

1

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COMPOSITION AND METHOD FOR THE PREPARATION OF PRODUCTS OF MOLYBDENUM CARBIDE

Pierre Vachet, Meudon, and René Molinier, Chambéry, France, assignors to Pechiney Compagnie de Produits Chimiques et Electrometallurgiques, Paris, France
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12 Claims. (Cl. 264-63)

This invention relates to the method of producing finished and semi-finished products of molybdenum carbide and to products resulting from same.

Molybdenum carbide embodies many interesting properties including a high melting point temperature of 2600° C.; an electrical conductivity which is about ten times that of graphite; and a heat conductivity which is about one-fifth that of graphite. Thus, molybdenum carbide finds many important applications in metallurgical processes including use as a refractory material for high temperature applications and as an electrical resistance for furnaces and the like.

Two processes have been developed for fabrication of products of molybdenum carbide. In one process, powdered molybdenum carbide is subjected to cold compression in metallic dies in combination with a binder such as zinc stearate, after which the cold compressed product is subjected to fritting.

In another process, the molybdenum carbide, in aqueous suspension, embodying a suspension agent of high viscosity such as sodium alginate is injected into a plaster mold and then fritted. It is impractical to make use of the first method in the formation of thin tubular members or of shaped elements of substantial lengths and the paste of the second method has only an insufficient initial strength and is incapable of use to form tubular elements.

Thus it is an object of this invention to provide a method for producing finished and semi-finished products of powdered molybdenum carbide and, more particularly, fabricated molybdenum carbide products of large dimension including thin wall tubing, round and flat bars, and the like in which such elements are of substantial lengths.

It is a related object to produce finished and semi-finished molybdenum carbide products of the type described.

In accordance with the practice of this invention, use is made of a composition formed of powdered or finely divided molybdenum carbide in admixture with a wax present in an amount within the range of 1 to 10 percent by weight of the carbide and an aliphatic saturated hydrocarbon present in an amount within the range of 5 to 20 percent by volume of the carbide. The mixture is heated and formed into a paste which can be cast when hot and which sets upon cooling. The hot mixture can be shaped into the desired product by one or more of the methods, such as simple molding in the form of compression molding, or molding and extrusion, in which the hot mixture is cast or compressed into a mold, cooled, dried and finally removed from the mold, or it may be formed to the desired shape by centrifugal molding in which the mixture is introduced into a preheated mold and formed centrifugally by rotation of the mold at high speed and then fritted by heating to high temperature, preferably in an oxidizing or inert atmosphere. In the preferred practice of this invention, the waxy component of the described mixture may be selected of bee's wax or carnauba wax, and as the saturated aliphatic hydrocarbon it is preferred to make use of a halogenated

2

aliphatic hydrocarbon such as carbon tetrachloride or trichlorethylene.

The following examples are given by way of illustration, but not by way of limitation, of the practice of this invention:

Example 1

Molding composition:

100 parts by weight powdered molybdenum carbide
1-5 parts by weight carnauba wax
8-15 percent by volume carbon tetrachloride based upon the powdered molybdenum carbide

The materials are kneaded together to form a paste composition at a temperature of about 60° C. The initial strength of the composition is dependent mainly upon the amount of wax component present in the composition while the fluidity or flowability of the composition for molding is more dependent upon the amount of carbon tetrachloride.

In practice, it is desirable to formulate for a paste that has sufficient plastic flow, when hot, for casting or molding but which is not so liquid or flowable as to enable sedimentation of the molybdenum carbide powder component after kneading or mixing to form the paste or to provide a setting point which is too low in response to chilling.

The paste, in a heated state of about 60° C., is then shaped, depending upon the form of the product, either in a single process step of simple moulding or centrifugal molding, or else in a two step process wherein the hot paste is first formed preferably by simple moulding into a billet which is there-after drawn or extruded to shape.

In the single step process, the hot paste at about 60° C. is cast or pressed into the mold and then chilled. Thereafter the cast material is dried in air or under vacuum prior to removal from the mold. In the process of centrifugal molding, the hot paste, at about 50-70° C., is placed in a mold heated to elevated temperature, such as 40-50° C. The mold is rotated at high speed, such as 500-1500 r.p.m. depending somewhat upon the diameter of the product to be molded. After rotation for about one to two hours, the molded product is removed from the mold.

In the two step process, the paste is introduced and compressed into billets, preferably using a mold formed of steel or other easily shaped material, and more preferably one which can provide a polished or smooth surface to ease removal of the billet from the mold and the forming or drawing operation. Particular care is required in the drying in order to preserve sufficient plasticity in the mold while excessive drying may lead to the formation of cracks in the drawn product.

The shaping and the drying of the paste is followed by fritting. The fritting operation may be performed in two stages—namely, a pre-fritting stage which covers the temperature range from ambient temperature to about 1350° C. during which little, if any, shrinkage of the heated product is observed. During the pre-fritting stage, the temperature is increased rapidly from ambient temperature to from 250-300° C., usually in less than 30 minutes, and thereafter the temperature is increased steadily at a rate of about 40° C. per hour until the temperature of 1350° C. is reached.

In the fritting stage, the rise in temperature is achieved at a higher rate, such as at a rate of 50-100° C. per hour, until the final fritting temperature is reached which is generally within the range of 1600-2300° C. The molded product is maintained at fritting temperature for a number of hours after which the product is cooled down slowly. The density of the fritted product will depend greatly upon the temperature and the time that the product is

maintained at fritting temperature. Fritting is desirably carried out in the absence of oxygen: it is generally effected in a neutral atmosphere, preferably under vacuum conditions.

Instead of making use of pure molybdenum carbide, use can be made of a mixture of molybdenum carbide powder with fritted material of the type described which has been reground for use. In such instance, the paste is molded preferably by simple compression molding, optionally followed by drawing or extrusion instead of by centrifugal molding because otherwise the centrifugal forces would tend to cause classification or separation between the heavier fritted particles and the unfritted powders. In the mixture of fritted and unfritted molybdenum carbide, the rapid rate in the initial rise in temperature during the pre-fritting stage would no longer be necessary. For this purpose, it is desirable to make use of fritted material reduced to granular size within the range of 1 to 2 millimeters in cross-section and the fritted material can be employed in the mixture in an amount up to 70 percent of the mixture but it is preferred to limit the use of the fritted component to an amount within the range of 0 to 50 percent by weight of the combined fritted and unfritted molybdenum carbide component.

The following examples are given by way of further illustration of the invention:

Example 2.—Preparation of a bar having a diameter of 30 millimeters and a length of 1000 millimeters

The bar is obtained by drawing or drafting a billet formed in a steel mold having a diameter of 97 millimeters and a length of 90 millimeters. The billet is molded of a paste formed of a mixture of molybdenum carbide kneaded with 3 parts by weight of carnauba wax per 100 parts by weight of the molybdenum carbide and 12 percent by volume of carbon tetrachloride. The cast material is partially dried by exhaustion to the atmosphere for about two hours.

The pre-fritting step is carried out by increasing the temperature to 300° C. in 20 minutes followed by increasing the temperature from 300° to 1350° C. under vacuum at a rate of 40° C. per hour.

The fritting step is carried out by increasing the temperature from 1350° to 1650° C. at a rate of 60° C. per hour, in an atmosphere of nitrogen, after which it is held at 1650° C. for about six hours.

The density increases from the 4.6 of the crude paste to 6.3 for the fritted product, the theoretical density of the molybdenum carbide being 8.9.

Example 3.—Preparation of molded tubing having an outer diameter of 100 millimeters, an inside diameter of 70 millimeters, and a length of 200 millimeters

Use is made of a mold of soft steel or graphite and the composition of the paste is the same as that of Example 2.

The pre-fritting and fritting cycle is the same as that of Example 2 except that the final fritting temperature is at 2100° C. at which temperature the product is maintained for about six hours.

In this instance, the final density is 8.1.

Example 4.—Preparation of a molded tubing having an outer diameter of 350 millimeters, an inside diameter of 320 millimeters, and a length of 400 millimeters

For this purpose, use is made of a mold and core formed of graphite.

The following is the paste composition which employed:

75 parts by weight powdered molybdenum carbide
25 parts by weight reground fritted molybdenum carbide having a grain size of from 1–2 millimeters
2 parts of the total weight of powder of carnauba wax
10 percent by volume of the powders of carbon-tetrachloride

During the pre-fritting step, the tubing is retained in its mold and the temperature is increased from room temperature to 1350° C. at the rate of about 40° C. per hour, under vacuum, and thereafter the tubing is removed from the mold.

In fritting the removed tubing, the temperature is increased from 1350° C. to 2000° C. at a rate of 60° C. per hour, and then held at this temperature for six hours in an atmosphere of nitrogen. The density is raised from a density of 5 for the crude paste to a density of 7 for the fritted product.

Example 5.—Preparation of molded tubing having an outside diameter of 245 millimeters, and inside diameter of 215 millimeters, and a length of 530 millimeters

Fritted molybdenum carbide reground into granules of 1–2 millimeters is introduced dry to fill the mold. The mold is heated to a temperature of 60° C. and the following hot fluid mixture is then cast into the mold:

70 percent by weight molybdenum carbide of less than 10 microns
26.5 percent by weight trichloroethylene
3.5 percent by weight carnauba wax

The mixture is introduced into the mold in the ratio of 2 parts by weight of the mixture per 3 parts by weight of the granules of fritted molybdenum carbide. The material flows between the granules of the fritted molybdenum carbide to fill the interstices. In the foregoing system, the materials can be varied plus or minus 10 percent without appreciable change in the results.

The tubing formed by extrusion of the paste into the mold filled with the fritted molybdenum carbide has a green density of 5.8 and results in a tubing density of 7 after the fritting steps.

When use is made of reground fritted molybdenum carbide, improvements are secured in the green content and density of the paste and in the final product; shrinkage during the fritting and heating steps is reduced; and the problems of fixation of the part in the furnace are simplified. It becomes possible to carry out the fritting and heating steps while the product is at rest in a horizontal position. This may be illustrated by Example 4 wherein, when only 25 percent fritted molybdenum carbide is used, the green density was only 5.

The results can be improved further by vibration of the paste during molding for purposes of densification and before removal of the product from the mold. For this purpose, use can be made of a shaker table on which the mold is placed during or after it is filled with the paste. Under such conditions, a green density of 6.2 instead of 5.8 is possible with a corresponding increase in the density of the final product from 7 to a level of about 7.5.

Instead of carrying out the fritting operation in two separate stages, the fritting and cure can be carried out in a single fritting cycle, the complete cycle comprising drying for several hours preferably by exhaustion under vacuum and then fritting by increasing the temperature at a rate of 30–70° C. and preferably 50° C. per hour until a temperature of 1600–2200° C. and preferably 2000° C. is reached. This results in a savings in time and power and any cracking in the first phase of the process is greatly minimized.

It will be understood that the solvent employed in the moldable composition may comprise other aliphatic saturated hydrocarbons in addition to or instead of trichloroethylene and carbon tetrachloride.

It will be further understood that changes may be made in the details of formulation and the temperature and conditions of processing without departing from the spirit of the invention, especially as defined in the following claims.

We claim:

1. A composition for use in the preparation of molded products of molybdenum carbide comprising a mixture of unfritted molybdenum carbide powder and granules of molybdenum carbide which has been heated to a temperature within the range of 1600–2300° C. and in which the latter makes up to 70 percent by weight of the carbide mixture and in which the carbides are mixed to form a paste consisting essentially of the carbide, a wax present in an amount within the range of 1 to 10 percent by weight of the carbide and a saturated organic hydrocarbon liquid present in an amount within the range of 5 to 20 percent by volume of the carbide.

2. A composition as claimed in claim 1 in which the wax is selected from the group consisting of carnauba wax and bee's wax.

3. A composition as claimed in claim 1 in which the saturated organic hydrocarbon liquid is selected from the group consisting of carbon tetrachloride and trichloroethylene.

4. The method of producing finished and semi-finished products of molybdenum carbide comprising the steps of providing the carbide in finely divided form, mixing the carbide to form a paste consisting essentially of the carbide, a wax and a saturated organic hydrocarbon solvent, said wax being present in the paste in an amount within the range of 1 to 10 percent by weight of the carbide, and said hydrocarbon being present in an amount within the range of 5 to 20 percent by volume of the carbide, molding the paste into a product of the desired shape, drying the molded product, heating to a temperature within the range of 250–300° C. and then heating more slowly at a rate of 40°–60° C. per hour to a temperature of 1350–1600° C., and thereafter heating the product to a temperature within the range of 1600–2300° C.

5. The method as claimed in claim 4 in which the wax component is selected from the group consisting of carnauba wax and bee's wax.

6. The method as claimed in claim 4 in which the saturated organic hydrocarbon is selected from the group consisting of carbon tetrachloride and trichloroethylene.

7. The method as claimed in claim 4 in which the paste is heated to an elevated temperature for molding.

8. The method as claimed in claim 7 in which the paste is heated to a temperature of about 60° C.

9. The method as claimed in claim 4 in which the heating step at 1600–2300° C. is carried out in a neutral atmosphere.

10. The method as claimed in claim 4 in which the heating step is carried out under vacuum conditions.

11. The method of producing finished and semi-finished products of molybdenum carbide comprising the steps of providing the carbide in finely divided form, said carbide consisting of unfritted molybdenum carbide powder and molybdenum carbide which has been heated to a temperature within the range of 1600–2300° C. with the latter being present in an amount up to 70 percent by weight, mixing the carbide to form a paste consisting essentially of the carbide, a wax and a saturated organic hydrocarbon solvent, said wax being present in the paste in an amount within the range of 1 to 10 percent by weight of the carbide, and said hydrocarbon being present in an amount within the range of 1 to 10 percent by volume of the carbide, molding the paste into a product of the desired shape, drying the molded product, heating to a temperature within the range of 250–300° C. and then heating more slowly at a rate of 40°–60° C. per hour to a temperature of 1350–1600° C., and thereafter heating the product to a temperature within the range of 1600–2300° C.

12. The method as claimed in claim 11 in which the molybdenum carbide heated to a temperature of 1600–2300° C. is first introduced dry into the mold and which includes the step of injecting the mixture of unfritted molybdenum carbide powder, wax and hydrocarbon into the mold to fill the interstices between the fritted molybdenum carbide.

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J. A. FINLAYSON, *Assistant Examiner*.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,277,222

October 4, 1966

Pierre Vachet et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, line 15, strike out "1 to 10 percent by" and insert instead -- 5 to 20 percent by vol- --.

Signed and sealed this 22nd day of August 1967.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents