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3,323,879

POWDERED METAL FILMS

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This invention relates to metal films or strips and to powder metallurgy techniques for fabricating such strips and is a continuation-in-part of United States application Ser. No. 105,891, filed Apr. 27, 1961, now abandoned, entitled "Powdered Metal Films."

It has been customary in the manufacture of strips or films formed from metal particles or powder to employ methods which require a considerable amount of compaction and considerable rolling and annealing to obtain the desired strip width and gauge. These methods necessitate use of expensive equipment and lengthy processing techniques.

Accordingly, it is an object of this invention to facilitate fabrication of metal strips or films in an improved yet simplified and relatively inexpensive manner.

A further object is to produce metal strip by powder techniques requiring a minimum amount of rolling and little or no annealing.

Another object of the invention is to facilitate accurate control over the percentage composition of metal alloy structures.

A still further object is to form a metal structure having an accurately controlled thickness and an accurately controlled density or porosity.

The foregoing objects are achieved in one aspect of the invention by the provision of a strip forming process which utilizes a combustible binder film incorporating metal particles in sufficient quantity to cause them to be essentially in contacting relation with each other and disposed substantially uniformly throughout the mass of the binder. The film can be subsequently processed to form a product such as a strip of metal by burning off the binder and sintering the metal powder. Such a strip has a prescribed thickness and a prescribed density as determined by the original binder and metal particle film thickness, the particle size, and the ratio of binder to metal particle composition. The sintered strip can be rolled to further reduce the thickness and to increase the density up to 100 percent, if desired.

Since the original film gauge formed in the above-described manner can be made much thinner than was previously possible with powder techniques, little rolling and little or no annealing need be used to achieve the desired results. Accordingly, with this thin gauge sintered process, very low density thin strips can be fabricated. Heretofore it was not possible to make low density thin strips because of the required heavy gauge of the original compacted metal which necessitated considerable rolling and, therefore, inherently produced very high strip density.

A low density metal structure having a uniform and controllable thickness and porosity has proven advantageous in numerous applications. For example, some of the electrodes in electron tubes have low densities in order to allow easy degassing during tube processing. Also, battery plate structures adapted for active material impregnation and restricted by space requirements as well as fuel cell separating materials are other examples of applications wherein porosities and thicknesses are critical perimeters.

Additionally, thin metal strips having a density as high as 100% are equally desirable and have many useful applications. Such strip is readily and economically provided

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by the invention since very little rolling is needed to densify and reduce the gauge of the initial thin-gauge strip.

Regarding alloy compositions, it has been found that the percentage composition of an alloy can be accurately determined when using powder metallurgy techniques so far as the original powder composition percentages are concerned. When utilizing the present invention, this accurate composition is further controlled and maintained by virtue of the fact that minimum rolling and annealing minimizes changes in homogeneity of the powder mix and minimizes the metallurgical changes in the composition normally brought about in rolling and annealing processes.

A preferred process for fabricating metal strip is the film technique described in Patent No. 2,965,927 of Crosby and Stoll. Therein, a self-supporting pliable film convertible to a self-supporting pliable metal strip is provided. This technique provides numerous advantages over the more frequently encountered spraying, painting, stroking, molding, and similar processes. For example, the thickness uniformity, porosity control, and consistency of the product are enhanced while such problems as variations due to air entrapment and nonhomogeneous distribution of the metal powders are virtually eliminated or at least greatly reduced.

This casting technique taken in conjunction with a suspension which includes metal particles homogeneously dispersed in an organic binder with a plasticizer and suitable solvents as disclosed in the copending application of Robert L. Lambert et al., Ser. No. 105,889, filed Apr. 27, 1961, now Patent No. 3,171,817, has provided films having unique and previously unobtainable qualities. Further, these films are convertible to self-supporting and pliable metal strip. As an example, a self-supporting pliable film having a thickness in the range of 0.001 to 0.010 inch, a density of about 2.0 gms./cm.³, and a homogeneous dispersion of metal particles therein was cast from the following suspension:

Toluene	-----ml.	360
Ethyl alcohol	-----ml.	80
Diethylene glycol monobutyl ether	-----ml.	16
Ethyl cellulose	-----gms.	24
Carbonyl nickel (3μ-4μ)	-----gms.	528

in which the ethyl cellulose had an ethoxyl content of between 47.5 and 49.0 percent by weight and a viscosity of approximately 200 centipoises in a 5 percent solution of 80:20 toluene to ethanol.

As to the binder, plasticizer, and solvents of the above formulation, the advantages and details as well as the unique results are clearly set forth in the above application of Lambert et al. Generally, a plurality of solvents having different boiling temperatures and evaporative ion rates is preferred in order to properly dissolve the organic material, render it easier to control the viscosity of the suspension, attain a predicted evaporation from the film casting, and insure a desired film porosity and strength.

The plasticizer renders pliability and flexibility as well as assistance in the removal of the casting from a temporary support. Moreover, the solvents, plasticizer, and binder material must be compatible and volatilize at a temperature lower than the sintering temperature of the metal in the film without leaving an undesired residue which might deleteriously affect the product wherein the film is used.

Additionally, the binder, solvents, plasticizer, and metal particles should be of a ratio such that a viscous mass is formed whereby the metal particles are maintained homogeneously dispersed in the suspension and in the film after the suspension is cast. This viscosity also permits the casting of the film having a uniformity of thickness, a surface smoothness, and a controlled porosity and

composition free from entrapped gasses which is believed to be unobtainable by other known methods.

As to the metal particles, it has been found that most all metals are applicable and appropriate so long as their form is solid rather than liquid and so long as the particles are sinterable. Also, the metal content should be in the range of about 75 to 97 percent by weight of the cast film. When less than about 75 percent metal content is used it has been found that the required contiguous relationship between the particles is most difficult to obtain and the metal strip resulting from the volatilization of the organic materials does not have the desired self-supporting qualities. On the other hand, a metal content greater than about 97 percent limits the organic material content such that the cast film does not have the strength nor the pliability necessary to provide a pliable and self-supporting film.

As to the thickness, density, and porosity of the film and strip, suspensions containing the above percentages of metal have been cast into self-supporting and pliable films having a density in the range of 0.9 to 3.3 gms./cm.³ with a thickness of about 0.001 to 0.100 inch. These films have then been converted by volatilizing the organic materials therefrom to pliable and self-supporting metal strip having a porosity of approximately 50 to 90 percent and a thickness of 0.0008 to 0.060 inch.

It has been found that films having a thickness greater than about 0.100 inch are difficult to cast in a manner which will provide smooth surfaces free from cracks and fissures. Experience indicates that the evaporation rate of the solvents or at least a major portion of the solvents should be equal to the diffusion rate of the solvents through the film and attempts to force dry the casting by vacuum and other normal techniques have not, thus far, been successful. Also, self-supporting films less than about 0.001 inch are difficult to handle without expensive and precise apparatus especially adapted to such techniques.

The above-mentioned combination of conditions necessary to provide a self-supporting and pliable film necessarily limit the density of the film. Also, the pliable self-supporting metal strip which results from the volatilization of the organic materials from the film is likewise limited in thickness and porosity.

As to the metal particle size and configuration, self-supporting pliable films convertible to self-supporting pliable metal strip have been cast with metal particles in the range of approximately 1μ to 50μ in size. Obviously, the smaller particle sizes are preferable for the thinner films in order to provide smooth film surfaces without protruberences as well as homogeneous distribution of the particles therein. Although particles smaller than 0.001 inch are applicable, their availability is limited and their use does not appear to be economically justified at present. Also, particles larger than 50μ do not appear to be compatible with desired uniform dispersal and smoothness in films greater than about 0.100 inch thick and strip in the range of 0.060 inch in thickness.

The particle shape is dependent upon the type of film and strip desired. For a more dense film or strip spherical particles are most applicable while a porous film or strip is more readily provided by particles having a dendritic configuration. Obviously, the increased surface area of the dendritic particles permits the necessary contiguous relationship therebetween at a reduced concentration.

As an example, dendritic-shaped carbonyl nickel particles in the range of 7μ to 9μ in size were included in the previously detailed formulation and cast according to the technique of Crosby and Stoll to a thickness of about 0.065 inch and a width of four inches. This casting was supported at ordinary room temperature until a major portion of the solvents had diffused therethrough and evaporated. The resultant self-supporting pliable film had a width of about four inches, a thickness of about 0.045 inch, and a density of approximately 1.5 gms./cm.³.

The film was then heated to a temperature of about 1100° C. whereby the organic constituents were volatilized and the powdered metal particles sintered. The resultant self-supporting pliable nickel strip had a width of about four inches, a thickness of approximately 0.038 inch and a porosity of 83 percent.

This metal strip was then cut to provide the supporting structure for a nickel-cadmium battery plate and, after impregnation, resulted in a battery plate having greater capacity per unit weight than is obtainable by any other known technique. Moreover, the technique is adapted to the fabrication of fuel cell separators of closely controlled porosity which, as far as is known, are unobtainable by any other process.

There are many advantages provided by the process and structure described herein. For instance, the film containing the proper percentages of metal powder can be produced close to desired finished size, and partially dense metal structures can be produced in desired gauges. With the control of thickness and density, limited or no annealing may be necessary in order to produce the metallic structure so that better control of the composition, e.g., alloy percentages, can be achieved. Also, thin gauge dense strips can be produced with little rolling and little or no annealing.

Although several embodiments of the invention have been described, it will be apparent to those skilled in the art that various changes and modifications may be made therein without departing from the scope of the invention as defined by the appended claims.

What is claimed is:

1. A self-supporting sintered pliable metal strip formed solely from a film casting and having a substantially uniform thickness not greater than 0.06 inch, comprising metal particles sintered together to provide a uniform and controlled porosity in the range of about 50% to 90%.

2. A self-supporting sintered pliable metal strip formed solely from a film casting and having a substantially uniform thickness in the range of about 0.0008 to 0.060 inch comprising metal particles sintered together and having a size in the range of 1μ to 50μ to provide a uniform and controlled porosity in the range of about 50% to 90%.

3. A self-supporting sintered pliable metal strip formed solely from a film casting containing metal particles in the range of about 75% to 97% by weight of the film comprising metal particles sintered together to provide a uniform and controlled porosity in the range of 50% to 90% and having a substantially uniform thickness of approximately 0.0008 to 0.060 inch.

4. A self-supporting sintered pliable metal strip comprising sintered metal particles having a size of about 1μ to 50μ and a uniform and controlled porosity of about 50% to 90%, and a thickness not greater than 0.06 inch.

5. A self-supporting sintered pliable metal strip formed solely from a film casting containing metal particles in the range of about 75% to 97% by weight of the film comprising sintered and compacted metal particles having a size of about 1μ to 50μ and a uniform and controlled density up to 100 percent, and a thickness not greater than 0.06 inch.

6. A self-supporting sintered pliable metal strip formed solely from a film casting containing metal particles in the range of about 75% to 97% by weight of the film comprising sintered and compacted metal particles having a size of about 1μ to 50μ and a uniform and controlled density up to 100% and a substantially uniform thickness in the range of 0.0008 to 0.060 inch.

7. A self-supporting sinterable pliable cast film having a uniform thickness and comprising metal particles homogeneously dispersed in an organic binder, said particles constituting about 75% to 97% of the film weight and said film having a density in the range of

about 0.9 gm./cm.³ to 3.3 gms./cm.³, said cast film having a thickness not greater than 0.10 inch.

8. A self-supporting sinterable pliable cast film having a uniform thickness and comprising sinterable metal particles homogeneously dispersed in an organic binder, said particles having a size in the range of about 1 to 50 microns and said film having a density in the range of about 0.9 to 3.3 gms./cm.³, said cast film having a thickness not greater than 0.10 inch.

9. A self-supporting sinterable pliable cast film having a uniform thickness and comprising sinterable metal particles homogeneously dispersed in an organic binder, said particles constituting about 75% to 97% of the film weight and said film having a thickness in the range of 0.001 to 0.100 inch.

10. A self-supporting sinterable pliable cast film having a uniform thickness and comprising sinterable metal particles homogeneously dispersed in an organic binder, said particles having a size in the range of about 1 to 50 microns and constituting 75 to 97 percent of the film weight and said film having a thickness in the range of about 0.001 to 0.100 inch with a density of approximately .9 to 3.3 gms./cm.³.

11. A cast film having a uniform thickness and comprising an organic binder, solvents for the binder, a plasticizer, and homogeneously dispersed powdered metal particles, said particles constituting 75% to 97% by weight of the film casting, said cast film having a thickness not greater than 0.10 inch.

12. A self-supporting pliable film having a uniform thickness in the range of about 0.001 to 0.010 inch and a uniform and controlled density of approximately 1.8 to 2.2 gms./cm.³ and cast from a viscous suspension consisting essentially of:

Toluene	ml.	360
Ethyl alcohol.....	ml.	80
Butyl carbitol.....	ml.	16
Ethyl cellulose.....	gms.	24
Carbonyl nickel (3μ-4μ).....	gms.	528

in which the ethyl cellulose has an ethoxyl content of between 47.5 and 49.0 percent by weight and a viscosity of approximately 200 centipoises in a 5 percent solution of 80:20 toluene to ethanol.

13. A process for fabricating a pliable self-supporting metal strip comprising the steps of:

casting onto a support a viscous suspension containing sinterable metal particles in contacting relationship and homogeneously dispersed in an organic binder, a binder plasticizer, and a volatile solvent;

drying said cast suspension to remove said solvent and provide a pliable self-supporting film;

removing said film from said support; and

heating said film sufficiently to volatilize said binder and plasticizer and sinter said metal particles to provide said metal strip, said strip having a substantially uniform thickness in the range of about 0.0008 to 0.060 inch and a uniform and controlled porosity in the range of about 50% to 90%.

14. A process for fabricating a pliable self-supporting metal strip comprising the steps of:

casting onto a support a viscous suspension containing sinterable metal particles in contacting relationship and homogeneously dispersed in an organic binder, a binder plasticizer, and a volatile solvent;

drying said cast suspension to remove said solvent and provide a pliable self-supporting film, said film containing metal particles in an amount of about 75% to 97% by weight thereof;

removing said film from said support;

heating said film sufficiently to volatilize said binder and plasticizer and sinter said metal particles to provide said pliable self-supporting metal strip; and compacting said metal strip to provide a uniform and controlled density of up to 100% of theoretical density.

15. A process for fabricating a pliable self-supporting metal strip comprising the steps of:

casting onto a support a viscous suspension containing sinterable metal particles in contacting relationship and homogeneously dispersed in an organic binder, a binder plasticizer, and a volatile solvent;

drying said cast suspension to remove said solvent and provide a pliable self-supporting film, said film having a uniform thickness in the range of 0.001 to 0.100 inch, a density of approximately 0.9 to 3.3 gms./cm.³, a metal particle content of about 75% to 97% by weight, and metal particles in the range of 1 to 50 microns;

removing said film from said support; and

heating said film sufficiently to volatilize said binder and plasticizer and sinter said metal particles to provide said metal strip, said strip having a substantially uniform thickness in the range of about 0.0008 to 0.060 inch and a uniform and controlled porosity in the range of about 50% to 90%.

16. A process for fabricating a pliable self-supporting metal strip comprising the steps of:

casting onto a support a viscous suspension containing sinterable metal particles homogeneously dispersed in an organic binder, a binder plasticizer, and at least one volatile solvent;

drying said cast suspension to remove said solvent and provide a pliable film having a substantially uniform thickness in the range of about 0.001 to 0.100 inch, a density of approximately 0.9 to 3.3 gms./cm.³, and a metal particle content of about 75% to 97% by weight of said film;

removing said film from said support; and

heating said film sufficiently to volatilize said binder and plasticizer and sinter said metal particles to provide said metal strip, said strip having a substantially uniform thickness in the range of about 0.0008 to 0.060 inch and a uniform and controlled porosity in the range of about 50% to 90%.

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