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(54) Method of making metal composite materials

(57) The present invention provides a method of producing a metal composite material by dissolving at least one inorganic metal salt of Mo and/or W optionally together with one or more organic iron group metal salts in water and possibly at least another polar solvent, complex binding the metals with at least one complex former comprising functional groups in the form of OH or NR_3, (R=H or alkyl). The amount of said salt of Mo and/or W in the solution should be no more than $4 \times 10^{-3} \times (\text{wt\% } H_2O)^2$ g/100 ml solution and not less than 10 wt-% water. The method further includes adding hard constituent powder to the solution, evaporating the solvent and heat treating the remaining powder in an inert and/or reducing atmosphere. As a result coated hard constituent powder is obtained which after addition of pressing agent and optionally with other coated hard constituent powders and/or carbon to obtain the desired composition can be compacted and sintered according to standard practice.

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Description

[0001] The present invention relates to a method of producing metal composite materials such as cemented carbide.

[0002] US 5,505,902 discloses a method in which one or more metal salts of at least one iron group metal containing organic groups are dissolved in at least one polar solvent such as ethanol, methanol, water and complex bound with at least one complex former comprising functional groups in the form of OH or NR_3, (R=H or alkyl). Hard constituent powder and, optionally, a soluble carbon source are added to the solution. The solvent is evaporated and remaining powder is heat-treated in inert and/or reducing atmosphere. As a result, hard constituent powder coated with at least one iron group metal is obtained which after addition of pressing agent can be compacted and sintered according to standard practice to a body containing hard constituents in a binder phase.

[0003] When making submicron cemented carbide i.e. with a WC grain size of <1 µm grain growth inhibitors have to be added in order to avoid WC grain growth during sintering. As grain growth inhibitors the metals V and Cr are often used but also Mo and W can be used.

[0004] According to US 5,993,730 the method disclosed in the above mentioned US-patent can be extended also to the precipitation of the metals of groups IVa, Va and VIa of the periodic system particularly V, Cr, Ti, Ta and Nb. However, it has been found that in case of the metals Mo and W porous structures are obtained.

[0005] It is thus an object of the present invention to provide a method of easy precipitation also of the metals Mo and W.

[0006] The process according to the present invention comprises the following steps where Me= one of the metals Mo and W:

1. At least one inorganic Me-salt, optionally combined with an addition of one or more organic iron group metal salt, is dissolved in water or mixtures of water + methanol or water + ethanol. The solution shall contain no more than 4 x 10^{-3} x (wt% $H_2O)^2$ g Me-salt / 100 ml solution and not less than 10 wt% water. Triethanolamine or other complex former especially molecules containing more than two functional groups, i.e. OH or NR_3 with (R = H or alkyl). 0.1-2.0 mole complex former/mole metal, preferably about 0.5 mole complex former/mole metal, is added under stirring.
2. Hard constituent powder such as WC, (Ti,W)C, (Ta,Nb)C, (Ti,Ta,Nb)C, (Ti,W)(C,N), preferably well-deagglomerated, e.g. by jet milling, is added under moderate stirring and the temperature is increased to accelerate the evaporation of the solvent. When the mixture has become rather viscous, the dough-like mixture is kneaded and, when almost dry, smoothly crushed in order to facilitate the evaporation (avoiding inclusions of solvent).
3. The loosened powder lump obtained in the preceding step is heat treated in nitrogen and/or hydrogen at about 400-1100°C, preferably 400-800°C. To achieve a fully reduced powder a holding temperature might be needed. The time of heat treatment is influenced by process factors such as powder bed thickness, batch size, gas composition and heat treatment temperature and has to be determined by experiments. A holding time for reduction of a 5 kg powder batch in a pure hydrogen atmosphere at 650°C of 60-120 minutes has been found suitable. Nitrogen and/or hydrogen are normally used but Ar, NH_3, CO and CO_2 (or mixtures thereof) can be used whereby the composition and microstructure of the coating can be modulated.
4. After the heat treatment the coated powder is mixed with a pressing agent in ethanol to form a slurry either alone or with other coated hard constituent powders and/or binder phase metals and/or carbon to obtain the desired composition. The slurry is then dried, compacted and sintered in the usual way to obtain a sintered body of hard constituents in a binder phase.

<u>Example 1</u>

[0007] A WC-0.9 wt%Mo-10 wt%Co cemented carbide was made in the following way according to the invention: 3.70 g ammonium molybdate tetrahydrate $(NH_4)6\ Mo_7O_{24}$ x $4H_2O$ was dissolved in 350 ml water (1.06 g/100 ml solution). 17.0 g cobalt acetate tetrahydrate ($Co(C_2H_3O_2)_2$ x $4H_2O$) was added to the solution. To this solution, 7 g triethanolamine ($(C_2H_5O)_3N$) was added during stirring. After that 200 g WC (d_{WC}= 2.1 µm) was added and the temperature was increased to about 100°C. Careful stirring took place continuously during the time the water was evaporating until the mixture had become viscous. The dough-like mixture was worked and crushed with a light pressure when it had become almost dry.

[0008] The powder obtained was fired in a furnace in a porous bed about 1 cm thick in nitrogen atmosphere in a closed vessel, heating rate 10°C/min to 500°C, completed with reduction in hydrogen for 90 minutes, finally followed by cooling in nitrogen atmosphere at 10°C/min. No cooling step between burning off and reduction step was used.

[0009] The powder obtained was mixed with pressing agent in ethanol with adjustment of carbon content (carbon black), dried, compacted and sintered according standard practice for WC-Co alloys. A dense cemented carbide structure was obtained with porosity A00 and hardness HV3=1400.

Example 2

[0010] A WC-0.9 wt%Mo-10 wt%Co cemented carbide was made in the same way as in Example 1 but with no addition of cobalt acetate tetrahydrate ($Co(C_2H_3O_2)_2$ x $4H_2O$) and only 1.7 g triethanolamine to the solution. The same result as in Example 1 was obtained.

Example 3

[0011] A WC-0.9 wt%Mo-10 wt%Co cemented carbide was made in the same way as in Example 1 but the solution used was a mixture of 250 ml methanol + 100 ml water (1.06 g ammonium molybdate tetrahydrate/100 ml solution). The same result as in Example 1 was obtained.

Example 4

[0012] A WC-0.9 wt%Mo-10 wt%Co cemented carbide was made in the same way as in Example 1 but the solution used was a mixture of 100 ml ethanol + 140 ml water (1.54 g ammonium molybdate tetrahydrate/100 ml solution). The same result as in Example 1 was obtained.

Example 5

[0013] A WC-0.9 wt%Mo-10 wt%Co cemented carbide was made in the same way as in Example 1 but the solution used was a mixture of 230 ml ethanol + 20 ml water (1.48 g ammonium molybdate tetrahydrate/100 ml solution). A cemented carbide structure with porosity A02, B04 was obtained.

Example 6

[0014] A WC-0.9 wt%W-10 wt%Co cemented carbide was made in the following way according to the invention: 2.90 g ammonium metatungstate hydrate $(NH_4)_6$ $H_2W_{12}O_{40}$ x H_2O was dissolved in 350 ml water (0.83 g/100 ml solution). 17.0 g cobalt acetate tetrahydrate ($Co(C_2H_3O_2)_2$ x $4H_2O$) was added to the solution. To this solution, 6 g triethanolamine ($(C_2H_5O)_3N$) was added during stirring. After that 200 g WC (d_{WC}= 2.1 µm) was added and the temperature was increased to about 100°C. Careful stirring took place continuously during the time the water was evaporating until the mixture had become viscous. The dough-like mixture was worked and crushed with a light pressure when it had become almost dry.

[0015] The powder obtained was fired in a furnace in a porous bed about 1 cm thick in nitrogen atmosphere in a closed vessel, heating rate 10°C/min to 500°C, completed with reduction in hydrogen for 90 minutes, finally followed by cooling in nitrogen atmosphere at 10°C/min. No cooling step between burning off and reduction step was used.

[0016] The powder obtained was mixed with pressing agent in ethanol with adjustment of carbon content (carbon black), dried, compacted and sintered according standard practice for WC-Co alloys. A dense cemented carbide structure was obtained with porosity A00 and hardness HV3=1400.

Example 7

[0017] A WC-0.9 wt%W-10 wt%Co cemented carbide was made in the same way as in Example 6 but with no addition of cobalt acetate tetrahydrate ($Co(C_2H_3O_2)_2$ x $4H_2O$) and only 1.0 g triethanolamine to the solution. The same result as in Example 6 was obtained.

Example 8

[0018] A WC-0.9 wt%W-10 wt%Co cemented carbide was made in the same way as in Example 6 but the solution used was a mixture of 175 ml methanol + 175 ml water (0.83 g ammonium metatungstate hydrate/100 ml solution). The same result as in Example 6 was obtained.

Example 9

[0019] A WC-0.9 wt%W-10 wt%Co cemented carbide was made in the same way as in Example 6 but the solution used was a mixture of 200 ml ethanol + 100 ml water (0.97 g ammonium metatungstate hydrate/100 ml solution). The same result as in Example 6 was obtained.

Example 10

[0020] A WC-0.9 wt%W-10 wt%Co cemented carbide was made in the same way as in Example 6 but the solution used was 200 ml ethanol with no water (1.45 g ammonium metatungstate hydrate/100 ml solution). A cemented carbide structure with high porosity A04, B08 was obtained.

Claims

1. Method of making a metal composite material comprising the following steps

- dissolving at least one inorganic metal salt or compound of at least one metal from the groups IVa, Va and VIa of the periodic system in water and possibly at least another polar solvent and complex binding said metal salt with at least one complex former comprising functional groups in the form of OH or NR_3, (R=H or alkyl)
- adding hard constituent powder and optionally

a soluble carbon source to the solution

- evaporating the solvent
- heat treating the remaining powder in inert and/or reducing atmosphere to obtain said hard constituent powder coated with said at least one metal
- adding pressing agent alone or with other coated hard constituent powders and/or carbon to obtain the desired composition to said coated hard constituent powder, compacting and sintering **characterised** in that said metal is Mo and/or W and that said metal salt is present in an amount of $<4 \times 10^{-3} \times (\text{wt\% } H_2O)^2$ g/100 ml solution and with not less than 10 wt% water in the solution.