Jan. 13, 1970 E. L. THELLMANN 3,489,555

METHOD OF SLIP CASTING TITANIUM STRUCTURES

Filed May 18, 1967 2 Sheets-Sheet 1

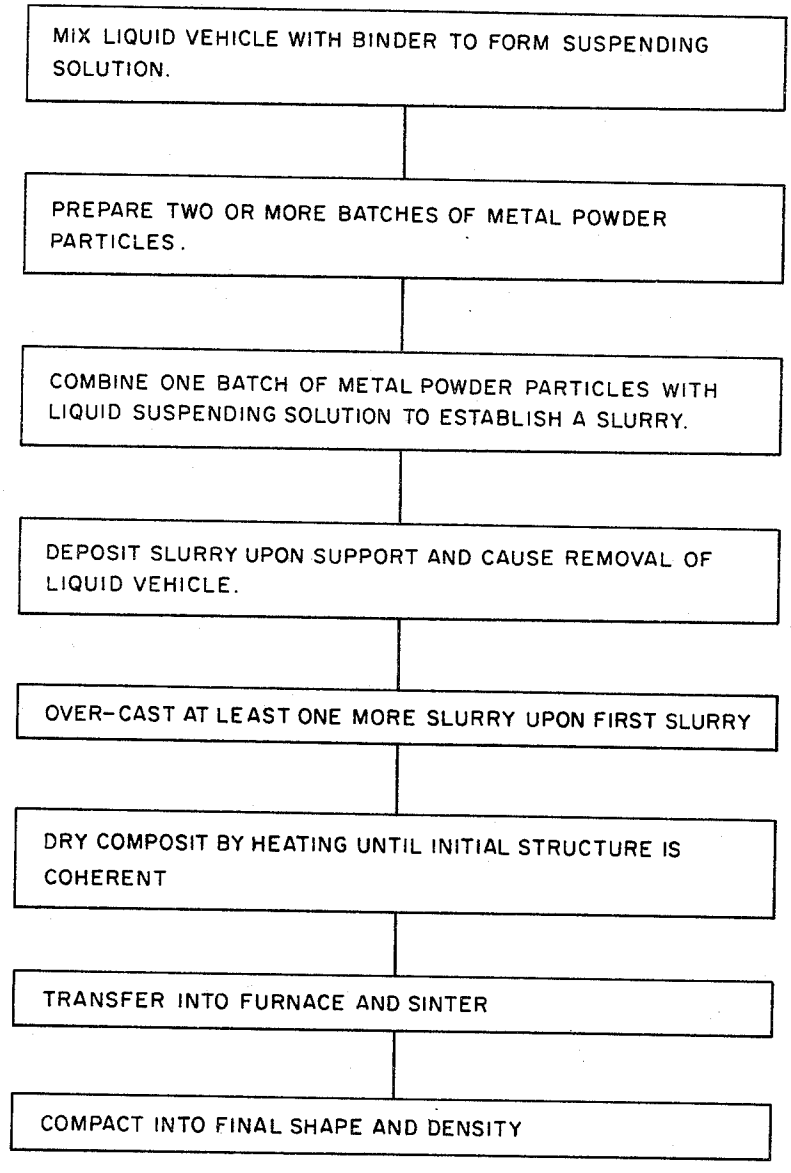


FIG. 1

INVENTORS
EDWARD L. THELLMANN
PAUL M. PHILLIPS
BY Edward L. Parker
ATTORNEY

Jan. 13, 1970 E. L. THELLMANN 3,489,555

METHOD OF SLIP CASTING TITANIUM STRUCTURES

Filed May 18, 1967 2 Sheets-Sheet 2

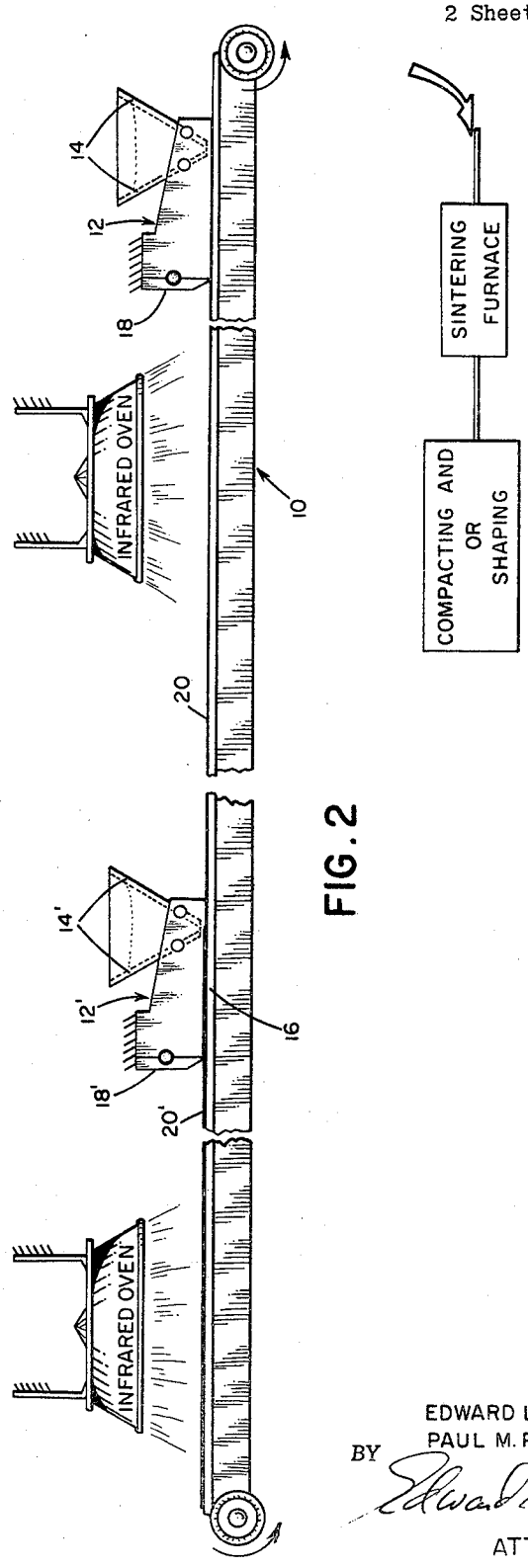


FIG. 2

INVENTORS
EDWARD L. THELLMANN
PAUL M. PHILLIPS
BY Edward L. Thellmann
ATTORNEY

United States Patent Office 3,489,555
Patented Jan. 13, 1970

3,489,555

METHOD OF SLIP CASTING TITANIUM STRUCTURES

Edward L. Thellmann, Bedford, and Paul M. Phillips, Cleveland, Ohio, assignors to Clevite Corporation, a corporation of Ohio

Filed May 18, 1967, Ser. No. 639,414
Int. Cl. C22f 1/00; B22f 3/16
U.S. Cl. 75—211 3 Claims

ABSTRACT OF THE DISCLOSURE

Preparing a liquid suspending agent of water, a binder, optionally a plasticizer and mixing each component with metal powders of a given size. Thereafter mechanically depositing the slip upon a support, then, if desired, slip casting a second layer upon the previously cast film and drying, sintering and compacting the composite. The slip is composed of metal powders, either titanium or nickel, a cellulose binder and, optionally, a plasticizer such as polyglycol.

The invention relates generally to a powder metallurgy process and, more particularly, to slip casting of single and multi-porosity structures. The invention is particularly adapted to be employed for making single and dual porosity filters, battery placques, metering devices, air bearings, electrodes for fuel cells, etc.

In the prior art it has been the practice to fabricate a multi-porosity structure by depositing a slurry upon a backing member and thereafter to work and sinter the slurry prior to applying a second slurry layer. This approach has some inherent shortcomings in that the working steps are very numerous and the resulting product is not of sufficiently uniform density and particle distribution. The slurry in the method of the prior art is usually produced by spooling the base structure through a trough which contains the liquid suspension. A representative illustration is shown in U.S. Patent 2,987,423. With such a process it is quite difficult, if not impossible, to control and maintain a uniform thickness of the film, at least not with the degree of accuracy required for many articles such as for example fuel cell electrodes. Further difficulties are encountered by virtue of the fact that the slurry must be made to adhere to the base material, and, therefore, the process can usually not be utilized for making a coherent and independent structure composed solely of the cast elements.

It is also known in the art to make multi-porosity structures by placing several layers of metal particle containing pastes into a container and extruding the container to a predetermined size. This process normally does not lend itself to mass production techniques and, moreover, it has been found that a clean transition zone between the various layers of paste cannot be readily maintained during the process nor established in the final article.

The compatibility of the materials hereinunder consideration, i.e., nickel and titanium, with materials and structures used in the process is of major significance due to their high reaction rate to form subcompounds with a great many other materials. Thus, for instance, titanium, cannot be used with paste suspending agents such as Vaseline and paraffin inasmuch as titanium will react therewith and the purity rate of the resulting structure will be detrimentally affected. The same difficulty is experienced as a result of contact between the titanium powders and metal tubes, or containers, conventionally utilized for the extrusion process mentioned above. The contamination of the metal powder particles causes a complete or partial inclusion of the porous structure and, frequently, results in a chemical reaction between the contaminants

and the particles establishing an alloying effect which lowers the corrosion resistance and affects ductibility, machinability and other properties. It has been shown that most known suspending agents react adversely with such titanium powders. While the reaction sensitivity of nickel powders with other materials is somewhat less than that of titanium it nevertheless is critical. Both metals also require due to the chemical sensitivity great care in the selection of compatible process equipment.

Applicant's invention enables the mass production of single and multi-porosity structures composed of pure titanium or nickel powders, and permits a close control over dimensional and density characteristics of the film.

In accordance with the invention, the porous structure is slip cast. This involves as a first step mixing a liquid vehicle with an organic binder to form a suspending solution. One or more batches of discrete metal powder particles are prepared in which the particles of each individual batch are of substantially or at least predominantly similar size but dissimilar relative to one or more other batches. In most instances at least one batch will contain relatively fine powder particles while another batch will be composed of comparatively coarse powder particles. The metal particles for a slip cast structure are either nickel or titanium. Thereafter, the liquid suspending solution is combined with one batch of powder particles in order to establish a slurry. The slurry is then mechanically deposited by means of a pig trough upon a flat support and the liquid vehicle is caused to be removed. For multi-porosity structures one or more additional slurries are then overcast, sequentially, upon the initial layer and thereafter the single or, alternatively, multi-slurry composite is dried until the resulting structure is sufficiently coherent to permit removal thereof from the support. Optionally, the first layer may be heat dried prior to overcasting. The structure is then sintered to the predetermined degree of density and compacted if desired to affect the porosity and final shape.

It is therefore the primary object of this invention to provide a method for making a single or multi-porosity structure composed of titanium or nickel which is more economical than prior methods and enables a greater degree of control over the dimension and uniform density of the final article.

It is the further object of this invention to provide a method for producing a porous structure of titanium or nickel particles having a high degree of purity.

It is a further object of this invention to provide a method in which the various components necessary for facilitating the production of the invention described in the preceding paragraph are metallurgically compatible with such particles and do not contaminate the metal powder matrix.

For a better understanding of the present invention, together with other and further objects thereof, reference is had to the following description taken in connection with the accompanying drawings, and its scope will be pointed out in the appended claims.

In the drawing:

FIG. 1 is a flowing sheet showing steps for practicing one embodiment of the invention;

FIG. 2 is a generally diagrammatic-schematic representation of the method.

As indicated in FIG. 1, the initial step in the process for making a multi-porosity structure is, preferably, the preparation of the liquid suspending agent. The basic vehicle of the suspending solution is water. To the water there is added an organic binder of cellulose powder which constitutes, approximately, ½ to 2 weight percent of the total suspending solution. Extensive tests with numerous organic binders have shown the binder of cellulose to be

the only known material suitable for producing a slip of either pure nickel or titanium which is reproducible and devoid of high reaction rate causing contaminants. The factors which enter into the selection of the binder are manifold and include criteria such as reproducibility, stability, residual behavior after sintering, bacteria resistance, pH sensitivity, etc.

It has been found that when the range of the above noted binder content is exceeded, one or more of the factors which entered into the desirability for choosing this particular binder are negated.

Preferably, although not absolutely essential for practicing the invention, approximately 0.25 weight percent of polyglycol is added to the solution when such solution is used in conjunction with nickel particles. The polyglycol addition acts as a plasticizer and promotes a ductile bond between the powder particles.

In the next step one or more batches of discrete metal powder particles of either nickel or titanium are prepared. Such preparation may involve cleaning, if necessary, and screening so that the particles of a given batch are substantially, or at least predominantly, of uniform size. For multi-porosity composites, for instance, dual porosity, it is of course desired that the particle size of the powders constituting the two layers be distinctly different.

Thereafter one batch of metal powder particles is combined with the liquid suspending solution to establish a slurry having a reasonably good viscosity.

The invention uses a conveyor-like structure **10**, part of the system being illustrated in FIG. 2. The slurry is deposited into a stainless steel pig trough and automatic strike-off machine **12** having two inclined walls **14**, adapted for adjusting the transverse dimension of the bottom opening of the trough in order to control the volume flow of the slurry upon a low friction support **16** which is suitably secured to the conveyor system **10**. The support **16** is preferably made of glass, although in some cases, stainless steel can be utilized. The rear end of the device **12** is provided with a vertically adjustable doctor blade **18** which bares upon the film **20** in a predetermined, spaced, relation to the support **16** to control the thickness of the layer or film **20**. The excess thickness is caused by the doctor blade **18** to be either swept forward together with the blade or flows sideways where the same may be readily removed.

The liquid vehicle is then removed by evaporation at room temperature, or by application of heat to accelerate the removal of the water.

Once the liquid vehicle has been removed, the slurry is now ready to be overcast with one or several additional slurries following the same procedure as outlined above. For this purpose there is stationed a second set of equipment identical to the one described above along the continuous conveyor system **10**. Like reference characters are utilized to designate such equipment, however prime marks distinguish the second set. It is obvious that the number of sets may correspond to the number of layers desired to facilitate the application of mass-production techniques.

The multi-slurry composite, or alternatively the initial and sole layer, is dried by application of heat, until the resulting structure is sufficiently coherent to permit removal thereof from the support **16**. The single or multi-slurry structure is then placed into a sintering furnace containing suitable atmosphere and temperature conditions to densify the composite to the degree desired.

Particular care must be exercised that the process equipment which comes in contact with the metal particles, particularly the titanium powder, is compatible therewith and will not contaminate the final article.

It has been found that a slurry containing approximately 40 to 90 weight percent nickel powder particles is usually desired. The exact composition is largely dependent upon the particle shape of the powder which influences the amount of fluid vehicle required to establish the desired viscosity. For certain applications requiring dual porosity, conditions can be optimized by using approximately 80 weight percent relatively fine nickel powder particles for the first slurry and for the second slurry, approximately 75 weight percent compartively coarse nickel powder particles.

For slurries containing titanium powder particles it has been found that 40 to 60 weight percent is the most suitable proportion for practicing the invention while approximately 55 percent titanium powder particles optimizes the results and provides a preferred structure.

The following are examples of specific methods and materials for slip casting titanium and nickel structures and these may be taken as illustrative for practicing the invention:

EXAMPLE I

A first batch of relatively fine porous nickel powder particles was prepared by screening same and selecting 0 to 5 micron size particles. The slip concentration consisted of 20 percent suspending agent of which 98½ percent was water and 1½ percent cellulose binder. The balance of 80 percent by weight was composed of the nickel particles. Prior to casting the slip upon the support **14**, the support was prepared with a releasing agent such as wax. The pig trough was adjusted to control the rate of deposit and the doctor blade was set at .015 to .017 inch. After the slip had been deposited upon the glass support, the liquid vehicle was removed by evaporation at room temperature.

A second batch of nickel powder particles was prepared. The particles were relatively coarse in that 60 percent thereof were of 10 to 15 micron size while the balance was 5 to 10 micron. Due to the particular shape and size of the nickel particles the slip concentration consisted of 75 percent by weight nickel particles and 25 percent by weight suspending solution which included 98½ percent water and 1½ percent cellulose binder. For the casting of this second slurry the doctor blade was set at .050 to .052 inch. The second slurry was deposited through the pig trough in the same manner as the first slurry and thereafter the multi-slurry composite was dried in an infrared oven for about one hour at about 140–150° F. The composite was then placed into a conventional sintering furnace with a dissociated ammonia atmosphere for a period of about 5–8 minutes at 1,850° F.

After sintering the multi-layer structure had a thickness of approximately .035–.037 inch. The structure was then compacted to the desired degree of denstiy and simultaneously shaped as required for the particular application.

EXAMPLE II

The procedure and material utilized was the same as described in the preceding example, except that after the first slurry was cast the same was dried in an infrared oven for one hour at a temperature of about 140–150° F. and allowed thereafter to cool to room temperature before the same was overcast with a second slurry.

EXAMPLE III

Metal powder particles of titanium were selected having a size of up to 150 micron. The slip concentration consisted of 55 percent by weight titanium particles with the balance being composed of 98 percent water and 2 percent cellulose binder. The support was again, as in the preceding example, waxed with a releasing agent and the doctor blade was set at .150 inch. Subsequent to depositing the slip into the pig trough and upon the glass support, the slurry was dried in an infrared oven for about two hours at a temperature of 130–140° F. Thereafter the cast structure was removed from the support plate and placed into a sintering oven for two hours in a vacuum at 1,850° F. The thickness obtained after sintering caused the film to shrink to approximately .095

inch. The structure was then compacted and shaped to the required degree of density and configuration.

EXAMPLE IV

The procedure outlined in the first example was generally followed, except that the structure was compacted to the desired shape and density prior to sintering.

While there have been described what are at present considered to be the preferred embodiments of this invention, it will be obvious to those skilled in the art that various changes and modifications may be made therein without departing from the invention, and it is, therefore, aimed in the appended claims to cover all such changes and modifications as fall within the true spirit and scope of the invention.

What is claimed is:

1. The method of slip casting a metal powder structure comprising:

mixing a water base liquid vehicle with a cellulose base binder to form a suspending solution;

combining discrete titanium particles with the suspending solution to establish a slurry in which the cellulose base binder constitutes approximately one-half to two weight percent of the total suspending solution;

mechanically depositing the slurry upon a support and causing a controlled removal of the liquid solution;

drying the slurry by application of heat until the resulting structure is sufficiently coherent to permit removal thereof;

and sintering said structure.

2. The method of slip casting according to claim 1, wherein the slurry contains approximately 40 to 60 weight percent titanium powder particles.

3. The method of slip casting according to claim 2, wherein the slurry contains approximately 55 weight percent titanium powder particles.

References Cited

UNITED STATES PATENTS

2,267,918	12/1941	Hildabolt	75—208 X
2,293,843	8/1942	Marvin	75—208
3,115,698	12/1963	St. Pierre	75—211 X
3,197,847	8/1965	Kerstetter	75—208 X
3,226,263	12/1965	Oswin	75—222 X
3,227,591	1/1966	Lambert	75—208 X
3,287,112	11/1966	Blaha	75—222
3,311,507	3/1967	Dittmann	75—208 X
3,323,879	6/1967	Kerstetter	75—208 X
3,323,915	6/1967	Lambert	75—208 X
3,350,200	10/1967	Stanstede	75—208

OTHER REFERENCES

Metal Progress, April 1967, vol. 91, No. 4, p. 64.

CARL D. QUARFORTH, Primary Examiner

A. J. STEINER, Assistant Examiner

U.S. Cl. X.R.

75—200, 222