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(54) Title: METALLIC CARBIDE-GROUP VIII METAL POWDER AND ITS PREPARATION

(57) Abstract

A transition metal carbide-Group VIII metal powder comprising discrete particles of a transition metal carbide and Group VIII metal wherein: substantially all of the particles have a size of at most 0.4 micrometer; the transition metal carbide is selected from carbides of the group consistig of tungsten, titanium, tantalum, molybdenum, zirconium, hafnium, vanadium, niobium, chromium, mixtures and solid solutions thereof; and the Group VIII metal is selected from the group consisting of iron, cobalt, nickel, mixtures and solid solutions thereof. Said powders were produced by heating an admixture comprising a finishing source of carbon (for example, acetylene black), a source of a group VIII metal (for example, Co_3O_4), and a particulate precursor to a temperature of 1173K to 1773K for a time sufficient to form a transition metal carbide-Group VIII metal powder, wherein at least 25 percent by weight of the carbide precursor is carburized in forming the transition metal carbide of the transition metal carbide-Group VIII metal powder. The particulate precursor generally contains less than 2.5 percent oxygen by weight and contains compounds which undergo carburization such as a transition metal (for example, W), lower valence transition metal carbide (W_2C) to form the transition metal carbide (for example, WC)-Group VIII metal powder.

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METALLIC CARBIDE-GROUP VIII METAL POWDER AND ITS PREPARATION

The invention relates to transition metal carbide-Group VIII metal powders and methods for preparing said powders. The invention relates, in particular, to tungsten carbide-cobalt powders.

Metallic carbide powders were used to make densified or sintered products. For example, it is well-known that monotungsten carbide (WC) is useful in the manufacture of commercially worthwhile items such as cutting tools, tool dies, blast nozzles and drill bits. In producing said WC items, it is common for a tungsten carbide powder to be combined with a metal such as cobalt and, subsequently, densified into a WC/Co cemented carbide by heating when making said tools.

As the particle size of the metallic carbide-metal powder decreases, the densified products generally exhibit improved properties such as increased strength and improved wear resistance. However, due to their high surface energy, if the particles were too small they may cause exaggerated grain growth to occur when forming a cemented carbide part. Exaggerated grain growth adversely affects properties such as strength. Grain growth can be controlled to some extent by addition of grain growth inhibitors such as VC, Cr_3C_2, or TaC or by starting with a WC having a narrow size distribution.

Densified metallic carbide-metal products having improved properties (for example, increased strength) were also generally achieved by homogeneously blending the metallic carbide and metal powders. Homogeneously blending the powders generally results in a more uniform microstructure resulting in less defects such as large grains due to exaggerated grain growth and pores in the densified body.

Monotungsten carbide is typically formed by the carburization of metal tungsten. Metal tungsten carburization processes typically make WC powders having a particle size of 0.8 micrometer and larger because of the difficulty in producing W metal much smaller than this size. Tungsten metal typically cannot be made much smaller than this size due to synthesis limitations and the tungsten powder being pyrophoric.

Methods which have attempted to make more homogeneously blended and smaller WC-cobalt powder (that is, WC-cobalt mixed powder) include the following. The article, "Production of WC Powder from WO_3 with Added Co_3O_4," by Ushijima, et al., published in the Japan Metal Society Journal, 42, No. 9, pages 871-875 (1978), describes a method to produce WC-cobalt powder by carbothermal reduction of WO_3 and Co_3O_4 in the presence of carbon in the form of carbon black and hydrogen. The WC-cobalt mixed powder formed by this method had a particle size of 0.6 micrometer or greater.

Pollizotti et al., (U.S. Patent No. 4,851,041) disclose a WC-Co powder produced by reduction decomposition of a suitable mixed metal coordination compound such as tris(ethylenediaminecobalt) tungstate resulting in an atomically mixed high surface area reactive intermediate product, followed by carburization reduction of the intermediate product in flowing CO/CO_2 gas. The WC-Co mixed powder is described as being composed of multiphase composite particles which were larger aggregates containing WC grains (particles) having a size of 10 to 20 nm in a matrix of beta-Co/W/C solid solution.

S. Takatsu in Powder Metallurgy International, Vol. 10, No. 1, pages 13-15, 1978, discloses a method to produce WC powder by reducing a mixed oxide of W and Co by reducing and carburizing with gaseous reagents using a rotary kiln. The mixed oxide is first reduced to metal in a hydrogen atmosphere, then carburized in a methane hydrogen gas mixture, and finally further treated in hydrogen or a methane-hydrogen gas mixture to remove excess carbon and convert W_3Co_3C to WC and Co. A homogeneous WC-Co mixed powder is disclosed having a mean particle size of greater than or equal to 0.4 micrometer.

It is desirable to provide a metallic carbide-metal powder and process to manufacture said powder wherein the powder has a particle size less than 0.4 micrometer.

A first aspect of the present invention is a method for preparing a transition metal carbide-Group VIII metal powder, the method comprises:

heating an admixture comprising:

a finishing source of carbon,

a Group VIII powder source of iron, cobalt, nickel or mixture thereof and

a particulate precursor comprised of a metal containing tungsten and a precursor carbide comprising a carbide of a transition metal selected from the group consisting of: tungsten; titanium; tantalum; molybdenum; zirconium; hafnium; vanadium; niobium; chromium and mixture thereof,

to a temperature of from 1173K to 1773K under a hydrogen-containing atmosphere for a time sufficient to form the transition metal carbide-Group VIII metal powder wherein at least 25 percent by weight of the precursor carbide is carburized and the transition metal carbide-Group VIII metal powder contains an amount of Group VIII metal of at least 0.25 percent to at most 50 percent by weight of the transition metal carbide-Group VIII metal powder.

A second aspect of the invention is a method for preparing a transition metal carbide-Group VIII metal powder, the method comprises:

heating an admixture comprising:

a finishing source of carbon,

a Group VIII powder source of iron, cobalt, nickel or mixture thereof and

a particulate precursor comprised of a precursor carbide comprising a carbide of a transition metal selected from the group consisting of: titanium; tantalum; molybdenum; zirconium; hafnium; vanadium; niobium; chromium and mixture thereof,

to a temperature of from 1173K to 1773K under a hydrogen-containing atmosphere for a time sufficient to form the transition metal carbide-Group VIII metal powder wherein at least 25 percent by weight of the precursor carbide is carburized and the transition metal carbide-Group VIII metal powder contains an amount of Group VIII metal of at least 0.25 percent to at most 50 percent by weight of the transition metal carbide-Group VIII metal powder.

A third aspect of the invention is a transition metal carbide-Group VIII metal powder comprising a mixture having particles of a transition metal carbide and Group VIII metal wherein:

at least 50 percent by number of the particles were discrete,

the particles have at most an average aspect ratio of 1.5,

substantially all of the particles have a size of at most 0.4 micrometer,

the transition metal carbide is a carbide selected from the group consisting of tungsten, titanium, tantalum, molybdenum, zirconium, hafnium, vanadium, niobium, chromium, and solid solution thereof,

the Group VIII metal is selected from the group consisting of iron, cobalt, nickel and solid solution thereof and

the transition metal carbide-Group VIII metal powder contains an amount of Group VIII metal of at least 0.25 percent to at most 50 percent by weight of the transition metal carbide-Group VIII metal powder.

A transition metal carbide-metal powder produced by a method described herein is useful to make coatings and sintered bodies displaying high hardness and good wear resistance properties. Suitable applications of said coatings and bodies include, for example, drill bits, blast nozzles, dies, punches and knives.

The first and second aspects of the invention were methods for preparing a transition metal carbide-Group VIII metal powder. The method comprises heating an admixture comprised of a finishing source of carbon, a source of Group VIII metal and a particulate precursor to a temperature from 1173K to 1773K under a hydrogen containing atmosphere for a time sufficient to form a transition metal carbide Group VIII metal powder, wherein at least 25 percent by weight of the precursor carbide is carburized in forming the transition metal carbide of the transition metal carbide-Group VIII metal powder. Herein, a Group VIII metal is iron, cobalt, nickel or mixture thereof. The carburization of the precursor carbide is believed to play a role in the formation of powder product having a small particle size.

Suitable Group VIII metal sources include metals, solid solution metals, oxygen containing compounds (for example, an oxide), nitrides and carbides of Ni, Co and Fe. Other suitable Group VIII metal sources include solid solution metals and carbide alloys of the aforementioned Group VIII metals and a transition metal selected from the group consisting of: tungsten; titanium; tantalum; molybdenum; zirconium; hafnium; vanadium; niobium; chromium and mixture thereof. Preferably the source of the Group VIII metal powder is an oxide. The average particle size of the powder is preferably less than 20 micrometers, more preferably less than 10 micrometers, and most preferably less than 5 micrometers to preferably greater than 0.5 micrometer.

The admixture desirably contains an amount of Group VIII metal source sufficient to make a transition metal carbide-Group VIII metal powder having a concentration of Group VIII metal of at least 0.25 percent by weight of said powder. Preferably the amount of group VIII metal source is sufficient to produce a transition metal carbide-Group VIII metal powder having a Group VIII metal concentration of at least 0.5 percent, more preferably at least 1 percent, and most preferably at least 2 percent to preferably at most 50 percent, more preferably at most 30 percent, even more preferably at most 20 percent and most preferably at most 15 percent by weight of the transition metal carbide-Group VIII metal powder produced.

The finishing source of carbon, in the admixture, is a separately added carbon, residual carbon from the formation of the particulate precursor or mixture thereof. The separately added carbon suitably includes those described hereinafter for a reducing source of carbon. Preferably the separately added carbon is a solid particulate carbon. More preferably the separately added carbon is a carbon black and most preferably acetylene black.

The finishing source of carbon is preferably present in an amount which results in a transition metal carbide-Group VIII metal powder having minimal or no free carbon after heating (reacting) the admixture. The amount of carbon advantageously ranges from 60 percent to 120 percent of the stoichiometric amount. The stoichiometric amount of carbon is the amount of carbon which would react with the oxygen to form carbon monoxide (that is, reduction reaction) in the particulate precursor (for example, WO_x), and Group VIII metal source (for example, Co_3O_4) and also carburize the transition metal compounds (for example, W, W_2C, WO_x) in the particulate precursor to a carbide of desired stoichiometry (for example, WC) in the absence of another reducing agent such as hydrogen, wherein "x" represents the amount of oxygen in the particulate precursor as determined by combustion analysis. When carbon is used in excess of the stoichiometric amount, a product containing little or no free

carbon can still be formed due to the loss of carbon from reaction with hydrogen (for example, formation of methane).

In the first aspect, the particulate precursor is comprised of a metal containing tungsten and a precursor carbide. The metal containing tungsten is suitably tungsten or a solid solution of tungsten and a transition metal selected from the group consisting of titanium; tantalum; molybdenum; zirconium; hafnium; vanadium; niobium; chromium and mixture thereof. The tungsten containing metal is suitably present in the particulate precursor in an amount of at least 5 percent by weight of said precursor. The amount is preferably at least 10 percent, more preferably at least 20 percent, and most preferably at least 30 percent to preferably less than 90 percent by weight of the particulate precursor.

The precursor carbide is suitably a transition metal carbide such as a carbide of Ti, W, Ta, V, Hf, Nb, Zr, Mo and Cr, wherein the valence of the transition metal is 2, 3 or 4 and the valence of the carbon is -4. For example, the carbide is preferably WC, W_2C, or mixture thereof, when forming a monotungsten carbide-Group VIII metal powder and specifically when forming a monotungsten carbide-cobalt powder. The precursor carbide is also suitably a solid solution transition metal carbide such as $(W,Ti,Ta)_xC$; $(Ti,Ta)_xC$; $(W,Ti)_xC$ or $(W,Ta)_xC$ wherein "x" is 1 to 2. Desirably at least 25 percent by weight of the precursor carbide is comprised of a transition metal carbide, wherein the valence of the transition metal in said carbide is lower than the valence of the transition metal in the following carbides: monotungsten carbide (WC), monotitanium carbide (TiC), monotantalum carbide (TaC), monovanadium carbide (VC), monohafnium carbide (HfC), mononiobium carbide (NbC), monozirconium carbide (ZrC), dimolybdenum carbide (Mo_2C), trichromium dicarbide (Cr_3C_2) or solid solutions thereof. More preferably the amount of lower valence carbide is at least 30 percent, and even more preferably at least 40 percent, and most preferably at least 50 percent by weight of precursor carbide.

The precursor carbide is desirably present in the particulate precursor in an amount of at least 20 percent by weight of the particulate precursor. Preferably the amount is at least 30 percent, more preferably at least 35 percent, and most preferably at least 50 percent to preferably at most 90 percent by weight of the particulate precursor.

The particulate precursor may also contain a Group VIII metal which is typically in a reduced form. For example, the Group VIII metal can be in the form of a metal, a metal in a metal solid solution, a carbide or a carbide alloy such as Co_6W_6C and Co_2W_4C when forming, for example, a WC-Co powder. The particulate precursor can also contain free carbon. The free carbon generally is a residue from the formation of the particulate precursor described hereinafter.

In a preferred embodiment of the first aspect of the invention in which WC-cobalt metal powder is formed, the particulate precursor desirably consists of tungsten, ditungsten carbide and monotungsten carbide. The tungsten is typically present in an amount of from 25 to 70 weight percent, more typically from 40 to 60 weight percent; ditungsten carbide is typically present in an amount of from 25 to 70 weight percent, more typically from 40 to 60 weight percent and monotungsten carbide is typically present in an amount of from 5 to 50 weight percent, more typically from 15 to 40 weight percent, based on the weight of the particulate precursor.

To minimize or avoid formation of water vapor which may cause unwanted particle growth during heating (reacting) of the admixture, the particulate precursor preferably has an oxygen content of less than 2.5, more preferably less than 2, and most preferably less than 1 percent by weight of the particulate precursor. To facilitate the production of a transition metal carbide-Group VIII metal powder having a small size, the particulate precursor desirably has a particle size that is less than or equal to 1.0 micrometer in diameter. Said particles were preferably at most 0.5, more preferably at most 0.4 micrometer, and most preferably at most 0.2 micrometer to preferably at least 0.01, more preferably at least 0.02, and most preferably at least 0.05 micrometer in diameter.

Particulate precursor of the second aspect:

The particulate precursor of the second aspect of the invention is comprised of a precursor carbide of a transition metal selected from the group consisting of: titanium; tantalum; molybdenum; zirconium; hafnium; vanadium; niobium; chromium and mixture thereof, wherein the stoichiometery of the particulate precursor is the same as described for the first aspect.

The precursor carbide of the second aspect is the same as the precursor carbide of the first aspect, except that the precursor carbide of the second aspect does not contain tungsten. That is to say, said precursor carbide does not contain a metal or carbide containing tungsten.

The precursor carbide can comprise all of the particulate precursor but preferably is present in an amount less than 100 percent to an amount greater than 50 percent by weight of the particulate precursor. For example, it is preferred that a transition metal(s) selected from the group consisting of: titanium; tantalum; molybdenum; zirconium; hafnium; vanadium; niobium; chromium and mixture thereof is present in an amount from 1 to 50 percent by weight of the particulate precursor. Said transition metal(s) can also be a solid solution metal of the aforementioned metals. The particulate precursor of this aspect of the invention may also contain a group VIII metal and free carbon as described for the particulate precursor of the first aspect. In addition, the particulate precursor of this aspect of the

invention preferably has an oxygen and particle size as described hereinabove for the first aspect of the particulate precursor.

The particulate precursor can be formed by any convenient method such as reduction by carbon and/or hydrogen and carburization of an oxygen containing transition metal compound, wherein the transition metal of the compound is tungsten, titanium, tantalum, molybdenum, zirconium, hafnium, vanadium, niobium, chromium or a mixture thereof. Herein, reduction is the removal of oxygen from a compound and carburization is described hereinafter. Preferably said transition metal compound is a transition metal oxide, acid (for example, tungstic acid) or ammonium compound (for example, ammonium paratungstate). For preparing solid solution metallic carbides, the transition metal oxide may be the oxide or oxides of more than one of the transition metals listed above. The source of the oxides or oxides of at least two transition metals may include separate oxide powders of the two transition metals or a single multimetallic alloy oxide containing two or more of the transition metals. The transition metal oxide is preferably the simple oxide of the metal, such as tungsten trioxide (WO_3), titanium dioxide (TiO_2) and tantalum pentoxide (Ta_2O_5).

A desirable source of tungsten oxide has particles which were less than or equal to 25 micrometers in diameter. A preferred particulate, WO_3, of this size is sold by GTE Products Corporation under the trade name "TO-3". Materials such as metatungstic acid, ammonium paratungstate or other tungsten oxides can be used in place of WO_3. "TITANOX™" from Velsicol Chemical Corporation, Chicago, Illinois, is a preferred source of TiO_2. "TITANOX" is a trademark for Velsicol's series of white pigments comprising TiO_2 in both anatase and rutile crystalline forms. Some "TITANOX" series pigments were extended with calcium sulfate, but these extended pigments were not preferred for use in the present invention. A preferred source of Ta_2O_5 is of less than 325 mesh (45 micrometers) size and greater than 99 percent purity, sold by Aldrich Chemical Company, Milwaukee, Wisconsin. The oxides of the other metals should be of comparable purity and particle size.

Preferably the particulate precursor is formed by heating the aforementioned transition metal compound with a reducing source of carbon to a temperature for a time under an atmosphere that is non-oxidizing and free of hydrogen sufficient to reduce the transition metal compound into the particulate precursor. The temperature is a temperature where the formation of the desired transition metal carbide is thermodynamically favored.

The reducing source of carbon is preferably a particulate carbon material such as carbon black or acetylene black. A particularly preferred acetylene carbon black is commercially available from Chevron Chemical under the trade designation "SHAWINIGAN." However, it is contemplated that other carbon solid sources would also be suitable. In addition, other sources of carbon such as organic polymers, carbohydrates and

hydrocarbons may be useful in place of all or part of a particulate carbon material. Carbon black having a specific surface area of 30 to 90 m^2/g has been found to be suitable for the invention.

The reducing source of carbon is used in an amount sufficient to form the particulate precursor described hereinabove. The amount of carbon is desirably an amount ranging from 60 percent to 120 percent by weight of the stoichiometric amount, the stoichiometeric amount being similar to the stoichiometeric amount for the particulate precursor previously described. That is to say, the stoichiometric amount of carbon is the amount of carbon which would react with the oxygen to form carbon monoxide (that is, reduction reaction) in the oxygen containing compound (for example, WO_3), and Group VIII metal source if present (for example, Co_3O_4) and also carburize the transition metal compounds (for example, WO_3) to a carbide of desired stoichiometry (for example, WC) in the absence of another reducing agent such as hydrogen.

A source of a Group VIII metal (that is, Fe, Co, and Ni) can also be admixed, heated and reduced along with the oxygen containing transition metal compound. A suitable Group VIII metal source and amount of said source is the same as those previously described. Preferably the source is an oxide of the Group VIII metal (for example, NiO or Co_3O_4).

The temperature is desirably equal to a temperature where the formation of the transition metal carbide having desired stoichiometry is thermodynamically favorable (that is, the free energy of the reaction to form said carbide is negative). The reaction temperature must also be less than the melting point of any intended reaction product(s). For mono tungsten carbide, a reaction temperature of at least 1273K is considered beneficial, while temperatures of from 1673K to 2673K were preferred, and temperatures of from 1823K to 2673K were more preferred. When a heating rate of 10,000K to 100,000,000K per second is employed, via the entrainment method discussed herein below, a reaction temperature of 1873 to 2423K is satisfactory. Approximate minimum temperatures at which the free energy of formation of the following specific reaction products is less than the free energy of formation of components of the finishing mixture needed to form the reaction products were as follows: tungsten carbide (WC) 950K; titanium carbide (TiC) 1555K; tantalum carbide (TaC) 1381K; vanadium carbide (VC) 932K; hafnium carbide (HfC) 1934K; niobium carbide (NbC) 1228K; zirconium carbide (ZrC) 1930K; dimolybdenum carbide (Mo_2C) 742K and trichromium dicarbide (Cr_3C_2) 1383K.

The time at the reaction temperature during the reduction depends in part upon the heating rate and reaction temperature, but must be high enough to reduce at least a major portion (that is, desirably greater than 90 percent by weight) of the transition metal

compound containing oxygen. The time is preferably in the range of 0.1 second to 1/2 hour, depending upon the heating method, heating rate, reaction temperature and the ultimate particle size desired. Whatever combination of reaction temperature, reaction time and heating rate is selected, however, it should be adequate to convert said transition metal compound containing oxygen into the particulate precursor described previously.

The particulate precursor is preferably prepared by the rapid carbothermal reduction method described below and described in more detail in U.S. Patent No. 5,380,688, incorporated herein by reference.

In preparing the particulate precursor by the method described by the '688 patent, an amount of reducing carbon (for example, acetylene black) is mixed with a transition metal compound containing oxygen (for example, WO_3). The amount of carbon used is the same as described before. An amount of a group VIII metal (for example, Co_3O_4) source can also be mixed with said carbon and transition metal compound. The reactants (for example, WO_3, C and, optionally, Co_3O_4) can be mixed by any convenient technique such as V-blenders, jet mills and ball mills, the latter containing a suitable milling media such as tungsten carbide-cobalt milling media.

The reactants were then heated advantageously at a rate of 100 to 100,000,000K/sec in a non-oxidizing atmosphere (that is, rapid carbothermal reduction). Generally, the heating rate for heating the reactants from room temperature to the reaction temperature is preferably at least on the order of 100 to 10,000K per second and optimally on the order of 10,000 to 100,000,000K per second.

The rapid carbothermal reduction can be performed by a drop or entrainment method as described in the '688 patent. In the drop method, the hot zone of an induction furnace is brought to the desired reaction temperature, as described further hereinbelow, and allowed to equilibrate for 30 minutes under a flowing non-oxidizing gaseous atmosphere such as argon. Aliquots of the reactants (for example, WO_3, C and, optionally, Co_3O_4) were dropped into a graphite crucible in the hot zone of the furnace. The extent of reaction is monitored by measuring the reaction by-product carbon monoxide level in the crucible as a function of time. When the carbon monoxide level decreases back to its baseline value, it is assumed that the reaction is over. After the reaction is assumed to be over, the crucible and reactant products were cooled as rapidly as possible back to a temperature, such as room temperature, sufficient to minimize particle agglomeration and grain growth.

It has been determined that the rates of heating in this drop method were from 100K per second to 10,000K per second. In the drop method, typical preferred residence times were from 5 minutes to 2 hours for a reaction temperature of 1773K with a heating rate of 100 to 10,000K per second.

The rapid carbothermal process can be carried out by the entrainment method as described in U.S. Patent No. 5,380,688. The entrainment method involves the use of a vertical graphite tube reaction furnace which is disclosed in U.S. Patent No. 5,110,565, incorporated herein by reference. The reactants were placed into a feed hopper, which allows flowing non-oxidizing gas, such as argon, to entrain the mixture and deliver it to the furnace's reaction chamber as a dust cloud. The powder or particulate mixture is immediately heated in the reaction chamber at rates of between 10,000 to 100,000,000K per second, while the average residence time of the particulate in the furnace is on the order of seconds. In the entrainment method, a residence time of from 0.2 to 10 seconds for a reaction temperature of 1823K or above with a heating rate of 10,000 to 100,000,000K per second is preferred. At the higher heating rate, residence times substantially greater than 10 seconds may undesirably produce sintered aggregates rather than particulate product. As for exiting the hot zone of the reaction chamber, the flowing gas carries the powder into a water-cooled stainless steel jacket which rapidly cools reacted powder below 283K. The entrainment method is the preferred method, as it has been shown to produce smaller size particulates than the drop method.

It is believed that reaction temperature, residence time and heating rate of the above methods were the main parameters controlling the size of the particles of the particulate precursor obtained. They do so by affecting both the nucleation rate for forming the metal and metal carbide particles and the growth rate of these particles once formed. For example, presuming that the particles were roughly spherical and the conversion of starting material to product occurs at a relatively constant volume rate, the growth rate of the particles should be proportional to the cube root of the residence time. In order to minimize the particle size of the resulting particulate precursor, the reaction temperature, heating rate and residence time should be selected to yield a particle nucleation rate which is higher than, and preferably significantly higher than, the particle growth rate.

To form a transition metal carbide-Group VIII metal powder, an admixture of the particulate precursor, Group VIII metal powder source and finishing source of carbon is heated to a temperature of from 1173K to 1773K under a hydrogen-containing atmosphere for a time sufficient to form a transition metal carbide-Group VIII metal powder, wherein at least 25 percent by weight of the particulate precursor is carburized to form the transition metal carbide-Group VIII metal powder. Said heating and subsequent carburization is referred to, hereinafter, as finishing or finishing reaction. The admixture of particulate precursor, Group VIII metal source and finishing carbon is referred to, hereinafter, as the finishing mixture.

During finishing, carburization of the precursor carbide occurs. Carburization, herein, is the chemical bonding of carbon to another element such as a carbon species reacting with a transition metal forming a carbide (for example, W + C = WC or W_2C) and carbon species reacting with a transition metal of a carbide, subsequently, forming a carbide wherein the transition metal has a higher valence (for example, W_2C + C = WC). During finishing, reduction by hydrogen and/or carbon (for example, $WO_3 + 3H_2 = W + 3H_2O$; WO_3 + 3C = W + 3CO) may also occur. Elimination of carbon may also occur by the reaction with hydrogen to form, for example, methane. Preferably at least two of the above-described reactions occur during finishing. More preferably all of the above reactions occur during finishing.

Mixing to form the finishing mixture may be done by any convenient mixing techniques such as those described previously, ribbon blenders, roller mills, vertical screw mixers and fluidized zone mixers such as those sold under the trade designation "FORBERG".

The finishing mixture can be static or moving during the finishing reaction. Preferably the finishing reaction is carried out by tumbling the finishing mixture in a rotary graphite crucible reactor. Other apparatus suitable for imparting motion to the finishing mixture during heating include a rotary calciner, fluidized bed and vibrating fluidized bed. The heating of the finishing mixture can be carried out in a number of ways, for example, by induction heating of the rotary graphite crucible.

The hydrogen-containing atmosphere advantageously contains at least 1 mole percent hydrogen with the balance being an inert gas such as argon. An atmosphere containing from 3 to 7 mole percent hydrogen in argon is particularly suitable. It is preferred that the atmosphere be a flowing atmosphere in order to carry away the gaseous by-products such as carbon monoxide and water vapor.

The temperature of reaction during the finishing reaction is typically from 900°C (1173K) to 1450°C (1723K). The temperature of the reaction may be used to manipulate the particle size of the product wherein a higher temperature generally leads to a product having a larger particle size. The finishing step is, typically, conducted for a period of time from 10 minutes to 2 hours. The lower the temperature that is used to carry out the finishing reaction, the longer the time will be to form the transition metal carbide-Group VIII metal powder.

The finishing step is conducted until the finishing mixture forms a product which is at least 95 percent by weight a transition metal carbide-Group VIII metal powder. More preferably the product is at least 98 percent by weight a transition metal carbide-Group VIII metal powder. Most preferably the product is at least 99 percent by weight transition metal carbide-Group VIII metal powder. Impurities may be present in the transition metal carbide-

Group VIII metal powder such as elemental transition metal, free carbon or transition metal-Group VIII-carbon alloys such as Co_6W_6C and Co_2W_4C. The powder desirably contains very little free carbon such as less than 0.2 percent of the total powder weight. Preferably the free carbon is at most 0.15 percent, more preferably at most 0.1 percent, and most preferably at most 0.05 percent by weight of the total powder. Preferably, the amount of transition metal and alloy impurity is below the powder X-ray diffraction detection limit as described in Elements of X-ray Diffraction, B. D. Cullity, Addison-Wesley, Reading MA, 1956, relevant portions incorporated herein by reference.

The transition metal carbide-Group VIII metal formed by the aforementioned methods were comprised of substantially discrete particles of a transition metal carbide and discrete particles of a Group VIII metal, wherein substantially means at least 50 percent of the particles by number were discrete particles. A particle is discrete when it is unconnected to any other particle. Preferably the number of particles that were discrete is greater than 60, more preferably greater than 75, even more preferably greater than 90, and most preferably greater than 95 percent by number. Said particles were uniformly and intimately mixed in the transition metal carbide-Group VIII metal powder. The amount of particles that were discrete can be determined directly by electron microscopy.

Generally, the particles of the transition metal-Group VIII metal powder were equiaxed. Herein, equiaxed describes particles having an average aspect ratio of at most 1.5 wherein the aspect ratio is the ratio between the longest and shortest dimension of a particle as measured by electron microscopy. Preferably the average aspect ratio is at most 1.2. Said particles desirably have a particle size in which substantially all of the particles were at most 0.4 micrometer in diameter. Preferably substantially all of the particles were at most 0.3 and more preferably were at most 0.2 micrometer in diameter. Said particles also preferably have a particle size in which substantially all of the particles were at least 0.01, more preferably at least 0.05, and most preferably at least 0.1 micrometer in diameter. The aforementioned aspect ratio and particle size can be determined by direct measurement of a number of particles using electron microscopy. Substantially all, as just used herein, equates to at least 95 percent by number of the particles falling within the specified sizes. It is also preferred that essentially all of the particles fall within the just specified particle sizes. Essentially all, as just used herein, equates to at least 99 percent by number of the particles falling within the specified particle sizes.

The transition metal carbide of the powder is selected from carbides of the group consisting of tungsten, titanium, tantalum, molybdenum, zirconium, hafnium, vanadium, niobium, chromium, solid solutions thereof and mixtures thereof. Preferably the transition metal carbide is monotungsten carbide (WC), WC containing solid solution such as WC-TiC-

TaC or mixture thereof. Most preferably the transition metal carbide is monotungsten carbide.

In a preferred embodiment, the powder is WC-cobalt powder having a particle size of at most 0.4 micrometer in diameter and a cobalt concentration of at least 1 percent by weight of the powder. Said powder is also preferred to have a particle size of greater than 0.1 micrometer in diameter. Said powder is even more preferred to have a particle size of at most 0.2 micrometer in diameter.

The following examples were illustrative only and should not be construed as limiting the invention in any way.

EXAMPLES

In the following examples, reference to "trace concentrations" equates to less than 5 weight percent; reference to "minor concentrations" equates to from 5 to less than 25 weight percent and reference to "major concentrations" equates to at least 25 weight percent.

The particle sizes in the following examples were crystallite mean number diameters measured from approximately 100 particles in random 50,000X scanning electron microscopy images.

Example 1

A tungsten carbide-containing particulate precursor was prepared using the entrainment method described above, wherein the temperature of the reaction was held at 1550°C (1823K), the atmosphere was argon, the reaction time was 2 to 4 seconds, the heating rate was 10,000 to 100,000,000K/sec and the reactive particulate mixture consists of 84.7 parts by weight of TO-3, (WO_3) and 15.3 parts by weight of Chevron acetylene black, as the source of carbon. 250 Grams of the resulting particulate precursor was homogenized in a 1-liter urethane-lined ball mill with 5 millimeter WC-Co milling media for 30 minutes, sieved through a 30-mesh screen, milled again for an additional 30 minutes and sieved again through a 30-mesh screen. The homogenized particulate precursor contains 1.29 weight percent of carbon and 4.12 weight percent of oxygen as measured by a combustion technique using apparatus manufactured by Leco Corporation (St. Joseph, MI).

86.1 Parts by weight (pbw) of the particulate precursor, 3.6 ppw of Chevron acetylene black and 10.3 ppw of Co_3O_4 (#22, 164-3 from Aldrich Chemicals, Milwaukee, Wisconsin) were milled together using the same milling procedure described for the homogenization of the particulate precursor to form a finishing mixture. The finishing mixture was formulated to obtain a product that has a weight ratio of WC/Co of 92/8 which corresponds to a carbon concentration of a bout 5.64 percent by weight.

50 Grams of the finishing mixture were placed in a quartz boat and the boat was placed in a tube furnace for conducting a finishing reaction. The finishing reaction was

conducted at 1100°C (1373K) for 120 minutes in a flowing atmosphere of 5 mole percent hydrogen in argon. The product from the finishing reaction contains WC and Co as shown by X-ray diffraction. The oxygen and carbon contents in the final WC-Co product were, respectively, 0.14 weight percent and 5.68 weight percent as measured by combustion analysis. 5.68 Weight percent was about the same carbon concentration as stoichiometeric amount desired. Scanning electron microscopic analysis of the product indicates that the average particle size was 0.1 micrometer.

Example 2

Example 1 was repeated except the finishing mixture consists of 86.6 parts by weight of the particulate precursor, 3.0 parts by weight of carbon, and 10.3 parts by weight of Co_3O_4 and the finishing temperature was 950°C (1373K). The formulation for the finishing mixture was based on forming a product having a WC/Co weight ratio of 92/8. The finished product has oxygen and carbon contents of 0.29 weight percent and 5.70 weight percent, respectively, an average particle size of 0.1 micrometer, a major concentration of WC and a minor concentration of Co.

Example 3

Example 2 was duplicated except that the time for the finishing reaction was 12 minutes. The oxygen and carbon levels in the finished product were 0.16 and 5.82 weight percent, respectively. X-ray diffraction analysis indicated that the final product had a major concentration of WC and a minor concentration of Co.

Example 4

In Example 4, the desired product was WC, WC-TiC-TaC solid solution and cobalt metal powder wherein the chemical composition of the powder as a whole has a molar ratio of 8(WC):1(WC-TiC-TaC):1(Co). In the absence of any free carbon, the desired powder product has a carbon concentration of 7.2 percent by weight. The solid solution contains about equal weights of the carbides. That was to say, the molar formula for the solid solution was approximately (WC-3.25(TiC)-TaC).

Tungsten trioxide (Scopino Yellow Oxide obtained from TACOW Trade Consultants, Ltd. Hockessin, Delaware), tantalum pentoxide (Zhuzhou-Grade FTa_2O_5, also obtained from TACOW Trade Consultants, Ltd.), titanium dioxide (Kronos K3020, obtained from Matteson-Ridolfi, Riverview, Michigan) and carbon black (Chevron Acetylene Black) were mixed by ball milling. The resultant reactant mixture contains 14.78 kg WO_3, 1.79 kg Ta_2O_5, 2.08 kg TiO_2 and 3.95 kg carbon black and was balled-milled for one hour in a 40-gallon ball mill that contains 400 lbs. of 0.5-inch (12.7 mm) diameter WC-6 percent Co milling media. After ball milling, said mixture was passed through a coarse (8 mesh, 2.36 mm) screen to remove the milling media.

Twenty-two (22) kg of said mixture were loaded into a feed hopper of a vertical graphite tube reaction furnace of the type disclosed in U.S. Patent Nos. 5,110,565 and 5,380,688. The furnace tube was 3.35 meters long and has a 15.2 centimeter inside diameter. The feed hopper was connected to a cooled reactant transport member of the furnace by a twin screw loss-in-weight feeder. The reactant transport member has an inside diameter of 1.3 cm and was maintained at a temperature of approximately 283K by water flowing through a cooling jacket. After the mixture was loaded into the feed hopper, the furnace tube was brought to a temperature of 2083K in 30 minutes as measured by optical pyrometers viewing the outside wall of the reaction chamber of the furnace tube. Argon gas flows into the reactant transport member at a rate of 3 scfm (85.05 slm).

The reactant mixture was then fed from the feed hopper into the cooled reactant transport member at a rate of 10 kg per hour (22 lbs per hour) by the twin screw feeder. The flowing argon gas entrains the particulate mixture and delivers it to the reaction chamber as a dust cloud. The particulate mixture was immediately heated in the reaction chamber at a rate of approximately 10,000 to 100,000,000K per second causing a carbothermal reduction reaction to occur. The average residence time of said mixture in the furnace was between 3 and 4 seconds.

After exiting the reaction chamber, the flowing argon and carbon monoxide (which was generated during the carbothermal reduction reaction) gas mixtures carry the particulate precursor into a water-cooled stainless steel jacket that rapidly cools the precursor below 283K. After exiting the reactor, the precursor was collected in a plastic bag that was placed in a stainless steel drum. The precursor was homogenized using a ball mill as described in Example 1. The homogenized precursor contains 2.39 weight percent oxygen and 6.78 weight percent carbon.

A finishing mixture containing 87.1 parts by weight of the precursor, 3.0 parts by weight carbon, and 9.9 parts by weight Co_3O_4 was made using the same milling procedure described in Example 1.

50 Grams of the finishing mixture were placed into a graphite tray and the tray was placed into a graphite furnace for conducting the finishing reaction. The finishing reaction was conducted at 1350°C (1423K) for 60 minutes in a flowing atmosphere of 5 mole percent hydrogen in argon. The product from the finishing reaction contains WC, a cubic solid solution WC-TiC-TaC carbide and Co as determined by X-ray diffraction. The oxygen and carbon contents in the final product were 0.19 weight percent and 6.60 weight percent, respectively. Scanning electron microscopy of the product indicates that the particle size was 0.3 micrometer. The product has a carbon concentration which was less than stoichiometeric (7.2 percent by weight).

Example 5

In Examples 5-7, the desired product was WC, WC-TiC-TaC solid solution and Ni metal powder wherein the chemical composition of the powder as a whole has a molar ratio of 8(WC):1(WC-TiC-TaC):1(Ni). In the absence of any free carbon, the desired powder product has a carbon concentration of 7.2 percent by weight. The solid solution contains about equal weights of the carbides. That was to say, the molar formula for the solid solution was approximately (WC-3.25(TiC)-TaC).

Example 4 was duplicated except that the finishing mixture contains 88.0 parts by weight of the precursor, 2.5 parts by weight carbon, and 9.5 parts by weight NiO and the finishing temperature was 1250°C (1523K).

The product contains WC, Ni and WC-TiC-TaC solid solution as determined by X-ray diffraction. The oxygen content was 0.95 percent by weight and the carbon content was 7.05 percent by weight. The carbon content was nearly the desired stoichiometeric amount (7.2 percent by weight). The particle size was 0.1 to 0.2 micrometer.

Example 6

Example 5 was repeated except that the finishing mixture contains 87.5 parts by weight of the precursor, 3.0 parts by weight carbon and 9.5 parts by weight NiO.

The product contains WC, Ni and WC-TiC-TaC solid solution as determined by X-ray diffraction. The oxygen content was 0.70 percent by weight and the carbon content was 7.34 percent by weight. The carbon content was nearly the desired stoichiometeric amount (7.2 percent by weight). The particle size was 0.1 to 0.2 micrometer.

Example 7

Example 6 was repeated except that the finishing reaction temperature was 1350°C (1623K).

The product contains WC, Ni and WC-TiC-TaC solid solution as determined by X-ray diffraction. The oxygen content was 0.15 percent by weight and the carbon content was 6.90 percent by weight. The carbon content was below the desired stoichiometeric amount (7.2 percent by weight). The particle size was 0.2 micrometer. For all of the above examples, the carbon concentration of the product was adjustable by the amount of carbon in the finishing mixture, temperature of the reaction and, to a lesser extent, by the time of the reaction. The optimum reaction parameters were empirically determinable.

WHAT IS CLAIMED IS:

1. A method for preparing a transition metal carbide-Group VIII metal powder, the method comprises:

(A) heating an admixture comprising:

a finishing source of carbon,

a Group VIII powder source of iron, cobalt, nickel or mixture thereof and

a particulate precursor comprised of a metal containing tungsten and a precursor carbide comprising a carbide of a transition metal selected from the group consisting of: tungsten; titanium; tantalum; molybdenum; zirconium; hafnium; vanadium; niobium; chromium and mixture thereof, to a temperature of from 1173K to 1773K under a hydrogen-containing atmosphere for a time sufficient to form the transition metal carbide-Group VIII metal powder wherein at least 25 percent by weight of the precursor carbide is carburized and the transition metal carbide-Group VIII metal powder contains an amount of Group VIII metal of at least 0.25 percent to at most 50 percent by weight of the transition metal carbide-Group VIII metal powder.

2. The method of Claim 1 wherein the particulate precursor is formed by

(A) heating a transition metal compound containing oxygen with a reducing source of carbon to a temperature under an atmosphere that is non-oxidizing and free of hydrogen for a time sufficient to reduce the transition metal compound into the carbide precursor wherein the transition metal compound contains a transition metal selected from the group consisting of: tungsten; titanium; tantalum; molybdenum; zirconium; hafnium; vanadium; niobium; chromium and mixture thereof.

3. The method of Claim 1 wherein the particulate precursor contains at most 2.5 percent oxygen by weight of said precursor.

4. The method of Claim 1 wherein the particulate precursor has a particle size of at most 0.4 micrometer in diameter.

5. The method of Claim 1 wherein the transition metal carbide is monotungsten carbide and the particulate precursor is comprised of ditungsten carbide, tungsten metal and monotungsten carbide.

6. The method of Claim 1 wherein the transition metal carbide-metal powder is comprised of particles in which 95 percent by number of the particles have a size of at most 0.4 micrometer in diameter.

7. The method of Claim 6 wherein the transition metal carbide-metal powder is monotungsten carbide-cobalt powder.

8. The method of Claim 7 wherein 95 percent by number of the particles have a size of at least 0.1 micrometer in diameter.

9. The method of Claim 1 wherein the hydrogen-containing atmosphere contains at least 1 mole percent hydrogen.

10. The method of Claim 9 wherein said atmosphere is a 5 mole percent hydrogen in argon gas mixture.

11. The method of Claim 1 wherein the solid solution carbide is WC-TiC-TaC.

12. The method of Claim 2 wherein an oxide of a Group VIII metal selected from the group consisting of iron, cobalt, nickel and mixtures thereof is admixed and heated with the transition metal compound.

13. The method of Claim 2 wherein the non-oxidizing atmosphere is argon.

14. The method of Claim 2 wherein the heating of step (A') is carried out at a rate of between 100K/sec to 100,000,000K/sec.

15. A method for preparing a transition metal carbide-Group VIII metal powder, the method comprises:

heating an admixture comprising:

a finishing source of carbon,

a Group VIII powder source of iron, cobalt, nickel or mixture thereof and

a particulate precursor comprised of a precursor carbide comprising a carbide of a transition metal selected from the group consisting of: titanium; tantalum; molybdenum; zirconium; hafnium; vanadium; niobium; chromium and mixture thereof, to a temperature of from 1173K to 1773K under a hydrogen-containing atmosphere for a time sufficient to form the transition metal carbide-Group VIII metal powder wherein at least 25 percent by weight of the precursor carbide is carburized and the transition metal carbide-Group VIII metal powder contains an amount of Group VIII metal of at least 0.25 percent to at most 50 percent by weight of the transition metal carbide-Group VIII metal powder.

16. The method of Claim 15 wherein the particulate precursor is formed by

(A) heating a transition metal compound containing oxygen with a reducing source of carbon to a temperature under a non-oxidizing atmosphere for a time sufficient to reduce the transition metal compound into the carbide precursor wherein the heating is carried out at a rate of 10,000 to 100,000,000K/sec and the transition metal compound contains a transition metal selected from the group consisting of: titanium; tantalum; molybdenum; zirconium; hafnium; vanadium; niobium; chromium and mixture thereof.

17. The method of Claim 15 wherein the particulate precursor contains a transition metal selected from the group consisting of: titanium; tantalum; molybdenum; zirconium; hafnium; vanadium; niobium; chromium and mixture thereof.

18. The method of Claim 15 wherein the transition metal carbide-Group VIII metal powder is comprised of particles in which substantially all of the particles have a size of at most 0.4 micrometer in diameter.

19. The method of Claim 15 wherein the particulate precursor contains the powder source of the group VIII metal.

20. The method of Claim 15 wherein the particulate precursor has a particle size of at most 0.4 micrometer in diameter.

21. A transition metal carbide-Group VIII metal powder comprising a mixture having particles of a transition metal carbide and Group VIII metal wherein:

at least 50 percent by number of the particles were discrete,

the particles have at most an average aspect ratio of 1.5,

substantially all of the particles have a size of at most 0.4 micrometer,

the transition metal carbide is a carbide selected from the group consisting of tungsten, titanium, tantalum, molybdenum, zirconium, hafnium, vanadium, niobium, chromium and solid solution thereof,

the Group VIII metal is selected from the group consisting of iron, cobalt, nickel and solid solution thereof and

the transition metal carbide-Group VIII metal powder contains an amount of Group VIII metal of at least 0.25 percent to at most 50 percent by weight of the transition metal carbide-Group VIII metal powder.

22. The transition metal carbide-Group VIII metal powder of Claim 21 wherein said powder is a monotungsten carbide-cobalt powder.

23. The transition metal carbide-Group VIII metal powder of Claim 22 wherein the monotungsten carbide-cobalt powder has a cobalt concentration of at least 1 percent by weight of the powder.

24. The transition metal carbide-Group VIII metal powder of Claim 21 wherein the size is at least 0.1 micrometer in diameter.

25. The transition metal carbide-Group VIII metal powder of Claim 21 wherein the size is at most 0.2 micrometer in diameter.

26. The transition metal carbide-Group VIII metal powder of Claim 21 wherein said powder contains a free carbon amount that is at most 0.2 percent by weight of the powder.

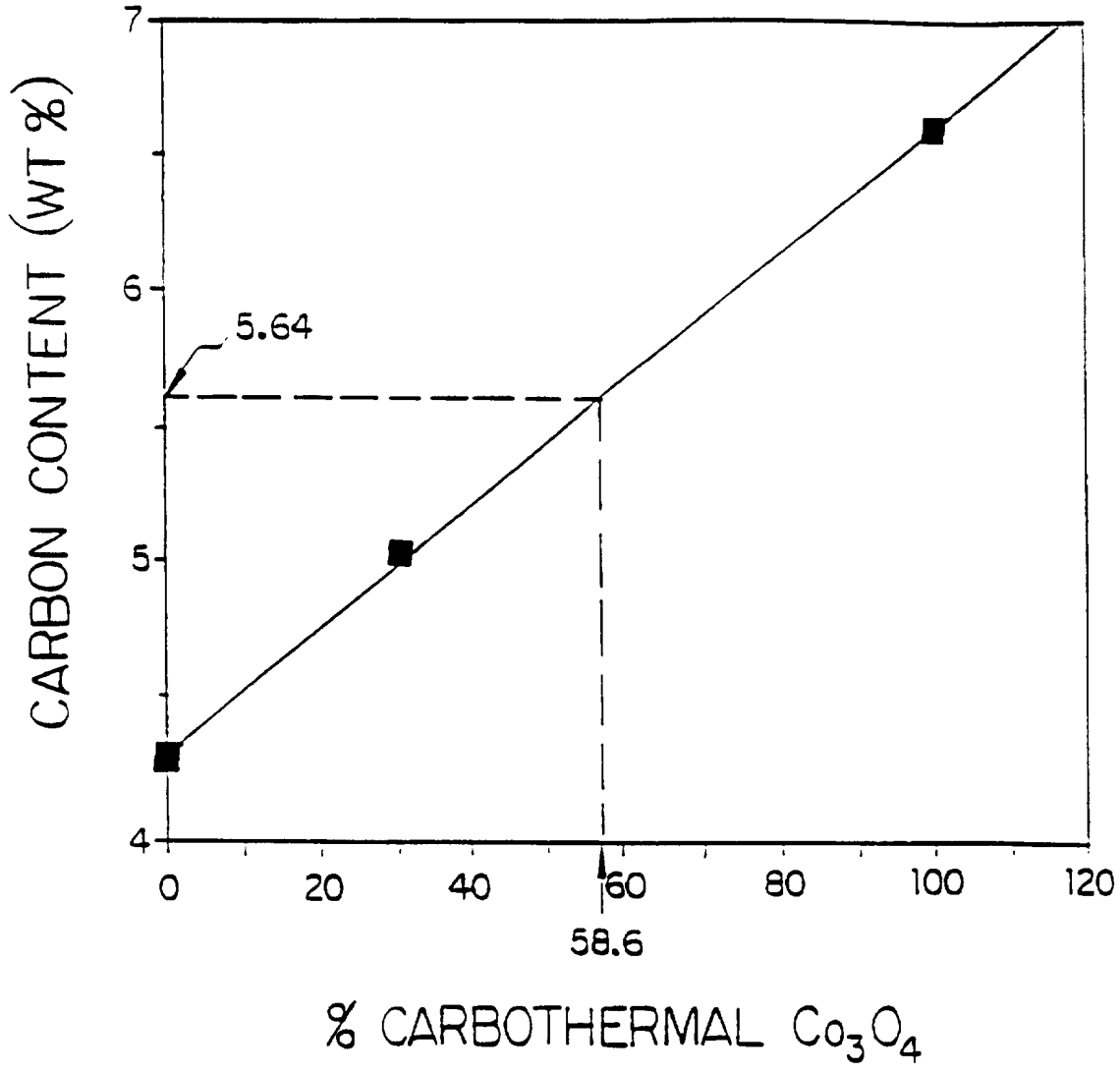

CARBON CONTENT (WT %)
7
6
5
4
5.64
0
20
40
60
80
100
120
58.6
% CARBOTHERMAL Co_3O_4

FIG 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/09680

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C04B 35/56; C22C 29/08
US CL : 75/ 240, 252, 351, 363, 369; 148/ 207, 237; 423/ 440
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 75/ 240, 242, 246, 252, 351, 363, 369; 148/ 207, 237; 423/ 440

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---- Y	US 3,713,789 A (RAMOVIST) 30 January 1973, column 3, line 15 to column 7, line 24.	21-26 -------- 1-20
Y	US 3,732,091 (PARIS et al.) 08 May 1973, column 6, lines 49-63.	21-26
X	US 5,380,688 (DUNMEAD et al.) 10 January 1995, see entire document.	1-26
Y,P	US 5,584,907 (MUHAMMED et al.) 17 December 1996, column 3, lines 5-10.	1-20
Y	USHIJIMA, K., et al., Mechanism of WC Formation from WO3 with Added Co3O4 and C, Japan Metal Society Journal, 1978, vol. 42, no. 9, especially page 8.	1-20

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"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
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"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
"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)	"&"	document member of the same patent family
"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		

Date of the actual completion of the international search 06 AUGUST 1997	Date of mailing of the international search report 26 SEP 1997
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