cast porous metal structures containing a plurality of random interconnecting passageways. It is a further object of the invention to provide a novel process for the production of the said porous structures. A still further object of the invention is to provide certain novel intermediate solid composite metallic structures which can be machined to any desired shape and dimension, and thereafter converted to a porous metal structure. Other objects of the invention will be apparent from the disclosures herein made.

Broadly speaking, and in accordance with the above and other objects of the invention, it has been found that porous metal structures can advantageously be made by preparing an initial supported or self-sustaining porous body composed of certain crystalline salts, introducing a molten metal into the said initial body to fill the spaces therein, cooling the composite salt and metal to solidify the metal and form a strong, composite, rigid intermediate body and leaching the salt from the intermediate body to produce a porous metal shape.

Any metal or alloy which melts and is castable, at a temperature lower than that of the salt selected for use in the process, can be used. Preferably, metals and alloys which melt and can be cast at temperatures below about 1360° C. are utilized in the process of the invention to form porous shapes. The M.P. temperature mentioned is that of calcium fluoride, which appears from the standpoint of convenience to be the highest melting soluble inorganic halide salt known which can be employed in the process. In the case of calcium fluoride, which is but

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slightly soluble in water, solutions of ammonium salts can be used for leaching out the salt. As will be pointed out more specifically hereinafter, beside water, other solvents and combinations of solvents can be used for leaching. Likewise, high-melting inorganic salts can be used in the process. Thus, for example, certain oxides can also be employed.

The inorganic, particulate salt which is employed to form the initial porous self-sustaining body can be any substantially anhydrous, soluble inorganic salt which is solid, inert toward the metal used and stable at a temperature above the melting point of the metal which is to be employed. Examples of salts which are conveniently employed (and which are employed in an exemplary sense hereinafter) are the alkali and alkaline earth metal halides, such as sodium chloride, potassium chloride, magnesium chloride, barium chloride, calcium fluoride; sulfates of these metals, such as sodium sulfate, magnesium sulfate, etc.; metallic oxides, such as magnesium oxide, strontium oxide and titanium dioxide, and the like. Obviously, the salt must also be substantially insoluble in the metals employed at the casting temperatures. Ordinarily, these salts are crystalline, but they may be amorphous; or the crystalline material can be ground, milled or otherwise treated to change the shape of this material or to reduce its size. Thus, for example, shapes approximating spheres can be used.

In forming the initial body, the salt is compacted, as by the use of pressure, into a body which is the same as that ultimately desired or which approximates this. If the compacted shape remains in the mold for later steps, no binder is ordinarily necessary. If it is to be removed and handled, the salt particles are conveniently bound by the addition of a small amount of solvent, which dissolves or softens the surfaces of the particles and on drying binds them firmly. The compacted shape contains voids which predetermine the ultimate porosity obtained in the finished metallic product. The size of the crystals used, and the degree to which these are compacted, control the amount of metal which can be introduced into the initial body, and also the size and numbers of the random-interconnected passageways which will be present in the final product.

Using crystalline or amorphous particles of about 12 to about 80 mesh, compacting them using from substantially no pressure up to about 10,000 p.s.i., porous metal objects having porosity ranging from about 40 to about 90 percent of the total volume are produced. Slight uniform wetting of the particles with from about 1 to 10 percent by weight of a solvent before compacting tends to make the salt easier to compact to initial shapes having a low percentage of voids, thus producing greater porosity in the final product; and in addition, this strengthens the preformed initial body and makes it easier to handle. When a solvent is used, it must of course be removed from the initial body by careful drying before introducing the molten metal.

If desired, the uniformity of the porosity may be enhanced by special molding techniques. For example, isostatic pressing may be performed by surrounding the salt preform with an impervious membrane and subjecting the encapsulated form to hydrostatic pressure. Elastomeric surrounds may also be used to accomplish the same condition of equal pressure throughout the preform.

After the initial body is prepared, it is placed in a

mold which more or less closely approximates its outer configuration and the selected metal, in molten condition and maintained at a temperature below the melting point of the salt, is introduced into the voids thereof. This can be accomplished to some degree by gravity where the average salt particle used in making the initial body is greater than about 8 mesh in size. Capillary action is also effective to a degree, especially when the pore size of the initial salt body is small. However, for best results, the molten metal is forced into the voids by pressure. Thus, for example, die-casting techniques can be used, or centrifugal force can be used to compel the metal to enter into and fill the voids throughout the initial shape. Alternatively, gas pressure can be employed, as by subjecting the mold containing the initial body, in a closed vessel, to reduction of atmospheric pressure to a very low level, introducing the molten metal, and again raising the pressure to atmospheric. The molten metal is thus forced to flow into and throughout the voids in the initial body. The procedure can be carried out in atmospheres of inert gases, and these may also be used to exert greater pressure in performing the casting operation. The resulting product is an intermediate composite metal and salt structure.

The intermediate composite is cooled to solidify the metal. If the mold has closely contacted the initial body over a sufficient area, thus exposing the surface pores so that leaching can be accomplished, this may now be done. Such may be the case, for example, where a simple cylindrical shape is used and the initial body is formed and compacted directly in a cylindrical refractory mold. However, the mold may be larger than the initial body, so that an impervious metal shell surrounds the composite intermediate. Portions of this shell are then removed so that leaching can be accomplished, as described hereinafter.

Another case may arise where it is desired to machine the composite intermediate to a predetermined size and shape. The composite intermediate is a strong, rigid structure which can be worked by the usual methods of the metal-working arts to produce any desired configuration. While in this form, it can easily be brought to close dimensional tolerances, and can be attached to or incorporated into other metallic structures. It should be noted, however, that the process of the present invention is especially useful in that porous metal structures having predetermined dimensions and porosity can be produced directly by casting.

When the composite intermediate has been wrought in the desired size and form, it is subjected to leaching to remove the salt. This can be done with water under various conditions of temperature and pressure, where water-soluble salts are used, or with other solvents such as acids or bases, or alcohols or other organic solvents appropriate to dissolve the salts which are present can be employed. It will be apparent that the solvent employed should not adversely affect or dissolve the metal. Thus water, for example, cannot be used with reactive metals such as the alkali metals. Likewise, acid- and base-solubility characteristics of the metals are well-known and those skilled in the art will have no difficulty in recognizing the adaptability of the solvent to be used in any particular case. For convenience, water-soluble salts are used and water is a preferred leaching solvent. Most inorganic salts are more soluble in hot water, while continuous agitation will assist in increasing the speed of the leaching process. Several changes of the leaching bath, using fresh solvent, are usually used to insure complete removal of the salt. The leached, porous metal skeleton is then dried and is ready for use.

Certain high-melting oxides, such as magnesium oxide which melts at 2642° C., are useful in producing porous structures of the higher-melting metals. While these oxides are not soluble in water, or other solvents which do not adversely affect the metals and alloys ordinarily

used, they can be removed, after formation of the intermediate composite, by a two-step leaching process. For example, magnesium oxide is known to be soluble in certain molten ammonium salts. Accordingly, the magnesium oxide is leached from the composite by means of a bath of molten ammonium chromium sulfate. The latter salt is conveniently removed from the porous metal by forcing it out in molten state using air pressure, while maintaining the system at a temperature above 100° C. Alternatively, but less rapidly, the ammonium salt is removed by leaching with water.

The porous metal bodies produced by the process of the invention are characterized by containing a plurality of random, interconnected tortuous passageways of predetermined size and shape substantially uniformly distributed throughout that part of the body which previously contained the salt. The walls of these passageways are replicas of the crystal faces or the exterior surfaces of other particles which were originally present, and may therefore be said to be internally molded or shaped. The passageways may be defined as having a predetermined replicate configuration.

Depending on the original degree of porosity of the compacted initial shape, the metal bodies produced by the process are more or less porous. Their utility rests upon their porosity. Thus they can be used as filters or screens for liquids or gases. A special and highly useful product employing the porous metal structures can be prepared by forming the structure into the shape of a propellant grain and introducing a solid rocket propellant, for example, a mixture of an oxidizer and a curable resinous oxidizable binder, in liquid form, into and throughout the structure. On curing by conventional means, a composite solid propellant grain is produced which is strengthened by the metal, and in which the porous metal serves to control the burning rate as well as to accomplish other desirable purposes.

The following tables set forth, respectively, a number of exemplary metals and alloys, and salts which can be used to make preformed porous salt structures for use in the process of the invention. The selection of the salt to be used with the particular metal selected must of course be made subject to the considerations set forth hereinabove.

TABLE I

Metal:	M.P. ° C.
Zirconium -----	1860
Chromium -----	1850
Platinum -----	1769
Titanium -----	1660
Iron -----	1537
Nickel -----	1453
Uranium -----	1133
Copper -----	1083
Phosphor bronze (96.84 percent Cu, 3.11 percent Sn, 0.02 percent P) -----	1065
Gold -----	1063
Aluminum brass (76 percent Cu, 22 percent Zn, 2 percent Al) -----	980
Cast iron -----	1980
Silver -----	960.8
Brass (70 percent Cu, 30 percent Zn) -----	954
Silver-copper eutectic (71.5 percent Ag, 28.5 percent Cu) -----	778
Aluminum -----	660.1
Magnesium -----	650
Engineering silver solders -----	620-775
Zinc -----	419.5
Lead -----	327.3
Tin -----	231.9
Soft solders -----	180-275
Woods metal -----	73

¹ And above.

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TABLE II

Salt:	M.P. ° C
MgO -----	2642
BeO -----	2530
SrO -----	2430
MnO -----	1785
TiO ₂ -----	1775
SiO ₂ -----	1713
Fe ₃ O ₄ -----	1597
MnS -----	1530
CaF ₂ -----	1360-1418
BaF ₂ -----	1350
CuO -----	1336
Cu ₂ O -----	1236
Fe ₃ C -----	1227
FeS -----	1195
Cu ₂ S -----	1130
CdF ₂ -----	1110
NiCl ₂ -----	1030
NaF -----	992
BaCl ₂ -----	960
Na ₂ S -----	919
SrCl ₂ -----	872
ZnF ₂ -----	872
LiF -----	870
KF -----	857
BaBr ₂ -----	845
CrCl ₂ -----	815
NaCl -----	800
CaCl ₂ -----	782
KCl -----	770
KBr -----	742
NaBr -----	755
CoCl ₂ -----	740
AgI -----	557
PbCl ₂ -----	498
AgCl -----	455

The following examples will more specifically illustrate the process and products of the invention. In the examples, all parts and percentages are by weight unless otherwise specified.

Example 1

A porous cylinder of -12+20 mesh (standard screen sizes) sodium chloride was formed by uniformly wetting about 30 g. of the salt slightly with about 0.6 ml. of water, pouring it into a 1" diameter cylindrical mold about 2" high and drying in a 105° C. oven for about one hour. This cylinder was placed in the bottom of a long cylindrical, quartz container about an inch in diameter. A 30 g. piece of 3/4" diameter aluminum rod was placed on the preformed salt body. The container and contents were brought to a temperature of 700° C. under vacuum (about 0.2 mm. of mercury). The aluminum melted and flowed down around and over the salt preform. Upon releasing the vacuum to restore atmospheric pressure the aluminum rapidly penetrated the salt preform. The metal-salt composite was cooled and after cooling, a 1/2 inch thick section was sawed from it using a metal-cutting saw. The aluminum-salt composite was then leached with water until all of the salt was removed. A porous, near-perfect aluminum replica of the salt interstices was obtained. This contained about 40-50 percent of free space. Water and gases passed freely through the structure, indicating that the passages therein were interconnected.

Example 2

Another run was made in the manner of Example 1 except that the moistened -12+20 mesh salt was tamped directly into the bottom of a quartz test tube about one inch in diameter. From this experiment was obtained a rod of aluminum-salt composite which after machining using an ordinary metal turning lathe was .914 inch diam-

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eter by 2.471 inches long. The composite slug weighed 59.28 grams. After leaching overnight in cold running water, and drying, the porous metal rod obtained weighed 30.22 grams. This weight corresponds to a porosity or void space amounting to 57 percent of its volume. Removal of the sodium chloride by leaching was complete. No chloride ion could be detected in the aluminum by chemical macro-analysis.

Example 3

One hundred and six grams of moistened (-70+80 mesh) sodium chloride was lightly tamped to a depth of four inches into a 1 inch I.D. quartz tube closed at one end. A piece of pure aluminum, 3/4 inch in diameter by 3 inches long, was placed on top of the salt. The pressure in the tube was then reduced to about 0.2 mm. of mercury and the temperature raised to about 700° C. over a period of 95 minutes. At this time the molten aluminum rested on top of the salt body with little or no tendency to flow into it. Upon restoration of atmospheric pressure the aluminum penetrated to the bottom of the salt preform in about one second. After cooling the tube carefully from one end (to prevent formation of a hollow shrinkage core in the center) the aluminum-salt composite was removed. A slug, 0.856 inch in diameter by 3.556 inches long and weighing 77.34 grams, was machined from the composite with a metal-cutting lathe. After leaching with water, a cylinder of porous aluminum was obtained with uniform fine voids amounting to 49 percent of its volume.

Example 4

Thirty six grams of -12+20 mesh sodium chloride moistened with about 3 percent by weight of water was placed in a one inch I.D. steel mold. The salt was compressed with a close-fitting ram, the following data being obtained:

Pressure (p.s.i.)	Percent voids in salt
0 -----	42
2000 -----	24.8
4000 -----	16.9
8000 -----	9.3

The salt preform compressed to 8000 p.s.i. was placed in a quartz container or mold which was about 1/16" larger in diameter than the preform which was located therein so as to center it. The porous salt preform was then impregnated with molten aluminum, using the technique of vacuum casting set out in the preceding examples. A half-inch thick transverse slice of the resulting aluminum-salt composite was sawed from the casting, leached with water, and dried, leaving a porous cylindrical body having an integrally bonded, imperforate shell, containing only 9.3 percent of aluminum, equivalent to a porosity of 90.7 percent. This structure presented the appearance of an aluminum tube filled with porous aluminum. The porous aluminum structure thus produced had appreciable strength and gases and liquids passed easily and uniformly through it.

Example 5

Thirty-eight grams of the moist salt used in Example 4 was compressed in a cylindrical mold one inch in diameter under 3000 p.s.i. The use of this pressure produces a preform having about 20 percent voids in the salt, by interpolation from the data given in Example 4. From the compressed salt slug a cylinder of porous aluminum was produced by the technique of the preceding examples. The casting was found to contain about 82 percent of voids.

Example 6

A sample of commercially available granulated sodium

chloride was found to have the following screen analysis:

Screen size (meshes per inch)	Percent by weight
—12+20 -----	0.0
—20+28 -----	20.3
—28+42 -----	71.6
—42+65 -----	7.2
—65 -----	.8
—65 -----	.8

From about 41 parts of this salt with the addition of about 2.27 percent by weight of water there was produced, using 3000 p.s.i., a preform having about 71 percent of voids. This salt preform was used to produce a porous aluminum cylinder containing 28.7 percent aluminum, following the procedure set forth in the preceding examples. This sample was intermediate in pore size and surface texture between the samples produced from —12+20 mesh salt and the —70+80 mesh salt.

Example 7

Fifteen grams of fused, crushed, barium chloride screened to —20+50 mesh was wet with about .4 gram of water and pressed into a 3/8" diameter graphite cylinder, using light pressure just sufficient to compact the mass. A piece of magnesium was placed on top of the salt preform. The graphite cylinder was then placed in a quartz tube and the entire assembly was placed in a vertical tube furnace. Reduced pressure of about 0.2 mm. of mercury was applied to the tube until the temperature reached 150° C. This operation removed the water and consolidated the salt preform. The pressure was then returned to atmospheric and heating was continued until the magnesium melted. A short reapplication and release of the reduced pressure removed air from the salt and forced the magnesium into the salt preform. After cooling and machining to cylindrical form, the barium chloride was leached from the composite in running tap water. A cylinder of porous magnesium was obtained having a porosity of about 60 percent of its volume.

What is claimed is:

1. A porous, cast metal structure containing many randomly interconnected empty chambers occupying substantially the entire volume thereof and connected at points of contact with each other thus forming random, tortuous passageways throughout its structure, said chambers corresponding in number, shape, size and position to a plurality of solid, leachable three-dimensional objects composed of a metal salt having a higher melting point than that of the metal, said metal salt objects being placed in contact as a mass serving as an internal mold used in making said structure.

2. A two-phase composite metal-salt structure consisting of, as a first continuous solid phase, a substantially anhydrous, heat stable, crystalline metal salt which is inert toward the metal used in the composite and which is soluble in a solvent which has no adverse effects on the said metal, said salt being in a configuration with the crystals thereof in contact, and containing numerous, randomly located interconnected passageways therethrough; and as a second continuous solid phase, dense cast metal having a melting point lower than that of the said salt filling the passageways in the said salt phase; the said structure having at least one face at which the salt phase is exposed to permit leaching of salt from the said two-phase structure.

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Disclaimer

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Hereby enters this disclaimer to claims 1 and 2 of said patent.

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