FORMATION OF CARBIDE COMPOUNDS BY VAPOR DEPOSITION ON GRAPHITE BODIES

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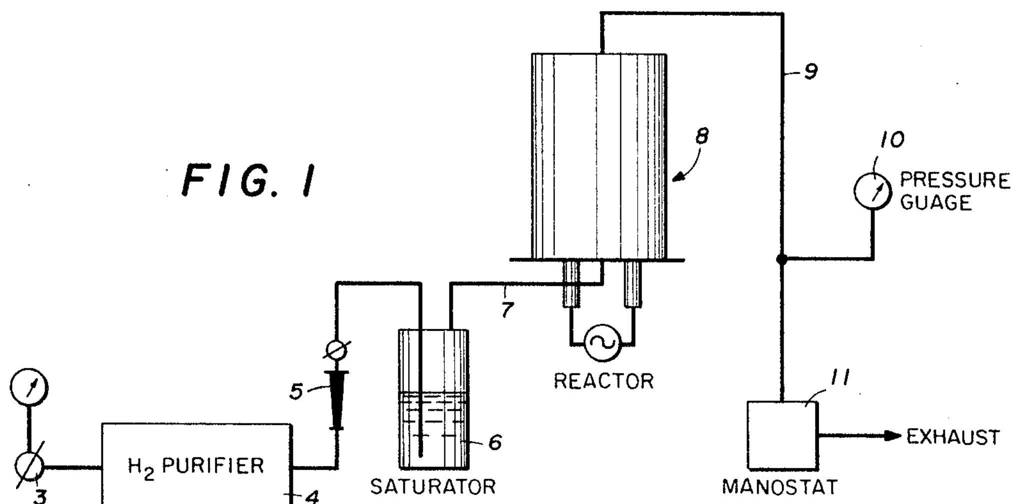

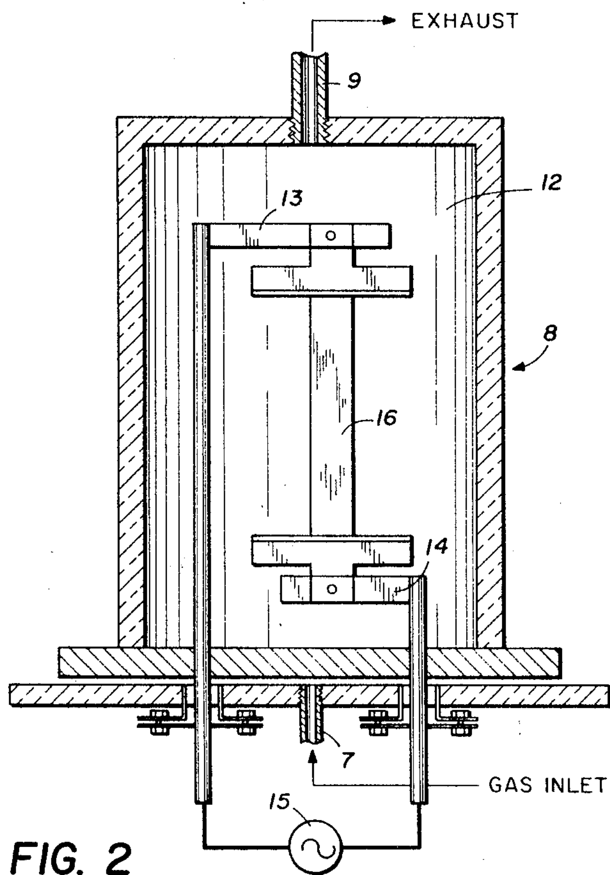

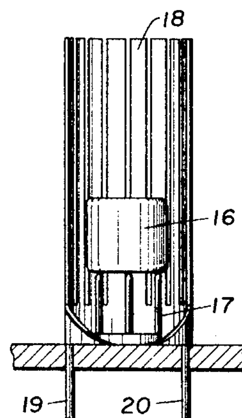

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FORMATION OF CARBIDE COMPOUNDS BY VAPOR DEPOSITION ON GRAPHITE BODIES

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ABSTRACT OF THE DISCLOSURE

A process for forming carbide compounds by heating a graphite body to an elevated temperature, passing a decomposable gaseous mixture of hydrogen and a compound of the element to be deposited over the graphite body, and subsequently elevating the temperature of the graphite body in order to effect penetration and conversion of the deposited element to a carbide of that element.

This application is a continuation-in-part of application Ser. No. 565,606, filed July 15, 1966, now abandoned, for Formation of Silicon Compounds.

This invention relates to a process for the formation of carbide compounds, and more particularly, but not by way of limitation, to the formation of such carbide compounds by deposition and infiltration of an element onto and into a graphite body with which it is to be reacted.

The hardness of carbide compounds, such as silicon carbide which has a Mohs' scale hardness of 9, has made them useful where wear resistant properties have been desired. Conventional methods for preparing carbide compounds, and in particular silicon carbide, leave rather crudely formed bodies. When a silicon carbide body having relatively precise dimensions is needed, a crudely formed silicon carbide body must be machined to desired tolerance. Due to the hardness of compounds, machining is very time consuming and expensive.

The present invention is particularly adapted to the forming of carbide compounds from a pre-shaped and machined body, the shaping and machining of which may be done relatively simply and cheaply. Such a use of the method of this invention is but illustrative, and other uses are contemplated.

The invention may be generally described as a method including the steps of heating a graphite body to a temperature between 900° C. and 1300° C. and passing over the body, while maintained between 900° C. and 1300° C., a gaseous deposition mixture of YH_aX_b and hydrogen for sufficient time to form a layer of Y on said body, and elevating the temperature of said body to a temperature greater than 1430° C. and less than 1900° C. for permitting the Y layer to penetrate and react with the body, where:

Y is selected from the group consisting of silicon, chromium, titanium, zirconium and vanadium, and

X is a halogen.

When Y is silicon, the integers $a+b=4$. These integers can assume any value between zero and four subject to the above condition. When Y is titanium, zirconium, chromium or vanadium, $a=0$ and b assumes a value compatible with the valence of the metallic element in the compound.

To be more specific, reference is here made to the drawings, in which:

FIGURE 1 is a schematic diagram of suitable apparatus for carrying out the invention;

FIGURE 2 is an enlarged diagrammatic illustration of the reactor of FIGURE 1; and

FIGURE 3 is a partial cutaway view in elevation of alternative apparatus for heating and suspending a body.

In FIGURE 1, hydrogen (H_2) is introduced through adjustable valve **3** into a deoxygenizing purifier **4**. From purifier 4, the hydrogen passes through volumetric measuring flow meter **5**. From flow meter **5**, the hydrogen discharges into and proximates the bottom of saturator **6**. The upper portion of saturator **6** communicates through conduit **7** with the bottom of reactor **8**. The top of reactor **8** communicates through conduit **9**, to which a pressure gauge **10** is connected, with a manostat **11** which exhausts to the atmosphere.

As illustrated in FIGURE 2, reactor **8** may comprise a gas tight chamber **12**, within which are supported electrodes **13** and **14** externally connected to an alternating current power source **15**. Between electrodes **13** and **14** is supported a body **16**, about which a gas entering chamber **12** through conduit **7** and exiting chamber **12** through conduit **9** will circulate. The equipment may be constructed of quartz, a mild steel or the like which is unreactive in the presence of the halides mentioned above and hydrogen.

An understanding of the inventive method may be gained by consideration of the following examples.

Example 1

The equipment illustrated in FIGURES 1 and 2 was utilized. A graphite bar having a density of 1.6 gms./cm.^{3} was suspended between electrodes **13** and **14**. The graphite body was 1/10" thick, 1" wide and 5" long. The body was raised to about 1000° C. by impressing a 15 volt potential across electrodes **13** and **14**, at which voltage the specimen drew 300 amperes of 60 cycles/sec. current. About 7.5 liters/min. of hydrogen was bubbled through saturator **6** which was filled with silicon tetrachloride. The gaseous mixture of silicon tetrachloride and hydrogen, which contained about 5–9 mole percent silicon tetrachloride, was circulated through reactor **8** for 45 minutes to form a layer of silicon on the graphite body which was maintained at approximately 1000°C. during the deposition. Manostat **11** was set to maintain the pressure in reactor **8** at atmospheric.

After the expiration of 30 minutes, gas flow through chamber **12** was terminated. The temperature of the graphite body was then raised to about 1430° C. and maintained at this temperature for 10 minutes during which the silicon layer melted, infiltrated the graphite body and reacted therewith to form silicon carbide.

It has been determined that deposition of the silicon layer on the graphite body is preferably done between about 900° C. and 1300° C., and the mole ratio of hydrogen to silicon tetrachloride is maintained within the range over which deposition of silicon will occur. The desired mole ratio of hydrogen to silicon tetrachloride for a given temperature-pressure system can easily be determined by use of published silicon-hydrogen-chloride equilibrium data, familiar to those skilled in the art. One such set of data may be found in Lever, "The Equilibrium Behavior of the Silicon-Hydrogen-Chlorine System," p. 460, IBM Journal (September 1964).

While silicon tetrachloride is a preferred source of silicon, the deposition of silicon can be effected by use of a silicon halide which term is used to include silicon-hydrogen-halide compounds.

While silicon fluorides (which term is used to include silicon-hydrogen-fluorine compounds) may be used, they are not preferred because of their low heat of reaction. Also, silicon iodides (which term is used to include silicon-hydrogen-iodine compounds) may be used, but are not preferred because of their low vapor pressure. Other

than silicon tetrachloride, the preferred silicon halides include trichlorosilane ($SiHCl_3$), dichlorosilane

(SiH_2Cl_2)

silicon dichloride ($SiCl_2$), silicon tetrabromide ($SiBr_4$), tribromosilane (SiH_3Br), dibromosilane (SiH_2Br_2) and silicon dibromide. Silicon dibromide and silicon dichloride only exist at higher temperatures and may be used to obtain faster deposition of silicon than obtainable with the other mentioned silicon bromides and chlorides (which terms are used to include silicon-hydrogen-bromine and silicon-hydrogen-chlorine compounds, respectively).

Example 2

For faster deposition, the equipment described above may be employed, but a bed of silicon heated to about 800° C. is interposed between the saturator **6** and reactor **8**. The gaseous mixture of silicon tetrachloride and hydrogen is passed through the bed and due to the unbalanced equilibrium of the system, silicon is etched from the bed forming a gaseous stream containing hydrogen and silicon dichloride. Upon introduction of the gas stream into the higher temperature zone of the reactor, approximately 1200° C., the equilibrium will again be imbalanced causing deposition of silicon on the graphite body. The exit gases, being depleted in silicon, may be recycled over the silicon bed and replenished in silicon. Thus enriched, the gas mixture can be used as feed gas. This procedure serves to lessen the net consumption of hydrogen and halide. After deposition of silicon for approximately 25 minutes, the gas flow may be terminated and the temperature raised to approximately 1430° C. for 10 minutes to permit infiltration of the silicon and reaction between the silicon and graphite.

Infiltration and reaction between the silicon and graphite is preferably carried out at a temperature between 1430° C. and 1850° C.

The time required to deposit a desired layer of silicon on a given graphite body will vary with the dimensions of the body, the temperature of the deposition and the amount of hydrogen and silicon halide being circulated through the reactor, all of which will be appreciated by those skilled in the art. Also, the time at which the body, after deposition, is maintained at the elevated temperature will depend upon the dimensions of the body and the degree of infiltration desired.

By use of the above described method, a relatively soft graphite body, premachined to a desired shape, may be converted to a silicon carbide body having the desired shape, thus eliminating the costly machining of a silicon carbide blank.

While deposition of silicon from a silicon halide is used in the above examples, there may be substituted a halide of chromium, titanium, zirconium and vanadium. The equilibrium data for these halides may be easily calculated by techniques such as those used by Lever, "The Equilibrium Behavior of the Silicon-Hydrogen-Chlorine System," p. 460, IBM Journal (September 1964). The various halides may be generally identified by formula:

$$YH_aX_b$$

When Y is silicon, the integers $a+b=4$. These integers can assume any value between zero and four subject to the above condition. When Y is titanium, zirconium, chromium or vanadium, $a=0$ and b assumes a value compatible with the valence of the metallic element in the compound.

Additionally, as indicated by FIGURE 3, a graphite body such as solid cylindrical shaped graphite body **16** may be supported at three points by a base **17** or the like and radiantly heated by a cylindrical slotted graphite heater **18**. Heater **18** is connected by electrodes **19** and **20** across a suitable power source, not illustrated. The structure illustrated in FIGURE 3 would of course be supported in a reactor body, such as illustrated in FIGURE 2, to permit circulation of a gaseous deposition mixture therearound and may be used in lieu of the resistance heating technique used in the FIGURE 2 reactor. Other heating techniques such as radio frequency inductive heating and radiative heating from other sources can also be employed.

While the invention has been described in connection with a rigid graphite body, it can be used as well to bond layers of a flexible graphite or carbon yarn, cloth or rope. for example, a graphite cloth may be formed into a desired shape such as a cone, cylinder, ring or the like and placed in a suitable reaction chamber. Silicon may be deposited thereon and reacted therewith to produce a relatively rigid silicon carbide body having much greater strength and hardness than bodies formed by bonding graphite yarns together with elemental carbon. With the flexibility permitted by graphite cloth and the like, an almost infinite number of silicon carbide bodies of differing shapes and physical characteristics could be formed by use of the present invention.

While rather specific terms have been used in describing the embodiment of the invention, they are not intended, nor should they be construed, as a limitation on the invention as defined by the claims.

What is claimed is:

1. A method for forming carbide compounds, comprising the steps of:

heating a graphite body to a temperature between 900° C. and 1300° C.;

passing over said body, while said body is maintained between 900° C. and 1300° C., a gaseous deposition mixture of H_2 and YH_aX_b for sufficient time to form a layer of Y on said body, wherein Y is an element selected from the class consisting of silicon, chromium, titanium, zirconium, and vanadium;

X is a halogen;

the subscript b is an integer representing the number of halogen atoms needed to form the compound, and the subscript a is an integer designating the number of hydrogen atoms in the molecule; and

elevating the temperature of said body to a temperature greater than 1430° C. and less than 1850° C. for permitting said Y layer to penetrate and react with said body, to form a carbide of said element.

2. The method of claim **1**, wherein:

YH_aX_b is silicon tetrachloride.

3. The method of claim **1**, wherein:

YH_aX_b is trichlorosilane.

4. The method of claim **1**, wherein:

YH_aX_b is dichlorosilane.

5. A method for forming silicon carbide, comprising the steps of:

heating a graphite body to a temperature of about 1000° C.;

passing over said body, while said body is maintained at about 1000° C., a gaseous deposition mixture of a silicon halide and hydrogen for sufficient time to form a layer of silicon on said body; and

elevating the temperature of said body to a temperature of about 1430° C. for permitting said silicon layer to penetrate and react with said body to form silicon carbide on the surfaces of and within said body.

6. A method for forming silicon carbide, comprising the steps of:

passing into a heated bed of silicon a gaseous etching mixture of a silicon tetrachloride and hydrogen for forming silicon dichloride which is capable of silicon deposition at temperatures between 900° C. and 1300° C.;

passing said silicon dichloride over a graphite body maintained between 900° C. and 1300° C. for depositing a layer of silicon on said graphite body; and

elevating the temperature of said graphite body after

deposition of said layer of silicon to a temperature greater than 1430° C. and less than 1850° C. for permitting said silicon layer to penetrate and react with said graphite body to form silicon carbide on the surface of and within said body.

7. The method of claim **6**, wherein the temperature of said silicon bed is about 800° C. and the mole fraction percentage of silicon tetrachloride in said silicon tetrachloride-hydrogen stream is between 5 and 9.

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