

[54] **PROCESSES FOR THE MANUFACTURE OF TUNGSTEN-BASED ALLOYS AND IN THE CORRESPONDING MATERIALS**

[75] Inventors: **André R. Hivert**, Pontoise; **Philippe M. Galmiche**, Clamart, both of France

[73] Assignee: **Office National d'Etudes et de Recherches Aerospatiales (O.N.E.R.A.)**, Chatillon-Sous-Bagneux, France

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Primary Examiner—Benjamin R. Padgett

Assistant Examiner—R. E. Schafer

Attorney, Agent, or Firm—Larson, Taylor and Hinds

[57] ABSTRACT

The process comprises sintering very fine tungsten powder mixed in the cold with a metallic binder occurring in the liquid state at the sintering temperature. This metallic binder is constituted by a very fine powder, of a granulometry of the order of several microns, containing 65 to 90% of nickel, 5 to 20% of chromium and 5 to 15% of phosphorus, the phosphorus being introduced in the form of an alloy powder containing one at least of the two other binder constituents.

14 Claims, No Drawings

PROCESSES FOR THE MANUFACTURE OF TUNGSTEN-BASED ALLOYS AND IN THE CORRESPONDING MATERIALS

The invention relates,

on the one hand, to processes for the manufacture of tungsten-based alloys, i.e. heavy alloys containing at least 50% of tungsten, such alloys being particularly sought for certain industrial applications and, especially, for the manufacture of perforating cores for munitions, of balancing weights for aerospace engines, etc.

and, on the other hand, to the materials constituted by such alloys, whether they are semi-fabricated products or completely finished parts.

It is known that tungsten can be easily obtained in the very fine powdered state by simple reduction, at about 900° C, from its oxide in hydrogen.

This has therefore led, for the manufacture of tungsten-based alloys, to the application of processes of powder metallurgy and, especially, processes of sintering bringing into use a metallic binder in the liquid state, such sintering processes enabling, if the metallic binder is suitably selected, particularly dense alloys to be obtained.

There was thus manufactured,

heavy tungsten-nickel-copper (W-Ni-Cu) alloys, using the nickel-copper alloy as binder,

and tungsten carbide-cobalt (WC-Co) cutting alloys using cobalt as binder.

However, these two categories of alloys have drawbacks, the abovesaid heavy alloys being relatively soft (hardness of 16 to 17 Rockwell C, being of the order of 210 Brinell), whilst the abovesaid cutting alloys have a troublesome fragility in their use for certain applications, especially for the manufacture of perforating projectiles.

It will be seen, in these circumstances, that it would be advantageous to have available tungsten-based alloys which are at the same time sufficiently hard and resilient.

It is a particular object of the invention to provide a process enabling the manufacture of tungsten-based alloys having the two qualities explained above, i.e. tungsten-based alloys which are at the same time hard (hardness greater than 40 Rc) and of low fragility.

The process according to the invention, for the manufacture of a tungsten-based alloy, consists of sintering very fine tungsten powder mixed in the cold with a metallic binder as a powder occurring in the liquid state at the sintering temperature, the abovesaid process being characterised by the fact that this metallic binder is constituted by very fine powder, of a granulometry of the order of several microns, containing 65 to 90% of nickel (Ni), from 5 to 20% of chromium (Cr) and from 5 to 15% of phosphorus (P), the phosphorus being introduced in the form of an alloy powder containing one at least of the two other constituents of the binder and, preferably, these two other constituents, the binder then having, in this latter case, the form of a nickel-based ternary alloy of the nickel-chromium-phosphorus type whose the constituents occur within the ranges of percentages by weight indicated above.

The proportion by weight of the binder thus constituted, in the mixture formed by the tungsten powder supplemented with the said binder, is preferably comprised between 5 and 20% and, preferably again, between 10 and 15%.

As for the sintering treatment proper, there is preferably adopted a treatment conducted in a halogenated-hydrogenated atmosphere at a temperature which is a function of the exact composition of the final alloy and in any case greater than the fusion temperature of the metallic binder used, this sintering temperature being then, generally, between 800° and 1150°C.

From the operational point of view, the best results have been obtained by starting first with a mixture in the dry or in a liquid medium of the powders introducing the tungsten and the constituents of the metallic binder, by then effecting a shaping in the cold, by mechanical or isostatic compression, in the presence of a conventional agglomerant (camphor e.g.) easily removable, by then proceeding to the elimination of this agglomerant by heating to a temperature at least equal to the volatilisation temperature of the said agglomerant but well below the fusion temperature of the metallic binder, and by finally effecting the sintering treatment.

It should be noted that the use of a binder of low melting point (less than or equal to 1000°C) enables the enlargement of the grains of tungsten to be avoided which could result from a recrystallization at a higher temperature. This enables the fine structure of the alloy to be preserved, and consequently, its resilience.

The invention enables the obtaining of tungsten-based alloys whose density varies from 14 to 16.5 according to the constitution and the proportions of the metallic binder, whose hardness is comprised between 40 and 45 Rc and whose resilience is good (no crumbling on grinding and behavior similar to that of hardened steel).

The hardness can be increased up to 60 Rc by adding a low proportion (below or equal to 5%) of a metallic carbide selected from among the hardest and with a heat of formation greater than that of tungsten carbide WC, such as the carbides of titanium or of zirconium, or, better still, tantalum carbide on account of its density.

There will accordingly be given below several examples of processes according to the invention, these being however purely by way of illustration and non-limiting.

For the majority of the examples, there is used a very fine tungsten powder (from one to several microns) and a metallic binder in a very fine powder (also from one to several microns) constituted by the ternary alloy Ni (77%) — Cr (13%) — P (10%).

This ternary alloy is sold commercially under the name "NICROBRAZ", by the American firm Wall Colmonoy Corporation of Detroit (Michigan), and it is in the form of a powder whose granulometry is about 40 microns, i.e. well above that desired (from one to several microns).

Crushing of this commercial ternary alloy powder is therefore first effected in a liquid medium (especially ethylene glycol) and the lenticular residual particles of too large size are removed before drying by sedimentation or by lutriation after drying (a gaseous fluid current carrying off the fines particles). In any case, there is thus obtained a very fine binder powder which is mixed dry or in a liquid medium with the tungsten powder, as already indicated, before proceeding to the shaping in the presence of an eliminable agglomerant, then to the operation of sintering after elimination of this agglomerant.

Taking into account these common data, the examples which follow differ from one another in the proportions of ternary binder and in the temperatures and durations of the sintering treatment.

EXAMPLE 1

The commercial NICROBRAZ powder (grains of 40 microns) is previously converted into a fine powder by the following process:

In a ball mill of two litres capacity, there are introduced 240 grams of NICROBRAZ in powder and a sufficient amount of ethylene glycol to form a fluid paste (50 to 100 cm³) and it is milled by rotation or vibration for about 10 hours. The paste extracted from the mill is supplemented by an equivalent volume of ethylene glycol. The mixture is allowed to stand for about two minutes to enable sedimentation of the coarsest particles, then the suspension is decanted into an other container. After sedimentation, the liquid is removed and three washings with distilled water are carried out. The powder obtained is dried in an oven at 120°C then screened on a 350 mesh screen.

In the same two litres mill, there is introduced 360 grams of tungsten as a fine powder (granulometry below three microns) freshly reduced in hydrogen and 8 grams of tantalum carbide as a fine powder (granulometry from one to three microns).

60 grams of fine powder NICROBRAZ provided by the treatment above is mixed with trichlorethylene in a sufficient quantity to form a fluid paste (30 to 80 cm³). It is milled by rotation or vibration for 3 hours. Then the paste is dried at 80°C and screened on a 350 mesh screen.

The powder obtained is supplemented with 4% of camphor by means of an alcoholic solution. After evaporation of the alcohol, the mixture is granulated on an 80 mesh metallic gauze.

The granulate obtained is introduced into a rubber bag of diameter 20 mm and length 70 mm.

The whole is subjected to an isostatic compression of 1.5 t/cm².

The cylinders obtained are arranged upright on plates of molybdenum covered with a fine layer of magnesium fluoride to avoid sticking. The whole is placed in a partially sealed casing of chromed iron at the bottom of which there is placed a bed of 2 to 3 cm of chrome granulate (2 to 3 mm) including a small amount of bivalent chromium fluoride and of ammonium acid fluoride. A chromed nickel gauze caps the parts to be sintered. The box provided with its cover is placed in a vertical oven of the bell type supplied with a light current of hydrogen.

The program of heating is arranged so as to describe the following cycle :

1. from 20° to 150°C in an one-half hour,
2. from 150° to 200°C in 3 hours (starting with the camphor),
3. from 200° to 850°C in about 3 hours,
4. stationary at 850°C, 1 hour (solid state deoxidation)
5. from 850° to 950°C in 1 hour,
6. stationary at 950°C, 1 hour,
7. slow cooling in the oven to 850°C,
8. rapid cooling in a bell with hydrogen protection.

The sintered parts have a density of 15.50 and a hardness of 685 Vickers (53 Rockwell C).

Their grinding is carried out without difficulty with the conventional means used for grinding hardened steel.

EXAMPLE 2

Procedure is as in Example 1 but without tantalum carbide.

The sintered parts obtained have a density of 15.7 and a hardness of 43 Rockwell C.

EXAMPLE 3

In a ball mill of two litres, there is introduced 370 grams of tungsten in freshly reduced fine powder, 60 grams of milled NICROBRAZ and 8 grams of chromium in a plasticised fine powder.

The remainder of the manufacture is similar to the case of Example 1 except for the final sintering temperature which is brought from 950°C to 990°C. The density of the parts obtained is 15.25 and their hardness is 46 Rockwell C.

EXAMPLE 4

The NICROBRAZ is replaced by a nickel alloy (74%) — phosphorus (10%) — chromium (16%) reduced to a powder of granulometry of 40 microns by pulverisation in a liquid state. This powder is milled under the same conditions as the NICROBRAZ of the Example 1.

In a ball mill of two litres, there are introduced 360 grams of tungsten in freshly reduced powder, 8 grams of tantalum carbide and 60 grams of the abovesaid alloy.

The sequence of the process is identical with that of Example 1 and the sintered parts obtained have a density of 15.2 and a hardness of 55 Rockwell C.

EXAMPLE 5

There is prepared by electrolysis of a mixture of sodium phosphate and nickel oxide the compound Ni₃P. The latter, which is fragile, is crushed then milled as in the case of Example 1.

In a ball mill of two litres, there are introduced 360 grams of tungsten as a freshly reduced fine powder, 40 grams of powder of the above compound Ni₃P, 12 grams of ex carbonyl nickel powder (3 microns) and 8 grams of fine pure chromium powder (1 micron).

The sequence of the process and the results obtained are the same as in the case of the Example 1.

As is self-evident and as is also apparent already from the preceding description, the invention is in no way limited to those of its methods of application, nor to those of its methods of production of its various parts, which have been more especially indicated; it embraces, on the contrary, all variations.

We claim:

1. Process for the manufacture of tungsten-based alloys, comprising forming a mixture of very fine tungsten powder with a metallic binder and sintering said mixture in a non-oxidizing, halogenated atmosphere, said binder occurring in the liquid state at the sintering temperature and being constituted by a very fine powder, containing as the only three constituents 65 to 90% of nickel, 5 to 20% of chromium and 5 to 15% of phosphorus, the phosphorus being introduced in the form of an alloy powder containing one at least of the two other constituents of the binder.

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2. Process according to claim 1, wherein said alloy powder contains also said two other constituents, the binder then being in the form of a nickel-based ternary alloy of the nickel-chromium-phosphorus type whose constituents are within the above-indicated ranges of percentage by weight.

3. Process according to claim 1, wherein the proportion by weight of the binder, in the mixture formed by the tungsten powder supplemented with said binder, is comprised between 5 and 20%.

4. Process according to claim 3, wherein the proportion by weight of the binder in the mixture formed by the tungsten powder supplemented with the said binder, is comprised between 10 and 15%.

5. Process according to claim 1, wherein said sintering is conducted in a halogenated-hydrogenated atmosphere at a temperature which is a function of the exact composition of the final alloy and above the fusion temperature of the metallic binder used.

6. Process according to claim 5, wherein said sintering temperature is between 800° and 1150° C.

7. Process according to claim 1, comprising first forming a mixture of the powders, introducing the tungsten and the constituents of the metallic binder, then cold shaping the mixture by compression in the presence of an easily removable conventional agglomerant, then removing said agglomerant by heating at a temperature at least equal to the temperature of volatisation of said agglomerant but well below the

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fusion temperature of the metallic binder, and lastly carrying out the sintering.

8. Process according to claim 7, wherein said agglomerant is camphor.

9. Process according to claim 1, comprising adding to the mixture, in a proportion at least equal to 5%, a hard metallic carbide having a heat of formation higher than that of tungsten carbide.

10. Process according to claim 9, wherein said hard carbide is titanium carbide.

11. Process according to claim 9, wherein said hard carbide is zirconium carbide.

12. Process according to claim 9, wherein said hard carbide is tantalum carbide.

13. A material constituted by a sintered mixture of fine tungsten particles and a metallic binder, said binder consisting of 65 to 90% nickel, 5 to 20% chromium and 5 to 15% phosphorus, the density of said material being between 14 and 16.5 and the hardness of said material being between 40 and 45 Rc.

14. A material constituted by a sintered mixture of fine tungsten particles, at least 5% by weight of tantalum carbide and a metallic binder, said binder consisting of 65 to 90% nickel, 5 to 20% chromium, and 5 to 15% phosphorus, the density of said material being between 14 and 16.5 and the hardness of said material being between 40 and 60 Rc.

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