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SINTERED HARD ALLOY AND METHOD OF MAKING

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6 Claims

ABSTRACT OF THE DISCLOSURE

A sintered hard metal alloy useful as a cutting tool bit and a process of making same comprising a metallic hard material phase having a nitrogen base and comprising nitrides or nitride-carbide mixtures or carbonitrides or mixtures thereof, preferably with metals of the transition metal Groups IVa and Va of the periodic table. The hard material phase is bonded by an auxiliary alloy phase comprising a mixture of metals from the iron group metals and from the chromium group metals.

Sintered hard metals are alloys of a metallic hard material, for example, a carbide, bonded with an auxiliary metal alloy phase. The sintered hard metals are useful, for example, as bits for metal cutting tools. The first usable sintered hard metals consisted of tungsten monocarbide (WC) with an addition of an auxiliary-metal selected from the iron group metals, preferably cobalt. Later, for machining long-chipping materials poly-arbide hard metals with a WC-TiC-Co base and a WC-TiC-TaC-Co base were developed, a substantial portion of the carbides being present as carbide solid solutions. Most recently successful attempts were made with a total or partial replacement of the TaC in the above mentioned hard-metals by HfC or HfC/NbC solid solutions or mixtures.

The properties of other metallic hard materials such as nitrides, borides, and silicides of the transition metals of the IVa, Va and VIa groups of the periodic system have been investigated for quite some time. However, it has not been possible to prepare or use any tough hard-metals combined with auxiliary-metals for machining purposes. On the one hand, the above metallic hard materials are always much more brittle than the corresponding carbides, and on the other hand, they generally react in an undesirable manner with the auxiliary-metals which are liquid during sintering thus forming brittle compound alloys.

Tests of a structuro-chemical nature have been made on carbonitrides, that is, on solid solutions of isotypic nitrides and carbides, but nothing positive have been reported on an achievable bonding of such metallic hard materials into more or less tough hard-metals and their use for machining purposes.

It has now been found that nitrides and carbide-containing nitrides, the latter preferably in the form of solid solutions, produce tough sintered hard-metal alloys if they constitute at least 35 percent by weight of the hard-substance (metallic hard material) phase, and in particular exhibit an oxygen content of less than 0.15 preferably less than 0.05% by weight, and if auxiliary-metal alloys of metals of the iron group (Fe, Ni, Co) and metals of the chromium group (Cr, Mo, W) are used. Special measures must be employed in the preparation of the hard-substance phase and especially in sintering.

Particularly favorable properties are found in an alloy whose hard-substance phase contains nitrides and/or nitride-carbide mixtures and/or carbonitrides of the transition metals of the Groups IVa and Va of the periodic system, preferably in amounts of at least 50 percent by

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weight. Here the nitride phase and/or carbonitride phase may contain 5–50 percent by weight and preferably 10–30 percent by weight of free carbides possibly in the form of a solid solution.

It is practical to combine specific nitrides with specific carbides, such as TiN-TiC or HfN-HfC; however, the nitride and carbonitride phase may also contain nitrides and carbides of different metals selected from the IVa or Va group of the periodic system.

The auxiliary-metal phase comprises, for example, 3–35 percent by weight and of the hard metal preferably 7.5–20 percent by weight and consists of metals of the iron group and metals of the chromium group, the latter constituting 5–40 percent by weight and preferably 10–30 percent by weight of the auxiliary-metal alloy.

In the process for preparing the new hard metal alloys, according to this invention, a batch is prepared comprising 0.5–5 percent by weight, and preferably 1–3 percent by weight of metals of the chromium groups, preferably molybdenum, further, oxygen-free or low-oxygen nitrides and/or nitride-carbide mixtures and/or carbonitrides with an oxygen content preferably of less than 0.15 percent by weight, more particularly below 0.05 percent by weight, possibly with an addition of free carbides and carbide solid solutions. The batch is then wet-ground and dried. To this batch is added auxiliary metal alloys of metals of the iron and chromium groups. The alloys may, for example, be powdered. The batch is then shaped, for example, by pressing. The shapes are subsequently sintered in nitrogen at underpressure.

In case of a nitrogen loss the nitrogen pressure may be increased to 1–30 atm. for a short time during sintering, such as for 5 to 20 minutes to replace the lost nitrogen.

In making nitrides and nitride-rich carbonitrides it is extremely difficult to obtain initial and final products that are low in oxygen, since, for instance, the isotypic monoxides of the transition metals in Groups IVa and Va of the periodic system form very stable oxynitrides and oxycarbonitrides that are unusually brittle and do not allow themselves to be wetted practically at all. Particularly low-oxygen nitride-carbide mixtures and carbonitrides can best be prepared from the pure metallic components and not from metal oxides. Thus, for instance, TiN, HfN, VN, or TaN are yielded from pure metallic powders or pure pulverulent metal hydrides and purified nitrogen. The carbonitrides Ti(N, C), V(N, C), or Ti, V(N, C) or Ti, Ta(N, C) are produced from low-oxygen nitrides and vacuum-purified carbides. The high-vacuum deoxidation of oxynitrides, such as Ti(N, O) with carbon into TiN and carbon monoxide takes place basically in the same way as the refining of oxycarbonitrides, such as V(N, C, O) with carbon (lamp black) into V(C, N) + CO. But it presents difficulties relative to the stoichiometry of the compounds containing nitride and carbonitride, since in a high vacuum at high temperatures the mentioned hard-substances lose nitrogen.

In order to obtain nitrides or carbonitrides that are especially low in oxygen, in accordance with the invention it has proven particularly favorable to subject nitridic, still oxygenic initial materials to a refining annealing treatment at roughly 1500–1800° C. at a nitrogen underpressure (50–300 mm. Hg) and with an addition of 0.5–5 percent by weight, and preferably 1–3 percent by weight of metals of the chromium group preferably molybdenum. The metals of the chromium group cause an excellent deoxidizing reaction. The oxygen content can readily be pushed down to 0.05 percent by weight and therebelow. If during deoxidation there is also an undesired reduction in the nitrogen, this may be compensated for by raising the nitrogen once more to 1–30 atm. toward the end of the refinement.

In sintering nitrides and carbonitrides with auxiliary-metals there are additional precautions that must be taken. Hydrogen, the traditional protective gas for carbide-cobalt hard metals, is out of the question since nitrides and carbonitrides react with hydrogen, and the nitrogen is lessened. Vacuum sintering which is used almost exclusively for hard-metals containing TiC, NbC, TaC, and HfC is also out of the question due to undesired nitrogen losses. In the process of the invention purified nitrogen has given satisfactory results as the sintering atmosphere, best of all at an underpressure of 200–500 mm. mercury.

By way of comparison, if pure iron metals, for instance either traditional powdered cobalt or nickel in amounts of 5–25 percent by weight are used for bonding the nitride-containing hard materials, only brittle materials will be obtained that have a bending strength of roughly 30–50 kg./mm.², strength properties that are too low for many applications, particularly for machining purposes.

Surprisingly, however, it has been found, according to the present invention, that auxiliary-metal alloys of iron metals and metals of the chromium group distinguish themselves by their high degree of strength and toughness. For instance, the following alloys have proven satisfactory: alloys of Ni with 15–27 percent by weight Mo, Ni with 20–40 percent by weight Cr, Ni with 15 percent by weight Cr and 15 percent by weight Mo, Co with 25 percent by weight W, Co with 30 percent by weight Cr and 5 percent by weight Mo, Co with 25 percent by weight Cr and 15 percent by weight W, Ni with 20 percent by weight Fe and 20 percent by weight Mo, Fe with 30 percent by weight Ni and 20 percent by weight Cr, Ni with 15–20 percent by weight Cr, 1–2 percent by weight Ti and 1–3 percent by weight Al. With such auxiliary-metal alloys it was possible to attain bending strengths of 110–150 kg./mm.² depending on the amount of auxiliary-metal used.

Binders of Ni-Mo, Ni-Cr, Co-Cr and Stellite-type binders have also been successfully tried with carbide metallic hard materials and served to increase their resistance to scaling and to corrosion. However, a substantial portion of the VIa metals enter the carbide phase during sintering because the VIa metals form very stable carbides and carbide solid solutions. But in the nitride-rich hard-substance alloys of the present invention no reaction with the nitride nitrogen or the nitrogen of the sintering atmosphere takes place. The nitrides of the chromium disintegrate almost completely in the presence of liquid iron metals, and the nitrides of molybdenum and of tungsten don't even form or are completely unstable in the presence of iron metals and high temperatures.

In other words, this means that in the case of the invention the auxiliary-metal alloys used are preserved along with their good strength properties even after sintering. Surprisingly these alloys also wet the nitrides, the nitride-carbide mixtures, and the carbonitrides better than the pure iron metals, which result in an improved dense-sintering, a lesser microporosity, plus an additional deoxidation of the oxygen brought in by the wet grinding.

As already mentioned above, a mixture of nitrides and/or carbonitrides with free carbides and/or carbide solid solutions (cf. Examples 5 and 7–9 below) can be used as the hard substance phase in place of pure nitrides and carbonitrides.

The invention will be more fully explained with the aid of the following examples:

EXAMPLE 1

Ninety percent by weight TiN powder with a O₂ content of 0.05% obtained from highly pure Ti powder are mixed with 10 percent by weight of a Ni-Mo-mixture (80:20), are ground, compressed, and sintered at 350 mm. mercury in nitrogen at about 1450° C. A Vickers

hardness of about 1500 (load 3 kg.) was obtained, as well as a bending strength of 80–90 kg./mm.².

EXAMPLE 2

A mixture of 85 percent by weight TaN with a O₂ content of 0.06% (obtained from the purest tantalum hydride powder) is mixed with 15 percent by weight of a Ni-Mo-powder mixture (75:25), and is ground. The tips pressed at about 0.5 t./cm.² are sintered at a nitrogen pressure of about 600 mm. mercury. The hard-alloys obtained have a Vickers hardness of about 1600–1700 with a bending strength of 105–115 kg./mm.².

EXAMPLE 3

Eighty-two percent by weight TiN are converted with 10 percent by weight TiC into a carbonitride through an annealing treatment at 1800° C. under 3 atm. nitrogen. The comminuted carbonitride with a O₂ content of 0.05% is ground with 8 percent of a Ni-Mo-alloying powder (80:20) and is compressed. The pressed blanks are sintered at 250–400 mm. mercury nitrogen pressure at 1550° C. The Vickers hardness obtained was 1500 with a bending strength of 100–110 kg./mm.².

EXAMPLE 4

Fifty-five percent by weight TiN, 15 percent by weight TiC, and 12 percent by weight HfC are converted into a carbonitride solid solution, as described in Example 3. The comminuted hard-substance powder is mixed with 18 percent by weight Ni, Mo, and Cr in a ratio of 70:15:15 and is wet ground with acetone. The sintering of the dried and compressed mixture is similar to that described for Examples 1–3, a Vickers hardness of 1650 and a bending strength of 120–145 kg./mm.² being achieved.

EXAMPLE 5

A mixture of 70 percent by weight TiN with a O₂ content of 0.05% and 20 percent by weight vacuum purified VC are bound with 10 percent by weight of an alloying powder of Hastelloy (60 Ni, 20 Fe, 20 Mo). Vickers hardness: 1550, bending strength: 95–105 kg./mm.².

EXAMPLE 6

Fifty percent by weight VN and 30 percent by weight NbC are converted into a carbonitride with a O₂ content of 0.04%, cf. the alloys according to Examples 3–5. A powder mixture of 20 percent by weight Co-W-Cr (65:10:25) serves as auxiliary-metal. Vickers hardness fluctuates between 1450 and 1550, the strength between 90–105 kg./mm.².

EXAMPLE 7

Seventy percent by weight TiN and 10 percent by weight TiC are converted into a solid solution with a O₂ content of 0.06% in the manner described above. During wet grinding 10 percent by weight free WC with a grain size of 1/10μ plus 10 percent by weight of a Co-Ni-Cr mixture (45:40:15) are added. Sintering is done at 0.5 atm., and finally at 15 atm. nitrogen in an autoclave. A Vickers hardness of 1650 was obtained, and the bending strength values exceeded 120 kg./mm.².

EXAMPLE 8

Forty-five percent by weight TaN, 5 percent by weight ZrN, and 10 percent by weight TiC are converted into low-oxygen carbonitrides with a O₂ content of 0.03% as described above. During wet grinding a carbide solid solution contributing for 12.5 percent by weight TiC, 10 percent by weight WC, and 2.5 percent by weight TaC in the end product plus 15 percent by weight of a cobalt super-alloy are added. (Analysis of the super-alloy: 35 Fe, 25 Co, 25 Ni, 10 Cr, 5 Mo.) The hardness and bending strength correspond approximately to the alloys of Examples 2 and 3.

EXAMPLE 9

Sixty percent by weight TiN and 20 percent by weight TaN are converted in the manner described above into oxygen-free or low-oxygen nitrides in solid solution with an O₂ content of 0.05%. In wet-grinding with tetraline a carbide mixture of 5 percent by weight TiC, 4 percent by weight WC, 1 percent by weight Mo₂C, plus 10 percent by weight of an 80/20 Ni/Mo alloy are added. Hardness and strength correspond approximately to the alloy of Example 7.

Having thus described the invention with detail and particularly as required by the patent laws, what is desired protected by Letters Patent is set forth in the following claims.

I claim:

1. Sintered hard metals comprising a metallic hard material having a nitride base bonded in an auxiliary metal alloy, said metallic hard material consisting of at least 35 percent by weight of metallic carbonitrides of the transition metals of Groups IVa and Va and the remainder, if any, consisting essentially of metallic carbides, the oxygen content of the said carbonitrides and carbides being less than 0.15% by weight oxygen, said auxiliary metal alloys comprising mixtures of at least one metal selected from the iron group of metals and at least one metal selected from the chromium group metals.

2. Sintered hard metals according to claim 1 in which the metallic hard material comprises 5 to 50 percent by weight carbides.

3. Sintered hard metals according to claim 1 in which the metallic hard material comprises 10 to 30 percent by weight carbides.

4. Sintered hard metals according to claim 1 in which each of the carbonitrides consists of a solid solution of a carbide and a nitride of the same metal.

5. Sintered hard metals according to claim 1 in which the auxiliary metal comprises 3 to 35 percent by weight of the sintered alloy, said auxiliary metal alloy comprising 5 to 40 percent by weight of the chromium group metals, and the remainder iron group metals.

6. Sintered hard metals comprising metallic hard material having a carbonitride base bonded in auxiliary metal alloy, said metallic hard materials selected from the group consisting of carbonitrides, carbides and mixtures thereof, said metallic hard materials being at least 50 percent carbonitrides, said carbonitrides, carbides and mixtures thereof being of the transition metals in Groups IVa and Va of the periodic system and containing less than 0.15 percent by weight of oxygen, said auxiliary metal alloys comprising 7.5 to 20 percent by weight of said sintered hard metal, said auxiliary metal alloy comprising 10 to 30 percent metals of the chromium group and the remainder metals of the iron group.

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