

April 13, 1971

D. A. TARVER
CVD PROCESS FOR PRODUCING TUNGSTEN CARBIDE
AND ARTICLE OF MANUFACTURE
Original Filed Aug. 5, 1964

3,574,672

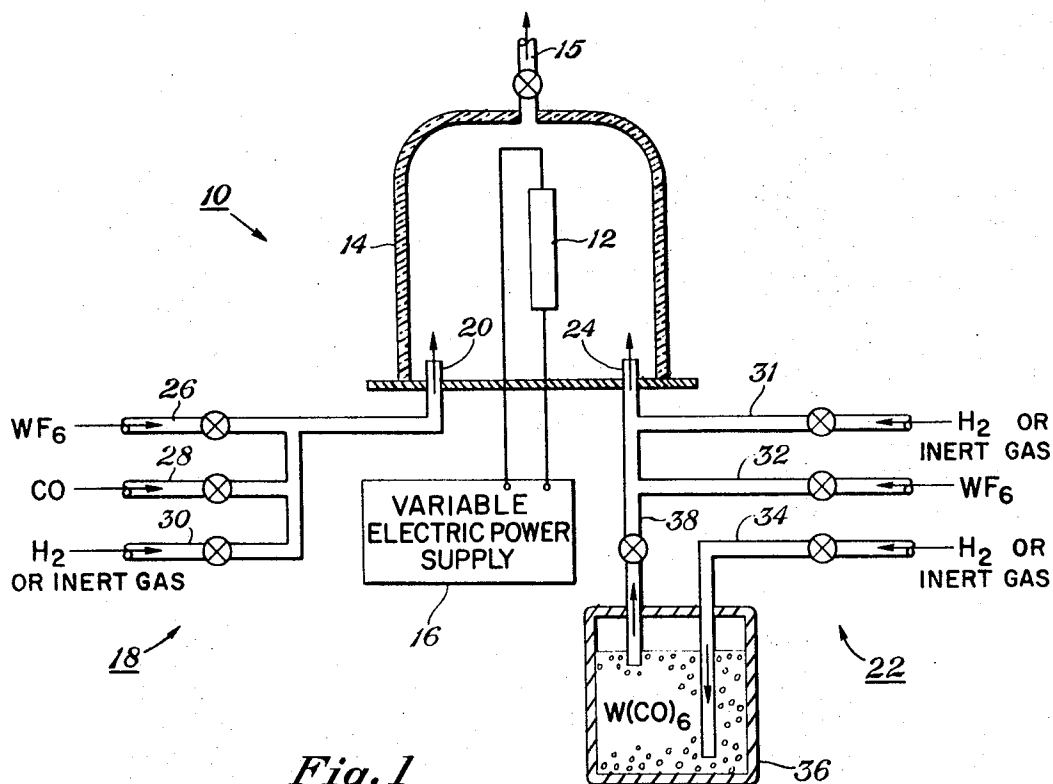


Fig. 1

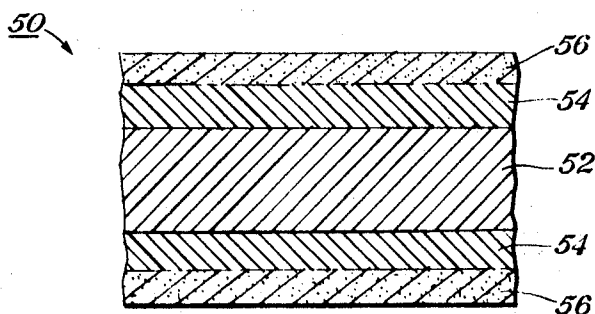
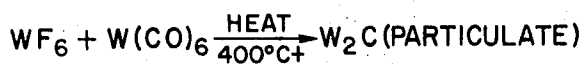
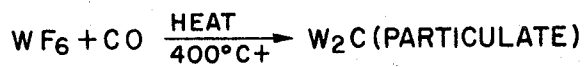


Fig. 2

INVENTOR
Donald A. Tarver
BY *E. Mickey Hubbard*
Attorney

1

2

CVD PROCESS FOR PRODUCING TUNGSTEN CARBIDE AND ARTICLE OF MANUFACTURE

Donald A. Tarver, Richardson, Tex., assignor to Texas Instruments Incorporated, Dallas, Tex.

Original application Aug. 5, 1964, Ser. No. 387,613, now Patent No. 3,389,977. Divided and this application Apr. 24, 1968, Ser. No. 761,354

Int. Cl. C23c 13/04

U.S. Cl. 117-106

7 Claims

ABSTRACT OF THE DISCLOSURE

Disclosed is a process for depositing a metal carbide in the form X_2C where X is taken from the group consisting of tungsten, molybdenum and chromium by heating a substrate to a temperature between about 400° C. and about 1300° C. and passing a reactant stream comprising a halide of the metal and carbon monoxide at about atmospheric pressure, or greater, over the substrate. The addition of hydrogen to the reactants results in a coherent mass of the carbide. A coherent layer of the carbide may be adherently deposited on a substrate such as steel by first passing a reactant stream comprising a halide of the metal X and hydrogen as a reducing agent over the heated substrate to deposit a thin layer of the metal X, then adding the carbon monoxide to the reactant stream to produce the metal carbide. The halide of the metal X is preferably a hexafluoride of the metal X and the carbon monoxide is preferably provided by the carbonyl of the metal X.

This is a division of application Ser. No. 387,613, filed Aug. 5, 1964, now Pat. No. 3,389,977.

The present invention relates to the production of metal carbides and more particularly, but not by way of limitation, relates to a chemical vapor deposition process for producing either particulate or coherent tungsten carbide in the form W_2C .

Since the first World War, tungsten carbide has been extensively used for machine tools and other applications which require extreme hardnesses. Insofar as is known, all commercial tungsten carbide is produced by a process whereby particulate tungsten and particulate carbon are intermixed, usually with a metal binder, then compressed and sintered to produce a congealed mass of tungsten carbide. This type of tungsten carbide has a significant metal phase which provides the tensile strength necessary for most commercial applications, but which also tends to reduce the hardness of the material.

Various attempts to produce tungsten carbide by chemical vapor techniques have been reported in the literature, but for various reasons these processes are not commercially feasible. In one group of reactions, tungsten, hydrogen and a hydrocarbon were reacted, sometimes with the addition of nitrogen, to produce tungsten carbide. However, these reactions require very high temperatures, approximately 2,000° C., and long reaction times for appreciable carbide production, and are therefore not commercially feasible. Further, the characteristics of the carbide produced are in general not attractive from a commercial standpoint. Another reaction used in an attempt to produce metal carbide was based on the pyrolysis of molybdenum, chromium and tungsten carbonyls at pressures as low as 10 millimeters of mercury in the presence of hydrogen. While molybdenum and chromium carbides were achieved, it was stated that hexagonal tungsten carbide was never produced. Attempts have also been made to pyrolyze tungsten carbonyl to tungsten and then subsequently carbonize the tungsten with carbon mon-

oxide to produce WC tungsten carbide, but the researcher concluded that at temperatures of approximately 1,000° C. the formation of tungsten carbide was uneconomically slow.

In accordance with the present invention, tungsten carbide in the preferred form W_2C , rather than the more readily available form WC , is produced at a commercially feasible rate at reasonably low temperatures and at atmospheric pressures. By reason of its purity and freedom from a metal phase, the tungsten carbide produced by this invention has a Knoop hardness ranging from about 1700 to about 2700 which is over twice the hardness of commercially available tungsten carbide. Further, the tungsten carbide can be formed as a coherent mass free of a substrate, as a powder free of the substrate, as a thin coherent coat adherent to a thick substrate, as a thick coherent coat adherent to a thin substrate, or as a thin coherent coat adherent to a thin substrate. Because of the predominant commercial interest, this invention is primarily concerned with the formation of tungsten carbide, and in particular with the formation of coherent tungsten carbide on steel. However, it will also be appreciated by those skilled in the art that additional useful metal carbides can be produced using the process of the present invention, such as, for example molybdenum, chromium and other refractory metal carbides.

In accordance with the broader aspects of this invention, a metal carbide is produced by reacting a halide of the metal with carbon monoxide at a temperature in excess of about 400° C. and preferably in excess of about 600° C. The metal halide may be a fluoride of the metal and the carbon monoxide may be in the form of gas, or may be furnished by a carbonyl or other compound which contains or produces carbon monoxide. Thus when producing tungsten carbide, for example, tungsten hexafluoride may be reacted with carbon monoxide, or with tungsten hexacarbonyl.

The form of the metal carbide material may be controlled by using either hydrogen or an inert gas as a carrier for the reactants. If the reaction is carried out in the presence of hydrogen, a dense coherent mass will be produced. The dense coherent mass may be adherently bonded to a substrate such as steel with relative assurance, provided the mismatch in thermal coefficients is accommodated. The mismatch may be accommodated by keeping either the coat of metal carbide thin, or using a thin steel substrate, or both, so that the thin material will have sufficient elasticity to prevent spalling of the tungsten carbide. In some cases, relatively thick carbide coatings have been successfully bonded to relatively thick substrates. A coherent mass free of a substrate may be produced by taking steps to prevent adherence to the substrate, such as by first carbonizing a steel substrate. Or the metal carbide may be produced in particulate or powder form by using an inert carrier gas and carrying out the reaction substantially free from hydrogen.

In accordance with another aspect of the present invention the tungsten carbide may be more adherently bonded to a steel substrate by first depositing a very thin film of tungsten metal on the surface of the substrate by a suitable deposition technique, preferably by the reduction of a tungsten halide such as tungsten hexafluoride, then depositing the coat of tungsten carbide by the reaction of a tungsten halide, such as tungsten hexafluoride, and carbon monoxide in the presence of hydrogen.

This process produces tungsten carbide in the form W_2C which is a coherent, dense mass free from any metal phase, and which has a Knoop hardness in the range from about 1700 to about 2700 which is substantially harder than tungsten carbide heretofore commercially available.

Therefore an important object of the present invention

is to provide a process for producing metal carbides that is commercially practical.

Another object of the present invention is to provide a process for producing metal carbides which may be carried out at relatively low temperatures, at atmospheric pressure, and at commercially feasible rates.

A still further object of the present invention is to provide a process for producing a metal carbide in either coherent or particulate form by chemical vapor deposition techniques.

A further object of the invention is to provide an improved tungsten carbide in the form W_2C that is substantially free from any metal phase.

A further object of the invention is to provide dense, coherent tungsten carbide that is adherently bonded to a steel substrate.

Many additional objects and advantages will be evident to those skilled in the art from the following detailed descriptions and drawings, wherein:

FIG. 1 is a schematic diagram of an apparatus which may be used to carry out the process of the present invention, and

FIG. 2 is a sectional view of a product produced by the process of the present invention.

Referring now to the drawings, a system for carrying out the process of the present invention is indicated generally by the reference numeral 10. A substrate 12 is suitably supported within a reaction chamber 14 which is adapted to control the atmosphere about the substrate. The substrate 12 may be resistively heated by a variable electric power supply to any desired temperature which may be monitored by any suitable means (not illustrated) such as a thermocouple, pyrometer or other conventional device. It is to be understood that the substrate 12 may be heated in any manner such as by radiation or induction.

The conduit system indicated generally by the reference numeral 18 and associated with the inlet 20 to the chamber 14 may be used for carrying out one specific process of the present invention, while the conduit system indicated generally by the reference numeral 22 and associated with the inlet 24 may be used to carry out another specific process in accordance with this invention. The conduit system 18 is comprised of a valved conduit 26 which is connected to a source of tungsten hexafluoride in gaseous form. The valved conduit 28 is connected to a source of carbon monoxide gas, and the valved conduit 30 is connected to a source of hydrogen gas. If desired, both the tungsten hexafluoride and carbon monoxide gases may be mixed with a carrier gas comprised of either hydrogen or an inert gas. The three conduits 26, 28 and 30 are connected to the inlet 20 so as to be adequately mixed. If desired, the gases may be admitted to the chamber 14 through separate conduits and mixed within the chamber. A valved outlet 15 is provided for withdrawing the gases from the chamber 14 so as to provide a flow of reactants past the substrate and thereby maintain a greater diffusion gradient for supplying reactants to the surface of the heated substrate.

The conduit system 22 is comprised of a valved conduit 31 which is connected to a source of hydrogen or inert gas and the valve conduit 32 is connected to a source of tungsten hexafluoride gas. A valved conduit 34 is connected to a source of hydrogen or an inert carrier gas and extends to the bottom of a container 36 which contains solid particles of tungsten hexacarbonyl. The particulate material is heated by a suitable means to a temperature which will produce a tungsten hexacarbonyl vapor pressure sufficient to result in the desired concentration of tungsten hexacarbonyl in the hydrogen or other carrier gas as the gas is passed through the container. The mixture of hydrogen and tungsten hexacarbonyl is then passed through valved conduit 38, which is heated to maintain the tungsten hexacarbonyl vapor pressure at the desired level, and mixed with the tungsten hexafluoride

and hydrogen or inert gas before introduction to the chamber 14 through the inlet 24.

In accordance with a specific aspect of the present invention, tungsten carbide in the form W_2C is produced by the reaction of tungsten hexafluoride and carbon monoxide in the presence of hydrogen using the apparatus 10 and the conduit system 18. In carrying out this process, the substrate 12 is mounted in the reaction chamber 14 and the chamber purged and filled with hydrogen gas. The substrate is heated by the electric power source 16 to a temperature in excess of $400^\circ C.$ and preferably in the range from about $600^\circ C.$ to about $1,000^\circ C.$ If it is desired to adherently deposit the carbide on the substrate, the substrate should first be thoroughly cleaned by standard techniques. If the carbide is not to be adherently deposited, then the substrate should be prepared as hereafter described, then hydrogen is circulated through the valved conduit 30 and out the exhaust conduit 15 to purge the system. Next the valved conduits 26 and 28 are opened to six tungsten hexafluoride and carbon monoxide with the hydrogen and the mixture passed by the substrate and through the chamber 14 for the duration of the process. Coherent tungsten carbide will then be formed on the surface of the substrate. The exact chemical reaction resulting from the process is not known, nor is the function of the hydrogen in the process. However, when hydrogen is used, a coherent mass of tungsten carbide is produced; without hydrogen, particulate tungsten carbide tends to be produced.

Based upon data heretofore obtained, it appears that any temperature above $400^\circ C.$ will result in the formation of tungsten carbide in the form W_2C . The maximum temperature appears to be limited only by practical considerations such as the properties of the substrate and the form of the resulting product, and may go as high as about $1500^\circ C.$ More specifically, a run of the process conducted at $400^\circ C.$ resulted in no appreciable deposition of tungsten carbide, while a run conducted at $600^\circ C.$ produced tungsten carbide at a commercial rate. In general, the greater the temperature of the substrate the more rapid the rate at which tungsten carbide is formed. However, the greater the rate of carbide formation, the greater the tendency for the carbide to form as spiked crystals on the surface rather than as a uniform coat. Therefore, some practical operating temperature less than $1,000^\circ C.$ and greater than $600^\circ C.$ produces the best deposition product at the best deposition rate. A temperature of about $800^\circ C.$ is preferred.

Based upon available data, almost any ratio of tungsten hexafluoride, carbon monoxide and hydrogen will produce the tungsten carbide. The following percentages of the total mixture for the three gases have been successfully used:

	Percent
Tungsten hexafluoride -----	12.5-40
Hydrogen -----	12.5-62.5
Carbon monoxide -----	12.5-75

Thus the ratio of tungsten hexafluoride to carbon monoxide ranges from about 0.3 to about 6.0. These percentages do not indicate limits, but merely the ratios which have been successfully used. No ratio used to date has been unsuccessful. A typical mixture is 12.5% tungsten fluoride, 37.5% hydrogen, and 50% carbon monoxide. Further, the deposition rate does not appear to be appreciably affected by the ratio of gases used. The deposition rate appears to be primarily dependent upon the temperature of the substrate so long as an adequate flow of reactants is passing through the chamber. However, as the quantity of hydrogen available diminishes toward zero, a powdery or particulate tungsten carbide is produced rather than the coherent mass which is produced when an adequate supply of hydrogen is present. Deposition at high temperatures tends to produce a high deposition rate and needle-like crystals.

In accordance with another more specific aspect of the present invention, the reactants introduced to the chamber may comprise a metal hexafluoride, a carbonyl, and hydrogen or inert carrier gas. For producing tungsten carbide, tungsten hexafluoride and tungsten carbonyl are the preferred reactants. When carrying out this process, the chamber 14 may be purged with hydrogen from the valved conduit 30. After the substrate 12 has been heated to the desired temperature in excess of 400° C. tungsten hexafluoride may be introduced through the valved conduit 32, and hydrogen passed through the container 36 from the valved conduit 34 so as to entrain vapors from the heated tungsten hexacarbonyl. The three process streams are mixed and introduced to the chamber 14 through the inlet 24. It is believed that the tungsten hexacarbonyl undergoes thermal decomposition and provides the necessary carbon monoxide so that the reaction produces the same result as heretofore described with no discernible difference. The desired flow rates of the gases in the process stream may be controlled by adjustment of the valves in the various conduits. The concentration of tungsten hexacarbonyl in the carrier gas is controlled by the temperature of the particulate material in the container 36. There are indications from the data that coherent tungsten carbide may be produced even when using an inert carrier gas rather than hydrogen. It is believed that this is due to the additional tungsten available in the carbonyl.

As in the process previously described, no particular ratio between the reactants appears to be critical and the deposition rate is controlled primarily by the temperature of the substrate 12. No ratio of reactants which has been used to date has failed to produce tungsten carbide and a typical mixture is tungsten hexafluoride 50%, tungsten hexacarbonyl 10% and hydrogen 40%.

The tungsten carbide or other metal carbide can be produced in several forms using the processes heretofore described. By eliminating the hydrogen from the process and using an inert carrier gas to purge the chamber 14 and transport the reactants, the tungsten fluoride-carbon monoxide process using the temperature heretofore described will result in a powdery or particulate tungsten carbide on substrate 12 which may be easily removed by scraping or other mechanical means. However, if it is desired to produce dense, coherent tungsten carbide, the tungsten hexafluoride and carbon monoxide, or other carbon monoxide-bearing reactant, may be reacted in the presence of hydrogen. If it is desired to form the tungsten carbide free from a substrate, the substrate may be pretreated to prevent adherence, such as by carberizing the surface of the substrate prior to beginning the above-described processes. However, a coat of tungsten carbide may be produced which is adherent to a substrate, such as a steel or other metal substrate, even though the coefficient of thermal expansion of steel is over twice that of tungsten carbide. This may be accomplished if the steel substrate is clean.

In accordance with an important aspect of the invention, the adherence of a tungsten carbide coating to a steel substrate may be materially improved by using the following process. First the substrate 12 is placed in the chamber 14 and the chamber purged with hydrogen. The substrate is cleaned in a suitable atmosphere, then adjusted to a deposition temperature from about 600° C. to about 1,000° C. Next, tungsten hexafluoride is mixed with hydrogen and passed through the chamber 14 for a short period of time. This produces a thin film of tungsten metal on the surface of the substrate 12 as the result of the reduction of the tungsten hexafluoride. After a sufficient period of time has passed to deposit a thin tungsten film, carbon monoxide, either in the form of gas or the vapors of tungsten hexacarbonyl, is mixed with the tungsten hexafluoride and hydrogen mixture to carry out the process heretofore described for depositing a tungsten carbide coating. The process is continued until the desired thickness is obtained.

In one example of the process of the present invention, the product 50 illustrated in FIG. 2 was produced. The substrate 52 was a strip of SAE 1010 steel having a length of 1.5 inches, a width of 0.125 inch and a thickness of 0.006 inch. The steel substrate was heated to a temperature of 800° C. and first a mixture of tungsten hexafluoride and hydrogen passed through the chamber, then carbon monoxide added to the process stream for a total of about twenty minutes. A tungsten metal film 54 approximately 0.002 inch thick was first deposited on both sides of the steel substrate, then a tungsten carbide film 56, also approximately 0.002 inch in thickness, was deposited over the tungsten film. The tungsten carbide was strongly adherent to the substrate and did not spall when the substrate was cooled or upon subsequent temperature cycling.

The tungsten carbide produced by the above-described process is in the form W_2C and, when using hydrogen in the reaction, is a coherent, dense mass having a Knoop hardness in that range from about 1700–2700, with the average produced having a hardness of about 220. This is over twice the hardness of commercially available tungsten carbide manufactured by sintering processes. The tungsten carbide has no metal phase detectable by X-ray or other analysis. The tungsten carbide may be produced as a coherent mass free from any substrate or as a powdered particulate material. An article of manufacture also may be produced which comprises a metal substrate, such as steel, with a thin coating of tungsten carbide covering and adherently bonded to the substrate. Or a thick tungsten carbide coating may be applied to a thin steel or other metal substrate. Or an article may be produced comprised of a thin steel or other metal substrate and a thin tungsten carbide coating adherently bonded thereto. A thin film of tungsten metal may be used to provide a gradient in coefficients of thermal expansion as well as to improve the bonding characteristics between the tungsten carbide and steel. It is believed that the increased hardness of the tungsten carbide is due to its purity and freedom from a metallic phase such as is present in the sintered tungsten carbide heretofore available.

The process has been described in connection with tungsten carbide and steel because of the commercial importance of these materials. However, the process is applicable to the formation of other metal carbides and the metal carbides may be bonded to substrates of other metals and materials. Generally, bonding tungsten carbide to steel represents the most difficult task because the difference in physical properties and thermal expansivity of the two materials is greater than in almost any other combination of metal carbide and substrate material which it might be desired to use.

Although several preferred embodiments of the invention have been described in detail, it is to be understood that various changes, substitutions and alterations can be made therein without departing from the spirit and scope of the invention as defined by the appended claims.

What is claimed is:

1. A process for producing a metal carbide in the form X_2C where X is a metal taken from the group consisting of tungsten, molybdenum and chromium, which comprises heating a substrate to a temperature of 400°–1000° C. and contacting the heated substrate with a reactant stream comprising hydrogen, a halide of the metal, and a carbonyl of the metal at about atmospheric pressure or greater whereby said metal carbide is deposited on the substrate.

2. The process of claim 1 wherein the metal is tungsten and the metal halide is tungsten hexafluoride.

3. The process of claim 2 wherein said carbonyl is tungsten hexacarbonyl.

4. The process of claim 1 wherein the metal is molybdenum and the metal halide is molybdenum hexafluoride.

5. The process of claim 4 wherein the carbonyl is molybdenum hexacarbonyl.

6. A process for producing tungsten carbide in the form W_2C which comprises heating a substrate to a temperature between 40–1000° C. and contacting the heated substrate with a reactant stream comprising 12.5%–62.5% hydrogen, 12.5%–40% tungsten hexafluoride, and 12.5%–75% carbon monoxide at about atmospheric pressure or greater whereby W_2C is formed on the substrate.

7. The process of claim 6 wherein the carbon monoxide is supplied as tungsten hexacarbonyl.

References Cited

UNITED STATES PATENTS

2,601,023	6/1952	Hurd	23—208(A)
2,690,980	10/1954	Lander	117—106(C)UX
3,054,694	9/1962	Aves, Jr.	117—71(M)X
3,077,385	2/1963	Robb	23—208(A)

FOREIGN PATENTS

468,758	10/1950	Canada.
1,056,449	4/1959	Germany 117—106(C)

OTHER REFERENCES

Von W. G. Burgers and J. C. M. Bassart, Über die Bildung hochschmelzender Metallcarbide beim Glühen eines Kohlenfadens im Dampf einer flüchtigen Halogen Verbindung des Metalles in Zeitschrift für anorganische und allgemeine Chemie, Vol. 216 1934, p. 210.

C. F. Powell, I. E. Campbell, B. N. Gonser: Vapor Plating, John Wiley and Sons, N.Y. 1955, pp. 74 and 83.

ALFRED L. LEAVITT, Primary Examiner

C. K. WEIFFENBACH, Assistant Examiner

U.S. Cl. X.R.

23—208; 117—71M, 169 R