United States Patent Office

3,501,287
Patented Mar. 17, 1970

3,501,287

METAL-METAL OXIDE COMPOSITIONS

Frank Mercer Lever, Pinner, England, assignor to P. R. Mallory & Co. Inc., Indianapolis, Ind., a corporation of Delaware

No Drawing. Continuation-in-part of application Ser. No. 421,104, Dec. 24, 1964. This application July 31, 1968, Ser. No. 748,919

Int. Cl. B22f *9/00;* C22b *5/00*

U.S. Cl. 75—.5 4 Claims

ABSTRACT OF THE DISCLOSURE

A method of making a uniformly mixed metal-metal oxide composition. An aqueous solution containing an unstable-oxide-forming metal and another metal is mixed with an aqueous solution containing a soluble hydroxide or carbonate causing co-precipitation of the metals as metal hydroxides or metal carbonates. The precipitate is then heated at an elevated temperature to form a mixed metal-metal oxide composition. Alternatively, a reducing agent can be added to the solution causing co-precipitation of the unstable-oxide-forming metal as a metal and the other metal as a metal hydroxide or metal carbonate. This precipitate can then be heated to form a mixed metal-metal oxide composition.

This application is a continuation-in-part of application Ser. No. 421,104, filed Dec. 24, 1964, now abandoned.

This invention relates to improvements in and relating to the production of metal-metal oxide alloys or compositions suitable for use as electrical contact material or for other purposes.

Metal-metal oxide alloys or compositions are well-known in the metallurgical art and may be prepared either by directly mixing powders of a metal and a metal oxide or metal oxides in the required proportions and pressing and sintering the mixture, or by forming an alloy of two or more metals, at least one of which is oxidizable, and then internally oxidizing the oxidizable metal or metals.

A typical example of such a metal-metal oxide composition is a silver-cadmium oxide material usually composed of about 90% silver and 10% cadmium oxide, which is well-known for use as contact material in aircraft relays.

The first method of manufacture suffers from the disadvantage that uniformity and consistent operating characteristics of the material cannot be guaranteed mainly due to the difficulty in obtaining a uniform mixture of the constituent powders.

The internal oxidation method offers an improved product but is not entirely satisfactory in a number of respects and material made by this method does not entirely adequately meet the severe conditions called for by modern technological developments. The method, moreover, is not applicable to powder metallurgical techniques.

In the production of metal-metal oxide compositions, particularly if such compositions are intended to use as contact materials, it is highly desirable that the oxide constituent be of very small uniform particle size and that the particles be uniformly distributed throughout the metal matrix, in order that the material shall exhibit consistently uniform characteristics in use.

An object of this invention is to overcome the disadvantages hitherto associated with the production of metal-metal oxide compositions and to provide an improved method of making such compositions.

Another object of the invention is to provide a method of making metal-metal oxide compositions which ensures that the oxide constituent shall be uniformly finely dispersed or distributed throughout the metal constituent.

A further object of the invention is to provide an improved method of making a metal-metal oxide composition by powder metallurgical techniques.

A still further object of the invention is to provide an improved metal-metal oxide composition, which exhibits consistently uniform characteristics when used as contact material, regardless of the thickness of the material used or the degree of wear to which it has been subjected.

A more limited object is to provide a silver-cadmium oxide contact material which is more efficient in use than such material as heretofore produced.

According to one feature of this invention, therefore, there is provided a method of making a metal-metal oxide composition which comprises the steps of forming a mixture of aqueous solutions of compounds of at least two metals capable of precipitation by reaction with a soluble carbonate or hydroxide and one of which metals forms an unstable oxide (unstable-oxide-forming metal) while the other metal or metals form a stable metal oxide (stable-oxide-forming metal); contacting said mixture with a solution containing a water soluble carbonate or hydroxide to cause co-precipitation of the metals of said mixed solutions in the form of their respective carbonates or hydroxides and subsequently treating the mixed precipitate to cause a reduction or conversion of the unstable oxide-forming-metal compound to metallic form, and of the other compound or compounds to the oxide form and to form a metal-metal oxide composition.

The reduction of the compound of the unstable oxide-forming-metal may be effected by the action on the mixed precipitate of a reducing agent prior to conversion of the other metallic constituent or constituents thereof to the stable oxide form.

According to another feature of the invention, there is provided a method of making a metal-metal oxide composition which comprises the steps of forming a mixture of aqueous solutions of compounds of at least two metals capable of precipitation by reaction with a soluble carbonate or hydroxide, and one of which metals forms an unstable oxide; contacting said mixture with a solution containing a soluble carbonate or hydroxide and a reducing agent to cause co-precipitation of the unstable oxide-forming-metal of said mixed solutions in metallic form and of the or each other metal in the form of its carbonate or hydroxide and subsequently treating the mixed precipitate to cause reduction of the compound or compounds thereof to the oxide form and to form a metal-metal oxide composition.

According to a further feature of the invention, there is provided as an article of manufacture, a metal-metal oxide composition which has been formed by the co-precipitation of the carbonates or hydroxides of two or more metals, one of which forms an unstable oxide from a mixture of solutions of compounds thereof capable of precipitation by reaction with a soluble carbonate or hydroxide, by reaction of said mixture with a soluble carbonate or hydroxide and the subsequent treatment of the co-precipitate to cause reduction of the unstable oxide-forming-metal compound to metallic form and of the other compound or compounds to the oxide form.

According to a still further feature of the invention, there is provided as an article of manufacture, a metal-

metal oxide composition which has been formed by the co-precipitation from a mixture of solutions of compounds of two or more metals, capable of precipitation by reaction with a soluble carbonate or hydroxide and one of which metals forms an unstable oxide, by reaction of said mixture with a solution containing a soluble carbonate or hydroxide and a reducing agent, of the unstable oxide-forming-metal in metallic form and of the, or each, other metal in the form of its carbonate or hydroxide and the subsequent treatment of the co-precipitate to cause conversion of the compound or compounds thereof to the oxide form.

In carrying out the invention in practice, the metal compounds, used as starting materials, may comprise any water soluble form of the metal which include the nitrate, sulphate, oxalate, citrate and/or chloride forms (the last-mentioned should not be used with silver and/or lead), and the unstable oxide forming metal may be silver, copper or nickel, the choice of any particular combination depending on the purpose for which the product is intended.

It must be mentioned, however, that in selecting any desired combination, care must be taken to ensure that, in the case where heating in hydrogen is necessary to effect a reduction of the unstable oxide-forming-metal compound to the metal, such as is necessary in the case of nickel or copper oxide, the final oxide-forming compound or compounds must not also form a hydrogen reducible oxide. For example, nickel and cadmium compounds cannot be used to form a nickel-cadmium oxide composition, or copper and tin compounds to form a copper-tin oxide composition as in each case the oxides of both metals are reducible in hydrogen. Subject to the above limitation, however, any suitable combination of compounds may be used. For example, a composition in accordance with this invention may comprise silver plus cadmium oxide; silver plus magnesium oxide; silver plus lead oxide; silver plus refractory oxide, such as silica, alumina or beryllia; silver plus tin oxide or silver plus two or more such oxides. A suitable contact material may, for example, advantageously consist of silver plus cadmium oxide, tin oxide and/or magnesium oxide. A particularly suitable composition will be found to be a silver-cadmium oxide composition containing 5% to 25% cadmium oxide. The silver content may, moreover, be wholly or partly replaced by copper, nickel or any other suitable metal.

In general, any soluble carbonate or hydroxide is suitable as long as it is capable of reacting with the metal compounds to form a metal precipitate. In particular, the alkali metal and ammonium carbonates or hydroxides are preferred and such include sodium carbonate, sodium hydroxide, ammonium carbonate, ammonium hydroxide, potassium carbonate and potassium hydroxide which are especially preferred.

The preferred soluble starting materials used in carrying out the method of the invention for the preparation of a silver-cadmium oxide contact material are a mixture of solutions of silver nitrate and cadmium nitrate.

The mixture of solutions can be contacted with a solution containing a carbonate or hydroxide, preferably sodium carbonate or sodium hydroxide, the resulting mixed precipitate heated to a temperature of about 450°–750° C. to form the metal-metal oxide composition, which may then be sintered for subsequent fabrication.

In the case in which a soluble reducing agent is incorporated in the carbonate or hydroxide solution for the purpose of obtaining direct reduction of the unstable oxide-forming-metal compound to the metal, the reducing agent used is preferably hydrazine, although other reducing agents may, if desired, be employed. Typical of such reducing agents include inorganic compounds such as hydroxylamine, phosphites and hypophosphites and the like, and organic compounds such as hydroquinone, phenylhydrazine and the like.

The following examples illustrate the manner in which the method of the invention may be carried out as applied to the manufacture of silver-cadmium oxide and silver-magnesium oxide compositions.

EXAMPLE I

1 kg. of a silver-cadmium oxide composition containing 10% of cadmium oxide was made by dissolving 1417 grams of silver nitrate ($AgNO_3$) and 240.2 grams of cadmium nitrate [$Cd(NO_3)_2 \cdot 4H_2O$] in 3 liters of water and the mixed solution was added slowly to a solution containing 900 grams of sodium carbonate in 18 liters of water, thereby causing coprecipitation of silver carbonate and cadmium carbonate.

The co-precipitate was filtered, washed to remove sodium nitrate and excess sodium carbonate, and dried and then heated in air at 450°–750° C. The silver carbonate was thereby converted to metallic silver and the cadmium carbonate to cadmium oxide, carbon dioxide and oxygen being evolved to produce a silver-cadmium oxide powder suitable for fabrication by powder metallurgical techniques.

EXAMPLE II

1 kg. of a silver-cadmium oxide composition containing 15% of cadmium oxide was prepared in the same manner as described in Example I, except that a 3 liter aqueous solution containing 1339 grams of silver nitrate ($AgNO_3$) and 360.3 grams of cadmium nitrate [$Cd(NO_3)_2 \cdot 4H_2O$] was used.

EXAMPLE III

The same procedure as in the previous examples was employed to prepare 1 kg. of a silver-magnesium oxide composition containing 10% magnesium oxide, a solution containing 1417 grams of silver nitrate ($AgNO_3$) and 635.9 grams of magnesium nitrate [$Mg(NO_3)_2 \cdot 6H_2O$] in 3 liters of water being used.

In each of the above examples a solution containing 600 grams of sodium hydroxide may be used in place of the 900 grams sodium carbonate solution.

If desired, in accordance with a modified method of carrying out the invention, the metallic constituent of the final composition may be precipitated directly from the solution used, as the metal, by the addition to the carbonate or hydroxide solution of a suitable reducing agent, such as hydrazine. For example, in the above examples 300 cc. of 40% hydrazine hydrate may be added to the carbonate or hydroxide solution before the solution of nitrates is added.

Or, alternatively, the metallic constituent of the final composition may be precipitated directly from the carbonate or hydroxide by the action on the mixed precipitate of 1200 cc. of a 10% hydrazine hydrate solution.

This modified method of preparation will be found to facilitate the fabrication of the finished material as it improves the "flowability" of the powder and thus assists the production of compacts of consistently uniform weight. This is thought to be due to the fact that, during the heating stage, there is only one carbonate constituent to be reduced by removal of carbon dioxide and consequently less "exploding" of the particles occurs during heating. The particle size of the powder is thus less irregular, resulting in an improved "flow" characteristic.

As will be readily appreciated, the invention is in no way limited to, or by, the above example, but other metal-metal oxide compositions may be prepared in a similar manner, except that as previously pointed out, in certain instances, for example, in the production of a nickel-magnesium oxide composition, it will be necessary to effect a final heating in hydrogen in order to reduce the nickel oxide formed to metallic nickel.

Metal-metal oxide alloys or compositions embodying the invention will be found to offer greatly improved characteristics compared with existing metal-metal oxide compositions and, when used as a contact material in the

form of a silver-cadmium oxide composition, will be found to exhibit consistently uniform characteristics in use.

Tests carried out on silver-cadmium oxide contact material in accordance with this invention, and also on contact material made by the known method of internal oxidation of a silver-cadmium alloy have shown that the strength of the onweld, produced by overload, with the material of the invention is only about half that produced with the internally oxidized material.

The material may, moreover, be subjected to a considerable degree of cold-work with annealing being necessary only at infrequent intervals.

Having thus described the invention, its features are pointed out in the appended claims.

What is claimed is:

1. A method for making a uniformly mixed metal-metal oxide composition comprising forming an aqueous solution containing an unstable-oxide-forming metal selected from the group consisting of silver, copper, nickel, and mixtures thereof, and another metal selected from the group consisting of cadmium, magnesium, lead, tin and mixtures thereof, a soluble carbonate or hydroxide, and a reducing agent selected from the group consisting of hydrazine, hydroxyl amine, phosphites, hypophosphites, hydroquinone, phenylhydrazine, and mixtures thereof, whereby said metals are co-precipitated with the unstable-oxide-forming metal precipitating and the other metal precipitating as a metal hydroxide or

metal carbonate, and heating said co-precipitate at a temperature from about 450° C. to about 750° C., thereby forming said composition.

2. A method according to claim **1** wherein said soluble hydroxide or carbonate is an alkali metal hydroxide or carbonate or ammonium hydroxide or carbonate.

3. A method according to claim **1**, wherein said unstable-oxide-forming metal is silver and said other metal is cadmium.

4. A method according to claim **3**, wherein said reducing agent is hydrazine.

References Cited

UNITED STATES PATENTS

3,241,949	3/1966	Kunda	75—0.5
2,254,976	9/1941	Powell	75—0.5
2,375,506	5/1945	Turk	75—0.5
3,085,876	4/1963	Alexander et al.	75—0.5
3,369,886	2/1968	Metzger et al.	75—0.5
3,390,981	7/1968	Hoffman	75—0.5

L. DEWAYNE RUTLEDGE, Primary Examiner

T. R. FRYE, Assistant Examiner

U.S. Cl. X.R.

75—108, 206