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(56) Documents cited
GBA 2070646
GBA 2005311
GB 1510684
GB 1506915
GB 1419278
GB 1348569
GB 1115908
GB 1077921
GB 1061166
GB 0912341
GB 0753454
GB 0708525
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(71) Applicant **Metallurg Inc.** **(USA—New York),** **25 East 39th Street, New York, N.Y. 10016, United States of America**
(72) Inventors **Fred Woodcock Hall,** **Dr. Hans-Joachim Retelsdorf**
(74) Agent and/or Address for Service **Pollak Mercer and Tench,** **High Holborn House,** **52/54 High Holborn,** **London WC1V 6RY**

(54) Sintered hardmetals

(57) Spinodally-decomposing mixed crystals of vanadium and niobium carbides, optionally including one or more carbides of titanium and other metals of Group Va of the Periodic Table of the Elements, are used in making sintered hardmetals based on tungsten carbide. One or more iron group metals or alloys, preferably cobalt or a nickel alloy, is or are used as a binder. The sintered hardmetals possibly include carbonitrides and are preferably made by a 2-stage process, mixed crystal material comprising vanadium and niobium carbides being formed in the first stage and being combined with the binder and tungsten carbide in the second stage. Process variations which encourage spinodal decomposition of the mixed crystal material are also disclosed.

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SPECIFICATION
Sintered hardmetals

This invention relates to sintered hardmetals, which comprise mixed carbides of metals selected from Groups IVa to VIa of the Periodic Table of the Elements and possibly other metals, in conjunction with binder metals or alloys of the iron group. As is well-known, the properties of hardmetals include extreme hardness and wear-resistance and these properties generally make hardmetals very suitable for use as tools or tool tips, for use in machine tools, and for dies and components generally where wear-resistance is essential.

For over five decades, hardmetal components intended for machining materials which produce short chips have consisted of tungsten carbide, WC, with cobalt as the customary iron group binder metal or alloy. For machining materials which produce long chips, it has been the practice for over the past three to four decades, to modify the hardmetals used by additions of titanium carbide, TiC, and tantalum carbide, TaC. These developments led to the discovery of the now classic WC—TiC—Co and WC—TiC—TaC—Co hardmetals.

Hardmetals of the latter type, in which the WC—TiC mixed crystal incorporates TaC, exhibit improved hot hardness and cutting endurance. Hafnium carbide, HfC, has a similar effect which can be ascribed to its similar characteristics to TaC, though HfC has the disadvantage of being rarer and therefore even more expensive than TaC.

Metallographic and X-ray examination of hardmetals of the latter type, which incorporate TaC and possibly other additional ingredients, reveals a structure having three main phases:

(1) a hexagonal (α) WC phase;

(2) cubic (β) TiC phase, containing variable amounts of TaC and WC in solid solution; and

(3) another mostly cubic (γ) Co phase, containing small amounts of W, Ti, Ta and C in solid solution.

Because of the greatly-increasing use of tantalum in condensers, as a result of which about 55% of world Ta production goes into capacitors, a general scarcity of tantalum with a consequent increase in cost, could arise, making it unacceptably expensive for use in hardmetals.

Thus attempts for cost-saving and other reasons to find partial replacements for tungsten, in the original cobalt-bound tungsten carbide hardmetals, have been followed by many attempts to find partial replacements for some or all of the added components, such as TiC, TaC and VC. Replacement of tantalum carbide with hafnium carbide does yield some improvement in properties, but as indicated this replacement gives no improvement in the raw material situation, merely a move to a rarer and more expensive material. A partial solution to this cost problem is replacement of some TaC by niobium carbide, NbC, which is much more plentiful and cheaper. Up to 40% of the TaC content of the hardmetal can be successfully replaced by NbC, but greater amounts cannot conveniently be used, as the products exhibit reduced strength and hardness. Attempts to replace TaC by Cr_3C_2, Mo_2C, ZrC and VC have proved ineffective.

Within the last few years, discoveries have been made of fully-miscible mixed crystal systems having miscibility gaps, for example TiC—ZrC, TiC—HfC, VC—NbC and VC—TaC. The advantageous properties of hardmetals containing such spinodally-decomposing mixed crystal material comprising zirconium and hafnium carbides, as a replacement for tantalum carbide, are disclosed in our GB-PA 7940140 (Specification Serial No. 2063922) and those of hardmetals containing spinodally-decomposing mixed crystal material comprising zirconium and titanium carbides are disclosed in our GB-PA 8007382 (Specification Serial No. 2070646).

It has now been surprisingly found that a spinodally-decomposing mixed crystal based on VC and NbC can be used as a complete and economic replacement for TaC in hardmetals based upon WC, TiC and an iron group metal or alloy binder.

It is remarkable and unexpected that a mixed crystal comprising vanadium and niobium carbides should operate like tantalum carbide and serve as a replacement for it, because pure NbC has the detrimental effects mentioned above, whilst pure VC produces a marked brittleness, mainly due to its high solubility in the binder phase.

According to one aspect of this invention, therefore, a sintered hardmetal comprises a tungsten carbide component, an optional titanium carbide component, a spinodally-decomposing mixed crystal containing vanadium carbide and niobium carbide and a binder comprising one or more metals or alloys of the iron group. The mixed crystal is preferably present in an amount in the range from 2% to 20% by weight and, most preferably, 4% to 12% by weight. The mixed crystal material preferably comprises, by weight, 5% to 50% VC and 95% to 50% NbC, most preferably from 10% to 30% VC and 90% to 70% NbC. The sintered hardmetal will usually include a titanium carbide component, which may be present wholly as TiC or is partially replaced by one or more of TaC, HfC and ZrC. This titanium carbide component, however constituted, can desirably form part of the spinodally-decomposing mixed crystal component of the hardmetal.

According to another aspect of the invention, a process of manufacture of a sintered hardmetal comprises heating a first mixture comprising vandium and niobium carbides under such conditions that the resultant first product comprises mixed crystal capable of spinodally decomposing, forming a second mixture from the first product in comminuted form, a tungsten carbide component, with or without at least one other hardmetal material and one or more metals or alloys of the iron group and heating the second mixture under such conditions that the resultant second product comprises a sintered hardmetal comprising spinodally-decomposed mixed crystal, a titanium carbide component optionally being included in either or both of the first and second mixtures.

In the hardmetal products of the invention, it is preferable for the VC—NbC to be combined in mixed crystal form with some TiC and WC. In other words, it is preferable, in manufacturing a hardmetal according to the invention, to form first a quaternary VC—NbC—TiC—WC mixed crystal rather than to use VC—NbC, VC—NbC—TiC or VC—NbC—WC. Before using this quaternary mixed crystal to produce the desired hardmetal product, by adding it to the WC and binder constituting the order components, it preferably comprises about 30%—60% of WC, i.e. the amount which would normally be taken up by a cubic VC—NbC—TiC mixed crystal when sintered with WC and a binder at the usual sintering temperature in the range from 1375°—1600°C.

An exception to the above is represented by a preferred feature, whereby nitrogen (preferably about 1%—15% of the carbon content) is introduced into the mixed crystal. In this case, it is advisable to limit the amount of WC in the mixed crystal to not more than 25% by weight and, preferably, from 10%—25%. Otherwise there is a danger that free C may be present, resulting in appreciable microporosity in the hardmetal.

The following Examples illustrate the invention in more detail, but are not intended to be limitative. In all the examples, the TiC and WC introduced into the quaternary mixed crystal can alternatively be added as TiC—WC mixed crystal. Amounts are given in parts by weight or percentages by weight.

EXAMPLE 1

0.5 part of VC and 3.5 parts of NbC were mixed with 5 parts of TiC and 11 parts of WC and converted to mixed crystal form by being heated in vacuum at 1700°C. The mixed crystal so obtained, after being finely milled, was then mixed with 70 parts of WC (<1 μm) and 10 parts of Co and wet-milled with acetone in an "Attritor". The wet slurry was spray-dried, pressed and sintered at 1400°C. The resultant hardmetal, with a composition of 81% WC, 5% TiC, 3.5% NbC, 0.5% VC and 10% Co, had a hardness of 81 HR_c and a bend strength of 180—200 kg/mm^2.

EXAMPLE 2

1.5 parts of VC and 5.5 parts of NbC were mixed with 8 parts of TiC and 15 parts of WC and converted to mixed crystal by heating under vacuum at 1800°C. The finely-milled mixed crystal obtained from this product was mixed with 61 parts of WC (<1.5 μm) and 9 parts Co and wet-milled under benzene in an "Attritor". The wet slurry was spray-dried, pressed and sintered at 1425°C. The hardmetal, with a composition of 76% WC, 8% TiC, 5.5% NbC, 1.5% VC and 9% Co, had a hardness of about 90 HR_c and a bend strength of 150—175 kg/mm^2.

EXAMPLE 3

2.5 parts of VC and 6.5 parts of NbC were mixed with 15 parts of TiC and 8 parts of WC and converted to mixed crystal by heating under vacuum at 1600°C. The furnace was then flooded with nitrogen so that on cooling about 0.5% N was taken up, observable as a brownish colouration of the mixed crystal cake. The finely-milled mixed crystal obtained from this product was mixed with 58.5 parts of WC (0.5—0.8 μm), 6.5 parts of Co, 0.5 part of Cr, 0.5 part of Mo and 1.5 parts of Ni and converted to hardmetal as in Examples 1 and 2. The resultant hardmetal, with a slight microporosity, had a hardness of HR_c 91.5 and a bend strength of 110—140 kg/mm^2. HIPping (hot isostatic pressing) at 1400°C and 300 atms of argon gave a fine grane structure completely free from microporosity and increased the bend strength to 150—180 kg/mm^2.

The general machining performance of this hardmetal, the composition of which was 66.5% of WC, 15% of TiC, 6.5% of NbC, 2.5% of VC, 0.5% of Cr, 0.05% of Mo, 1.5% of Ni, 0.5% of N and 6.5% of Co, was equal to that of the classical P10 hardmetal containing 67.5% of WC, 16% of TiC, 8% of TaC and 8.5% of Co and in a milling operation it was appreciably better.

As is well-known in the art, the hexagonal WC may be replaced by (WMo)C or, in the case of nitrogen-containing hardmetals, the W(CN) may be replaced by (WMo)(CN) and the cubic TiC may be partially replaced by HfC and/or TaC.

As is also well-known in the art, the Co binder may be replaced or partially replaced with other metals of the iron group and by alloy binders such as Ni—Mo, Ni—Cr, Co—Cr, Co—Cr—Mo and Co—Re, and components made from hardmetals of the invention may be provided with a wear resistant coating, e.g. TiC, TiN(TiC, N), HfN or Al_2O_3.

CLAIMS

1. A sintered hardmetal, comprising a tungsten carbide component, an optional titanium carbide component, a spinodally-decomposing mixed crystal containing vanadium carbide and niobium carbide and a binder comprising one or more metals or alloys of the iron group.

2. A sintered hardmetal according to claim 1, wherein the spinodally-decomposing mixed crystal is present in amounts of 2% to 20% by weight.

3. A sintered hardmetal according to claim 2, wherein the spinodally-decomposing mixed crystal is present in an amount of 4% to 12% by weight.

4. A sintered hardmetal according to any preceding claim, wherein the spinodally-decomposing mixed crystal comprises, by weight, 5% to 50% VC and 95% to 50% NbC.

5. A sintered hardmetal according to claim 4, wherein the spinodally-decomposing mixed crystal comprises, by weight, 10% to 30% VC and 90% to 70% NbC.

6. A sintered hardmetal according to any

preceding claim, wherein the spinodally-decomposing mixed crystal also includes the TiC component of the hardmetal.

7. A sintered hardmetal according to claim 6, wherein the spinodally-decomposing mixed crystal contains the TiC component of the hardmetal and 30% to 60% by weight of WC.

8. A sintered hardmetal according to claim 6 or 7, wherein the TiC component partially comprises one or more of TaC, HfC and ZrC.

9. A sintered hardmetal according to any preceding claim, which contains carbonitrides in an amount equivalent to a nitrogen content in the range from 1% to 15% by weight of the carbon content.

10. A sintered hardmetal according to claim 9, wherein the WC content of the spinodally-decomposing mixed crystal is up to 25% by weight.

11. A sintered hardmetal according to any preceding claim, wherein the tungsten carbide component comprises (WMo)C.

12. A sintered hardmetal according to claims 9 and 11, wherein the tungsten carbide component comprises (WMo) (CN).

13. A sintered hardmetal according to any preceding claim, wherein the binder comprises cobalt.

14. A sintered hardmetal according to claim 13, wherein the binder comprises cobalt in conjunction with one or more of Ni, Fe, Mo, Cr and Re.

15. A sintered hardmetal according to any of claims 1 to 12, wherein the binder comprises a nickel alloy containing one or more of Cr, Mo and Re.

16. A sintered hardmetal according to any preceding claim, which has been consolidated by hot isostatic pressing.

17. A tool, tool tip, die or component made from a sintered hardmetal as defined in any previous claim.

18. A tool, tool tip, die or component according to claim 17, having a wear-resistant coating, for instance selected from TiC, TiN, Ti(CN), HfN and Al_2O_3.

19. A process of manufacture of a sintered hardmetal, which comprises heating a first mixture comprising vanadium and niobium carbides under such conditions that the resultant first product comprises mixed crystal capable of spinodally decomposing, forming a second mixture from the first product in comminuted form, a tungsten carbide component, with or without at least one other hardmetal material and one or more metals or alloys of the iron group and heating the second mixture under such conditions that the resultant second product comprises a sintered hardmetal comprising spinodally-decomposed mixed crystal, a titanium carbide component optionally being included in either or both of the first and second mixtures.

20. A process according to claim 19, wherein the TiC content of the hardmetal is incorporated into the first mixture.

21. A process according to claim 20, wherein WC is incorporated into the first mixture comprising VC, NbC and TiC, in an amount in the range from 30% to 60% by weight.

22. A process according to any of claims 19 to 21, wherein the TiC component partially comprises one or more of TaC, ZrC or HfC.

23. A process according to any of claims 19 to 22, wherein nitrogen is present in the form of one or more carbonitrides in an amount equivalent to a nitrogen content of 1% to 15% by weight of the carbon content.

24. A process according to claim 23, wherein the WC content of the mixed crystal is up to 25% by weight.

25. A process according to any of claims 19 to 24, wherein the tungsten carbide component comprises (WMo)C.

26. A process according to any of claims 19 to 25, wherein the spinodally-decomposing VC—NbC mixed crystal is incorporated in tungsten carbide in an amount in the range from 2% to 20% by weight.

27. A process according to claim 26, wherein the amount of VC—NbC mixed crystal incorporated is in the range from 4% to 12% by weight.

28. A process according to any of claims 19 to 27, wherein the spinodally-decomposing VC—NbC mixed crystal contains 5% to 50% by weight VC and 95% to 50% by weight NbC.

29. A process according to claim 28, wherein the VC—NbC mixed crystal comprises 10% to 30% by weight VC and 90% to 70% by weight NbC.

30. A process according to any of claims 19 to 29, wherein the hardmetal product is consolidated by hot isostatic pressing.

31. A process according to any of claims 19 to 30, substantially as described with reference to any of the foregoing Examples.

32. A sintered hardmetal, when made by a process according to any of claims 19 to 31.

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