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CASTING METAL POWDERS

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1 Claim. (Cl. 29—182)

This invention relates to a method for forming metal articles having relatively complex shapes and more particularly to a method and composition providing for slip casting of metal powder to produce green ware of good strength and uniformity.

This application is a continuation-in-part of copending application Serial No. 751,901, filed July 30, 1958, now abandoned, and assigned to the same assignee as the present invention.

Due to the requirements of present-day technologies, an increasing number of metals and alloys are being developed which possess special mechanical and thermal properties rendering them particularly applicable for use in special situations. However, since these metals and alloys must very often be formed into selected and often relatively intricate shapes, the ease with which they can be fabricated becomes a material consideration. Some metals, such as molybdenum and tungsten, among others, are difficult to work and therefore require special processing. Even then, the production cost is high and the reject rate is above that of more easily worked materials, this feature further increasing the unit cost of the final product.

Although some fabrication difficulties have been overcome by resorting to powder metallurgy techniques, in general the shapes which can be made by this process are restricted. This restriction results, at least to some extent, from the fact that high compacting pressures are normally used and the receptacle holding the metal powder must be able to withstand the forming pressures.

As a possible solution to the problem of shaping powder metals into intricate shapes, it was attempted to fluidize metal powders and cast them in a manner analogous to slip casting. Due to various factors, however, this method has not been adopted because of its unreliability in producing strong, sound green castings for subsequent firing into metal articles.

It is a principal object of this invention to provide a process and a composition for slip casting metal powder.

It is another object of this invention to provide a composition containing finely divided metal powders which can be used in a slip casting process to consistently produce articles of good green density and strength.

Still another object of this invention is to provide a process and a slip composition for forming articles of molybdenum and/or tungsten powder.

Other objects and advantages of the present invention are in part obvious and in part explained in the accompanying specification.

Briefly, the present invention comprises a process for slip casting metal powders, and more particularly refractory metals such as molybdenum and tungsten, and utilizes a slip composition comprising a fluidized metal powder, a viscosity controlling addition, and anti-foaming agent to reduce the formation of bubbles, and an additive to promote uniform wetting of the metal particles, the last-mentioned feature being important from the standpoint of obtaining reproducible results.

Several factors must be considered in preparing a slip composition capable of use for the casting of metal powders into preselected shapes. For example, the solid-to-liquid ratio of metal to liquid, the type and particle size of metal which is being cast, the nature of the oxide coating on the metal, the acidity or basicity of the slip, and the foaming characteristics of the final composition.

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These factors are discussed more fully later and although the discussion is directed primarily toward the slip casting of molybdenum and tungsten, it is to be understood that other metals and alloys having similar properties can be cast in the same way.

Considering each of the various factors mentioned in the preceding paragraph, the particle size of the powder metal particles is of particular importance, since it determines whether the system is controlled principally by physical considerations. If the particle size exceeds a certain maximum, the system is regulated principally on the basis of physical phenomena, whereas if this maximum size is not exceeded, chemical considerations prevail and the ionic atmosphere of the slip is important. That is, the rheology of the slip is determined principally from the standpoint of the chemical and ionic conditions rather than by the effects of gravity.

In preparing a slip of either molybdenum or tungsten powder, for example, it has been found that about 90 percent of the powder should be of 10 micron size or smaller. If the percentage of particles greater than 10 micron size exceeds 90 percent, then the system is controlled primarily by gravitational considerations rather than by chemical considerations. Of the 90 percent of the particles which fall within the range of from 0 to 10 microns, at least 50 percent of these particles should be less than 5 microns in particle size, although if all of the particles are within the 10 micron range, the chemical properties of the system will still control. The metal powders are preferably dry milled in a porcelain ball mill using porcelain balls and in an inert atmosphere or inert liquid environment which precludes any unnecessary oxidation of the particles. Milling in water or other oxidizing environment promotes oxidation, this oxide then dissolving in the slip liquid and causing the slip to sit up and gel after a short time.

The finely divided molybdenum or tungsten powder is then mixed with a suitable volume of liquid to render it sufficiently fluid to enable pouring into an absorbent mold, a mold similar to that ordinarily used in slip casting processes being acceptable. It is desirable to make the powder-liquid mixture as dense as possible consistent with pourability, preferably so that there is a volume ratio of from 1.25 to 2.5 parts of liquid to one part of solid, although as much as 5 parts of liquid to one part of solid can be used. The liquid referred to includes not only water but also all of the additional liquid modifying agents used in the slip. Use of large quantities of liquid can increase the expense of the casting operation both by requiring additional materials and by necessitating a longer time for removal of the liquid into the porous mold. The small particle size of the metals, in addition to its other requirements and advantages, permits the use of quantities of liquids smaller than could be used with larger particles. Another feature which must be considered is the hydrogen ion concentration of the mixture. When casting finely divided metal powders, it has been found that the pH should fall within the range of from 3 to 9. For molybdenum powder, for example, the preferred pH is from 6 to 7, whereas for tungsten powder, a pH of about 4 to 6.

The pH of the system is felt to have some effect upon the quality of the final green casting primarily in its effect upon the oxide coating contained on the individual powder particles. Control of pH is readily effected through the use of suitable acid or base additions. In the present case, hydrochloric acid is used to increase the acidity of the slips while ammonium hydroxide has been found effective in increasing the basicity of the slips. In an extremely fine material of the type being used in the present invention, the ratio of oxide coating to parent metal is much greater than it is where the particles are

large enough to be primarily controlled by gravity. Therefore, the amount or degree of hydrolysis of oxide coating has an effect upon the quality of the casting obtained and upon the reproducibility of results. That is, if the oxide coating does not hydrolyze to the same degree in each batch of slip, the resulting green castings will vary. Therefore, one of the factors which controls the hydrolyzation of the oxide coatings is the pH and strict control over this will assist in achieving reproducible results.

The apparent viscosity of the slip should approximate the viscosity of a liquid such as glycerin at room temperature, this being the usual viscosity of mixtures used in slip casting. It has been found that a 1 to 5 percent aqueous solution of polyvinyl alcohol will form a suitable liquid vehicle at the proper viscosity for pouring. Other recognized viscosity-controlling agents such as sodium or ammonium alginate or methyl cellulose may be used to locate the viscosity of the slip within the proper range.

Also important to the attainment of a proper casting is the inclusion of a suitable antifoaming agent such as one of the silicones, octyl alcohol or amyl alcohol. Other and well known antifoamants may also be used. The function of the antifoaming agent is to prevent the formation of air bubbles within the slip which would present the possibility of air bubbles being trapped in the green ware. If air bubbles are trapped in the wall of the articles being cast, it is obvious that the final product will be structurally weak. The amount of antifoamant used in a given situation will vary, since the removal of foaming is essentially a surface reaction. For example, a slip held in a shallow container causing a large surface area to be present will require more antifoamant than the identical slip in a deep container causing a comparatively small surface area of the slip to be exposed. Also, when a quantity of slip is poured from a container into a mold, a great deal of the antifoamant is lost from the surface of the slip so that additional quantities may have to be used.

The final agent used in the present slip composition is a wetting agent such as "aerosol OT" which is dioctyl sodium sulfosuccinate, a wetting agent produced by the American Cyanamid Company. The "aerosol OT" is not the only wetting agent which can be used, although it is an extremely effective one in the refractory metal systems and preferred for that reason. Other sulfonated organic wetting agents may be substituted for it. The wetting agent insures that each of the individual particles will be uniformly wetted so that from batch to batch the same degree of wetting will always occur, thus insuring reproducibility of results. Generally, it has been found that a small but effective amount, between 0.01 to 0.50 gram of the wetting agent per 100 cubic centimeters of metal in the slip will ensure the proper degree of wetting, with an addition of 0.1 gram being preferred in most instances. The use of the wetting agent assists uniform hydrolyzation of the oxide coating in each instance.

As an example, a molybdenum slip made according to the present invention was prepared by mixing 125 cubic

centimeters of 3 weight percent aqueous polyvinyl alcohol with 100 cubic centimeters of molybdenum, the molybdenum particle size all being within the 10 micron limit. A small amount of antifoam was added, the amount not being critical, and 0.1 gram of wetting agent (aerosol OT) was also introduced. The entire mixture was poured into an absorbent mold and when the desired wall thickness was reached, the remaining slip was poured out. The resulting green ware was found to have excellent green strength and density. Upon firing at 1900° C. in hydrogen, the resulting body was not only substantially free from pores but also presented a pleasing appearance and had excellent mechanical strength.

A tungsten slip was also made according to the invention by mixing 100 cubic centimeters of tungsten powder of which at least 90 percent was less than 10 micron particle size with 200 cubic centimeters of 3 weight percent polyvinyl alcohol solution. To this was added about 0.1 gram of wetting agent (aerosol OT) to insure uniform hydrolyzation of the powder. The pH, which was initially slightly in excess of 5, was reduced to 4.5 through suitable addition of hydrochloric acid. This mixture was then poured into an absorbent mold, the liquid withdrawn, and the resulting green body fired similarly to the molybdenum powder previously described to produce a body of uniform quality and excellent mechanical strength.

Thus, the present invention has described a method and a composition whereby metal slips can be prepared and cast to make bodies having sufficient green density to form metal bodies. As already mentioned, the various factors can be controlled to suit the requirements of similar metals.

What I claim as new and desire to secure by Letters Patent of the United States is:

A slip composition of pH of from about 3 to about 9 for forming metal powder castings having high green strength and substantially uniform thickness, said slip consisting essentially of metal powder at least 90 percent of which does not exceed 10 micron particle size, from about 1.25 to 5.0 parts of a water carrier for each part of metal powder to fluidize said metal powder for pouring into an absorbent mold, an amount of polyvinyl alcohol dissolved in said liquid carrier sufficient to form a 1 to 5 weight percent solution, an antifoaming agent selected from the group consisting of silicone antifoamants, amyl alcohol and octyl alcohol to reduce formation of bubbles and assist production of a sound casting, and from about 0.01 to 0.50 gram of a sulfonated organic wetting agent promoting uniform hydrolyzation of said metal powder and improving the rheological characteristics of the slip.

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