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MANUFACTURE AND PRODUCTION OF FINE METAL AND ALLOY POWDERS

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This invention relates to the production, in the form of fine powders, of metals or alloys capable of being produced by the conversion of their compounds into metal by a process of reduction or dissociation carried out at a temperature below the melting point of the metals or alloys. If powdered reducible compounds of these metals are subjected to reduction by heating in the presence of reducing agents, or are dissociated by heating, the particles of the metals formed coalesce to form larger aggregates which it is impossible to comminute by mechanical means by reason of their malleability.

According to this invention the said metals or alloys thereof are obtained in the form of fine powder by carrying out the dissociation or reduction of one or more suitable compounds of these metals in the presence of a suitable distributing or dispersing agent (hereinafter termed a distributing agent) which is capable of being removed without detriment to the powdered metal or metals or alloys formed and then removing the distributing agent.

Metals which can be produced in powdered form by the process of this invention include copper, silver, gold, iron, nickel, cobalt, and the platinum group metals or alloys of two or more of these metals or alloys of one or more of these metals with one or more fusible metals (as for example, tin, lead, zinc or cadmium) which can be reduced below the melting point of the alloy formed.

For example an oxide, hydroxide or carbonate of one of the said metals may be co-precipitated with the oxide, hydroxide or carbonate of another metal incapable of reduction or dissociation, for example of the alkaline earths or magnesium, the resulting mixed precipitate washed free from soluble salts, dried and then subjected to a dissociation or reduction treatment whereby the said metal compound is converted to metal which remains in a finely divided state evenly distributed throughout the finely divided oxide of the other metal constituting the distributing agent. The distributing agent is then removed, for example by leaching out with a suitable solvent. In some cases, the finely divided metal may be floated away from the distributing agent by the use of a liquid of suitable specific gravity or by the use of the usual oil flotation process.

Alternatively the distributing agents may be impregnated with a solution of a suitable compound of the metal, the resulting mixture then being worked up in the same way as the mixed precipitate referred to above.

The temperature and duration of the dissociation or reduction treatment influences the grain size of the resulting metal powder, the powders tending to be finer the lower the temperature used.

The proportion of distributing agent used also tends to influence the size of the particles of the resulting metal powder, the particles being smaller the larger the amount of distributing agent used.

According to this invention it is possible to obtain metal powders in such a state of fineness that they will remain suspended in water for relatively long periods.

The fine metal powders obtainable according to this invention may be used for example for the decoration of ceramic ware, for the production of conducting surfaces on non-conducting materials, for the preparation of metallic paints and also in powder metallurgy.

When using a mixture of two or more compounds of the said metals, as for example silver and copper nitrates, it is possible by selecting a suitable temperature in the dissociation or reduction treatment to obtain a powdered alloy because by reason of the very fine state of subdivision of the metals, diffusion takes place rapidly during the heating. It is thus possible to obtain such alloys in the form of very fine powders.

While in the case of tin, for example, powdered metal cannot be obtained by the method according to this invention, since at the temperature necessary for reduction, namely at least 600° centigrade, the metal melts and runs together, I have found that by using a tin compound in admixture with a metal compound capable of reduction below the melting point of the alloy formed, there is formed by the reduction treatment a powdered alloy; this is possible because the melting point of the alloy formed from the tin and the other metal or metals is higher than that of tin. Other metals may also be added in the form of reducible compounds, so that alloys are obtained in the form of fine powders.

For example with copper or precious metal compounds, tin compounds may be used in any proportion provided that the alloy produced melts at above the reduction temperature (the temperature of the reduction treatment being above 600° centigrade) and cadmium and zinc compounds may be used in amounts of not more than

about 10 per cent by weight (the temperature of the reduction treatment being for example between 700° and 800° centigrade). If larger amounts of cadmium or zinc are used, volatilisation occurs.

Iron, cobalt, nickel, gold and the platinum metals, or alloys of these metals in any proportion may also be obtained in the form of powders by the process of this invention. In these cases the reduction treatment is effected at a temperature above the reduction temperature of the metal compounds used. Alloys of silver and copper, alloys of gold and nickel, copper, iron or platinum, or various carat gold alloys containing not more than 10 per cent of zinc or cadmium may likewise be prepared in the form of fine powders.

The powdered alloys according to this invention are very useful for example for soldering parts which are difficultly accessible and for many other purposes.

The following examples will further illustrate how the said invention may be carried out in practice, but the invention is not restricted to these examples.

Example 1

A mixture of silver nitrate and calcium or magnesium nitrate (corresponding to a ratio by weight of Ag:CaO or MgO=1:1) is dissolved to give a 10 per cent aqueous solution and the solution poured into an amount of a boiling solution of sodium carbonate or caustic soda more than sufficient to precipitate the corresponding carbonates or hydroxides. The resulting precipitate is washed with hot water to remove soluble salts, and dried. The resulting mixture is then subjected to a dissociation or reduction treatment as follows. For the purposes of dissociation, the mixture is heated in air at a temperature of from 300° to 900° centigrade. Higher temperatures may be used but in this case the silver melts and forms minute spheres. The reduction treatment may be carried out by heating the mixture, for example in an atmosphere of hydrogen, at a temperature of from 200° to 900° centigrade. The product of either the dissociation or reduction treatment is a finely divided silver powder homogeneously dispersed throughout the distributing agent, i. e., calcium or magnesium carbonate or oxide. The distributing agent is then separated, for example by leaching with a suitable dilute acid, such as acetic acid.

The resulting silver powder, especially when the lower temperatures mentioned are used, is extremely fine and will remain in suspension in water for an appreciable time, and shows no tendency to cake together when it is washed and dried.

Example 2

Fine copper powder is prepared in a manner similar to that described in Example 1, but in this case the metal oxide must be subjected to a reducing treatment since copper oxide does not dissociate on heating. The starting materials may be mixtures of copper and calcium nitrates, copper and magnesium sulphates or copper and magnesium chlorides.

Example 3

For the production of an alloy of silver and copper in the finely powdered form a mixture of silver and copper nitrates in such a proportion as to give the desired copper-silver ratio in the alloy, is dissolved in water to give a 10 per cent solution, which is mixed with an equal volume of a 10 per cent aqueous solution of calcium or magnesium nitrate, and the mixed solution is poured into an amount of a boiling solution of sodium carbonate or caustic soda more than sufficient to precipitate the corresponding carbonates or hydroxides. The resulting precipitate is washed with hot water, dried and subjected to a reduction treatment at a temperature of from 300°–900° centigrade, in an atmosphere of a reducing gas, as for example hydrogen, water gas, or producer gas, whereby all the copper and silver compounds are reduced to the corresponding metals. In this way a silver-copper alloy is obtained in the finely powdered form, intimately mixed with calcium or magnesium oxides. The distributing agent is then removed, for example by leaching with a suitable dilute acid such as acetic acid or sulphuric acid.

Example 4

Fine gold and fine platinum and other platinum metals may be obtained by impregnating an excess of calcium or magnesium carbonates with solutions of the chlorides of the metals, drying the resulting mixture and heating it in air or in the presence of a reducing agent to produce an intimate mixture of the precious metal with the distributing agent consisting of calcium or magnesium carbonates and chlorides. The distributing agent is then leached out with dilute hydrochloric acid. The precious metals are thus obtained in an extremely finely powdered form.

Example 5

To produce an alloy of gold and platinum in the finely divided form, a mixture of the chlorides of the two metals in the desired proportions is dissolved in a small quantity of water and the solution mixed with a large excess of calcium or magnesium carbonates to produce a damp powdery mixture, which is then dried and heated in air at about 1000° centigrade for half to one hour. After cooling, the calcium or magnesium oxides and chlorides, which have acted as the distributing agent, are removed by leaching with dilute hydrochloric acid. There is thus obtained an extremely finely powdered gold-platinum alloy which can be used in powder metallurgy.

Example 6

Iron, copper and nickel sulphates (the ratio by weight of the metals contained therein being 1:3:1) are dissolved in water to give a 10 per cent solution which is then mixed with an equal volume of a 10 per cent aqueous solution of magnesium sulphate, and the mixed solution is poured into a hot 20 per cent aqueous solution of sodium carbonate containing more than sufficient carbonate to precipitate the iron, copper, nickel and magnesium as carbonates.

The precipitate is washed and dried and then heated in an atmosphere of hydrogen at about 800° centigrade. The product consists of a finely powdered alloy of iron, copper and nickel homogeneously distributed in magnesium oxide. The latter is removed by extraction with dilute sulphuric acid leaving the alloy in a very finely divided state. This may be used as a magnetic powder.

A similar method may be used for production of iron, nickel and cobalt in the form of fine powders. In this case the mixture which is poured into the sodium carbonate solution con-

sists simply of iron, nickel or cobalt sulphate, nitrate or chloride mixed with the corresponding magnesium salt, or if the nitrate or chloride solution is used, the corresponding calcium salt. In this way it is possible to prepare iron, nickel or cobalt in a very fine powdered form suitable for use in powder metallurgy.

Alloys of other metals may be produced in a corresponding manner.

In the present specification and the appended claims I mean by "conversion operation" the operation of converting a compound of a metal or a mixture of compounds of a plurality of metals into the corresponding metal or alloy by reduction with a suitable reducing agent or by heating to such a temperature that the compound or compounds is or are dissociated to leave the free metal or alloy. This latter occurs only in the case of compounds of the precious metals, i. e. gold, silver and the platinum group metals.

By "distributing agent" I mean a substance which prevents the aggregation or sintering of the particles of a metal or metals into relatively coarse particles. Usually when a metal oxide is reduced by hydrogen or other gaseous or solid reducing agents the fine particles of metal first formed coalesce into much coarser particles or grow together to form relatively large crystals. The purpose of the distributing agent is to prevent this sintering or grain growth and to keep the reduced metal in the form of a very fine powder.

By "capable of being removed without detriment to the powdered metal or metals or alloys formed" I mean that the substance used as a distributing agent can be dissolved in solvents which do not attack the finely powdered metal, metals or alloy or can be removed by mechanical processes, such as flotation or treatment with a heavy liquid, without contaminating the finely powdered metal, metals or alloy produced by the conversion operation.

Where in the claims the expression "metal compound" or "compound of a metal" is used such expression is intended to include one or more metal compounds or the compounds of one or more metals, since, as pointed out in the examples, where a single metal compound is used the product is a single metal and where more than one metal compound is used the product is an alloy.

What I claim is:

1. A process of producing in the form of fine powder a metal capable of being produced from its compounds by a conversion operation at a temperature below its melting point, which consists in forming by coprecipitation from a solution of suitable salts an intimate mixture of a water-insoluble compound of the metal and a distributing agent which prevents aggregation of the particles of the metal and is capable of being removed without detriment to the metal, subjecting the coprecipitated mixture to the conversion operation for converting the whole of the metallic content into a fine metallic powder and then removing the distributing agent.

2. A process of producing a fine metallic powder which consists in subjecting a solution containing a salt of a metal capable of being produced from its compounds by a conversion operation at a temperature below its melting point and a salt of a metal selected from the group alkaline earths and magnesium, to a precipitation operation to produce an intimate mixture of an insoluble compound of the first-named metal with a distributing agent selected from the group oxides, hydroxides, and carbonates, of metals selected from the group magnesium and the alkaline earths, subjecting said mixture to the conversion operation at a temperature below the melting point of the first-named metal, and then removing the distributing agent.

3. A process of producing in the form of a fine powder a metal capable of being produced from its compounds by a conversion operation at a temperature below its melting point which consists in forming by coprecipitation from a solution of suitable salts an intimate mixture of a water-insoluble compound of the metal and a distributing agent which prevents aggregation of the particles of the metal and is capable of being removed without detriment to the metal, subjecting the coprecipitated mixture to the conversion operation in the presence of a reducing agent and then removing the distributing agent.

4. A process of producing a fine metallic powder which consists in forming by a precipitation operation an intimate mixture of a compound of a metal capable of being produced from its compounds by a conversion operation at a temperature below its melting point with a distributing agent which prevents aggregation of the particles of metal and is capable of being removed without detriment to the metal, subjecting the resulting intimate mixture of insoluble metal compound and distributing agent to the conversion operation in the presence of a reducing agent and then removing the distributing agent.

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