This invention relates to the manufacture of hard alloys for tools and similar articles, the said alloys being of the kind in which tungsten carbide is the principal constituent, while there is also present an auxiliary metal, of much lower melting point than the tungsten carbide, comprising one or more of the metals iron, nickel or cobalt.

Henceforth it has been proposed to improve the properties of sintered hard alloys having a tungsten carbide base and also containing an auxiliary metal such as iron, cobalt or nickel having a substantially lower melting point than that of the tungsten carbide by the addition of another hard carbide or carbide-nitride having a high melting point. Thus it has been proposed to add to a mixture comprising tungsten carbide and up to 20 per cent of an auxiliary metal of lower melting point such as iron, cobalt or nickel one or more carbides of tantalum, niobium or vanadium in quantities of 0.01 to 30 per cent and to work up this mixture further in the usual way. Furthermore, tool alloys have been proposed comprising a sintered product containing at least two carbides of tungsten, molybdenum, boron, silicon, titanium, zirconium and vanadium which are obtained entirely in the form of mixed crystals by heating to a sufficient extent and an addition amounting to 3 to 20 per cent of one or more metals such as nickel, cobalt and chromium; the most favourable results were stated to have been obtained with mixed crystals of the system molybdenum carbide—tungsten carbide. Moreover, metal carbo-nitrides have been proposed for imparting a high degree of hardness to alloys, the carbo-nitrides with or without nitrides of metals or metalloids being added to the various metals or alloys as constituents; an example of this procedure was the increase of the solidity and hardness of known hard alloys consisting chiefly of tungsten or molybdenum carbides by additions of the said carbo-nitrides—necessarily the case of tungsten carbide as the principal constituent and small percentages of chromium carbo-nitride, tungsten carbo-nitride, cobalt and tungsten. There have also been proposed hard metal alloys comprising zirconium or thorium carbide or both in a quantity not exceeding 20 per cent, cobalt up to 10 per cent and tungsten carbide as the remainder. Lastly there have been proposed sintered hard alloys consisting of tungsten carbide, a metal of lower melting point than that of the tungsten carbide in an amount of up to about 25 per cent and a mixture of hard titanium compounds such as titanium carbide and titanium nitride in an amount up to 50 per cent of the total alloy.

The present invention has for its object to effect still further improvements in the properties which are essential for the quality of metals for cutting tools, and for this purpose the sintered alloys according to the present invention comprise at least 50 per cent of tungsten carbide, a quantity up to 20 per cent of one or more of the metals iron, cobalt and nickel, and a quantity of 2 to 30 per cent of hard mixed carbides of carbides or carbides and nitrides formed from a carbide or nitride of a metal of the fourth group of the periodic system and a carbide or nitride of a metal of the fifth group of the periodic system. The hard mixed crystals of carbides or carbides and nitrides should be completely formed before their addition to the other constituents of the alloy, namely tungsten carbide and one or more of the metals iron, cobalt or nickel.

It is known that mixtures of many hard substances and compounds having a high melting point, more particularly of certain carbide mixtures or even carbide-nitride mixtures, show considerable solubility or form a considerable amount of mixed crystals with one another. In certain individual cases, where there is a close relationship of the substances as regards structure, an unlimited flawless formation of mixed crystals may result. Furthermore, it is known that by the formation of mixed crystals the hardness of alloys is as a rule very considerably increased. This is also the case with the hard carbide systems and carbide nitride systems utilized in the production of the alloys according to the present invention, for example with the systems TiC—TaC, TiC—NbC, TiC—VC, ZrC—TaC, ZrC—NbC, ZrC—VC, HfC—TaC, HfC—NbC, HfC—VC, TiN—TaC, TaN—TIC and similar mixtures. The maximum hardness is mostly present, although not always, when the two constituents are mixed in equimolecular proportions, for example in the system TaC—TiC in the proportion of 23.7 per cent by weight TiC to 76.3 per cent by weight TaC. The increase in hardness is particularly noticeable when one component of the mixed crystal consists of a hard nitride, for example in the system TiN—TaC or TaN—TIC.

The production of hard alloys which, apart from an addition up to 20 per cent of one or more of the metals iron, cobalt and nickel, consist exclusively of several carbide or carbide nitride mixed crystals, is possible per se, but by utilizing the hardness of the mixed crystals described by...
adding them in accordance with the present invention in quantities of 2 to 30 per cent to tungsten carbide and one or more of the additional metals, iron, cobalt and nickel the presence of the latter produces a substantial lowering of the heat conductance which has proved to be favourable in practice.

It has likewise been found practical to employ an alloy of an iron metal with a metal of the 10 4th, 5th or 6th group of the periodic system or with boron instead of one or more additional metals of the iron group, such as iron, cobalt or nickel. It is particularly advisable, in this instance, to select the components of the alloy in molecular proportion, so that intermetallic compounds result. Such compounds, for example of the cobalt or nickel with tungsten or molybdenum are produced in that the molecular quantities of the individual components corresponding to the chemical formula WCo, WNbc, MoCo, MoNi as metal powder are thoroughly mixed and then sintered in an electric furnace in a reducing atmosphere at a temperature between 1200° and 1600° C, which lies below their melting point. When employing the borides cobalt or nickel are thoroughly mixed in the molecular proportion corresponding to the chemical formulae NiB, CoB, NbB2, CoB2, NiB2, Co3B and sintered in a vacuum at a temperature between 800° and 1300° C.

After these compounds have been produced, they are thoroughly mixed in quantities up to 20% with the other hard metal components such as the tungsten carbide and the mixed crystal formed from carbides of metals of the 4th and 5th group of the periodic system, and after the powders have been pressed, sintered at a temperature between 1400 and 1700° C, slightly higher than the melting point of the additional metal alloy.

The toughness and strength are not affected by employing the additional metal alloy. The density and hardness of the hard metal alloy is, however, increased by the possibility of applying a higher sintering temperature.

If the sintering is carried out, as usual, in a tubular coal furnace through which hydrogen flows, the additional metal compounds, owing to the great mutual chemical affinity of their components, remain unchanged at sintering temperatures up to 1700° C. For example, recarbonisation of the compound WCo is not caused by the presence of tungsten carbide, such as is the case when free tungsten is added to the tungsten monocarbide whereupon lower tungsten carbides form.

In carrying out the present invention in order to produce the hard mixed crystals desired the most possible components, for example TiC and TaC, are intimately mixed together in molecular proportions and then heated for such a long period in a tubular coal furnace traversed by hydrogen that a formation of mixed crystals is brought about. In the example selected, the components must be heated at 2000° C. for half-an-hour for 15 this purpose, although in certain cases a temperature between 1500° C. and 2000° C. is sufficient. The mixed crystals, which remain at the room temperature after cooling off, are now added in a quantity of about 10 per cent by weight to a hard metal powder consisting of 95 per cent tungsten carbide and 5 per cent cobalt. The mixture is ground in a known manner for a lengthy period in ball mills, pressed and finally sintered during a period of 1 to 3 hours at between 1600° C. and 1800° C., say about 1500° C. for a tubular coal furnace traversed by hydrogen.

In some cases, a high temperature sintering in a nitrogen current or a hydrogen-nitrogen current or even in a gaseous current charged with ammonia is suitable with subsequent annealing in a nitrogen atmosphere between 1200° C. and 1600° C.

I claim:

1. Sintered hard metal alloy for tools and similar articles, consisting of at least 50% tungsten carbide, up to 35% of an additional metal alloy of a metal of the iron group with boron and 2 to 30% of a hard mixed crystal of carbides of an element of the 4th group with an element of the 5th group of the periodic system.

2. Sintered hard metal alloy for tools and similar articles, consisting of at least 50% tungsten carbide, up to 25% of additional metal of the iron group and 2 to 30% of a preformed hard mixed crystal of only one pair of carbides selected from the following groups, namely: TiC—NbC, ZrC—NbC, HfC—TaC, HfC—NbC, HfC—VC.

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