(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 443 048 A1**

(12) **EUROPEAN PATENT APPLICATION published in accordance with Art. 158(3) EPC**

(21) Application number: **90913553.5**

(51) Int. Cl.⁵: **B22F 3/10**, C22C 1/05

(22) Date of filing: **12.09.90**

(86) International application number: **PCT/JP90/01171**

(87) International publication number: **WO 91/04119 (04.04.91 91/08)**

(30) Priority: **14.09.89 JP 238849/89**

(43) Date of publication of application: **28.08.91 Bulletin 91/35**

(84) Designated Contracting States: **CH DE FR GB IT LI NL**

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(54) METHOD OF PRODUCING CEMENTED CARBIDE OR CERMET ALLOY.

(57) A method of producing cemented carbide or cermet alloy comprising mixing and kneading cemented carbide powder or cermet alloy powder with an organic binder, molding this mixed powder into a predetermined shape by injection molding, removing the organic binder from the resulting mold and sintering the mold to obtain a compact alloy. The removal of the organic binder is carried out in a first removing step in an inert gas atmosphere and subsequently in a second removing step in vacuum of 1 Torr or below. In the first removing step, the pressure of the atmosphere is kept at or above the atmospheric pressure so as to prevent the occurrence of defects in the mold. After continuous fine pores are formed inside the mold, the pressure of the atmosphere is kept near vacuum in order to promote the evaporation of the gas from the surface and the release of the gas generated inside the mold.

Field of the Invention

The present invention relates to a method of preparing a cemented carbide or a cermet alloy, and more particularly, it relates to a method of preparing a cemented carbide or a cermet alloy by shaping cemented carbide powder or cermet alloy powder into a prescribed configuration by an injection molding method, thereafter removing an organic binder and sintering the compact.

Background Art

A cemented carbide and a cermet alloy are materials having high melting points. In order to obtain a cemented carbide sintered compact or a cermet alloy sintered compact, therefore, a powder metallurgy method of press-molding or CIP-molding a powder raw material and thereafter sintering the same has generally been employed. In this method, however, manufacturable configurations are significantly restricted. In order to obtain a complicated final configuration, it is necessary to grind the sintered compact with a diamond grindstone after sintering, leading to an extremely high cost.

A technique of molding plastic by an injection molding method is widely known. Japanese Patent Publication No. 62-33282 discloses a method of kneading metal powder or ceramics powder with an organic binder and shaping the same into an article having a complicated configuration by injection molding.

When such a powder injection molding technique is applied to a cemented carbide or a cermet alloy, however, the following problems take place: Cemented carbide powder or cermet alloy powder is fine powder whose particle diameter is about 1 µm. Further, such an alloy has large gravity. In addition, tolerance for carbon concentration in the alloy is small. Due to such material properties of the cemented carbide or the cermet alloy, deformation and imperfection are easily caused during debinder processing. Besides, it is impossible to obtain an alloy of good quality, due to an influence exerted by residual carbon which is caused by decomposition of the organic binder. In order to avoid such problems, it is necessary to perform debinder processing for an extremely long time. Due to presence of the aforementioned problems, an injection molding technique for a cemented carbide and a cermet alloy has not yet been substantially put into practice.

Disclosure of the Invention

An object of the present invention is to provide a method which can obtain a cemented carbide or a cermet alloy of high quality by efficiently shaping cemented carbide powder or cermet alloy powder by an injection molding method, and through subsequent debinder processing and sintering processing.

Another object of the present invention is to provide a method which causes no deformation and imperfection of a compact in debinder processing.

Still another object of the present invention is to provide a method which can perform debinder processing in a short time.

A method of preparing a cemented carbide or a cermet alloy to be the premise for the present invention comprises a step of mixing/kneading cemented carbide powder or cermet alloy powder with an organic binder, a step of shaping this mixed powder into a prescribed configuration by an injection molding method, and a step of thereafter removing the organic binder from the compact and sintering the same. In such a method, the present invention is characterized in that removal of the organic binder is first performed in an inert gas atmosphere as a first removal step, and then performed in a vacuum of not more than 1 Torr in continuation as a second removal step.

According to one aspect of the present invention, the organic binder contains a plurality of types of binders, which are divided into a group removable under a low temperature and a group removed under a high temperature. Compositions of the respective binders contained in the organic binder are selected to satisfy such a condition that the loss rate of the high-temperature removal group is within 5 % when the low-temperature removal group is lost by 30 % of the whole in an inert gas atmospheric pressure heating loss test (TG) for only the organic binder. Preferably the rate of the binder belonging to the low-temperature removal group with respect to the overall organic binder is set to be at least 30 % and not more than 90 %.

According to another aspect of the present invention, a temperature for transition from the first removal step to the second removal step is selected to satisfy the following condition: The condition is such a condition that the amount of removal of the binder belonging to the low-temperature removal group is at least 30 % with respect to the overall organic binder, while the residual rate of the binder belonging to the high-temperature removal group is at least 5 % with respect to the overall organic binder. A binder for serving as the main component of the low-temperature removal group is preferably prepared from wax having hydrophilic polar groups, with a melting point of not more than 80° C.

After the organic binder is removed from the compact by the aforementioned method, sintering processing may be performed in continuation. Alternatively, the compact may be once cooled after the organic binder is removed, to be thereafter sintered.

An injection-molded compact is formed by powder and a binder, substantially with no voids. When the compaot is subjected to temperature rising in this state, the binder first escapes by expansion of the binder, and then debindering progresses due to evaporation from the surface. When debindering of 30 % progresses by such a process, pores communicating with the surface are formed in the interior of the compact. Gas generated in the interior of the compact is removed through the pores, to further promote debindering. However, if the gas is generated in the interior of the compact in a debindering state of less than 30 %, the compact is cracked or blistered. In order to prevent such cracking or blistering of the compact, it is necessary to suppress generation of the gas in the interior of the compact with a loose programming rate. Therefore, a long time is required for the debinder processing. Wax for serving as a plasticizer and high polymer resin for serving as a binder are required as the binders. Since wax evaporates at a low temperature with no decomposition, it is possible to relatively easily perform debindering. On the other hand, high polymer resin is apt to cause imperfection in the compact in an initial stage of debindering, since the same generates a large quantity of gas by decomposition.

The inventors have noted the aforementioned points, to achieve the present invention. In more concrete terms, selected is high polymer resin which will start no decomposition even if the temperature reaches such a level that the wax is removed by at least 30 % of the whole, and this high polymer resin is mixed with the wax. In an initial state of debinder processing, debindering of at least 30 % is facilitated by evaporation of the wax alone, to form continuous pores in the interior of the compact. After the pores are formed, decomposition of the high polymer resin is made to start.

Hoechst wax, carnauba wax, montan wax, ozokerite wax, auriculine wax, candelilla wax, beeswax, microcrystalline wax and the like can be cited as major wax materials of the low-temperature removal group. Low density polyethylene, low molecular weight polyethylene, ethylenevinyl acetate, polypropylene, acrylic resin and the like can be cited as binders of the high-temperature removal group.

In the initial state of debinder processing, the atmosphere pressure is maintained in excess of the atmospheric pressure, thereby preventing the compact from imperfection. After continuous pores are formed in the interior of the compact, the atmosphere pressure is brought into a decompressed state, or a state close to a vacuum, thereby facilitating evaporation of gas from the surface and desorption of gas generated in the interior of the compact.

Note the strength of the injection-molded compact. When the high molecular resin serving as a bonding agent is removed, bonding strength between the powder particles is extremely reduced, such that a cemented carbide etc. having high specific gravity inevitably collapses. In order to prevent this, it is necessary to attain strength by bonding powder materials for forming the alloy. However, since the surfaces of the alloy powder materials are covered with thin oxide films, bonding is hardly caused by diffusion. The inventors have found that, when removal of the binder is performed in a vacuum state, the surfaces of the alloy powder materials are deoxidized by ambient carbon, whereby bonding strength is attained between the alloy powder materials. Thus, according to the present invention, debindering in the vacuum state is facilitated thereby bonding the powder particles with each other. When the powder particles are bonded with each other, the compact will not collapse until debindering is terminated. In a preferred embodiment of the present invention, the debinder processing is performed in two stages of a first removal step and a second removal step. The first removal step is carried out under an atmospheric pressure atmosphere, and the second removal step is carried out under a vacuum atmosphere. In transition from the first removal step to the second removal step, the bonding agent must be left by at least 5 %. If the residual amount of the bonding agent is not more than 5 %, the compact will collapse before bonding strength is attained between the powder particles.

The atmosphere for the debinder processing is now described. The first removal step is preferably carried out in an atmosphere of inert gas such as N_2 or Ar. If the debinder processing is performed in an oxidizing atmosphere such as the air, surface oxidation of Co, Ni and the like inevitably progresses during progress of the debindering. If such surface oxidized layers are present, bonding strength by reduction is inevitably lowered in the second removal step. Further, since oxidation of only a portion exposed to the ambient atmosphere progresses with progress of debindering, carbon concentration in the alloy is ununiformalized and a liquid phase appearance temperature in sintering is ununiformalized, to significantly reduce dimensional accuracy. It is conceivable to attain reduction of the oxide films on the surfaces of the alloy powder materials, by carrying out the second removal step not in a vacuum but in an H_2 atmosphere. If debinder processing is performed in an H_2 atmosphere, however, simultaneously caused is such reaction that carbide C, which is a hard phase forming component of the cemented carbide or the cermet alloy, reacts with hydrogen to form CH_4. Thus, the carbon content of the alloy is reduced.

The types of wax are now described. The surface of cemented carbide powder or cermet alloy powder is hydrophilic. On the other hand, wax such as n-paraffin is hydrophobic. Therefore, wettability between wax such as n-paraffin and cemented carbide powder or cermet alloy powder is inferior. In order to attain viscosity which is required for injection molding, therefore, it is necessary to use a larger amount of wax. The inventors have studied various wax materials, to find that the amount of the binder can be reduced by employing a certain type of natural wax having hydrophilic polar groups. When the compact is taken out from a metal mold in injection molding, the compact is easily broken since wax is friable. In order to prevent such breakage, it is preferable to use wax at least having a melting point of not more than 80 °C. So far as the wax has hydrophilic polar groups with a melting point of not more than 80 °C, its effect remains unchanged whether the same is a synthetic or natural one. While stearic acid or the like may be employed as a lubricant, the effect of the present invention remains unchanged even if such a minor additive is employed.

Best Modes for Carrying Out the Invention

Example 1

80 % of WC powder having a particle diameter of 2 to 4 µm, 10 % of TiC powder having a particle diameter of 1 to 2 µm, and 10 % of Co powder having a particle diameter of 2 to 4 µm were mixed in a wet ball mill for 3 hours, and dried. 6.0 % of beeswax and 1.0 % of low molecular weight polyethylene were added to 100 % of this mixed powder, and these were kneaded at 120 °C for 30 minutes. Then, this raw material mixture was cooled/solidified and thereafter pulverized, to prepare raw material particles of 0.5 to 2.0 mm in particle diameter. Then, injection molding was performed with a mold (20 × 20 × 6 mm) having the configuration of a throw-away tip, to prepare a compact. The compact was arranged in a furnace, and the interior of the furnace was held at 1 atm. in an Ar atmosphere. The temperature in the furnace was raised up to 425 °C at a programming rate of 8 °C/h. under a condition of an Ar flow rate of 3 ℓ/min., to perform debinder processing. Then the temperature in the furnace was raised up to 700 °C at a programming rate of 50 °C/h. in a state maintaining the interior of the furnace not more than 0.5 Torr with a vacuum pump, and the furnace was held at the temperature for one hour, and thereafter cooled. Thus, the debinder processing was terminated. Then, the interior of the furnace was brought into a vacuum state of 0.05 Torr and the temperature was raised up to 1400 °C at 200 °C/h., and the furnace was held at the temperature for one hour, and thereafter cooled. The as-formed sintered body had absolutely no imperfection, and was excellent in view of alloy characteristics. A heating loss test for the binders used in this Example was carried out, whereby the beeswax was lost by 95 % before reaching 425 °C under conditions of N_2 and 1 atm. On the other hand, the loss of the low molecular weight polyethylene was 13 % at 425 °C.

Example 2

90 % of WC powder having a particle diameter of 0.5 to 2 µm and 10 % of Co powder having a particle diameter of 2 to 4 µm were mixed in a wet ball mill for 20 hours, and dried. 5.5 % of carnauba wax and 1.0 % of low molecular weight polypropylene were added to 100 % of this mixed powder, and kneaded at 140 °C for 30 minutes. Then, this raw material mixture was cooled/solidified and thereafter pulverized, to prepare raw material particles of about 0.5 to 2.0 mm in particle diameter. Then, injection molding was performed in a mold (20 × 20 × 6 mm) having the configuration of a throw-away tip. This compact was arranged in a furnace. The interior of the furnace was under an Ar atmosphere of 1 atm., and its temperature was raised up to 430 °C at a programming rate of 10 °C/h. under a condition of a flow rate of 3 ℓ/min., to perform initial debinder processing. Then, the temperature was raised up to 700 °C at a programming rate of 50 °C/h. while maintaining the interior of the furnace not more than 0.2 Torr with a vacuum pump, and the furnace was held at the temperature for one hour. Thus, the debinder processing was terminated. Thereafter the temperature in the furnace was raised up to 1350 °C at 200 °C/h. in a vacuum of 0.05 Torr, and the furnace was cooled after the same was held at the temperature for one hour. The as-formed sintered body had absolutely no imperfection, and was excellent in view of alloy characteristics. A heating loss test was performed on the binders employed in this Example, whereby the carnauba wax was lost by 92 % before reaching 430 °C under conditions of N_2 and 1 atm. On the other hand, loss of the low molecular weight polypropylene was 8 % at 430 °C.

Example 3

88 % of WC powder having a particle diameter of 0.1 to 1 µm, 6 % of Co powder having a particle diameter of 2 to 4 µm and 6 % of Ni powder having a particle diameter of 2 to 4 µm were mixed in a wet ball mill for 25 hours, and dried. 0.5 % of beeswax, 4.5 % of n-paraffin, 0.2 % of stearic acid, 0.5 % of ethylene-vinyl acetate and 1.0 % of low molecular weight polyethylene were added to 100 % of this mixed powder, and kneaded at 120° C for 30 minutes. Then this raw material mixture was cooled/solidified and thereafter pulverized, to prepare raw material particles of about 0.5 to 2.0 mm in particle diameter. Then, injection molding was performed with a mold (20 × 20 × 6 mm) having the configuration of a throw-away tip. This compact was arranged in a furnace. The interior of the furnace was set in an N_2 atmosphere of 1 atm., and its temperature was raised up to 380° C at a programming rate of 13° C/h. under a condition of a flow rate of 2 ℓ/min., to perform initial debinder processing. Then, the temperature was raised up to 700° C at a programming rate of 50° C/h. while maintaining the interior of the furnace not more than 0.5 Torr with a vacuum pump, and the furnace was cooled after the same was held at the temperature for one hour. Thus, the debinder processing was terminated. Then, the interior of the furnace was brought into a vacuum of 0.05 Torr, and its temperature was raised up to 1350° C at 200° C/h., and cooled after the same was held at the temperature for one hour. The as-formed sintered body had absolutely no imperfection, and was excellent in view of alloy characteristics. A heating loss test was performed on the binders employed in this Example, whereby the beeswax was lost by 60 % and the n-paraffin was lost by 100 % before reaching 380° C under conditions of N_2 and 1 atm. On the other hand, loss of the low molecular weight polyethylene was 7.0 % and loss of the ethylene-vinyl acetate was 10 % at 380° C.

Example 4

88 % of WC powder having a particle diameter of 1 to 2 µm and 12 % of Co powder were mixed in a wet ball mill for 15 hours, and dried. 5.5 % of montan wax and 0.8 % of low density polyethylene were added to 100 % of this mixed powder, and kneaded at 120° C for 3 hours. Then, this raw material mixture was cooled/solidified and thereafter pulverized, to prepare raw material particles of about 0.5 to 2.0 mm in particle diameter. Then injection molding was performed with a mold (20 × 20 × 6 mm) having the configuration of a throw-away tip. This compact was arranged in a furnace. The interior of the furnace was set in an Ar atmosphere of 1 atm., and its temperature was raised up to 350° C at a programming rate of 10° C/h. under a condition of a flow rate of 3 ℓ/min., to perform initial debinder processing. Then, the temperature was raised up to 650° C at a programming rate of 50° C/h. while maintaining the interior of the furnace not more than 0.5 Torr with a vacuum pump, and the furnace was cooled after the same was held at the temperature for one hour, to terminate the debinder processing. Then, the interior of the furnace was brought into a vacuum of 0.05 Torr, the temperature was raised up to 1400° C at 200° C/h., and the furnace was cooled after the same was held for one hour. The as-formed sintered body had absolutely no imperfection, and was excellent in view of alloy characteristics. A heating loss test was performed on the binders employed in this Example, whereby loss of the montan wax was 93 % before reaching 350° C under conditions of N_2 and 1 atm., while loss of the low density polyethylene was 0 % on measurement at 350° C.

Example 5

Cermet powder (50 % of TiCN, 10 % of TaC, 12 % of Mo_2C, 13 % of WC, 5 % of Ni and 10 % of Co) having a particle diameter of 0.5 to 1 µm was mixed in a wet ball mill for 10 hours, and dried. 7.8 % of montan wax, 2.7 % of n-paraffin, 2.7 % of low density polyethylene and 0.3 % of stearic acid were added to 100 % of this mixed powder, and kneaded at 120° C for 3 hours. Then, this raw material mixture was cooled/solidified and thereafter pulverized, to prepare raw material particles of about 0.5 to 2.0 mm in particle diameter. Then, injection molding was made into a mold having a ball end mill configuration of 10 mm in diameter, to obtain a compact. This compact was arranged in a furnace. The interior of the furnace was set in an Ar atmosphere of 1 atm., and its temperature was raised up to 350° C at a programming rate of 10° C/h. under a condition of a flow rate of 3 ℓ/min., to perform initial debinder processing. Then, the temperature was raised up to 650° C at a programming rate of 50° C/h. while maintaining the interior of the furnace not more than 0.5 Torr with a vacuum pump, and the furnace was cooled after the same was held at the temperature for one hour, to terminate the debinder processing. Then, the interior of the furnace was brought into a vacuum of 0.05 Torr and the temperature was raised up to 1400° C at 200° C/h., and the furnace was cooled after the same was held for one hour, and thereafter HIP processing was performed at

1350° C. The as-formed sintered body had absolutely no imperfection, and was excellent in view of alloy characteristics. A heating loss test was performed on the binders employed in this Example, whereby loss of the montan wax was 93 % under conditions of N_2 and 1 atm. before reaching 350° C and loss of the n-paraffin was 100 %, while loss of the low density polypropylene was 0 % on measurement at 350° C.

Example 6

A plurality of raw material particle compacts were prepared under the same conditions as those in Example 1. With respect to these compacts, the programming rate in the first removal step of debinder processing and a transition temperature to the second removal step were changed, to examine states after debindering. Table 2 shows the results. Table 1 shows results of heating loss tests of beeswax and low molecular weight polyethylene (PE). As obvious from the results of Tables 1 and 2, excellent states are attained after debindering according to the inventive method, and debindering times can be shortened.

Table 1

Heating Loss Rate (N_2 1 atm, Temperature Rising at 10°C/min.)

T	250°C	300°C	350°C	375°C	400°C	425°C	450°C	475°C
Beeswax (xT)	0.03	0.12	0.32	0.50	0.74	0.95	0.99	1.00
Low Molecular Weight PE (yT)	0.01	0.03	0.05	0.07	0.09	0.13	0.30	0.85

Table 2

Test Result of Transition Temperature to Second Removal Step

Test No.	Transition Temperature to 2nd Removal step	1st Removal Step Programming Rate	Beeswax Loss Rate a × xT	PE Residual Rate b × (1-yT)	State After Debindering
1	300	8°C/h.	0.10	0.14	bursting state
2	300	4	0.10	0.14	significantly cracked and blistered
3	350	8	0.27	0.14	5 cracks
4	350	4	0.27	0.14	good
⑤	375	8	0.43	0.13	good
⑥	400	8	0.64	0.13	good
⑦	425	8	0.81	0.12	good
⑧	450	8	0.85	0.10	good
9	475	8	0.86	0.02	collapsed

○: Inventive Method

a = 0.86
b = 0.14

Example 7

8 types of samples were prepared by using alloy powder which was similar to that of Example 1 and changing the rate of beeswax to low molecular weight polyethylene (PE) as to binder compositions (tests Nos. 10 to 17), to perform debindering tests. Table 3 shows the results. The transition temperature from the first removal step to the second removal step was set at 450° C. As obvious from the results of Table 3, it is recognized that the inventive compositions are excellent.

Table 3

Test Condition and Result

Test No.	Binder Composition Beeswax/Low Molecular Weight PE	1st Removal Step Programming Rate	Beeswax Loss Rate $a \times x_{450}$	PE Residual Rate $b \times (1-y_{450})$	$b \times y_T$ ($a \times x_T = 0.3$)	State after Debindering
10	6.5/0.5	10°C/h.	0.92	0.05	0.005	partially deformed
⑪	6.0/1.0	10°C/h.	0.85	0.10	0.008	good
⑫	5.0/2.0	10°C/h.	0.71	0.20	0.018	good
⑬	4.0/3.0	10°C/h.	0.57	0.30	0.032	good
⑭	3.0/4.0	10°C/h.	0.42	0.40	0.045	good
⑮	3.0/4.0	4°C/h.	0.42	0.40	0.045	good
16	2.0/5.0	10°C/h.	0.28	0.50	not reaching $a \times x_T = 0.3$	significant-ly cracked
17	2.0/5.0	4°C/h.	0.28	0.50	not reaching $a \times x_T = 0.3$	2 cracks

○: Inventive Method
Binder Composition: Rate with respect to 100% of Alloy Powder

Example 8

Alloy powder similar to that of Example 3 was used and debindering tests were performed by changing types and compositions of binders. Table 4 shows the results. Debindering conditions were identical to those of Example 3. Good injection and debindering were possible in the tests Nos. 18 to 20. In the test No. 21 employing n-paraffin, however, it was impossible to make good injection unless the amount of n-paraffin was increased. In the test No. 22, on the other hand, distortion was caused in debinder processing. In the test No. 23 of mixing beeswax and n-paraffin at 1/1, no deformation was recognized in debindering although it was necessary to add a slight amount of the binder.

Table 4

Wax Type and Result

Test No.	Wax Type	Binder Composition Wax/Low Molecular Weight PE	Injection	Debinder State
⑱	Carnauba Wax	5.0/1.5	possible	good
⑲	Beeswax	5.0/1.5	possible	good
⑳	Montan Wax	5.0/1.5	possible	good
21	n-Paraffin	5.0/1.5	impossible	---
22	n-Paraffin	7.0/1.5	possible	distorted
㉓	Beeswax+ n-Paraffin	3+3/1.5	possible	good

○: Inventive Method
Binder Composition: Rate with respect to 100% of Alloy Powder

Example 9

In a preparation method similar to the test No. 5 of Table 2, atmospheres for the first removal step and the second removal step were varied as shown at tests Nos. 24 to 30 in Table 5. As obvious from the results of Table 5, it is recognized that the inventive atmospheres are effective. It was impossible to advance the samples of the tests Nos. 26 and 29 to sintering steps, since the same collapsed in debindering. Other samples were capable of progressing to sintering steps.

Table 5

Test No.	1st Removal Step: up to 350°C			2nd Removal Step: 350 to 700°C			Result (Sintered Body)
	Gas	Flow Rate	Pressure	Atmosphere	Flow Rate	Pressure	
⑤	Ar	3ℓ/min.	Atmospheric Pressure	Vacuum		0.5Torr	good
㉔	Ar	0.1ℓ/min.	Atmospheric Pressure	Vacuum		0.5Torr	good
㉕	N_2	3ℓ/min.	Atmospheric Pressure	Vacuum		0.5Torr	good
26	N_2	3ℓ/min.	Atmospheric Pressure	N_2	3ℓ/min.	Atmospheric Pressure	Collapsed (in debindering)
㉗	N_2	3ℓ/min.	600Torr	Vacuum		0.5Torr	good
28	Air	3ℓ/min.	Atmospheric Pressure	Vacuum		0.5Torr	distorted, cracked
29	Ar	3ℓ/min.	Atmospheric Pressure	Ar		5Torr	collapsed
30	N_2	3ℓ/min.	Atmospheric Pressure	H_2	3ℓ/min.	Atmospheric Pressure	low carbon abnormal phase caused

○: Inventive Method

Industrial Availability

The present invention is effectively applied to a method of preparing a cemented carbide or a cermet alloy by shaping cemented carbide powder or cermet alloy powder into a prescribed configuration by an injection molding method and thereafter sintering the compact upon removal of an organic binder.

Claims

1. A method of preparing a cemented carbide or a cermet alloy by mixing/kneading cemented carbide powder or cermet alloy powder with an organic binder, shaping this mixed powder into a prescribed by an injection molding method and thereafter removing said organic binder from this compact and sintering the same in order to obtain a dense alloy, characterized by

   removal of said organic binder being first performed in an inert gas atmosphere as a first removal step, and then performed in a vacuum of not more than 1 Torr in continuation as a second removal step.

2. The method of preparing a cemented carbide or a cermet alloy in accordance with claim 1, wherein

   said organic binder contains a plurality of types of binders being divided into a group removable under a low temperature and a group removed at a high temperature, and

   assuming that a_1, a_2, ..., a_i represent rates of respective binders of said low-temperature removal group including i types of binders with respect to overall said organic binder, b_1, b_2, ..., b_j represent rates of respective binders of said high temperature removal group including j types of binders with respect to overall said organic binder ($\Sigma a_i + \Sigma b_j = 1$), xT_1, xT_2, ..., xT_i represent loss rates of a single substance of respective said binders belonging to said low-temperature removal group at a certain temperature T in inert gas atmospheric pressure heating loss tests (TG), and yT_1, yT_2, ..., yT_j represent loss rates of a single substance of respective said binders belonging to said high-temperature removal group at said certain temperature T in inert gas atmospheric pressure heating loss tests, compositions of respective said binders contained in said organic binder are selected to satisfy the following conditions:

   $\Sigma(b_j \times yT_j) \leqq 0.05$
   $\Sigma b_j \geqq 0.1$

   at said temperature T for which $\Sigma(a_i \times xT_i) = 0.3$.

3. The method of preparing a cemented carbide or a cermet alloy in accordance with claim 2, wherein said temperature T for transition from said first removal step to said second removal step is selected to satisfy the following conditions:

   $\Sigma(ai \times xT_i) > 0.3$
   $\Sigma\{b_j \times (1 - yT_j)\} > 0.05$

4. The method of preparing a cemented carbide or a cermet alloy in accordance with claim 2, wherein said low-temperature removal group includes wax having hydrophilic polar groups with a melting point of not more than 80 ° C.

5. A method of preparing a cemented carbide or a cermet alloy in accordance with claim 3, wherein said low-temperature removal group includes wax having hydrophilic polar groups with a melting point of not more than 80 ° C.

INTERNATIONAL SEARCH REPORT

International Application No PCT/JP90/01171

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl^5 B22F3/10, C22C1/05

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC	B22F3/10, C22C1/05

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

Jitsuyo Shinan Koho	1926 - 1990
Kokai Jitsuyo Shinan Koho	1971 - 1990

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
P	JP, A, 2-11703 (Mitsubishi Seiko K.K.), 16 January 1990 (16. 01. 90), (Family: none)	1 - 5
P	JP, A, 2-70004 (Mitsubishi Metal Corp.), 8 March 1990 (08. 03. 90), (Family: none)	1 - 5
A	JP, A, 51-126308 (Shinroku Saito), 4 November 1976 (04. 11. 76), (Family: none)	1 - 5
A	JP, A, 57-16104 (Witec Cayman Patent, Ltd.), 27 January 1982 (27. 01. 82) & EP, A1, 32404 & US, A, 4305756 & CA, A1, 1177291	1 - 5
A	JP, B1, 41-21321 (Barzels Patent und Richantts Anschutalt), 13 December 1966 (13. 12. 66), (Family: none)	1 - 5

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search November 27, 1990 (27. 11. 90)	Date of Mailing of this International Search Report December 10, 1990 (10. 12. 90)
International Searching Authority Japanese Patent Office	Signature of Authorized Officer