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CASTING SLIPS FOR FABRICATION OF REFRACTORY METAL WARE

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The present invention relates to slip casting, and more particularly to the slip casting of refractory heavy metals such as tungsten, molybdenum and tantalum.

There are many difficulties in fabricating various types of tungsten articles by conventional metallurgical techniques. To make a crucible or a thin-walled tube of tungsten, one method which may be essayed is to form the article from sheet stock on a mandrel and butt weld the joint. Here the difficulties encountered are the brittleness of the material, which makes forming on a mandrel difficult, and the absence of a well developed technique for welding tungsten. The conventional powder metallurgy technique of dry pressing and sintering the thin tube is severely limited with respect to minimum wall thickness in that the strains induced by pressing may result in a warped final product. On the other hand, a shape such as a thick-walled blank suitable for deep drawing into a long, thin-walled capsule is difficult to form by pressing, punching or forging without numerous defects. The thick blank is difficult to prepare by machining because of the extreme intransigence of tungsten to machining operations.

It is known that prior workers in the art have investigated various slurries or suspensions for the slip casting of tungsten and other metals. Such compositions have invariably been aqueous, and were found to be inadequate in that they do not consistently produce high density, crack free castings. Either the green castings are cracked, crack during sintering, or are not sufficiently close to maximum percentage of theoretical density after final sintering. While new types of aqueous slips have been investigated in the work leading to the present invention and some satisfactory results are obtainable therewith, the most outstanding results occur with the slips disclosed and claimed below, compositions which use only organic vehicles and additives.

The primary object of the present invention is to provide compositions for slip casting tungsten articles which are free of cracks and other defects in the green state and may be sintered to obtain finished shapes of high density which are similarly free of defects.

Another object is to provide such compositions in which the vehicle and additives are non-aqueous.

A further object is to provide such a non-aqueous slip which casts walls of intricate shape with uniform thickness and which drains readily from the interior of the cast surface.

Another object is to provide such a slip which is not unduly dilute, i.e., in which the tungsten or other metal is the major fraction of the weight of the entire slip.

A good tungsten slip must permit wall formation uniformly from top to bottom of mold, i.e., without settling of the heavy tungsten particles, but at the same time is not unduly dilute. One technique for accomplishing this objective is to use metal powders in as small a particle size as possible. This has been done in the present invention by using the minimum size which is commercially available, and further by ball milling such powder to even smaller sizes.

Such an attack is limited however, and the alternate possibility of holding the metal powder in suspension with carefully selected vehicles must be pursued, requiring of such vehicle that it not unduly dilute the metal powder and have the other properties required of a casting slip—non-reactive, good drainage characteristic, reasonably safe to use, etc.

Although many organic vehicles have been investigated, a single organic material satisfying all such requirements has not been found. It has been found necessary to use at least two substances other than the metal powder itself, one the basic vehicle itself, furnishing the necessary fluidity and good drainage, the other a thickening agent which aids in holding the metal particles in suspension during the casting process and considerably reduces the quantity of basic vehicle otherwise required. The thickening agent found peculiarly suitable with all of the basic organic vehicles of the present invention is ethyl cellulose. This material also adds green strength to the castings.

The preferred basic vehicle of the present invention is methyl chloroform, which may be replaced in whole or in part by one or more of n-butyl acetate, isobutyl acetate, o-xylene, and 1,1,2,2 tetrachloroethane. It is noted that due to their very nature, each of methyl chloroform, n-butyl acetate, isobutyl acetate, o-xylene, and 1,1,2,2 tetrachloroethane possess the properties of being non-aqueous, relatively non-reactive toward both the plaster mold and the material being suspended, and prone toward not being hygroscopic.

It has also been found advantageous to use a minor proportion of one or more wetting agents, i.e., materials that promote wetting of the metal particles by the other constituents of the slip. The preferred such wetting agent is dioctyl sodium sulfosuccinate, a material available under the proprietary name of Aerosol OT and having the incidental benefit of preventing the gelling of the slip. Another suitable wetting agent is pentachloroethane.

Another useful additive is a minor fraction of one or more materials which act as deflocculants, dispersing the metal particles without conglomeration, and/or thinning the slip to promote better drainage. Suitable such materials, together or separately, are oleic acid, which also prevents gelling and mold sticking, n-octyl alcohol, 1,1,2,2 tetrachloroethane and triethanolamine. N-octyl alcohol has the added benefit of inhibiting or preventing "skin effect," the formation of an impervious skin on a green casting which inhibits drying and causes bursting during firing.

EXAMPLES

Commercially available tungsten powders were used for all average particle sizes of 0.9 micron and larger, a particular source being the Reduction and Refining Corporation, especially for 0.9 micron material. For smaller sizes, this material was milled in polyethylene lined jars using tungsten carbide balls and a carbon tetrachloride vehicle to an average particle size of 0.74 micron. The milled slurry was evaporated to dryness and ignited at 600° C. in an H_2 atmosphere. After ignition, the powder was screened through a 400-mesh U.S. Standard sieve to eliminate agglomerates.

The moulds employed were ordinary plaster molds, sometimes uncoated but more often coated with a mold release. A satisfactory coating, used in all of the specific examples below, consists of approximately equal parts by weight of oleic acid and triethanolamine. These materials are dissolved in water in varying concentrations, e.g., 7 grams of each in 500 to 3000 cc. of water, and are either sprayed on the mold cavity surfaces or quickly poured in and out of the mold cavity.

The tungsten powder, vehicle, suspending agent, wetting agent, deflocculent-thinner, etc., were thoroughly mixed in standard laboratory stirrer until all entrapped air was removed, only a few minutes being required.

The slip was then poured into the previously coated mold, a typical size being 1 inch I.D. by 1⅝ inches high, and allowed to stand for the time required to cast a wall of the desired thickness, 1 to 10 minutes per 1/16 inch. The excess slip was then poured out, and the casting allowed to stand for a few minutes to dry sufficiently for ready removal from the mold. The green castings were sintered in a hydrogen atmosphere.

Specific compositions, conditions and results follow. All castings were well consolidated and free from defects.

Example 1

Composition:

100 grams tungsten powder, average particle size 0.9 micron
13 cc. of a solution or suspension of 5 grams of ethyl cellulose in 400 cc. o-xylene
0.7 cc. n-octyl alcohol

A 1/16 inch wall was cast in 3 to 4 minutes. Density was 94% of theoretical when fired at 1830° C. for 13 hours. This density increased to greater than 97% of theoretical when the piece was fired an additional 59 hours at 1890–1900° C. Fired shrinkage (based on mold diameter) was 41% at 94% density, 42.5% at 97% density.

Example 2

Composition:

400 grams tungsten powder, average particle size 0.9 micron
52 cc. of a solution or suspension of 7.5 grams of ethyl cellulose in 400 cc. methyl chloroform
1.2 cc. n-octyl alcohol

A cylindrical crucible having a 1/16 inch wall was cast in 5 to 8 minutes. The green casting was placed in the hydrogen furnace and fired for 72 hours at 1800–1850° C. to increase its density to 97% of theoretical, with a shrinkage of 36%.

Example 3

Composition:

100 grams tungsten powder, average particle size 0.9 micron
12.5 cc. of a solution or suspension one-half of which was o-xylene and one-half methyl chloroform containing 20 grams of ethyl cellulose per 400 cc. methyl chloroform
0.8 cc. of a solution of 10 grams of dioctyl sodium sulfosuccinate in 100 cc. of methyl chloroform
0.4 cc. n-octyl alcohol
0.18 cc. pentachloroethane

The casting rate was 1/16 inch of wall in 2 minutes. The pieces were fired at 1900° C. for 59 hours to yield sintered cylinders having a density which was 98% of theoretical, with a shrinkage of 45%.

Example 4

Composition:

200 grams tungsten powder, average particle size 1 to 1.3 microns
21 cc. of a solution or suspension three-fourths by volume being tetrachloroethane and one-fourth methyl chloroform containing 10 grams of ethyl cellulose per 400 cc. methyl chloroform
0.17 cc. sulfonated castor oil
1 cc. of a solution of 10 grams of dioctyl sodium sulfosuccinate in 100 cc. 1,1,2,2 tetrachloroethane

This slip cast a 1/16 inch wall in 2 minutes. It was fired for 72 hours at 1800–1850° C. to yield finished ware having densities in the range 95.3 to 96%, with accompanying shrinkages of 29 to 32%.

Example 5

Composition:

100 grams tungsten powder, average particle size 0.9 micron

16 cc. of a solution or suspension consisting of 14.5 cc. of n-butyl acetate or isobutyl acetate for each 10.5 cc. of methyl chloroform containing 20 grams of ethyl cellulose per 400 cc. methyl chloroform
1 cc. of methyl chloroform containing 10 grams of dioctyl sodium sulfosuccinate per 100 cc. methyl chloroform
1.4 cc. oleic acid

Casting time was about 1/16 inch in 2 minutes. The pieces were fired at 1850° C. for from 13 to 72 hours to obtain densities varying from 93 to 97% of theoretical.

Example 6

Composition: Identical to that of Example 5 with the addition of 0.03 cc. of triethanolamine.

Casting rate was 1/16 inch in 1½ minutes. A density of 92.7% of theoretical obtained upon firing at 1850° C. for 13 hours (shrinkage 42.3%). With a 76 hour soak at 1850° C., the density of the finished ware was 95.6 to 96% (shrinkage 43.9%).

Example 7

Composition:

100 grams tungsten powder, average particle size 0.74 micron
11 cc. of a suspension or solution containing 14.5 cc. of isobutyl acetate for each 10.5 cc. of methyl chloroform containing 20 grams of ethyl cellulose per 400 cc. methyl chloroform
0.6 cc. oleic acid
0.6 cc. of methyl chloroform containin 10 grams of dioctyl sodium sulfosuccinate per 100 cc. methyl chloroform

The slip cast a wall at the rate of 1/16 inch in 7 minutes. A final product having a density of 96 to 96.4% of theoretical, with a shrinkage of 30 to 31%, was obtained after firing at 1850° C. for 60 hours.

What is claimed is:

1. A composition suitable for slip casting articles of tungsten metal consisting essentially of the said metal in finely divided form with an average particle size in the range of 0.7 to 1.3 microns, at least one organic vehicle selected from the class consisting of methyl chloroform, o-xylene, n-butyl acetate, isobutyl acetate, and 1,1,2,2 tetrachloroethane, an ethyl cellulose suspending agent with the approximate ratio of said vehicle to said metal being 12 cc. of a solution containing from 5 to about 20 grams of said ethyl cellulose in 400 cc. of the said organic vehicle per 100 grams of metal.

2. The composition of claim 1 which also contains about 0.2 cc. per 100 grams of the said metal of at least one wetting agent selected from the class consisting of sulfonated castor oil and pentachloroethane.

3. The composition of claim 1 which also contains about 0.5 cc. per 100 grams of the said metal of at least one deflocculent thinner selected from the class consisting of oleic acid and n-octyl alcohol.

4. The composition of claim 3 which also contains about 1 cc. of methyl chloroform containing 10 grams of dioctyl sodium sulfosuccinate per 100 cc. of methyl chloroform.

5. The composition of claim 3 which contains approximately 100 grams of said metal per 13 cubic centimeters of a solution of approximately 5 grams of ethyl cellulose in 400 cubic centimeters of o-xylene, and 0.7 cc. n-octyl alcohol and the said metal has an average particle size of about 0.9 micron.

6. The composition of claim 3 which contains approximately 400 grams of said metal per 52 cubic centimeters of a solution of 7.5 grams of ethyl cellulose in 400 cubic centimeters of methyl chloroform and 1.2 cc. of n-octyl alcohol and the said metal has an average particle size of about 0.9 micron.

7. The composition of claim 4 which contains approxi-

mately 100 grams of said metal per 16 cc. of a solution consisting approximately of 10.5 cc. of methyl chloroform containing 20 grams of ethyl cellulose per 400 cc. methyl cellulose and 14.5 cc. of an organic vehicle selected from the class consisting of n-butyl acetate and isobutyl acetate, 1 cc. of methyl chloroform containing 10 grams of dioctyl sodium sulfosuccinate per 100 cc. methyl chloroform and about 1.4 cc. oleic acid and the said metal has an average particle size of about 0.9 micron.

8. The composition of claim 4 which contains about 100 grams of said metal per 11 cc. of a solution consisting approximately of 11 cc. of methyl chloroform containing about 20 grams of ethyl cellulose per 400 cc. methyl chloroform and 14.5 cc. of an organic vehicle selected from the class consisting of n-butyl accetate and isobutyl acetate, about 0.6 cc. of oleic acid, and about 0.6 cc. of methyl chloroform containing 10 grams of dioctyl sodium sulfosuccinate per 100 cc. methyl chloroform and the said metal has an average particle size of about 0.7 micron

References Cited in the file of this patent

UNITED STATES PATENTS

2,082,354	Reichmann	June 1, 1937
2,979,401	Szymaszek	Apr. 11, 1961

OTHER REFERENCES

Weber et al.: American Ceramic Society Bulletin, vol. 37, No. 7, July 1958, pages 334–339.