

1

3,577,226

## METAL BODIES OF UNIFORM POROSITY

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2 Claims

### ABSTRACT OF THE DISCLOSURE

Sintered porous metal sheet, having not more than about one pore per twenty-five (25) square feet of sheet with a size larger than three times the average pore size of said sheet.

This application is a division of application Ser. No. 650,250, filed June 30, 1967, now U.S. 3,433,632, which is, in turn, a continuation-in-part of application Ser. No. 484,123 filed Aug. 31, 1965, and now abandoned.

This invention relates to porous metal bodies. More particularly the invention is directed to porous metal sheet and to an improved process for producing it.

A number of methods have been employed heretofore in producing porous metal bodies, particularly porous metal sheet. These methods include sintering of metal particles, the use of materials which liberate gas at elevated temperatures in order to introduce voids into a metal product, and the use of slip casting techniques in which metal particles are suspended in a variety of liquid or solid binders and then heated to eliminate the solvent or binder. All of these methods were subject to one or both of the disadvantages of non-uniform porosity in the product or difficulties in continuous large scale production.

It is an object of this invention to provide an improved process for producing porous metal bodies, including porous metal sheets, particularly very thin sheets of highly uniform porosity. A further object of the invention is to provide porous metal sheets of highly uniform porosity which can be produced in a continuous process.

According to the process of this invention a fluid mixture is prepared which comprises: (1) a metal powder, (2) an organic thickening agent, (3) an organic plasticizer, and (4) a volatile solvent. The fluid mix is then deposited in a thin layer on a backing sheet and allowed to dry, that is, the solvent is evaporated. This (substantially solvent free) material, referred to as "green sheet," is then subjected to further treatment to vaporize the organic material and sinter the metal particles. The sintered porous sheet can then be stripped from the backing sheet.

Any sinterable metal powder can be employed in this process, and suitable powdered metals include nickel, copper, cobalt, iron, tungsten, silver, stainless steel, other alloys such as nickel-base alloys, iron-base alloys, and cobalt-base alloys and the like. Typical stainless steel powders include types 304 and 316 as defined in the "Metals Handbook," 8th edition, pp. 408-409. Other illustrative alloy powders include (a) those having the composition (weight percent) nickel, 76%; chromium, 15.8%; iron, 7.2%; manganese, 0.2%; silicon, 0.2%; carbon, 0.04%; and copper, 0.1% and (b) those described in U.S. Pat. No. 2,703,277. The metal particle size is not critical, but generally particles having an average diameter in the range of 1 to 40 microns are preferred. The choice of particle size depends primarily on the desired pore size of the metal sheet, the smaller particles providing a product with a correspondingly smaller pore size.

2

Also, non-sinterable powders can be admixed with the sinterable metal powders. The sintered powder then provides a matrix which supports the non-sinterable material. Useful non-sinterable materials include carbon powder and Raney nickel powder.

The organic thickening agents (that is, agents whose function is to provide strength and durability to the green sheet and to define the structure of the porous sheet) which are useful in the process include plastic materials such as nitrocellulose, methyl cellulose, ethyl cellulose, and the like, and other organic materials such as the alginates.

The organic plasticizers are employed in order to improve the flexibility and ease of handling of the green sheet, and to improve the film-forming properties of the thickening agent. Useful plasticizers include conventional plasticizers such as paraffin oils, dimethylphthalate, polyoxyalkylene glycols, and the like.

The combination of organic thickening agent and plasticizer used in this invention differs from organic materials used as "binders" in prior art techniques in that green sheet ductility and flexibility are obtained without undesirable cracking, pinholing, and mud cracking. These properties are obtained by coating the individual metal particles with a mixture of organic materials not requiring thermal treatments.

The volatile solvents which are useful in the process of this invention include water, alcohols such as methanol, isopropanol, and the like, aromatic hydrocarbons such as benzene and toluene, and ketones such as acetone. Miscible mixtures of these solvents can also be used.

An organic wetting agent can be included in the fluid mixture as an optional ingredient. The wetting agent improves the homogeneity of the mix and the uniformity of dispersion of the metal particles. Suitable wetting agents include stearic acid and quaternary ammonium salts such as lauryl isoquinolinium bromide and dimethyl ammonium chloride.

All of the organic thickening agents, organic plasticizers, organic wetting agents, and solvents useful in this invention are materials which will either volatilize, completely decompose, or oxidize at elevated temperatures without leaving solid residues.

The backing sheet can be, for example, metal, porous metal, expanded metal, glassine paper, plastic coated paper, plastic sheet, and the like.

The fluid mix containing the metal powder, thickening agent, plasticizer, and solvent can be prepared by any convenient method. One such method is to first mix the thickening agent, plasticizer, and solvent, and then add the metal powder and continue mixing until a uniform suspension of metal powder is obtained. The relative amounts of the metal powder, thickening agent, plasticizer, and solvent which result in a uniform suspension depend upon the particular materials employed, and also on the particular metal and the particle size of the metal. The compositions of a number of satisfactory suspensions are given in the illustrative examples hereinbelow.

After the suspension of metal powder has been prepared, it can be deposited on the backing sheet by any convenient method. In continuous processes, it has been found particularly convenient to deposit the mix containing metal powder from a standard slit feeder onto a moving sheet of flexible material (herein referred to as the "backing sheet"), the desired thickness of the deposited layer being regulated by a leveling bar under which the moving sheet passes after the mix has been deposited thereon.

Of particular importance in producing the porous metal bodies of this invention is the ability to sinter either completely in the free shrinkage state or completely in the



restricted shrinkage state. Only under properly selected conditions can these states be realized. Failure to operate under these conditions results in sheets containing pinholes, cracks, warpage, and similar defects. In the case of free shrinkage, the unsintered sheet of metal powder suspended in a plastic matrix must be perfectly free to shrink in any direction during the sintering operation. In the case of the restricted shrinkage method, the unsintered sheet must be mechanically restricted, on a microscopic scale, from shrinkage appreciably in any direction except that vertical to the plane of the sheet.

It has been discovered that by proper selection and treatment of the backing sheet, the proper combination of nonmetallic ingredients in the mix, and the proper pre-compression of the unsintered sheet, the desirable result of either free or restricted shrinkage can be obtained. The examples hereinbelow illustrate some of the combinations which produce defect-free porous material. Excessive pre-rolling, sintering on backing strips not properly pre-treated, or excessive sintering during the initial stages all can cause sticking of the sintered sheet to the backing sheet precluding removal or can cause the generation of excessive defects in the finished porous sheet. In the case of free shrinkage, improper mixes which do not provide sufficient coherent material to bond the powder together during the initial sintering steps will result in sheets having excessive tears, pinholes, and the like defects.

The desirable shrinkage characteristics just described can be obtained when the ingredients used in the process of this invention are mixed in the weight ratios shown in Table I, the ratios being based on the amount of metal powder employed.

TABLE I

Ingredient:	Weight (grams)
Metal powder -----	100
Thickening agent -----	0.5-16
Plasticizer -----	0.5-9
Solvent -----	10-75
Wetting agent -----	0-3

These ratios also depend to some extent upon the powder characteristics and the desired final properties of the sheet. Therefore, in the case of a specific porous metal product, the weight ratios, while falling in this range, are held to much closer tolerance. For instance, the porous product obtained from nickel powders having average diameters of about 6 to 15 microns will have highly uniform properties if the ingredients used in the process are employed in the weight ratios given in Table II.

TABLE II

Ingredient:	Weight (grams)
Nickel powder -----	100
Thickening agent -----	3-5
Plasticizer -----	0.9-3.2
Solvent -----	15-20
Wetting agent -----	0-0.5

For smaller nickel metal powders, for example powders in the 3 to 5 micron diameter range, the same mix ingredient ratios given in Table II also apply except that the thickening agent can be used in amounts up to 8 grams per 100 grams of nickel powder and the solvent can be used in amounts up to 40 grams per 100 grams of nickel powder.

The ingredients of the metal powder containing mix, together with the other process variables referred to earlier, influence the shrinkage characteristics of the sheet, and therefore, its final properties. The non-metallic ingredients in the mix are added to the metal powder to provide handle-ability and strength to the green sheet. Excess amounts of these ingredients cause undue shrinkage and disruption when removed. Insufficient amounts make the mix difficult to handle and result in a weak green sheet. The proper amount fills the void structure formed by the

metal particles but does not significantly distend the metal structure. In this way cross shrinkage is prevented in the presintered state by virtue of the restraining powder particle network.

In addition to the factors described earlier with regard to free and restricted shrinkage, the relationship of sintering conditions (time, temperature, and atmosphere) to the powder characteristics is important. These characteristics are mainly the surface area, shape, size, agglomeration, and melting point of the powder. Each of these influence the degree of consolidation effected by a given set of sintering conditions. These basic factors dictate the sintering conditions for a given powder and structure. In general, the particle size of the powder and its melting point have the greatest influence on shrinkage during sintering. Low melting points and small particle size cause rapid sintering and lead to nonuniform shrinkage unless the sintering conditions are moderated to account for these tendencies.

The process of this invention is applicable to a wide variety of metal powders. Some powders have very sharp particle size distributions and pack to relatively high densities; other powders have very broad particle size distributions and are loose and fluffy in nature. However, in general, a sheet mated from any of these powders by the process of this invention will have a maximum individual pore size less than three times as large as the average pore size. The actual value will be dependent upon the particular powder used and is a characteristic of the powder and the thickness of the product sheet. In order to obtain this high degree of uniformity the green sheet should generally be sufficiently thick to obtain metal powder particle stacking of 15 particles or more. In the porous metal products of this invention, the pore size non-uniformity (many pores larger than 3 times the average pore size) which characterized previously known materials is practically eliminated. These large (non-uniform) pores will not occur more frequently than one per 25 square feet in the porous products of this invention. For example, the product of Example 1 hereinbelow has an average pore size of 6 microns (measured by the alcohol bubble pressure method) and a maximum pore size of 12 microns; pores as large as 18 microns occur not more than once per 25 square feet of product.

Where the metal powder is nickel powder, iron powder, or copper powder, the backing sheet is preferably pre-oxidized stainless steel.

After the green sheet has been deposited on the backing sheet, the final product can be obtained by several different series of steps. For example, in one embodiment of the invention the prerolled green sheet is sintered while still in contact with the backing sheet. The sintering operation, of course, serves to eliminate all volatile, decomposable, and/or oxidizable components as well as to effect sintering of the metal particles. The sintered metal powder layer is then stripped from the backing sheet and subjected to an additional sintering treatment. A rolling operation can be incorporated into the process between the two sintering treatments, if desired. In another embodiment of the invention, the green sheet is passed through rollers while still in contact with the backing sheet, subjected to the sintering operation while still in contact with the backing sheet, and thereafter the sintered porous metal sheet is stripped from the backing sheet.

Where paper or plastic backing sheets are employed, the sintering operation decomposes and/or oxidizes the backing sheet; preferably such backing sheets are separated from the green sheet prior to the sintering steps.

The thickness of the as deposited green sheet can vary from about 0.010 inch up to 0.062 inch or greater. During the evaporation of the solvent the thickness of the green sheet decreases by as much as 60 percent.

The removal of the volatile organic material and the sintering of the metal particles can be carried out in two separate steps or in a single combined step. To remove



5

the volatile, decomposable and/or oxidizable material it is preferable to heat the green sheet slowly to at least about 400° C. This can be conveniently done in a stream of inert gas which helps to carry away the volatilized components. The sintering operation is then carried out in a reducing atmosphere at temperatures of 700° C. or above, depending upon the particular metal powder. For example, where the metal is nickel or copper, a hydrogen atmosphere containing some water vapor is employed; where the metal is steel or iron an atmosphere or dry hydrogen is preferred.

The removal of decomposable and/or oxidizable material and the sintering operations can be conveniently combined in a continuous process, for example, by depositing the green sheet on a moving backing sheet which is continuously passed through a furnace. The furnace temperature and speed of the moving sheet are adjusted so that the green sheet is maintained at about 400° C. for about 5 minutes and is then heated at the sintering temperature of about 700° C. to about 1000° C., depending upon the metal used, for about 20 minutes. Cooling takes place on leaving the furnace. The entire furnace is flushed with dry or moist hydrogen or other neutral atmosphere depending on the metal involved.

The porous metal sheets produced by this process have thicknesses from as low as 0.003 inch up to 0.030 inch and above. The void fraction in the porous sheets can be as high as 60 percent and the average pore diameter can vary from as low as one micron up to about 50 microns.

The porous metal sheets produced by the process of this invention have a number of applications. Because of their uniformity and strength they are excellent, high quality filters. They are uniquely suited for use as electrodes in a wide variety of fuel cells and batteries. High porosity, large-pores structures can be made which serve as abrasable seal members, transpiration-cooling walls, and sound-suppression duct liners. Porous sheet, preferably copper or brass, can be impregnated with bearing alloys to make a high performance, long life bearing liner. The porous metal structures can be applied to solid heat exchanger surfaces to promote nucleated boiling. Also, the combination of the backing sheet and (unstripped) porous sheet can be used in fabricating boiling promoting surfaces in heat exchangers.

The following examples further illustrate the process and product of the present invention:

#### EXAMPLE 1

The following ingredients were mixed in a conventional paint shaker; 5900 grams of acetone, 1132 grams of nitrocellulose, and 680 grams of dimethylphthalate. After one hour of mixing, 32 kilograms of nickel powder (14 micron average diameter) were added and mixed for an additional two hours. The suspension containing nickel powder had a viscosity of 2500 centipoises. This mixture was allowed to stand for 24 hours to remove trapped gases, after which it was slowly rotated for two hours to re-homogenize the mix. The mixture was then loaded into a conventional slit feeder apparatus and forced by air pressure onto a moving belt of preoxidized stainless steel 0.008 inch thick and 12 inches wide. The use of mild steel or copper was not successful due to the formation of alloy between the nickel and the carrier belt which resulted in warpage and tearing of the sintered sheet. A leveling bar in front of the slit feeder insured sheet of uniform thickness. The leveling bar also defined the wet sheet thickness which was 0.029 inch. Upon drying the thickness reduced to 0.013 inch. The combination green sheet and stainless steel sheet was rolled to a thickness of 0.017 inch (green sheet thickness of 0.009 inch). This precompacting reduces nonuniformity, time required for sintering, and shrinkage during sintering. If the sheet is not precompacted, surface cracking frequently occurs along the edge of the sheet, these cracks reduce the uniformity and the strength of the sintered sheet. The pre-

6

rolled green sheet and support sheet combination was then passed through a belt furnace. The furnace temperature and belt speed were adjusted so that the green sheet was heated from room temperature to 800° C. in 5 minutes and was maintained at 800° C. for 20 minutes. This temperature of the initial pass is limited by alloying that occurs between the green sheet and the carrier belt; in this case it can be as high as 950° C. but, in Example 2, alloying would occur at this temperature. The furnace atmosphere was a mixture of 92.5 volume percent nitrogen and 7.5 volume percent hydrogen which had been passed through a water bubbler. The sintered sheet was cooled in a water-jacketed area of the furnace to about 160° C. before exiting from the furnace. The sintered sheet emerged completely separated from the stainless steel and was rolled up on a separate pickup roll. The sintered sheet was refurnaced (resintered) in the same atmosphere for 15 minutes at 950° C. to further reduce the porosity of the sheet. The finished sheet was 0.008 inch thick, 11 inches wide, and 200 feet long.

#### EXAMPLE 2

The following ingredients were mixed in a conventional paint shaker; 1504 grams of acetone, 311 grams of nitrocellulose, 170 grams of dimethylphthalate, and 70 grams of lauryl isoquinolinium bromide. After one hour of mixing, 5500 grams of nickel powder (4 micron average diameter) were added and mixed for an additional hour. The mix was then slowly rotated for 3 hours. The suspension containing nickel powder had a viscosity of about 4500 centipoises. The mix was then forced through a slit feeder onto a moving preoxidized stainless steel belt in the same manner as described in Example 1. The green sheet had a wet thickness of 0.037 inch and a dried thickness of 0.016 inch. The sheet was then rolled as in Example 1 to a thickness of 0.008 inch, and sintered as in Example 1 with the exception that it was not necessary to resinter this material. As noted in Example 1, higher temperatures during sintering will result in sticking to the carrier belt; this is a function of the nickel particle size.

#### EXAMPLE 3

The following ingredients were mixed for one hour on a conventional paint shaker; 160 grams of acetone, 40 grams of nitrocellulose, and 16 grams of dimethylphthalate. Eight hundred grams of 7 micron nickel powder were stirred into the plastic and this mixture was mixed for an additional hour. The mix was allowed to stand for one hour and was then cast onto a moving hard surface paper belt. The wet thickness was 0.030 inch which dried to 0.014 inch. The sheet was allowed to dry and the green sheet and paper sheet were separated. The green sheet was then rolled to 0.008 inch and sintered at 750° C. for 20 minutes in the same manner and atmosphere as in Example 1. For this type of operation the steps involving evolution of gases are important as the sheet is loose and weak at this point and furnacing at higher temperatures and faster rates frequently causes cracking of the green sheet. The maximum rate is dependent upon the thickness of the green sheet which controls its rigidity.

#### EXAMPLE 4

The following ingredients were mixed in a conventional paint mixer: 1000 grams of acetone, 200 grams of nitrocellulose, and 120 grams of dimethylphthalate. After one hour of mixing, 4950 grams of nickel powder (7 micron average diameter) were added and mixed for an additional hour. The suspension containing nickel powder had a viscosity of about 4000 centipoises. This mixture was allowed to stand for about a half hour to allow trapped vapor or air bubbles to escape. The mixture was then loaded into a conventional slit feeder apparatus. The mix containing metal powder was then forced by air pressure from the slit feeder onto a moving belt of preoxidized stainless steel .008 inch thick and 9 inches wide. The green sheet



7

which had a wet thickness of 0.024 inch was allowed to air dry for about 15 minutes. The thickness of the dry green sheet was about 0.012 inch. The combination green sheet and backing sheet was then prerolled at a thickness of 0.009 inch in order to precompact the metal powder. The prerolled green sheet-backing sheet combination was then passed through a furnace. The furnace temperature and belt speed were adjusted so that the green sheet was heated from room temperature to 950° C. in 9.2 minutes and was maintained at 950° C. for 37 minutes. The furnace atmosphere was a mixture of 95 volume percent nitrogen and 5 volume percent hydrogen which had been passed through a water bubbler. The sintered strip was cooled in a water jacketed area of the furnace to about 160° C. before emerging from the furnace. The sintered porous nickel, after stripping from the backing sheet was 0.0075 inch thick, 9 inches wide, 40 feet long and had a void fraction of 40 to 45 percent.

## EXAMPLE 5

An expanded metal-supported porous stainless steel sheet was prepared by casting a plastic mix containing stainless steel powder onto a carrier belt of expanded metal. The film-forming characteristic of the plastic mix permitted the mix to bridge the holes in the expanded metal, and the wetting characteristics of the mix caused the plastic mix to form a thin layer of material on both sides of the expanded metal. The plastic mix used consisted of 7500 grams of -325 mesh stainless steel (304) powder, 311 grams of nitrocellulose, 200 grams of dimethylphthalate, 752 grams of acetone, and 752 grams of toluene. The expanded metal used was made from 0.005 inch thick stainless steel sheet. The strand width was 0.007 inch wide and it was pulled to a 3/0 pattern, roughly 0.04 inch wide diamond pattern holes. The plastic mix was blended with the stainless steel powder by first shaking on a paint shaker for 30 minutes, then slowly rolling on a mill for 90 minutes. When it was cast, it had a viscosity of 4200 centipoises. The plastic material was cast onto the expanded metal following the general procedures of Example 1. The solvent evaporated rapidly and the mesh-mix combination quickly became self-supporting. The green sheet was prerolled to reduce its thickness by about 5 percent before sintering at 1200° C. for 3 minutes in a dry hydrogen atmosphere. The sheet was uniform and well bonded to the expanded metal.

## EXAMPLE 6

A large-pored, high void sheet was prepared by first preagglomerating nickel powder, and then casting it into

8

green sheet and sintering it so that the areas between the agglomerates formed the large pores, and the voids within the agglomerates aided in achieving a high void fraction. The same nickel powder used in Example 1 was presintered at 750° C. in a hydrogen atmosphere. The presintered stock was ground up and screened into specific screen sizes of -50 to +150, -150 to +250, and -250 to +325. A mix was made using 600 grams of the -50 to +150 mesh presintered nickel powder, 200 grams of toluene, 200 grams of acetone, 80 grams of nitrocellulose, and 50 grams of dimethylphthalate. The mix was blended by shaking on a paint shaker for one-half hour. The mix was then allowed to stand for one hour to remove trapped gas bubbles, and the powder which had settled from the plastic was redispersed by hand stirring. The mix was then cast on a tightly stretched nonsoluble plastic film. The material was removed from the plastic film before sintering and was sintered at 1100° C. for 12 minutes in a dry hydrogen atmosphere. The sintered sheet was 0.04 inch thick.

What is claimed is:

1. Sintered porous metal sheet having not more than about one pore per twenty-five (25) square feet of sheet with a size larger than three times the average pore size of said sheet and wherein said metal is selected from the group consisting of nickel, copper, cobalt, iron, tungsten, silver, stainless steel, a nickel-base alloy, an iron-base alloy and a cobalt-base alloy.

2. The sintered porous metal sheet as in claim 1 wherein said metal is nickel.

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