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[54] **SILICON CARBIDE SURFACED FILAMENTS WITH TITANIUM CARBIDE COATING**

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[52] **U.S. Cl.** .... **117/69,** 117/46 CG, 117/169, 161/172, 161/175
[51] **Int. Cl.** **D02g 3/00,** D02g 3/02
[58] **Field of Search** .... 161/175, 172; 117/46 CB, 117/46 CC, 46 CG, 71 M, 75, 106 C, 128, 69, 169

[56] **References Cited**

UNITED STATES PATENTS

3,306,764	2/1967	Lewis et al.	117/106 C X
3,366,464	1/1968	Guichet et al.	117/106 C X
3,556,836	1/1971	Basche et al.	117/106 C X
3,556,837	1/1971	Hammond	117/71 M
3,622,369	11/1971	Basche et al.	117/46 CG
3,702,261	11/1972	Feakes et al.	117/106 C

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[57] **ABSTRACT**

A composite filament suitable for use as a reinforcement in titanium or nickel matrices comprises a filamentary substrate having a silicon carbide surface layer and a thin, adherent outer layer consisting essentially of titanium carbide.

2 Claims, 2 Drawing Figures

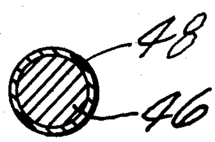

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FIG. 1

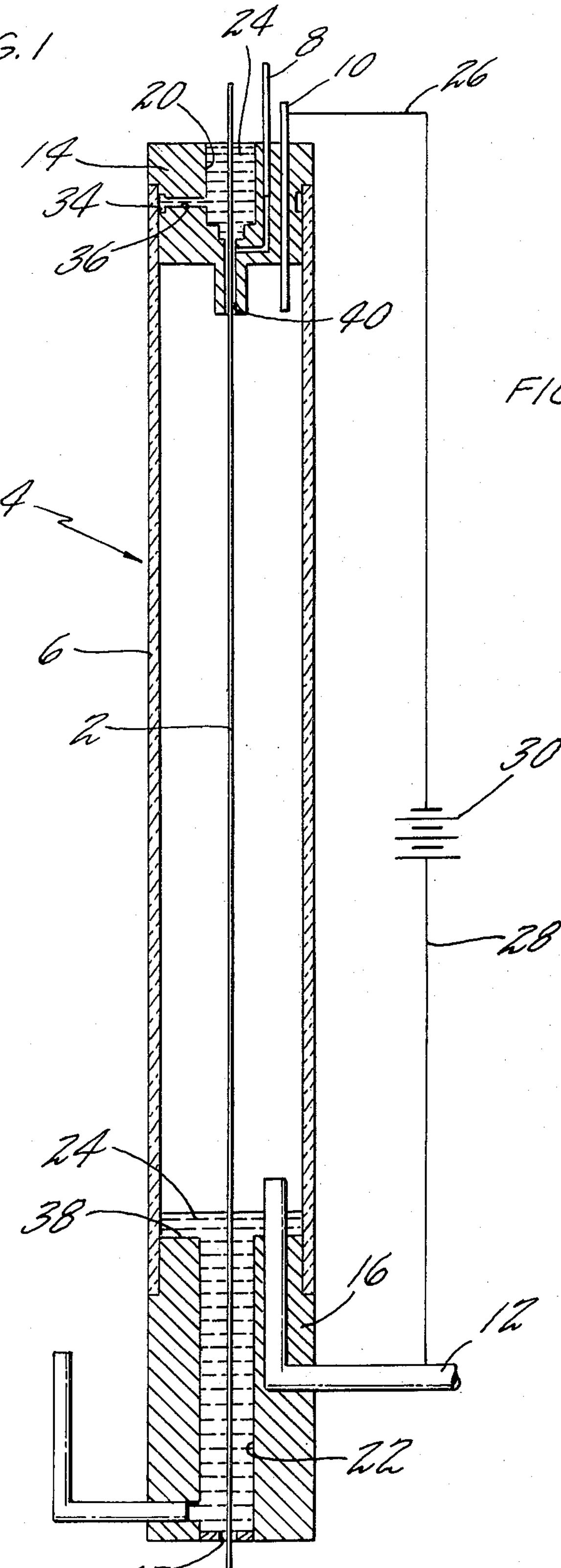

FIG. 2

SILICON CARBIDE SURFACED FILAMENTS WITH TITANIUM CARBIDE COATING

BACKGROUND OF THE INVENTION

It is known that silicon carbide surfaced filaments such as silicon carbide, silicon carbide coated boron and silicon carbide coated carbon are useful as reinforcing materials in composite structures, particularly silicon carbide coated boron filaments such as those taught in U.S. Pat. No. 3,622,369, commonly owned by the assignee of the present invention. In particular, usefulness of silicon carbide surfaced filaments as reinforcements in the resin matrices and in certain metal matrices such as aluminum and magnesium is recognized in the industry. While the reactivity of silicon carbide is lower than that of, for example, boron, it has itself been sufficiently high to necessitate the use of relatively low temperature or short time at temperature processes during fabrication of the filament reinforced metal composites in order to prevent fiber degradation. In addition, it limits the choice of metal matrix material and further, may well define the temperature to which the structure is limited in operation.

Accordingly, in power metallurgy or other processes wherein titanium or nickel is hot pressed with silicon carbide surfaced filaments such as silicon carbide coated boron filaments, pressing temperatures have been held below about 800°C to prevent fiber degradation. While temperatures below 800°C can be employed in such a hot pressing technique, they require inordinately high pressures which are not practical for the formation of larger pieces. As a consequence, realization of the full potential of silicon carbide surfaced filaments is seen to be dependent upon the development of techniques to enhance fiber matrix compatibility as hereinbefore discussed.

SUMMARY OF THE INVENTION

The present invention relates to composite filaments and, more particularly to silicon carbide surfaced filaments such as filaments of silicon carbide, silicon carbide coated boron, silicon carbide coated carbon and the like which are provided with a thin, adherent coating of titanium carbide.

Titanium carbide has been found to be compatible with silicon carbide surfaced substrates as well as with such metal matrix materials as titanium and nickel. It has been found that a titanium carbide coating on a silicon carbide surfaced filament to a thickness of only 0.03 mil will not only impart oxidation resistance to the filament but, in addition, will provide a diffusion barrier between the silicon carbide surfaced substrate and such matrix metals as titanium and nickel whereby fiber degradation is minimized in processes wherein temperatures above 800°C are employed.

Titanium carbide is advantageous in several respects. Because it may perform its principal function as surface protection for silicon carbide surfaced filaments, such as the high modulus, high strength, low density silicon carbide coated boron in very thin thicknesses, only a very small weight penalty is paid as a result of its addition. Furthermore, while there is a coefficient of thermal expansion mismatch in the use of titanium carbide, no problem in this regard has been presented in actual practice, primarily because of the thin film aspect.

BRIEF DESCRIPTION OF THE DRAWINGS

An understanding of the invention will become more apparent to those skilled in the art by reference to the following detailed description when viewed in light of the accompanying drawings, wherein:

FIG. 1 is a simple sketch, taken in elevation, of apparatus used in the production of the titanium carbide coating on the filaments of the present invention; and

FIG. 2 is an enlarged cross-sectional view through one of the filaments of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

As seen in FIG. **1**, the titanium carbide coating is produced on a resistively heated silicon carbide surface filament **2** which is drawn downwardly through a reactor **4** comprising a tubular containment vessel **6**, having dual gas inlets **8** and **10** at the upper end of the reactor and a single exhaust part **12** at the lower end thereof. Cooling hydrogen is fed to the reactor through inlet **8**, and inlet **10** is used for the introduction of a reactant gas mixture comprising methane and titanium chloride ($TiCl_4$). The containment vessel may be formed of Pyrex, although a number of other materials including Vycor and quartz will be found satisfactory. The gas inlets **8** and **10** and the exhaust **12** penetrate and are electrically connected to the metallic end plugs **14** and **16** which provide the end closure for the containment vessel and, also provide convenient means by which power may be supplied to the wire for resistance heating purposes.

The end plugs are each respectively provided with a well **20** and **22**, for containing a suitable conductive sealant **24**, such as mercury, which serves the dual purpose of providing a gas seal around the wire where it penetrates the end plugs, and further providing electrical contact between the moving wire and the respective end plugs which are in turn electrically connected through the tubes **10** and **12** and the leads **26** and **28** to a suitable DC power source **30**. The upper plug **14** is provided with a peripheral groove **34**, which communicates with the mercury well **20** through the passageway **36**, to provide peripheral sealing around the plug. Sealing between the end plug **16** and the lower end of the containment vessel **6** is provided by mercury contained in an annular well **38**.

The respective plugs are each formed with a centrally oriented orifice **40** and **42** which is large enough to accomodate the free passage of the wire **2** therethrough but which, in combination with the wire, is small enough to retain the mercury, through surface tension forces, in their respective wells.

The hydrogen admitted through the inlet **8** enters the reactant chamber immediately adjacent the wire inlet and is used primarily for cooling purposes at the end plug **14**. As shown in FIG. **2**, passage through the reactor results in a composite filament comprising a silicon carbide surfaced substrate **46** having a thin adherent coating of titanium carbide **48**. Subsequent to the formation of the titanium carbide layer, the filaments are consolidated and bonded to the desired matrix material by hot pressing.

Various process techniques and parameters may be utilized in producing filaments of the present invention, as indicated by the following examples.

EXAMPLE I

In a reactor of the type illustrated, utilizing an 8 inch long reactor formed from 25 mm Pyrex tubing and a reactant gas mixture of methane, hydrogen and titanium chloride, a titanium carbide coating was produced on silicon carbide coated boron filaments heated to 1150°C and passed through the reactor at a rate of 600 ft./hour (reactor dwell time: 4 seconds). The substrate filaments are commercially available from Hamilton Standard Division of United Aircraft Corporation and comprised 4 mil boron filaments having a 0.15 mil thick coating of silicon carbide and an average UTS of 410,000 psi. The total gas flow through the reactor was maintained at 500 cc/min. and the methane was saturated with $TiCl_4$ by passing CH_4 through $TiCl_4$ in a container and holding the condenser above its container at 18°–20°C ambient cold water temperature with the container pressure at 1 psig. Hydrogen was introduced separately into the reactor and the ratio of hydrogen to methane was maintained at 5 to 1.

The titanium carbide coating was verified by X-ray diffraction and electrical conductivity measurements showed marked decrease in resistance. The coating was found to be thin (0.03 mils) and adherent with the coated filament exhibiting a UTS of 360,000 psi.

EXAMPLE II

The same apparatus and conditions were utilized as in Example I except that substrate filament speed was 240 ft./hour (reactor dwell time: 10 seconds), substrate temperature was 1050°C and the hydrogen/methane ratio was 15 to 1. The adherent titanium carbide coating was approximately 0.02 mils thick and the coated composite filament exhibited a UTS of 300,000 psi.

EXAMPLE III

The same apparatus and conditions were utilized as in Example II except that substrate temperature was 1,100°C and the hydrogen/methane ratio was 5 to 1. Adherent titanium carbide coatings were approximately 0.02 mils thick, were produced on ten samples and the composite coated filament exhibited an average UTS of 372,000 psi.

EXAMPLE IV

The same apparatus and conditions were utilized as in Example I except that substrate filament speed was 150 ft./hour (reactor dwell time: 16 seconds), substrate temperature was 1,100°C and the hydrogen/methane ratio was 25 to 1. The titanium carbide coating was of similar thickness and quality as that produced in Example I and the filament had a UTS of 325,000 psi.

EXAMPLE V

Example IV was repeated except that substrate temperature was 1,150°C and the hydrogen/methane ratio was 15 to 1. The titanium carbide coated filament had a UTS of 365,000 psi.

EXAMPLE VI

In the reactor apparatus of Example I a thin, adherent titanium carbide coating is produced on a silicon carbide coated carbon filament (1 mil circular cross section carbon monofilament available from Great Lakes Carbon Corporation) heated to 1,100°C and passed through a reactant gas mixture of methane, hydrogen and titanium chloride in the reactor at a rate of 240 ft./hour (dwell time: 10 seconds). The total gas flow through the reactor is maintained at 500 cc/min. and the hydrogen/methane ratio is maintained at 5 to 1. The methane is saturated with $TiCl_4$ as in Example I.

EXAMPLE VII

Utilizing the apparatus and conditions of Example VI, a titanium carbide coating is produced on a silicon carbide filament (100μ continuous filament from Dow Corning or General Technologies Corporation).

In the course of experimentation, wire temperatures, speeds and gas compositions were varied. It is to be noted that in general, the UTS of the filament increases as temperature increases, increases as gas ratio increases and decreases as dwell time increases. Further, no TiC coating was detected by X-ray diffraction when, with a dwell time of 4 seconds, the wire temperature was 1050°C and the gas ratio 25 to 1 or when the wire temperature was 1100°C and the ratio 15 to 1. Likewise, with the dwell time increased to 10 seconds, no coating could be observed when the temperature was maintained at 1150°C with a gas ratio of 25 to 1. Finally, with the dwell period at 16 seconds, no coating was observed when the temperature was 1050°C with a gas ratio of 5 to 1.

As indicated in the examples above, the deposition of titanium carbide does result in a small reduction in average strength of the composite filament. This reduction is relatively slight, however, when the proper process conditions are observed. The parameters set forth in Example III, for example, show a reduction of only 7 percent (410,000 psi to 372,000 psi) in strength. This reduction is not considered significant in view of the fact that the TiC coated filaments allow bonding with titanium or nickel matrices which normally, at temperatures above 800°C, attack and destroy silicon carbide surfaced filaments. In the present case, titanium coated filaments were subjected to compatibility testing in matrices of nickel and titanium. Composites were prepared by hot pressing TiC coated silicon carbide surfaced filaments with Ti powder at 900°C and 5,000 psi for 30 minutes. They were also prepared by hot pressing with Ni powder at 850°C and 5,000 psi for 3 minutes. In all cases, the TiC coated filament was not attacked by either the titanium or the nickel.

While the invention has been described in connection with specific examples, numerous modifications to the process will be evident to those skilled in the art. The examples will, therefore, be understood to be illustrative only within the true spirit and scope of the invention as set forth in the appended claims.

What is claimed is:

1. A composite filament for use as a reinforcement in matrices of titanium and nickel comprising:

a filamentary substrate selected from the group consisting of silicon carbide, silicon carbide coated boron and silicon carbide coated carbon; and

a thin adherent outer layer which consists essentially of titanium carbide.

2. A composite filament according to claim 1 wherein said filamentary substrate is a silicon carbide coated boron filament.

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