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[54] **PROCESS FOR PYROLYTIC DEPOSITION OF BORON ON A METAL SUBSTRATE**

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Related U.S. Application Data

[63] Continuation of Ser. No. 540,091, April 4, 1966, abandoned.

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[51] **Int. Cl.** **C23c 13/02**

[58] **Field of Search** ..... 117/106 R, 107.2, 130 R, 117/130 E, 160 R, 227, DIG. 10

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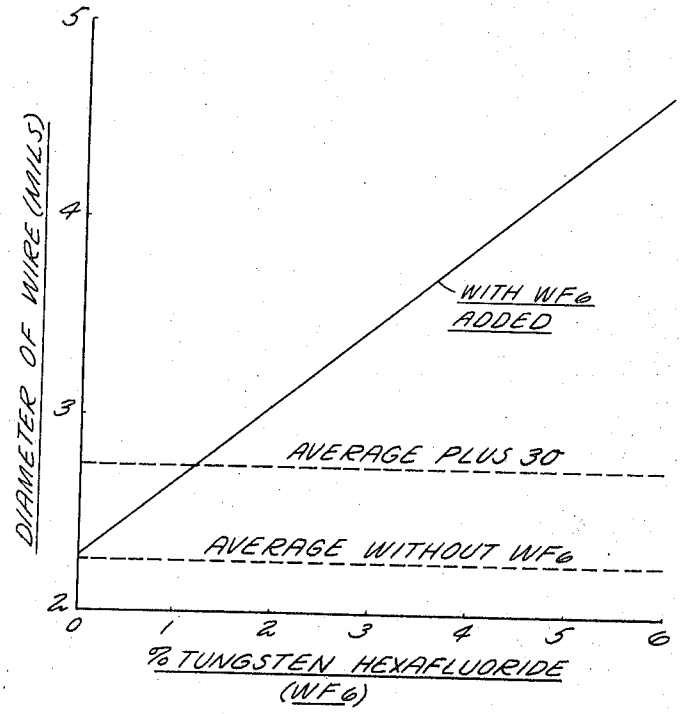
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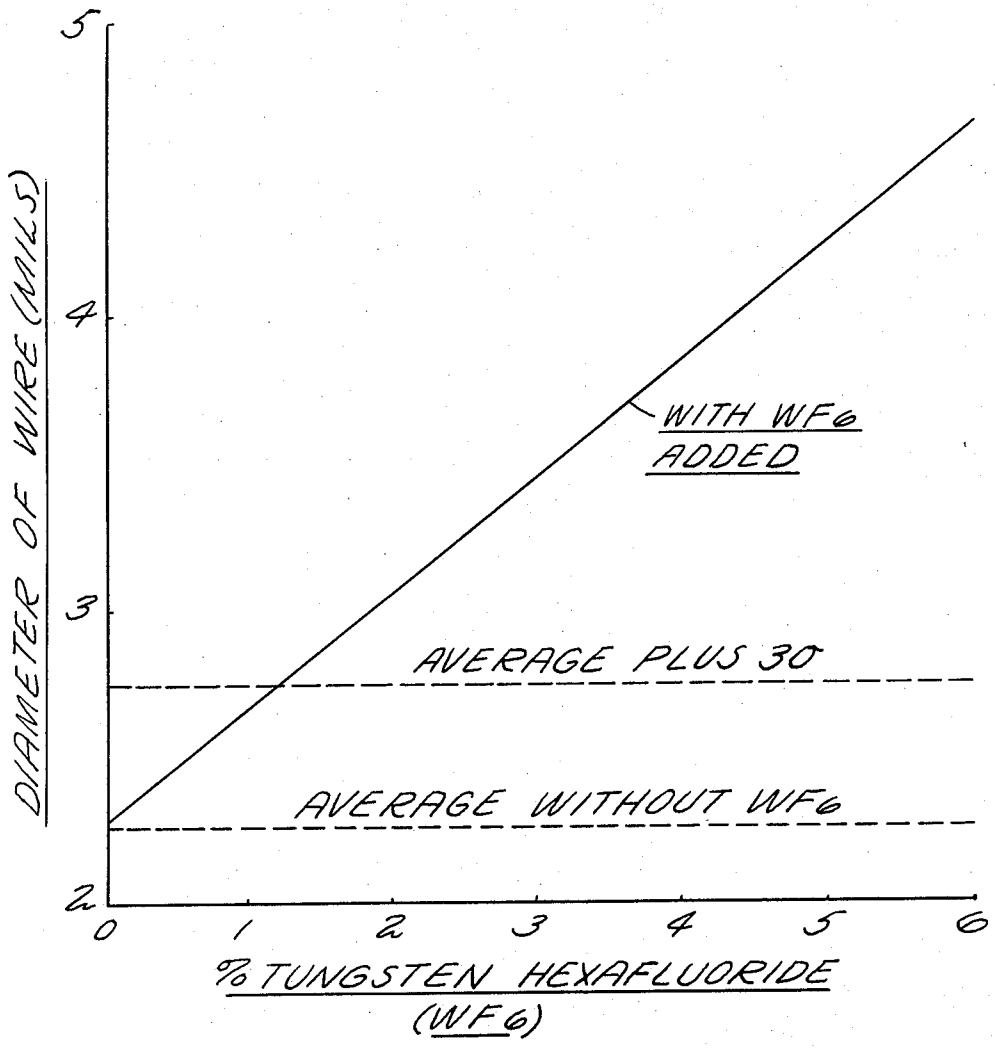
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[57] **ABSTRACT**

This invention provides a process for the pyrolytic deposition of boron on a substrate comprising bringing a pyrolytically decomposable gaseous boron-containing compound and a pyrolytically decomposable metal-containing gas into contact with a substrate, including a reducing gas at an elevated temperature sufficient to pyrolytically decompose both the boron-containing compound and the metal-containing gas, whereby the boron is deposited on the substrate at a rate higher than could be obtained in the absence of the metal-containing gas.

3 Claims, 1 Drawing Figure





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PROCESS FOR PYROLYTIC DEPOSITION OF BORON ON A METAL SUBSTRATE

This is a continuation of Ser. No. 540,091, filed Apr. 4, 1966, and now abandoned.

The invention herein described was made in the course of or under a contract, or subcontract thereunder, with the U.S. Department of the Air Force.

This invention relates to an improved process for pyrolytic deposition of boron on a suitable substrate. More particularly, the instant invention pertains to a process for increasing the rate of pyrolytic deposition of boron on a substrate such, for example, as a filamentary substrate. The process of this invention is of particular interest in effecting deposition of boron on fine metallic filaments for the production of boron fibers.

The pyrolytic deposition of boron on a metallic filament by the thermal decomposition of a boron halide at elevated temperatures in a reducing atmosphere is well known. A typical known process of the aforementioned type is the production of boron by reacting boron trichloride and hydrogen by passing the reactants over an electrically heated tungsten filament, the reaction being represented by the following:

$$2\ BCl_3 + 3\ H_2 = 2\ B + 6\ HCl.$$

In such reaction, the rate of boron deposition on the filament by decomposition of boron chloride is rapid during the first few seconds and then decreases considerably with time.

Objects and advantages of the invention will be set forth in part hereinafter and in part will be obvious herefrom, or may be learned by practice with the invention, the same being realized and attained by means of the steps and methods pointed out in the appended claims.

The invention consists in the novel steps and methods herein shown and described.

It is an object of this invention to provide a process wherein boron is deposited by a pyrolytic deposition on a suitable substrate at an improved rate over that achieved by the presently available processes. A further object of this invention is to provide a process for improving the rate of boron fiber growth on a metallic filament from the thermal decomposition of a boron halide in a reducing atmosphere.

It has been found that the objects of this invention may be realized by including in the reactant gases (e.g., boron trichloride and hydrogen) of a process for the pyrolytic decomposition of boron on a suitable substrate, a catalytic amount of a metal-containing gas, said metal-containing gas being other than a boron-containing gas and being capable of thermally decomposing under the conditions for pyrolytic deposition of boron whereby the metallic component of said gas is pyrolytically deposited on the substrate so as to keep a constant supply of such metal available at the surface of the substrate during boron deposition.

Hence, it has been found that the rate of pyrolytic deposition of boron on a substrate is increased by addition to the reacting gases of a metal-containing gas which serves as a catalyst in enhancing the rate of boron deposition. The term "catalyst" as used in the present disclosure means a metal-containing gas, which when present in small amounts compared to the boron-containing reactants, improves the rate of boron deposition on substrate, and wherein the catalyst may or

may not enter in the reaction. While the present invention is not dependent upon any theory of action, a possible mechanism for the improved results regarding the rate of deposition of boron is as follows:

Examination of cross-section boron fiber deposited on a tungsten filament by the conventional pyrolytic decomposition of boron on the tungsten filament shows that the reduction in the rate of deposition that occurs can be correlated with the loss of the tungsten core due to boron diffusion and the formation of borides. Accordingly, it was conceived that the presence of tungsten may be necessary for rapid boron deposition (i.e., rapid fiber growth).

More particularly, it was found that when tungsten in small amounts was codeposited with boron, the rate of boron deposition increased compared to deposition of boron alone. When such codeposition of boron and tungsten occurs, the tungsten probably forms borides and, therefore, is not recoverable as pure tungsten. It is believed that the boron diffuses into tungsten creating surface vacancies which act as nucleating sites for the deposition of fresh boron. Addition of tungsten-containing gases with the other gases insures that tungsten will be present, even after diffusion into the core of the tungsten-boron fibers has ceased.

In order to illustrate the process of the instant invention further, the following working examples are given. In such examples, the metal-containing gas catalyst is tungsten hexafluoride (WF_6) and the reactants for effecting pyrolytic deposition of boron on the tungsten filament substrate is a BCl_3/H_2 reactant mixture. A series of 13 individual runs were made using 0.5 mil tungsten filament as substrate in a static reactor. Six runs (as control) were made with no WF_6, and seven with WF_6 percentages from 0.05 to 5.00 percent. Where possible, the runs were of 5.00 seconds duration. However, since there was some variation in reaction time, all runs were normalized to a standard equivalent of 5 seconds duration.

The results of this series are shown in the FIGURE of the accompanying drawing. The standard deviation of the six runs at 0 percent WF_6 was calculated, as well as the average diameter. These were $\sigma = 0.157$ mils, $D_{AV} = 2.263$ mils. The line representing three σ's above the average at 0 percent WF_6 is included. It is evident that growth is strongly dependent on WF_6 concentrations. A statistically significant increase in boron deposition rate can be predicted for WF_6 in concentration of two percent or greater. Tests were limited to mechanical and microscopical measurements of final filament diameter.

In carrying out the process of this invention, any conventional reactor for pyrolytically depositing, batchwise or continuously, boron on a metallic substrate may be used. For example, a relatively simple apparatus may be used comprising a simple chamber through which the reactant and catalyst gases are passed and in which a filament substrate is supported in relation to the walls so gases can flow over the filament, the filament substrate being heated to the desired temperature by any conventional technique (e.g., electrical resistance, induction, radiation, etc.). Of course, the reactor is provided with suitable inlet means for feeding the reactant and catalyst gases to the reaction chamber and suitable outlet means for exiting the by-product and excess reactant gases. Examples of typical reactions that may be employed in carrying out the process of this in-

vention are those disclosed in U.S. Weintraub Pat. No. 1,019,934, U.S. Fetterley Pat. No. 2,542,916, U.S. Stern Pat. No. 2,839,357, and U.S. Robb Pat. No. 3,115,393.

It will, of course, be apparent to those skilled in the art, that instead of using boron trichloride as the reactant gas for pyrolytic decomposition to boron, other pyrolytically decomposable boron-containing gases may be used, particularly boron halides such, for example, as boron tribromide. In like manner, while a tungsten filament is specifically disclosed in the substrate for the boron other conventional metallic substrates may be used such, for example, as refractory metals like tantalum, titanium, zirconium, graphite, etc. Then, too, while tungsten hexafluoride is the metal-containing gas illustrated in the working example, other pyrolytically decomposable metal-containing gases capable of codepositing the metallic component thereof with boron may be used such as for example the halides of chromium, columbium, molybdenum, tantalum, titanium, vanadium, zirconium and hafnium, e.g., $ZrCl_4$, $TaCl_5$ and MoF_6. The aforementioned halides are the halides of subgroups IVb, Vb and VIb of the Periodic Table.

In general, in the process of this invention, the reaction is carried out at a temperature in the range of 700° to 1,400°C, and preferably 1,100° to 1,350°C, and the reaction is carried out at a pressure of 0.5 to 4 atmospheres, and preferably 1 to 3 atmospheres. In general, the boron containing gas is in an amount of 15 to 50 mol percent, and preferably 23 to 45 mol percent of the total reacting gases; the metal containing catalyst gas is in an amount of 0.05 to 5 mol percent, and preferably 0.5 to 3.0 mol percent of the total reacting gas; and, the remainder is a reducing gas, preferably hydrogen.

Apropos to the aforementioned proportion ranges is the fact that if the metal-containing catalyst gas is in an amount substantially below the above indicated minimum amount, no appreciable catalytic effect is obtained, while if the metal-containing catalyst gas is in an amount substantially above the above indicated maximum amount, there is formed a significant amount of undesirable metal borides.

The invention in its broader aspects is not limited to the specific steps and methods described, but departures may be made therefrom within the scope of the accompanying claims without departing from the principles of the invention and without sacrificing its chief advantages.

We claim:

1. A process for the pyrolytic deposition of boron and tungsten on a filamentary substrate comprising bringing 15 to 50 mol percent of pyrolytically decomposable gaseous boron trichloride and a catalytic amount of from 0.05 to 5.00 mol percent of tungsten hexafluoride into contact with the substrate in the presence of a reducing gas and at a temperature of 700° to 1,400°C. to pyrolytically decompose both said boron trichloride and said tungsten hexafluoride thereby depositing boron and tungsten on said substrate, the boron being deposited at a rate higher than would be obtained in the absence of said tungsten hexafluoride.

2. A process for the pyrolytic deposition of boron on a substrate according to claim **1** wherein the substrate is a filament of a material selected from the group consisting of tantalum, titanium, tungsten, zirconium and graphite.

3. A process for the pyrolytic deposition of boron on a metallic substrate according to claim **1** wherein the reactants include 23 to 45 mol percent of boron trichloride, as the boron-containing gas, and hydrogen, wherein the temperature is 1,100° to 1,350°C., and wherein the substrate is a tungsten filament.

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