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SLIP CASTING

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This invention relates to an improved method of forming shaped slip cast articles of metals and metallic compounds.

Articles of tungsten, molybdenum, tungsten carbide and other refractory metals and metallic compounds thereof are at present produced primarily by the customary powder metallurgical practice of compressing powders of the material into the desired shape at high pressure and sintering the object so produced. This method of producing articles involves the use of costly equipment since a multiplicity of press sizes and die shapes is required. The dies also must be replaced frequently due to wear. Another disadvantage of fabricating articles by compacting is the limitation in the sizes and shapes that may be produced because of the flow characteristics of certain powders during compression. Articles of complex design, such as those having re-entrant angles, external threads, two or more lateral projections, etc., cannot be fabricated by pressing.

Other methods of forming objects of the heavier metals and metallic compounds have been attempted in the past. Slip casting is well known and successful in the ceramics industry. Ceramic particles, due to the nature of their ionic charge, are inclined to repel each other in a suspending medium, thereby achieving the dispersed state suitable for slip-casting. Metal particles such as tungsten and molybdenum, on the other hand, do not have such a tendency to disperse readily. Sustained suspension of the metal powder in the slip is required to prevent premature settling and consequent variation in wall thickness but, because of the excessive weight of the heavy metal particles, it has been difficult, if not impossible, to produce objects having uniformly high density and suitably uniform wall thicknesses. For these reasons, up to the present time, the production of unusual shapes from such metals and their compounds has been an expensive, if not impossible, undertaking.

A further disadvantage of the normal slip-casting technique arises from the fact that water is commonly employed as a suspension agent for the material particles. This requires that the techniques be limited to materials and metals which are non-reactive in an aqueous environment.

It is, therefore, the primary object of the present invention to provide a novel method of forming slip cast articles of complex design from the heavier metals and compounds.

Further objects of the present invention are to provide a novel method of forming slip cast articles having a high density from the heavy metals and compounds; to provide a novel method of forming hollow slip cast articles having a uniform wall thickness; and to provide a novel method of slip-casting materials normally reactive in the presence of water.

Other objects, features and advantages of the present invention will become apparent from the following description and appended claims.

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According to the present invention articles may be formed from metals or metallic compounds by providing a mixture of a resin and an organic suspending medium, suspending a powder of the heavy metal or heavy metallic compound desired to be cast in such mixture and placing the mixture with the suspended powder in a porous mold. The suspending medium is then adsorbed through the mold, leaving a slip cast object which may be removed and sintered.

The phenomenon which enables the successful application of the slip casting technique to produce shapes of the heavy metals and their compounds resides in the recognition of the fact that, by coating the individual particles with a suitable resin, powders of these materials may be effectively dispersed in certain organic suspending media to produce slips having the required properties for casting into shapes. Thus, a well known ceramics process may be employed for the first time with heavy metal and heavy metal compound powders.

It is important in the practice of the invention that minute particles be employed so that a product having maximum density is obtained. Powders of a purity desired in the finished article should be employed and particle sizes ranging from 1 to 5 microns have proved satisfactory. Since the surface area of the particles varies with particle size, the quantity of resin to be employed is similarly effected. A quantity of resin equivalent to about 1 percent of the weight of powder utilized has been found sufficient in instances where the powder is of the order of 5 micron size. About 4 percent of the total weight of the powder is necessary when the particles size is from 1 to 2 microns.

Any organic or silicone resin capable of coating the individual metal particles may be employed. Methyl phenyl polysiloxane mixed with toluene ($\text{CH}_3\text{C}_6\text{H}_5$) and/or xylene ($\text{C}_6\text{H}_4(\text{CH}_3)_2$), the latter serving as organic media, has been found to be particularly effective although any organo siloxane resin could be used. It has also been found that such organo siloxane resin composition in a suitable organic solvent may be provided in situ by providing a hydrolizable silane substituted with an organic radical such as methyl, ethyl, and the like in the organic suspending medium together with a sufficient amount of water to form the organic siloxane resin. Similarly, any non-polar liquid in which the resins are soluble may be used as suspending media. In addition to its peptizing activities, silicone resin also serves to enhance the green strength of the slip cast ware.

In the practice of the invention the solid resin is first dissolved in the solvent to obtain the maximum dispersion. The powder is then added directly to the resin-solvent mixture and a solids content ranging from 80 percent to 98 percent may be achieved while still retaining the proper viscosity in the slip for casting. The slip is then gradually poured into a plaster mold; the plaster readily absorbs the liquid while the powder particles cling to the walls of the mold and progressively build up to the desired wall thickness. Some of the resin is carried into the mold by the solvent where it is there absorbed. Most of the resin, however, is retained on the particle. Additional slip is added as needed until the proper wall thickness is achieved, after which the excess slip is drained from the mold. When the article is sufficiently set, it is extracted from the mold and air-dried at room temperature for a period of time sufficient to allow the article to be handled and placed in a furnace, where it is sintered. The resin which coats the particles is decomposed and carburized during the sintering operation.

A good slip should have a minimum amount of dispersing medium and yet possess optimum fluidity. To

accomplish this, surface active agents may be used which peptize the suspension or deflocculate the particles in the slip. However, a good slip should be able to suspend materials without relying on a thixotropic gel. In addition, a slip should form quickly in the mold, be easily removed, and have sufficient rigidity to be handled without cracking or deforming. By the process of this invention, all of these requirements are met.

Sintering temperatures of from 1700° C. to 2000° C. have been found to be a useful range, with very excellent results having been obtained at 1900° C. A non-oxidizing atmosphere is necessary during sintering. Hydrogen serves with marked efficiency, except perhaps in a graphite furnace, where argon or some other gas that is non-oxidizing and which will not react with the carbon in the furnace, should be employed.

Example I

Tungsten powder totaling 904 grams of 99.6 percent purity and having an average particle size of between 2.0 and 2.2 microns was added to 90 ml. of a solution of methyl phenyl polysiloxane in xylene in which the resin was present in the organic mixture in an amount of 9 grams (approximating 1 percent of the weight of the tungsten). The solids content of the tungsten metal slip was about 90 percent and slip density was about 8.5 g./cc. Crucibles of 50 and 100 ml. capacity with $\frac{3}{32}$ inch thick walls were cast from this slip in a plaster mold. The cast and dried crucibles were sintered in a graphite tube furnace for one hour at 1900° C. in an argon atmosphere. A density of 18.3 to 18.6 g./cc. was obtained in the ware after sintering. Maximum variations in wall thickness for individual crucibles were from 0.010 to 0.015 inch.

Example II

Molybdenum powder totalling 906 grams of 99 percent purity, with 90 percent of the particles less than 5 microns size, was added to 188 ml. of a solution of methyl phenyl polysiloxane in xylene in which 40 grams of resin was present. This produced a slip having a 3.93 g./cc. density and a solids content of 85 percent. Crucibles of 50 and 100 ml. capacity with a $\frac{3}{32}$ inch wall thickness were cast in plaster molds and were subsequently sintered in a graphite tube furnace for one hour at 1900° C. in an argon atmosphere. Density of the crucibles after sintering was 9.2 g./cc., or 90 percent of theoretical density of molybdenum metal. Wall thickness of individual crucibles showed a maximum variation of 0.010 to 0.015 inch from top to bottom.

While the examples cited have been limited to tungsten and molybdenum, the invention is not to be so limited. The process disclosed is equally applicable for use with any metal or metallic compound but is particularly useful in applying slip casting techniques to those materials which have too great a density to form successful slips by conventional methods. The term "metal" as used in this disclosure includes silicon and the term "metallic

compound" comprises intermetallics and metalloids such as carbides, nitrides, borides, and silicides. The process is also operable with other compounds such as metallic salts or halides providing only that they be insoluble in the organic medium. A further advantage of the technique is that objects may be formed of the highly reactive metals which oxidize easily in the presence of water.

What is claimed is:

1. The method of forming cast articles of at least one material selected from the group consisting of metals and metallic compounds, comprising providing a powder of said selected material, coating the particles of said powder with a resin while suspending said coated particles in a non-polar organic suspending medium in intimate contact with a porous mold of desired shape, absorbing said organic suspending medium through said porous mold to form a green casting of selected material and desired shape in said mold, removing said green casting from said mold and sintering said green casting to form a strong dense article of desired shape.

2. The method in accordance with claim 1, wherein said resin is silicone resin.

3. The method in accordance with claim 1, wherein said suspending medium is a material selected from the group consisting of toluene and xylene.

4. The method of forming cast articles of at least one material selected from the group consisting of metals and metallic compounds comprising providing a mixture of a silicone resin and a non-polar liquid organic suspending medium, suspending powder of said selected material in said mixture to coat the particles of said powder with said silicone resin placing said suspension of said coated particles in intimate contact with a porous mold of desired shape, absorbing said organic suspending medium through said porous mold to form a green casting of selected material and desired shape in said mold, removing said green casting from said mold and sintering said green casting to form a strong dense article of desired shape.

5. The method of forming cast articles of at least one material selected from the group consisting of metals and metallic compounds comprising providing a suspension of resin coated particles of said material having an individual particle size of 1 to 5 microns in a non-polar organic suspending medium in intimate contact with a porous mold of desired shape, absorbing said organic suspending medium through said porous mold to form a green casting of selected material and desired shape in said mold, removing said green casting from said mold and sintering said green casting to form a strong dense article of desired shape.

References Cited in the file of this patent

UNITED STATES PATENTS

2,698,990	Conant et al.	Jan. 11, 1955
2,744,011	Samuel et al.	May 1, 1956