PROCESS FOR PRODUCING SINTERED METAL ARTICLES

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This invention relates to the production of sintered metal articles.

It is known that in powder metallurgy difficulties are often encountered by reason of the fact that the particles of the metal powders available for use do not sinter together sufficiently or only sinter together at very high temperatures. Even metal powders which are characterized by high purity do not have sufficient sinterability for many purposes.

We have now found that metal powders having especially good sinterability, in particular iron, nickel, cobalt, copper, and zinc powders, are obtained by precipitating hydroxy compounds of these metals from the salt solutions of the metals concerned by means of ammonia or ammonium carbonate, and then reducing them at elevated temperature, preferably with hydrogen and if necessary under pressure. The said hydroxy compounds may be hydroxides proper or basic salts of the said metals. By using ammonia or ammonium carbonate as the precipitant, a product is obtained which yields, by the subsequent reduction, for example with hydrogen, a metal powder the sinterability of which is considerably better than that of metal powders obtained by using other precipitants.

As the metal salts, it is preferable to choose the nitrates, but other salts, as for example chlorides or salts of the metals with organic acids, may also be used with advantage. In almost all these cases a thorough washing of the metal hydroxides or the basic metal salts can be dispensed with because during the subsequent reduction at elevated temperatures practically all impurities still present in the precipitate volatilize.

The precipitate obtained by using ammonia or ammonium carbonate may be readily reduced. Therefore the temperature of the reduction, generally ranging between about 300 and 800° C. in dependence on the nature of the metal compound to be reduced, may be chosen low while nevertheless obtaining a substantially reduced metal. A low reduction temperature of for example 400 to 600° C. has the advantage that the reduced metal is only slightly agglomerated by the heating during the reduction and therefore can readily be ground to very fine powder without waste. By heating to sintering temperature, such metal powders form sintered bodies without cracks, and these can readily be further consolidated by pressure treatment, such as pressing or rolling.

It is especially advantageous to use as the reducing agent a stream of pure hydrogen because then a great purity and a good sinterability of the reduced product is ensured by the low reduction temperature. The reducing effect may be supported and the temperature necessarily kept low by causing the hydrogen to act upon the metal compounds under increased pressure, e. g. up to 300 atmospheres.

In the case of metals, the salts of which form soluble complex compounds with ammonia, such as copper, nickel, cobalt and zinc, it is preferable first to bring the metal hydroxides into solution by the use of an excess of ammonia, to separate from this solution any solid impurities present, and then to precipitate the metal hydroxide from the solution by removing ammonia, for example by expelling it with steam or by neutralizing with acid. Metals which form ammonia-complex compounds, or initial materials containing such metals, are preferably brought into solution by treating them with ammoniacal ammonium carbonate solution under the action of an oxidizing agent, for example while leading in air, whereupon the precipitation is effected by removing ammonia.

In the case of many metals, the salts of which form complex compounds with ammonia, it is often difficult to precipitate the last traces of metal. In these cases it may be preferable to add to the residual solution oxalic acid or another organic precipitant having a similar action so that the amount of metal still contained therein is precipitated, for example in the case of cobalt in the form of cobalt oxalate. The precipitate, if desired after conversion into the oxide, may be worked up to metal powder by reduction, so that a practically complete yield of sinterable metal powder is obtained.

The process according to the present invention may also be used with advantage for solutions or metal-containing raw materials which contain a plurality of soluble metal salts or metals of the said kind. In this way it is possible to prepare in a simple manner very fine and intimate mixtures of metal powders which form alloys even after a short heat-treatment for diffusion.

The good sinterability of the metal powders prepared according to the present invention becomes evident in particular in the powder-metallurgical manufacture of pure, in particular ductile, sheets, wires or small tubes, such as are required for example in high vacuum technique. These metal powders may also find employment with special advantage in the preparation of sintered alloys, for example for permanent magnets.

The following examples will further illustrate the present invention but the invention is not limited to these examples.

Example 1
Copper turnings are treated at 50° C. in an ammoniacal ammonium carbonate solution with a mixture of ammonia, air and carbon dioxide until a concentrated deep blue copper-ammonia complex salt solution is formed. After separating off the undissolved residue, the ammonia is expelled from the solution by heating, whereby a basic copper carbonate is precipitated. The precipitate is separated, dried and reduced in a stream of hydrogen at a temperature of 500° C. The copper powder so obtained may be sintered into pieces by heating to 900° C. These pieces have a considerably higher density and strength than sinter pieces which have been produced under the same conditions from a powder which has been precipitated from copper salt solutions with sodium carbonate and after careful washing has likewise been reduced with hydrogen under the same conditions.

Example 2
A copper-ammonia complex solution is prepared from copper turnings in the manner described in Example 1 and to the solution there is added so much iron nitrate solution that in the precipitate of copper and iron hydroxides formed there are 10 parts of copper to about 30 parts of iron. The precipitate is separated from the liquid, dried and treated with hydrogen at 700° C. After short grinding, a copper-iron powder is obtained which is well suited for the preparation of sintered bearings.
Example 3

Cobalt cubes are dissolved in nitric acid while heating until a practically neutral, concentrated cobalt nitrate solution is formed. After separating undissolved constituents, the solution is diluted with water to about five times its volume and a 20% aqueous ammonia solution is added while stirring until no more cobalt hydroxide is precipitated. The cobalt hydroxide is filtered off, washed for a short time, dried and reduced in a stream of hydrogen at 750° C. The resulting, only slightly agglomerated metallic cobalt is ground for a short time in a ball mill and then heated in moulds to 1000° C. in a hydrogen atmosphere. In this way crack-free sintered pieces are obtained which can be worked up by forging and rolling into compact half-finished metal products.

If, however, cobalt is precipitated in the same way with sodium carbonate and the resulting precipitate is carefully washed, there is obtained after reduction under the above conditions a cobalt powder from which by sintering only pieces which are riddled with cracks can be obtained and which cannot be consolidated by forging and rolling.

The filtrate obtained after the precipitation with ammonia still contains small amounts of cobalt which cannot be satisfactorily precipitated with further amounts of ammonia. If oxalic acid be added to this filtrate, the residual cobalt is precipitated almost completely as cobalt oxalate which can be worked up in known manner into sinterable cobalt metal powder. In this way cobalt cubes can be converted into sinterable cobalt powder much more economically than when the whole amount of cobalt is worked up with the aid of oxalic acid.

This application is a continuation-in-part of our application Ser. No. 142,528, filed February 4, 1950, and now abandoned.

What we claim is:

1. The process of producing sintered metal articles which comprises sintering together powders of a sinterable metal from the group consisting of nickel, cobalt, copper and zinc previously derived by bringing said metal into solution as a complex ammonium salt of the metal by treatment with an ammoniacal ammonium carbonate solution and an oxidizing agent, precipitating said metal as a hydroxy compound from the solution, and reducing the precipitate to the metal with hydrogen at an elevated temperature not exceeding about 600° C.

2. The process of producing sintered metal articles which comprises sintering together copper powder previously derived by bringing metallic copper into solution as a complex ammonium salt of copper by treatment with an ammoniacal ammonium carbonate solution and an oxidizing agent, precipitating copper from the solution as a hydroxy compound, and reducing the precipitate to the metal with hydrogen at an elevated temperature not exceeding about 600° C.

References Cited in the file of this patent

UNITED STATES PATENTS

1,908,696 Dodge May 16, 1933
2,183,145 Michael et al. Dec. 12, 1939
2,400,098 Brogdon May 14, 1946

FOREIGN PATENTS

327,863 Great Britain Apr. 17, 1930
332,052 Great Britain July 17, 1930
420,544 Great Britain Oct. 4, 1944
593,959 Great Britain Oct. 30, 1947

OTHER REFERENCES