

[54] ROTARY FURNACE FOR CARBURIZATION

[75] Inventors: Akio Hara; Masaya Miyake, both of Itami, Japan

[73] Assignee: Sumitomo Electric Industries, Ltd., Higashi-ku, Osaka, Japan

[22] Filed: Oct. 12, 1971

[21] Appl. No.: 187,953

[30] Foreign Application Priority Data

Oct. 30, 1970 Japan..... 45-95243
Sept. 16, 1971 Japan..... 46-71233

[52] U.S. Cl..... 23/279, 423/440, 432/114, 219/389, 13/20, 13/21, 13/35, 266/5 E, 266/18, 23/277 R

[51] Int. Cl..... F27b 7/06, B01j 6/00

[58] Field of Search..... 23/279, 227 R, 288 J; 263/32; 219/389; 13/20, 21, 35; 266/5 E, 18; 423/440, 441; 432/114

[56] References Cited

UNITED STATES PATENTS

3,350,495 10/1967 Barnes et al..... 13/21 X

| | | | |
|-----------|---------|--------------------|--------|
| 1,700,942 | 2/1929 | Lederer | 13/20 |
| 3,111,394 | 11/1963 | Weber et al. | 23/279 |
| 3,422,205 | 1/1969 | Pisano et al. | 13/35 |

Primary Examiner—James H. Tayman, Jr.
Attorney, Agent, or Firm—Wenderoth, Lind & Ponack

[57] ABSTRACT

An improved furnace of the rotating type comprises a rod-shaped or tubular heating core of graphite or carbonaceous material fixedly arranged in the central portion of the furnace. A rotary cylinder having an inner wall of graphite or carbonaceous material is secured to rotate around the heating core. A casing is provided with means for rotatably holding the rotary cylinder, an opening for feeding a raw material, means for supplying electric power, an opening for discharging a product and a gas flow opening and is secured to hold an atmosphere of carburization inside the furnace.

9 Claims, 3 Drawing Figures

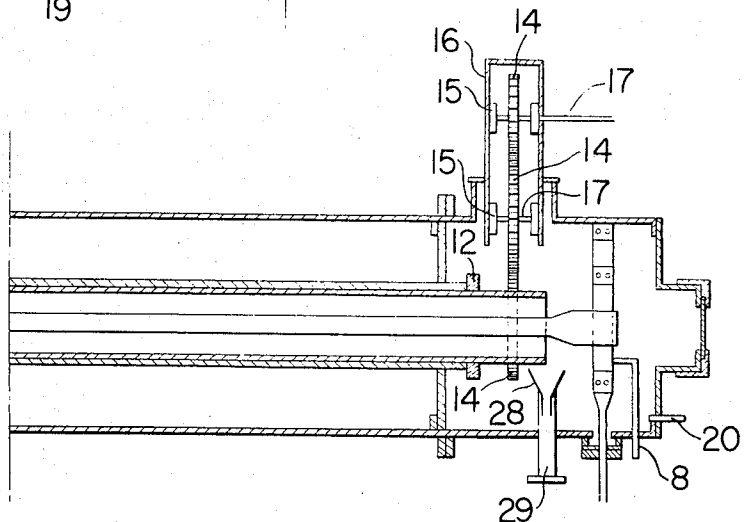
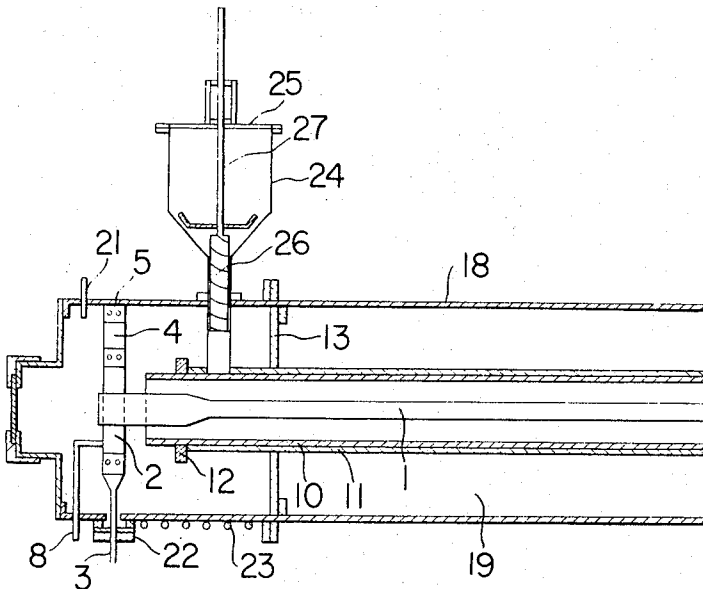


FIG. 1

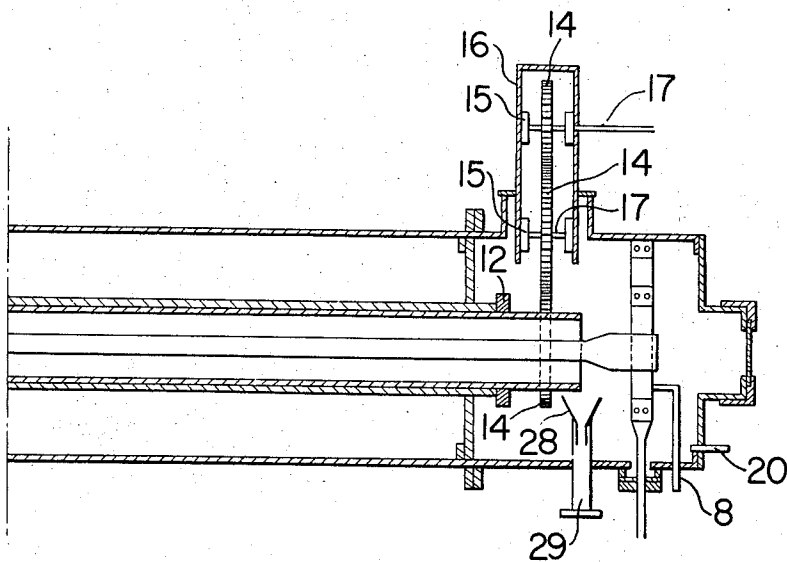
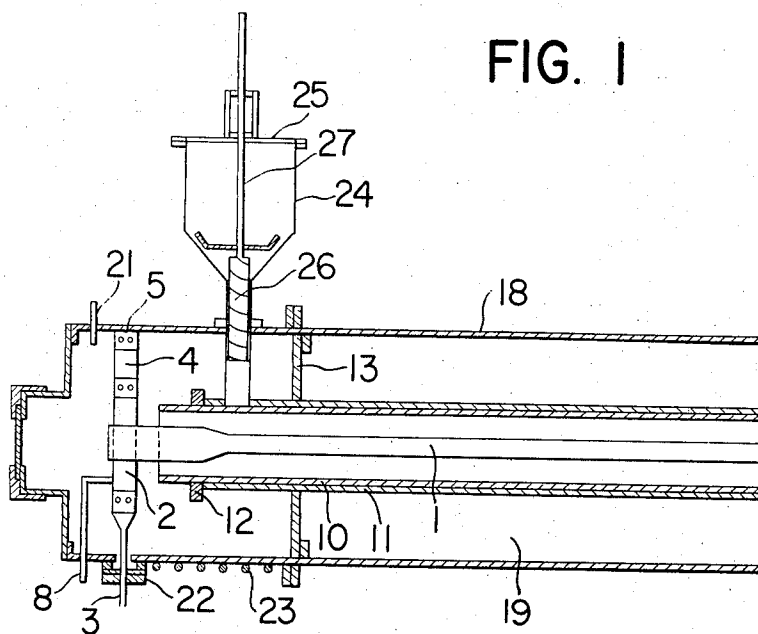


FIG. 2

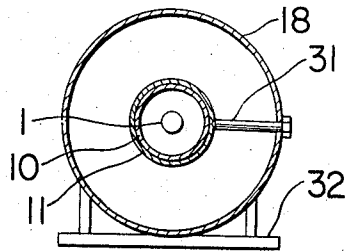
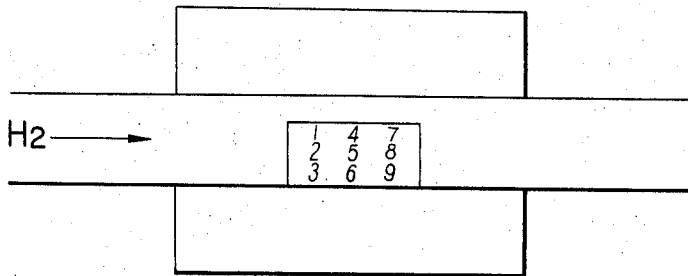


FIG. 3



ROTARY FURNACE FOR CARBURIZATION

BRIEF SUMMARY OF THE INVENTION

This invention relates to a furnace for carburization, and more particularly it is concerned with a rotary furnace for carburization, which is suitable for the production of carbides of elements of Groups IV-A, V-A and VI-A of Periodic Table, actinide elements, boron and silicon.

Various attempts to produce carbides of the kind by gaseous cementation have hitherto been made, but have proven unsatisfactory on an industrial scale. Only the method has been put to practical use wherein a powdered metal or metal oxide is mixed with a carbonaceous powder such as carbon black by means of a ball mill and, optionally after formed into a certain size by a press, the mixture is then charged in a graphite boat and heated in hydrogen or in vacuum. However, there is no choice but to do employ batch production by use of this method. Furthermore, this method has a disadvantage that, since the reaction of forming these carbides is accompanied by the generation of heat, an abnormal generation of heat takes place in the lower portion of the boat, resulting in a localized grain growth, and the degree of cementation differs between the upper portion and lower portion of the boat in the carburization in hydrogen, being accompanied by cementation, resulting in unevenness of the quantity of carbon combined. In order to solve this disadvantage, it is necessary to advance the reaction in a continuous manner with agitation of the reactants.

To this end, the use of rotary furnaces is recommended, but those used in the cement manufacturing industry or for the hydrogen reduction of tungsten oxide cannot resist high temperatures such as required for the production of the foregoing carbides. There is nothing but carbon as a material for the rotating tube used in a protective atmosphere such as hydrogen gas at a high temperature of up to 2,000°C. Carbon materials, however, are porous so that leakage of hydrogen gas occurs as a troublesome problem. The heating system of carbon materials, in addition, requires a large electric current and large slidable contacts. Therefore, rotation of the furnace itself is very difficult. Since carbon has such a high thermal conductivity that, when the temperature of the central portion of a carbon tube is raised to 800°-2,200°C, the end portion thereof will also be of a high temperature, and even bearings in the furnace system have to be resistant to high temperatures.

It is an object of the present invention to provide a rotary furnace for carburization, whereby the above mentioned disadvantages of the prior art are overcome.

It is another object of the invention to provide a rotary furnace for carburization, whereby carbides with a uniform composition and very narrow grain size distribution are produced continuously.

It is a further object of the invention to provide a process for the production of carbides by the use of this furnace for carburization.

Still more objects will be apparent from the following detailed description.

BRIEF DESCRIPTION OF THE DRAWING

The accompanying drawings are to illustrate the principle and merits of the invention in more detail.

FIG. 1 shows schematically one form of the rotary furnace for carburization according to the invention.

FIG. 2 shows a cross sectional view of the furnace of FIG. 1 at the central portion thereof.

Located at the center of furnace body 18 is heating core 1, around which rotating cylinder 10 and fixed cylinder 11 are arranged.

FIG. 3 shows a dispersion of the quantity of carbon in tungsten carbide powder carburized by the prior art furnace.

DETAILED DESCRIPTION OF THE INVENTION

It has been found as a result of various studies that the foregoing objects can be accomplished by providing a fixed, rod-shaped or tubular heating core of graphite or carbonaceous material in the center of a furnace for carburization and arranging a rotating cylinder having a graphite or carbonaceous material inner surface coaxially around such heating core.

That is to say, there is the provision of a rotary furnace for carburization, which comprises a rod-shaped or tubular heating core of graphite or carbonaceous material fixedly positioned in the central portion of the furnace, a rotary cylinder having an inner wall of graphite or carbonaceous material and positioned to rotate coaxially around the heating core, and a casing provided with means for rotatably supporting the rotary cylinder, an opening for feeding a raw material, means for supplying electric power, an opening for discharging a product and a gas flow opening and being constructed to maintain an atmosphere of carburization within the furnace. The most important aspect of this furnace lies in that rotation of the rotary cylinder is independent of the fixed heating core and, consequently, sliding electrical contacts are unnecessary. Since the furnace is of an internal heating type, an outer wall for shielding hydrogen gas can be kept at normal temperature by inserting a heat insulating material between the inner and outer walls, and the problems of insulating materials can thus be solved.

In accordance with the second feature of the invention, the rotating cylinder is modified into a double structure of a rotating cylinder and fixed cylinder. In this case, the furnace comprises a rod-shaped or tubular heating core of graphite or carbonaceous material fixedly positioned in the central portion of the furnace, a rotary cylinder having an inner wall of graphite or carbonaceous material and positioned to rotate coaxially around the heating core, a fixed cylinder fixedly positioned to surround the rotary cylinder, and a casing provided with means for rotatably supporting the rotary cylinder, means for fixedly supporting the fixed cylinder, an opening for feeding a raw material, means for supplying electric power, an opening for discharging a product, a gas flow opening, and being constructed to maintain an atmosphere of carburization with the furnace.

By these carburizing furnaces, carbides of high melting point metals such as tungsten, titanium, tantalum, columbium, hafnium, zirconium, vanadium, chromium and molybdenum having a substantially stoichiometric amount of combined carbon and a very narrow grain size distribution are economically produced from the high melting point metals or oxides thereof. The features and merits of these furnaces are summarized below:

1. Since rotation of the rotary section is independent of the fixed heating core, slidable contacts for supplying electric power are not necessary.

2. Since the furnace is of the internal heating type with a heating core provided therein, it is relatively easy to maintain high temperatures, the raw material is directly exposed to the heat radiation from the heating core, and the furnace can be adapted for the continuous production of hard carbides without the use of expensive heat insulating materials.

3. Since the heating core is fixedly arranged in the central portion of the furnace, the thermal efficiency is raised and a large electric current can be supplied independently of the rotating mechanism of the cylinder.

4. Since the cylinder is of a double structure of a rotary cylinder and fixed cylinder, rotation of the cylinder can smoothly be effected, and accordingly, feeding of powdered raw materials can be carried out corresponding to movement of the powder in the cylinder. Moreover, leakage of hydrogen gas can be prevented.

5. Since the cylinder is of a double structure, the furnace structure is so simple that the driving mechanism is composed of shafts only.

Reactants fed into the rotary furnace of the invention flow down between the inner wall and the heating core little by little in the form of powder or granules. The diameter of the heating core and the inner diameter of the rotary cylinder may be varied with the quantity of reactants and reaction temperature. When it is further desired to increase the surface area of the heating core, it may be tubular shaped. Moreover, the inclination of the furnace body may be varied depending on the desired reaction speed.

The invention is further illustrated in the accompanying drawings. With particular reference to FIG. 1, carbon heating core 1 is fixed by copper electrode 2 and furnished with a large electric current through bus bar 3, which is fixed by insulator 4 and supported by metal fitting 5. Copper electrode 2 is cooled by water supplied by conduit 8. Rotary cylinder or tube 10 is located coaxially around heating core 1 and rotated within and in contact with fixed cylinder or tube 11 and carbon ring 12. That is to say, rotary cylinder or tube 10 is set by carbon ring 12 and moved in fixed cylinder or tube 11. Fixed cylinder or tube 11 is positioned in the center of the furnace by carbon disk 13. The driving mechanism of rotary cylinder 10 consists of stainless steel gears 14 supported by carbon bearings 15 and shafts 17 in gear box 16, the driving being effected through shafts 17. The above mentioned mechanism is enclosed in furnace body or casing 18. The space between fixed cylinder 11 and furnace body 18 is filled with heat insulating material 19 so that the temperature of the central portion may be raised up to 2,200°C. Hydrogen gas enters hydrogen inlet 20 and leaves from hydrogen outlet 21. Teflon 22 is used for the purpose of insulation and preventing leakage of hydrogen from around bus bar 3. Furnace body 18 is provided with cooling water tube 23 on the outer surface thereof to prevent it from overheating.

Referring to FIG. 2, carbon tube pyrometer 31 for measurement of the outer surface temperature of rotary cylinder 10 is positioned to extend through furnace body 18 and fixed cylinder 11. Furnace body 18 is mounted on support frame 32 in such a manner that its inclination may be varied in accordance with the desired reaction speed.

In operation of this furnace for carburization, a raw material powder is charged in hopper 24 from a feed opening (not shown) of hopper cover 25 and moved downwardly by screw 26 upon rotation of shaft 27. Then the raw material powder is fed to rotary cylinder 10 through a hole in fixed cylinder 11 when such hole aligns with a hole formed in rotary cylinder 10. The powder is reacted while flowing through cylinder 10, and the reacted powder is discharged from discharge port 29 via receiver 28.

Using the rotary furnace for carburization according to the invention, as illustrated above, various reactions for the production of carbides are carried out and the following results are obtained.

EXAMPLE 1

Using a rotary furnace of the invention (having no fixed cylinder), tungsten carbide was produced by the following condition:

| | |
|---|----------|
| Inner diameter of rotary cylinder (graphite tube) | 60 mm |
| Outer diameter of heating core (carbon) | 30 mm |
| Whole length of rotating part | 2 m |
| Inclination of furnace body | 4° |
| Rotation Speed | 6 rpm |
| Flow rate of hydrogen | 10 l/min |
| Electric power | 20 KW |

A mixed powder of tungsten and carbon was pressed in a mold and crushed, and the resulting granule was continuously fed, while keeping the furnace at 1,450°C over about 60 cm, thus obtaining continuously tungsten carbide with a uniform property at a rate of 8 kg/hour.

EXAMPLE 2

Tungsten powder of 0.7 μ was mixed with 6.25 % of carbon powder in a ball mill and the granulated powder having a grain size distribution of 1 mm to 0.02 mm was obtained. The resulting granulated powder was subjected to carburization reaction by the use of a rotary furnace for carburization according to the invention as shown in FIGS. 1 and 2, to obtain WC powder. The various conditions of the furnace are as follows:

| | |
|-----------------------------------|--------------|
| Inner diameter of rotary cylinder | 60 mm ϕ |
| Outer diameter of heating core | 20 mm ϕ |
| Whole length of rotating part | 1500 mm |
| Inclination of furnace body | 4° |
| Rotation speed | 2 rpm |
| Flow rate of hydrogen | 15 l/min |
| Electric power | 10 KW |
| Carburization temperature | 1400 °C |

The granulated powder was fed in the hopper and moved at a rate of 5 kg/hr continuously in the cylinder. The reaction proceeded smoothly and the product was discharged as WC powder without adhesion to the inner wall of the cylinder. No troubles occurred when 1 ton of the product was produced.

In the case of carrying out the reaction using a carbon case in a horizontal Tammann furnace according to the carburization method of the prior art, there occurred a dispersion of the quantity of carbon depending on the position in the boat, as shown in FIG. 3. When the position in the carbon case was numbered to the flow of hydrogen gas as follows:

Front upper 1 Center upper 4 Back upper 7
 middle 2 middle 5 middle 8
 lower 3 lower 6 lower 9

the quantity of carbon (% by weight) in the each position was as tabulated below.

| | | | | | |
|---|------|---|------|---|------|
| 1 | 6.39 | 4 | 6.37 | 7 | 6.28 |
| 2 | 6.14 | 5 | 6.06 | 8 | 6.06 |
| 3 | 6.18 | 6 | 6.20 | 9 | 6.15 |

When carburization was continuously carried out using the furnace of the invention, on the other hand, the fluctuation of carbon quantity was much reduced as shown in Table 1.

TABLE 1

| Dispersion of carbon quantity of WC powder in rotary furnace for carburization | | |
|--|-------------------|------------------|
| | TC (Total Carbon) | FC (Free Carbon) |
| 1 | 6.17 | 0.05 |
| 2 | 6.17 | 0.05 |
| 3 | 6.18 | 0.05 |
| 4 | 6.18 | 0.05 |
| 5 | 6.17 | 0.06 |
| 6 | 6.16 | 0.07 |
| 7 | 6.17 | 0.05 |

Note: Sampling was carried out every 15 minutes.

EXAMPLE 3

Tungsten powder of 2μ was mixed with 6.25 % of carbon powder in a ball mill, pressed in a mold under a pressure of 1 ton/cm² and crushed to obtain a powder having a grain size distribution of 0.5 mm to 0.02 mm. The resulting powder was subjected to carburization using the carburizing furnace of the invention under the following conditions:

| | |
|-----------------------------------|--------------------|
| Inner diameter of rotary cylinder | 80 mmφ |
| Outer diameter of heating core | 20 mmφ, rod-shaped |
| Inclination of furnace body | 6° |
| Rotation speed of rotary cylinder | 2 rpm |
| Flow rate of hydrogen gas | 10 l/min |
| Electric power | 12 KW |
| Carburization temperature | 1500 °C |

The reactants were fed to the furnace body from the hopper at a rate of 10 kg/hr. The so obtained WC powder had a total quantity of carbon of 6.19 % and free carbon of 0.06 %, and the grain size distribution was much better than in the case of using a carburizing furnace of the prior art.

To this WC powder was added 7 % of cobalt powder and mixed with acetone for 100 hours in a ball mill having an inner diameter of 200 mmφ and cylinder length of 270 mm, followed by drying by heating at 100 °C.

The resulting mixed powder was pressed in a mold under a pressure of 1 ton/cm² and sintered at 1,450 °C for 1 hour in vacuum. The mechanical properties of the resulting alloy are shown in Table 2:

TABLE 2

| | SG | H _{RA} | H _V | TRS | 4πσ | H _C |
|----------------------------|-------|-----------------|----------------|-----|-----|----------------|
| WC powder of the invention | 14.90 | 91.2 | 1500 | 210 | 140 | 165 |
| WC powder of the prior art | 14.87 | 91.0 | 1475 | 170 | 140 | 160 |

Note:

- SG = specific gravity
- H_{RA} = Rockwell hardness, A scale
- H_V = Vickers hardness
- TRS = transverse rupture strength
- 4πσ = saturated magnetisation quantity
- H_C = coercive force

From the WC powder produced by the prior art method and from the WC powder produced by means of the carburizing furnace of the invention alloys were respectively prepared and compared regarding their properties. The latter is favourably compared with the former in the fact that the grain size distribution of WC in the alloy is better, abnormally grown WC crystals are less and the transverse rupture strength is higher.

EXAMPLE 4

As in Example 3, tungsten powder of 5μ was mixed with 6.25 percent of carbon powder in a ball mill, pressed in a mold under a pressure of 1 ton/cm² and then crushed to obtain a powder having a grain size distribution of 0.5 mm to 0.02 mm. The thus size-controlled powder was subjected to carburization using the carburizing furnace of the invention under the following conditions:

| | |
|-----------------------------------|----------|
| Inner diameter of rotary cylinder | 80 mmφ |
| Outer diameter of heating core | 20 mmφ |
| Inclination of furnace body | 4° |
| Rotation speed of rotary cylinder | 2 rpm |
| Flow rate of hydrogen | 10 l/min |
| Electric power | 18 KW |
| Carburization temperature | 2000 °C |

The reactants were fed to the furnace from the hopper at a rate of 10 kg/hr. The so obtained WC powder had a total carbon quantity of 6.23 % and free carbon quantity of 0.10 and the grain size distribution was much better than in the case of using a carburizing furnace of the prior art.

To this WC powder was added 10 % of cobalt powder and mixed with acetone for 80 hours in a ball mill having an inner diameter of 200 mmφ and cylindrical length of 250 mm, followed by drying by heating at 100 °C. The resulting mixed powder was pressed in a mold under a pressure of 1 ton/cm² and sintered at 1,450 °C for 1 hour in vacuum. The mechanical properties of the resulting alloy are shown in Table 3.

TABLE 3

| | SG | H _{RA} | H _V | TRS | 4πσ | H _C |
|----------------------------|-------|-----------------|----------------|-----|-----|----------------|
| WC powder of the invention | 14.60 | 87.0 | 1100 | 300 | 196 | 70 |
| WC powder of the prior art | 14.60 | 86.5 | 1080 | 270 | 190 | 65 |

From the WC powder produced by the prior art method and from the WC powder produced by means of the carburizing furnace of the invention alloys were respectively prepared and compared regarding their

properties. The latter is favourably compared with the former in the fact that the grain size distribution of WC in the alloy is better, abnormally grown WC crystals are less and the transverse rupture strength is higher.

EXAMPLE 5

Tungsten oxide (WO_3) powder of 0.2μ was mixed with 16 % by weight of carbon powder and 2 % by weight of stearic acid in a ball mill, pressed in a mold under a pressure of 1 ton/cm² and then crushed to give a powder having a grain size distribution of 2 mm to 0.2 mm. The resulting powder was subjected to carburization in two steps by the use of the rotary carburizing furnace of the invention. The first step was carried out at 1,400 °C in nitrogen and the second step, at 1,800 °C in hydrogen. Various conditions of the furnace are shown in Table 4.

TABLE 4

| | First step carburization | Second step carburization |
|-----------------------------------|--------------------------|---------------------------|
| Inner diameter of rotary cylinder | 60 mmφ | 80 mmφ |
| Heating core | rod-shaped heating core | tubular heating core |
| Dimension of heating core | 20 mmφ × 1700 | 30mmφ × 20mmφ × 1700 |
| Inclination of furnace | 6 ° | 4 ° |
| Rotation speed | 4 rpm | 2 rpm |
| Atmosphere | N ₂ | H ₂ |
| Carburization temperature | 1400 °C | 1800 °C |

The WC powder had a total carbon quantity of 6.32 % and free carbon quantity of 0.20 % and a grain size of 1μ .

EXAMPLE 6

Hafnium oxide (Hf_2O_5) powder of 0.2μ was mixed with 15 % by weight of carbon powder and 2 % by weight of stearic acid in a ball mill, pressed under a pressure of 1 ton/cm² and then crushed to obtain a powder having a grain size of 1 mm to 0.1 mm. The thus size-controlled powder was subjected to carburization in two steps using the rotary furnace of the invention. The first step was carried out at 1,600 °C in argon and the second step, at 1,900 °C in hydrogen. Various conditions of the furnace are shown in Table 5.

TABLE 5

| | First step carburization | Second step carburization |
|-----------------------------------|--------------------------|---------------------------|
| Inner diameter of rotary cylinder | 60 mmφ | 80 mmφ |
| Heating core | rod-shaped heating core | tubular heating core |
| Inclination of furnace | 6 ° | 4 ° |
| Rotation speed | 4 rpm | 2 rpm |
| Atmosphere | Ar | H ₂ |
| Carburization temperature | 1600 °C | 1900 °C |

The HfC powder had a total carbon quantity of 6.44 % and free carbon quantity of 0.20 %, and a grain size of 1μ .

EXAMPLE 7

Titanium hydride (TiH_2) powder was mixed with 21 % of carbon and 5 % of stearic acid for 20 hours in a ball mill, pressed in a mold and crushed to obtain a size-

controlled powder having a grain size distribution that 80 % consists of 10 meshes to 20 meshes. The thus size-controlled powder was reacted at 1,200 °C in H₂ atmosphere by means of the furnace as shown in Example 2. Feeding of the powder was carried out in such a manner that the thickness thereof did not exceed 5 mm in the cylinder. A TiC powder with a combined carbon of 19.5 % was obtained without explosive reaction in a yield of 98 %.

The thus obtained TiC powder was mixed with 10 % of nickel powder and 10 % of molybdenum powder for 10 hours by means of a vibrating mill using balls each having a diameter of 10 mm and being a cermet ball and alcohol in an amount of two times the powder. The mixed powder was pressed under a pressure of 2 tons/cm² and sintered at 1,375 °C for 1 hour in a vac-

uum having a degree of vacuum of 2×10^{-4} to obtain an alloy having the following characters:

TABLE 6

| SG | H _{RA} | H _V | TRS | 4πσ |
|------|-----------------|----------------|-----|-----|
| 5.55 | 91.9 | 1570 | 170 | 60 |

EXAMPLE 8

52 % of tungsten powder of 1μ and 30 % of titanium dioxide (TiO_2) powder of 0.2μ were mixed with 18 %

of carbon powder and 2 % of stearic acid for 1 hour by the use of a high speed mixer. The mixture was pressed by a powder roller and passed through a sieve to obtain a size-controlled powder having a grain size distribution of 1.0 mm to 0.1 mm. The resulting size-controlled powder was reacted at 2,000 °C in hydrogen using the rotary furnace of the invention under the following conditions:

TABLE 7

| | |
|-----------------------------------|--|
| Inner diameter of rotary cylinder | 150 mm ϕ |
| Heating core | tubular, outer diameter 50 mm ϕ inner diameter 30 mm ϕ |
| Whole length of rotating part | 3 m |
| Inclination of furnace body | 8° |
| Rotation Speed of cylinder | 6 rpm |
| Carburization temperature | 1900 °C |
| Electric power | 30 KW |

Using the above mentioned furnace, a solid solution of (W.Ti)C was produced at a rate of 20 kg/hr, having the following composition.

TABLE 8

| | | | | | |
|--------|--------|--------|----------------|----------------|----------------|
| TC | FC | CC | O ₂ | H ₂ | N ₂ |
| 9.80 % | 0.02 % | 9.78 % | 0.02 % | 0.0003 % | 0.0002 % |

From the resulting solid solution (W.Ti)C and WC powder of 2 μ obtained in Example 3 a cemented carbide was prepared by the following recipe:

Table 9

| 2 μ WC (W.Ti)C solid solution cobalt powder | Blending composition | |
|---|----------------------|-----------|
| | 50 % | by weight |
| | 40 | do. |
| | 10 | do. |

The foregoing composition was ball-milled for 100 hours and sintered by holding at 1,450 °C for 1 hour in a high vacuum furnace. At the same time, another cemented carbide was prepared from WC and (W.Ti)C solid solution type carbide obtained by the prior art method. Comparison of their cutting properties was carried out by the following cutting test:

Workpiece Cr-Mo steel, hardness H_B 250

Cutting speed 110 m/min, feed 0.54 mm/rev, depth of cut 2 mm

As a result of this test it was found that our cemented carbide had a life of about 1.3 times as long as the comparative cemented carbide, such life being that continued until the Flank wear reached 0.3 mm.

EXAMPLE 9

30 % of tungsten powder, 22 % of tantalum oxide (Ta₂O₅) powder and 30 % of titanium dioxide (TiO₂) powder were mixed with 18 % of carbon powder for 1 hour by means of a high speed mixer. The mixture was granulated by a pan type granulator while spreading acetone thereon. The thus granulated powder was subjected to carburization under the following conditions:

| | |
|-----------------------------------|------------------------------------|
| Inner diameter of rotary cylinder | 150 mm ϕ |
| Heating core | 80 mm ϕ × 60 mm ϕ × 2500 |
| Inclination of furnace body | 10° |
| Rotation speed | 2.5 rpm |
| Flow rate of hydrogen | 20 l/min |
| Carburization temperature | 1900 °C |

The granulated powder was fed to the furnace in such a manner that the thickness thereof equaled 10 mm and stirring was adequately carried out to complete the reaction. The charge was processed at a rate of 15 kg/hr thus to obtain a complete solid solution of (W.Ti.Ta)C. The carbide of such solid solution type was well available as a raw material of cemented carbides.

EXAMPLE 10

Chromium oxide (Cr₂O₃) powder was mixed with 26 % of carbon powder and 2 % of stearic acid in a ball mill, pressed under a pressure of 1 ton/cm² and crushed to obtain a powder having a grain size distribution of 2 mm to 0.2 mm. The thus size-controlled powder was subjected to carburization by the rotary furnace of the invention at 1,500 °C in hydrogen. The conditions of the furnace are as follows:

| | |
|-----------------------------------|--------------------------|
| Inner diameter of rotary cylinder | 80 mm ϕ |
| Outer diameter of heating core | 20 mm ϕ |
| Inclination of furnace body | 6° |
| Rotation speed | 2 rpm |
| Flow rate of hydrogen | 10 l/min |
| Electric power | 12 KW |
| Carburization temperature | H ₂ , 1500 °C |

Thus a Cr₂O₃ powder with a quantity of carbon combined of 12 % was given.

EXAMPLE 11

Columbium oxide (Cb₂O₅) powder and 24 % of carbon powder were ball-milled, pressed and crushed to obtain a controlled grain size. The resulting powder was heated at 1,500 °C in hydrogen by the use of the rotary furnace of the invention to give a CbC powder with a theoretical amount of carbon, TC 11.50 % and FC 0.05 %. The conditions of the furnace are as follows:

| | |
|-----------------------------------|--------------------------|
| Inner diameter of rotary cylinder | 80 mm ϕ |
| Heating core | rod shaped, 20 mm ϕ |
| Inclination of furnace body | 4° |
| Rotation speed | 1 rpm |
| Flow rate of hydrogen | 5 l/min |
| Whole length of rotating part | 3 m |

The furnace, yielding the product at a rate of 5 kg/hr, was fit for use as a rotary furnace on a commercial scale.

EXAMPLE 12

Tantalum oxide (Ta₂O₅) powder and 16 % of powder were ball-milled, pressed and crushed to obtain a controlled grain size. The resulting powder was heated at 1,700 °C in hydrogen by the use of the rotary furnace of the invention to give a TaC powder with a theoretical amount of combined carbon, TC 6.30 % and FC 0.11 %. The conditions of the furnace are as follows:

| | |
|-----------------------------------|--------------------------|
| Inner diameter of rotary cylinder | 80 mm ϕ |
| Heating core | rod-shaped, 20 mm ϕ |
| Inclination of furnace body | 6° |
| Rotation speed | 2 rpm |
| Flow rate of hydrogen | 5 l/min |
| Whole length of rotating part | 3 m |

The furnace, yielding the product at a rate of 5 kg/hr, was fit for use as a rotary furnace on a commercial scale.

EXAMPLE 13

Vanadium oxide (V₂O₅) powder and 29 % carbon powder were ball-milled, pressed and crushed to obtain a controlled grain size. The resulting powder was

heated at 2,100 °C in hydrogen by the use of the rotary carburizing furnace to give a V₄C₃ powder with a theoretical amount of carbon, TC 19.00 % and FC 4.02 %. The conditions of the furnace are as follows:

| | |
|-----------------------------------|-----------------|
| Inner diameter of rotary cylinder | 80 mmφ |
| Heating core | tubular, 30 mmφ |
| Inclination of furnace body | 4 ° |
| Rotation speed | 2 rpm |
| Flow rate of hydrogen | 5 l/min |
| Whole length of rotating part | 3 m |

The furnace, yielding the product at a rate of 3 kg/hr, was fit for use as a rotary furnace on a commercial scale.

EXAMPLE 14

Zirconium oxide (ZrO₂) and 23 % of carbon powder were ball-milled, pressed and pulverized to obtain a controlled grain size. The resulting powder was heated at 2,100 °C in nitrogen by the use of the rotary furnace of the invention to give a ZrC powder with TC 11.30 % and FC 0.20 %. The conditions of the furnace are as follows:

| | |
|-----------------------------------|-----------------|
| Inner diameter of rotary cylinder | 100 mmφ |
| Heating core | tubular, 40 mmφ |
| Inclination of furnace body | 4 ° |
| Rotation speed | 3 rpm |
| Flow rate of nitrogen | 5 l/min |
| Whole length of rotating part | 3 m |

The furnace, yielding the product at a rate of 7 kg/hr, was fit for use as a rotary furnace on a commercial scale.

What is claimed is:

1. A rotary furnace for carburization which comprises:

an enclosing casing constructed to maintain a carburization atmosphere within said furnace, said casing having an opening at the upper portion thereof for feeding a solid raw material therein, an opening at the lower portion thereof for discharging a carburized product therefrom, a gas feed inlet, a gas exhaust outlet, and being inclineable to provide a downward slope thereof;

a raw material feeding means communicating with said upper opening;

a product collecting means communicating with said lower opening;

a rotary hollow cylinder of graphite or carbonaceous material having a large ratio of length to diameter, tubular supporting member means of graphite or

carbonaceous material arranged in said enclosing casing, said rotary hollow cylinder being rotatably mounted on said supporting member means and having means to receive said raw material from said raw material feeding means and to discharge said carburized product to said product collecting means;

an elongated heating core of graphite or carbonaceous material fixedly positioned substantially coaxially at the center of said rotary cylinder;

means for supplying electric power to said heating core and connected with the end of said heating core;

drive means for rotating said rotary hollow cylinder; and

a heat insulating material arranged round said rotary hollow cylinder independently of the rotation thereof.

2. The rotary furnace according to claim 1, wherein said supporting member means is a fixed hollow cylinder of graphite or carbonaceous material having a slightly larger diameter than said rotary hollow cylinder, the inner periphery of said fixed hollow cylinder being in contact with the outer periphery of said rotary hollow cylinder, and said fixed hollow cylinder being fixed to said enclosing casing.

3. The rotary furnace according to claim 2, wherein said rotary and fixed hollow cylinders have holes therein, and said raw material is fed to said rotary hollow cylinder when said holes coincide.

4. The rotary furnace according to claim 2, wherein said fixed hollow cylinder is fixed to said enclosing casing by means of a carbon disk.

5. The rotary furnace according to claim 1, wherein said gas feed inlet is provided at the product discharge end of said casing, and said gas exhaust outlet is provided at the raw material feed end of said casing.

6. The rotary furnace according to claim 1, wherein said raw material feeding means is a vertical screw feed device.

7. The rotary furnace according to claim 1, wherein said electric power supplying means is a bus bar fixed by an insulator and supported by a metal fitting.

8. The rotary furnace according to claim 1, wherein said drive means comprises a gear mechanism.

9. The rotary furnace according to claim 8, wherein said gear mechanism comprises a plurality of gears and shafts supported by carbon bearings, one of said shafts being air-tightly connected to a power source outside said enclosing casing.

* * * * *

55

60

65