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3,013,875

METHOD OF MANUFACTURING HOMOGENEOUS CARBIDES

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The present invention relates to an improved process for the production of hard metal compounds, and in particular to a method for the manufacture of carbide mixtures suitable for the production of cemented carbides and cemented carbide strip. This is a continuation-in-part of my earlier filed application Serial No. 566,767, filed February 21, 1956, now Patent No. 2,893,859, issued July 7, 1959, and entitled "Method of Manufacture of Homogeneous Compositions."

Generally, the production of cemented carbides starts with the production of a single carbide whereby pulverized metals or their oxides are carburized with solid carbon below the melting point of the carbide and usually at temperatures between 1200° C. and 1900° C. In the production of multicarbide powders, generally the method consists in carburizing mechanical mixtures of metal oxides or metals with lampblack, or diffusion heat treatment of mechanical mixtures of individual carbides.

The carbide powders are then mixed with a binder metal powder, usually cobalt or nickel, in a procedure requiring a high order of skill, close controls, especially with regard to particle size, and comparatively high expense. It has been found necessary to grind the mixture for a period ranging between several hours and several days to a point where the binder metal can no longer be separated magnetically from the metal carbide. The grinding is usually done with hard balls in wear-resistant mills, such as those with Stellite or tungsten carbide liners. Some oxidation and pickup of the grinding media results from this step. In order to prevent such oxidation, it has been found necessary to grind under an atmosphere of hydrogen, or in the presence of a nonoxidizing liquid. In the latter operation, the powders must be subjected to a reduction step to dry them and remove any oxides.

The powders at this point are difficult to mold and generally are too fine to flow evenly into dies. Therefore, it has been found necessary to mix the powders with a binder and briquette such mixture into simple shapes which are then reground in order to make the powders flow easier. Even at this stage, the powders are not easily pressable, and only simple shapes may be pressed. The resulting compacts are then presintered to give them some strength and to evaporate the lubricant. The compacts are then further shaped with the help of various mechanical operations, such as diamond saw cutting and grinding. The compacts are further sintered to near 100% density and the parts are then brought to the final dimensions by grinding. It will thus be appreciated that the production of sintered carbides requires a great many steps, much special equipment, and a great deal of special precautions; and as a result of this complexity in processing, these materials are relatively expensive.

Broadly, it is the object of the present invention to provide an improved process for the production of intimate mixtures of hard metal compounds and binder metals which obviate one or more of the aforementioned difficulties. Specifically, it is within the contemplation of the present invention to provide a simplified process for the manufacture of carbide mixtures. The present method finds application in making single carbide-single binder mixtures, multicarbide-multibinder mixtures, multicarbides of metals which exhibit both solid solution and

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non-solid solution, and other combinations of the aforementioned materials, including cemented carbide strip.

Advantageously, the process eliminates long grinding steps, avoids contamination from ball mills, and eliminates briquetting and further grinding to agglomerate the particles. The process results in an intimate homogeneous mixture of the desired elements, produces a powder with a priori good flow characteristics, excellent green strength when pressed, and allows for manufacturing in a manner compatible with mass production techniques and at cost factors which are favorable as compared to known processing methods.

In accordance with the generalized method of the present invention, a homogeneous composition of the several elements may be prepared from a homogeneous solution of the several elements in a volatile solvent. The term "solution" is intended to include true solutions, colloidal suspensions, and fine dispersions. The solution is dried under conditions appropriate to drive off substantially all of the volatile solvents, without causing segregation of the several elements. The drying action, which may be characterized as quick drying, forms a homogeneous mixture of the several elements in solid form, which may be further treated to obtain a near molecular mixture in powdered form. This homogeneous mixture is then reduced and carburized to form intimate mixtures of carbides with or without other metals.

Carbide-metal powders which may be formed according to this invention include those mixtures which can be reduced and carburized from a mixed oxide below the melting temperature of the compound, and below the temperature at which one or more of the constituents will melt and separate from the unreduced oxides and/or uncarburized metals. Examples of combinations which can be made are, without limitation, cobalt-tungsten carbide, nickel-cobalt-tungsten carbide-molybdenum carbide, nickel-molybdenum carbide-vanadium carbide, tungsten-carbide-titanium carbide, and cobalt-tungsten carbide-titanium carbide.

In its specific aspect, the present invention includes seven main processing steps which are as follows:

(1) A solution and/or suspension is made of the desired elements, by dissolving the elements, their oxides, ores, or compounds, in an appropriate volatile solvent such as ammonia, acetic acid, nitric acid, sulfuric acid, or water or combination thereof.

(2) The solution made according to (1) is subjected to "quick-drying." Most of the volatile solvents are quickly evaporated and no segregation occurs in the non-volatile elements which ultimately make up the end product. Most of the volatile solvent which evaporates may be collected in its original form or in a form which can readily be converted to the original state.

(3) Optionally, the product may be ground to the appropriate size desired in the end product.

(4) The homogeneous mixture from (2) and (3) is heated to drive off any residue of the volatile solvent. Once again the volatile solvent may be recovered. This product is now a molecular or near molecular mixture of the several elements.

(5) The product is now ground to the desired size of the end product.

(6) The ground solid mixture is now reduced and carburized to a metal-carbide mixture, or all-carbide mixture. The steps may be done in one operation or in several steps.

(7) The product from step (6) is now deagglomerated to its prereduction size. In the case where metal-carbide mixtures are made, the product may be used as is. In the case where straight carbide mixtures are made, the products may be recycled through steps (1)-(7), to ob-

tain a metal coating on the mixed carbides; or the metal coating may be obtained in the more conventional manner.

To facilitate a more thorough understanding of the present invention, details of each step of the present process will be set forth.

In accordance with step (1), the preparation of the homogeneous solution of the several elements in a volatile solvent achieves a molecular mixture of the elements. In the case of a solution-dispersion, the system achieves a homogeneous wetting and absorption on all the solid particles of the material in suspension.

In accordance with step (2), a homogeneous, easily friable solid mixture of the desired elements is produced. In the case where a dispersion was made, a homogeneous, easily friable solid, consisting of fine particles coated with homogeneous oxides is produced. The volatilization of the volatile solvent may consist of total volatilization, partial volatilization, or volatilization of one component and retention of the others. For example, if an ammoniacal solution of tungsten trioxide and cobalt sulfate was quick dried, most of the ammonia would be volatilized but none or little of the sulfur trioxide would be evolved.

The product after step (2) may be ground to increase its bulk density and thereby increase the capacity of the equipment used in step (4).

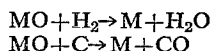
Step (4) completes the removal of the volatile elements and completes the homogenization and interaction of the remaining oxides. The product is now a synthetic mineral or a mixture of oxides in a near molecular dispersion.

Step (5) grinds the easily friable oxides into the desired size of the finished product and a hammer mill or like apparatus may be used.

Step (6) involves the reducing and carburizing of the homogeneous composition in powder form from step (5). Several approaches may be taken at this point and they depend on the elements in the homogeneous mixture.

In the case where the elements are fairly easily reducible and further carburization of part of the elements can be made at a temperature where the binder metal will not segregate from the remaining carbides, then the following procedure is desirable.

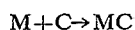
(6A) The homogeneous oxides are reduced into an alloy, or near atomic mixture of metals and the reducing gases may be hydrogen, methane, cracked natural gas, blue water gas, or a solid carbonaceous reductant with the following equations describing the generalized reaction:



A rotary kiln or a continuous belt furnace may be used for this operation.

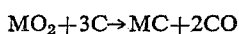
(6B) The product from step (6A) is now deagglomerated in a hammer mill or like apparatus to its prereduction size and blended with lampblack in preparation for the carburizing step.

(6C) The product is now heated in a tube furnace or like apparatus to effect the following reaction:



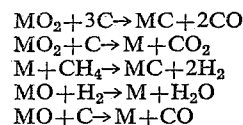
(7) The slightly sintered mass is now ground to its prereduction size in a hammer mill or like apparatus and the resulting powders consist of a molecular mixture of carbides and metal atoms and is now ready for briquetting in the final desired shapes.

In the case where some of the elements are more easily reduced to metal form than the others, then the procedure can be modified to reduce the binder metal first as described under (6A) but leaving the carbide forming elements in their oxide states, and then blending the resulting powder with fine carbon and effecting the carbide reaction directly from the mixed oxides as described by the following equation:



On the other hand, reduction of the binder metal, and partial carburization may be done in one step and final carburization in a second step according to the following generalized procedure:

(6AA) The homogeneous powders resulting from step (5) may be blended with lampblack and heated in a rotary kiln or continuous belt furnace under a neutral, reducing and/or carburizing atmosphere such as CH_4 , H_2 , CO , or a combination of any or all of the gases to effect the following reactions:



(6BB) The product is now deagglomerated and analyzed for carbon and oxygen. Additional carbon may be added, if needed, and blended with the product.

(6CC) The blended product is now heated in a pusher type furnace to effect final carburization. The product is now similar to the product obtained under (6C).

In the case where only a homogeneous mixture of carbides is wanted or where the carburization temperature is so high that the binder metal would segregate from the carbide forming metals, then a procedure may be employed to produce these homogeneous mixed carbides similar to that under step (6AA) or to carburize the blended oxides-lampblack mixture in an induction furnace. If this mixed carbide product is recycled through steps (1) to (7), then the final product will be a homogeneous mixture of carbides of finite size covered uniformly with a layer of binder metal.

In all other cases the product would be a homogeneous molecular or near molecular mixture of carbides and binder metal so that a maximum uniformity and the ultimate in fineness of the individual carbide particles are achieved. In all cases, the mixtures of carbides themselves would be in the order of solid solutions but the compositions are not limited to those carbides capable of existing in solid solution.

In the case where cemented carbide strip is desired, the following procedures would be used.

(8A) The product from steps (6C) or (6CC) is now added to a powder rolling mill and because of the high green strength of these carbide-binder metal mixtures, a "green strip" can be achieved.

(9A) This strip is now sintered at a temperature and time sufficient to effect a near 100% theoretical densification of the strip.

(8AA) The product from step (6A), a homogeneous mixture of metals, is now added to a powder rolling mill and a "green strip" is obtained.

(9AA) This strip is now sintered at a time and temperature to effect a near 100% theoretical densification.

(10) This strip is now carburized by solid or gaseous diffusion by

(A) Covering it with the necessary amount of lampblack and heating in a neutral atmosphere until full carburization is achieved.

(B) Heating the strip in a carburizing gas such as methane until the necessary carburization is achieved.

Now that the process has been revealed, various specific examples will be described to illustrate the process, but it is to be expressly understood that the process is not limited to these examples:

EXAMPLE I.—90% WC, 10% Co

(1) 56.5 parts WO_3 were dissolved in 100 parts strong aqueous ammonia. 24.0 parts $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ were dissolved in a little water and this latter solution was added to the tungstic oxide solution.

(2) The solution was fed dropwise onto a hot metal surface maintained at 200°C . and allowed to remain there for 30 seconds.

(3) The product was easily ground in a hammer mill so that 90% was finer than 200 mesh.

(4) The material was further heated to 800° C. in air and the material lost 21% of its input weight.

(5) The product was then deagglomerated so that 90% passed through 200 mesh.

(6) The homogeneous composition was then reduced to a homogeneous molecular mixture of metals by reduction in a tube furnace under a hydrogen furnace at 900° C. for one hour.

(6B) The resulting product was easily ground in a hammer mill so that 90% passed through a 200 mesh screen. This homogeneous "alloy" powder was then blended with 6.6% lampblack and was heated at 1200° C. for two hours in a carbon covered Alundum boat under a hydrogen atmosphere. A grey mass resulted which.

(7) was easily ground to minus 200 mesh. The resulting powder was analyzed and was found to have the composition of 90% WC, 10% Co.

The product, a free flowing, heavy grey powder was pressed without lubricants at 25 tons per square inch into a test bar. The resulting bar which was 59% of theoretical density, and mechanically strong, was sintered for three hours in a carbon covered Alundum boat in a carbon tube furnace at 1500° C. under a hydrogen atmosphere. The resulting bar had uniformly shrunk to approximately 100% density and showed the characteristic high hardness and transverse rupture strength of cemented carbides of this composition.

EXAMPLE II.—90% WC, 10% Co STRIP

The carbide powder from Example I, step (6C) was fed to a powder rolling mill and easily rolled into a "green" strip approximately 0.030 inch thick, and having good handling strength. This strip was sintered at 1500° C. for three hours between carbon blocks under a hydrogen atmosphere. A strip, of approximately 100% density, resulted having the high hardness and strength of such carbide compositions. This material was suitable for liners which require great hardness and low thickness and for tool bits requiring thin carbide tips.

As a variant on the above procedure, powder from step (6B), a homogeneous alloy of cobalt and tungsten was fed to a powder rolling mill and a continuous strip resulted having excellent strength. This material was sintered at 1100° C. for 1 hour under a hydrogen atmosphere. This strip was then coated with lampblack by painting on the strip a colloidal suspension of lampblack. The lampblack amounted to 6.6% of the strip weight. The strip was placed between two carbon plates in an Alundum boat, covered with lampblack and heated at 1500° C. for three hours. A dense hard strip resulted having the composition of 90% WC, 10% Co.

EXAMPLE III.—45% Mo₂C, 45% WC, 5% Co, 5% Ni

(1) 79 parts 85% MoO₃ were dissolved in 200 parts aqueous ammonia; 56.5 parts WO₃ were dissolved in 100 parts aqueous ammonia; 22.3 parts NiSO₄·6H₂O and 23.9 parts CoSO₄·7H₂O were dissolved in a little water. All the solutions were mixed and

(2) Fed dropwise onto a hot metal surface maintained at 200° C. and removed after 30 seconds. An easily friable, khaki colored powder resulted.

(3) This powder was easily ground so that 90% passed through a 200 mesh screen.

(4) The powder was heated to 800° C. in air; the total heating time was 30 minutes.

(5) The resulting powder was easily deagglomerated and

(6A) Reduced at 800° C. for 60 minutes under a dry hydrogen atmosphere. The product, a homogeneous atomic mixture of metals, was bright grey in color and had sintered slightly.

(6B) This alloy powder was easily deagglomerated into its prereduction size.

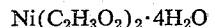
(6C) The resulting powder was mixed with 5.9% lampblack and placed in an Alundum boat and covered with a carbon plate. The material was heated at 1200° C. under a dry hydrogen atmosphere for two hours.

(7) The resulting product, a grey material, was easily deagglomerated in a hammer mill to finer than 200 mesh and analyzed. The product was found to have the composition of 45% Mo₂C, 45% WC, 5% Ni, 5% Co.

The powder was tested by briquetting it without a lubricant at 25 tons per square inch. The resulting bar was 62% of theoretical density and mechanically strong. The bar was sintered at 1500° C. for 3 hours in an alundum boat covered with a carbon plate. The resulting bar had uniformly shrunk to approximately 100% density and exhibited the characteristic high hardness and high strength of cemented carbides of this composition.

EXAMPLE IV.—42.5% VC, 42.5% Mo₂C, 15% Ni

(1) 61.4 parts V₂O₅ were dissolved in 200 parts strong aqueous ammonia; 72.2 parts (NH₄)₆Mo₇O₂₄·4H₂O were dissolved in 200 parts strong ammonia; 63.6 parts



were dissolved in 50 parts water. The solutions were all mixed together and

(2) Fed dropwise onto a metal surface maintained at 200° C. and left there for 30 seconds. The easily friable

product was tan in color and

(3) Was easily ground so that 90% was finer than 200 mesh.

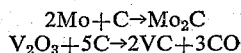
(4) The powder was then heated to 550° C. in air; the operation took 30 minutes.

(5) The product was then deagglomerated and

(6A) Reduced at 900° C. for one hour under a dry hydrogen atmosphere. The resulting product was a cermet containing an alloy of nickel and molybdenum with a molecular dispersion of an oxide of vanadium.

(6B) The slightly sintered mass was then deagglomerated in a hammer mill and blended with 23.9% lampblack and

(6C) Reduced to effect the following reactions:



The product was heated at 1200° C. in an alundum boat with a carbon cover in a tube furnace under a hydrogen atmosphere for two hours.

(6D) The product was deagglomerated and analyzed for carbon. The carbon content was found to be less than theoretical (10.6%) and therefore the product was blended with sufficient lampblack to bring the carbon content back to theoretical.

(6E) Again the powder was heated to 1200° C. for two hours under a hydrogen atmosphere.

(7) The product, a homogeneous carbide, was ground in a hammer mill until it all passed a 200 mesh screen and was analyzed. The product was found to have the composition of 42.5% VC, 42.5% Mo, 15% Ni.

The product was tested by pressing the powder at 30 tons per square inch without lubricant into a test bar. The bar was 70% of theoretical density and had good handling strength. The bar was sintered at 1450° C. for three hours under a slow hydrogen flow and the resulting product was a uniformly shrunk bar of approximately 100% density which showed the characteristic high hardness and high strength of this composition of cemented carbides.

EXAMPLE V.—13.3% TiC, 86.7% WC

(1) 139 parts of WO₃ were dissolved in 300 parts aqueous ammonia. 48.0 parts TiO₂ were added to this solution with stirring forming a very stable suspension. The stability of the suspension may be attributed to perhaps

the formation of NH_4TiO_3 on the surface of the particles.

(2) The homogeneous dispersion was fed dropwise onto a hot metal surface maintained at 200°C . and allowed to remain there for 30 seconds. An easily friable light yellow powder was obtained and

(3) This powder was ground so that 90% passed through a 200 mesh screen.

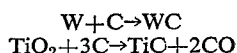
(4) The resulting powder was calcined at 900°C . in air for 30 minutes.

(5) The product, a bright yellow slightly sintered mass was easily deagglomerated.

(6) The powder was then reduced at 1000°C . under a dry hydrogen atmosphere for one hour. A dark grey powder was obtained and

(6B) This powder was deagglomerated to its prereduction size. This powder, a homogeneous cermet, composed of W and TiO_2 ,

(6C) Was blended with 14.9% lampblack. This amount of lampblack was 10% more than the theoretical to effect the following reactions:



The blended cermet-lampblack mixture was heated in an alundum boat, with a carbon cover at 1600°C . for 3 hours. The resulting mass was a homogeneous solid solution carbide.

(7) The slightly sintered mass was ground in a hammer mill until it all passed at 325 mesh screen and was then analyzed. The product was found to have the composition of 13.3% TiC, 86.7% WC.

EXAMPLE VI.—12% TiC, 78% WC, 10% Co

(1) 90 parts of —325 mesh 13.3% TiC, 86.7% WC powder from Example V, step (7) were added to 150 parts of an aqueous solution containing 50.9 parts $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$.

(2) The solution was stirred vigorously and with stirring was fed dropwise onto a hot metal surface maintained at 200°C .

(3) The product was ground in a hammer mill and

(4) Heated in nitrogen to 500°C .

(5) The resulting product was ground so that 90% passed through a 200 mesh screen.

(6A) The product was then reduced under hydrogen at 800°C . for 30 minutes, to form a homogeneously cobalt covered solid solution of TiC and WC.

(7) The product was deagglomerated to its prereduction size and analyzed. The product had the composition of 12 TiC, 78WC, 10Co.

The product was tested by pressing it into a test bar. The bar had good handling strength. The bar was sintered at 1450°C . for three hours in an alundum boat covered with a carbon plate. The product had uniformly shrunk to a near 100% density and exhibited the high hardness and high transverse rupture strength of materials of this composition.

A latitude of modification, change and substitution is intended in the foregoing disclosure and in some instances some features of the invention will be employed without a corresponding use of other features. Accordingly it is appropriate that the appended claims be construed broadly and in a manner consistent with the spirit and scope of the invention herein.

What I claim is:

1. In a method for manufacturing homogeneous compositions of carbide-metal compositions in powder and

strip form, the steps of preparing a homogeneous solution of the several elements in the composition in a volatile solvent, subjecting said solution to quick drying to drive off a substantial amount of the volatile solvent under conditions selected to preclude segregation of the several elements and to assure the formation of a homogeneous molecular mixture of said several elements in solid form, treating said molecular mixture to obtain a powder, reducing said mixture, carburizing said mixture, and grinding said mixture, and then rolling said mixture into a strip.

2. The method according to claim 1, including the further step of sintering said strip.

3. In a method for manufacturing homogeneous compositions of carbide-metal compositions in powder and strip form, the steps of preparing a homogeneous solution of the several elements in the composition in a volatile solvent selected from the group consisting of ammonia, acetic acid, sulfuric acid, nitric acid and water, subjecting said solution to quick drying at a temperature in the range of 150°C . to 450°C . to drive off a substantial amount of the volatile solvent under conditions selected to preclude segregation of the several elements and to assure the formation of a homogeneous molecular mixture of said several elements in solid form, further heating said molecular mixture to drive off any residue of said volatile solvent, treating said molecular mixture to obtain a powder, reducing said mixture, and carburizing said mixture, and then rolling said mixture into a strip.

4. The method according to claim 3, including the further step of sintering said strip.

5. In a method for manufacturing homogeneous compositions of carbide-metal compositions in powder and strip form, the steps of preparing a homogeneous solution of the several elements in the composition in a volatile solvent, subjecting said solution to quick drying to drive off a substantial amount of the volatile solvent under conditions selected to preclude segregation of the several elements and to assure the formation of a homogeneous molecular mixture of said several elements in solid form, treating said molecular mixture to obtain a powder, reducing said mixture, rolling said mixture into a strip, sintering said strip, and thereafter carburizing said strip.

6. In a method for manufacturing homogeneous compositions of carbide-metal compositions in powder and strip form, the steps of preparing a homogeneous solution of the several elements in the composition in a volatile solvent selected from the group consisting of ammonia, acetic acid, sulfuric acid, nitric acid and water, subjecting said solution to quick drying at a temperature in the range of 150°C . to 450°C . to drive off a substantial amount of the volatile solvent under conditions selected to preclude segregation of the several elements and to assure the formation of a homogeneous molecular mixture of said several elements in solid form, further heating said molecular mixture to drive off any residue of said volatile solvent, treating said molecular mixture to obtain a powder, reducing said mixture, and carburizing said mixture at a temperature in the range of 1200°C . to 1600°C ., for at least two hours, and then rolling said mixture into a strip.

7. The method according to claim 6, including the further step of sintering said strip.

References Cited in the file of this patent

UNITED STATES PATENTS

1,319,589	Jones	Oct. 21, 1919
2,893,859	Triffleman	July 7, 1959