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[54] **HIGH STRENGTH METAL CARBONITRIDED COMPOSITE ARTICLE**

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[58] **Field of Search** 29/191, 191.2, 191.4, 192, 29/191.6; 148/16.5; 23/359, 191

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[57] **ABSTRACT**

A high strength, light weight, composite article is provided which contains as reinforcing elements, members formed of metal substrates which are, for example iron or titanium, carrying solid solution layers of metal carbonitrides such as titanium carbonitride about their periphery. In one embodiment the reinforcing element is in the form of a sheet, and the composite body is formed by interposing sheets of metal between the elements and then fastening the metal sheets and element sheets together by diffusion bonding. In another embodiment the reinforcing elements are in the form of strips or filaments which are placed within a matrix of plastic, such as epoxy or polyimide, or metal, such as aluminum.

8 Claims, No Drawings

HIGH STRENGTH METAL CARBONITRIDED COMPOSITE ARTICLE

This invention relates to high strength composite articles. In another aspect, this invention relates to composite articles which find particular utility in the aircraft industry. In still another aspect, this invention relates to novel composites which contain as reinforcing elements, metallic members which carry a coating of a metal carbonitride.

In an attempt to obtain very high strength but relatively light weight construction materiasl for applications such as in the aerospace and aircraft industries, recent emphasis have been directed to research on the use of light weight, high strength ceramics as reinforcing elements in structural components. This research has generally been limited to methods of utilizing reinforcing amounts of the ceramic type materials in a matrix to form a structurally sound, composite article.

Conventional composites generally comprise ceramic-type filaments incorporated within a plastic or metal matrix. Boron filaments have been developed for such use. These boron filaments generally comprise a very fine tungsten substrate core which has been vapor deposited with boron to form a composite filament. For example, a popular boron filament includes 0.5 mil tungsten substrate core which has been uniformly coated with boron by vapor phase deposition to form a 4 mil diameter reinforcing filament.

Problems have occurred using these boron filaments in the presence of matrix materials such as aluminum at higher temperatures (temperatures generally about 250° C) because the filaments react with the matrix materials and degrade. Attempts have been made to coat these boron filaments with protective coatings of carbides or nitrides, but such procedures are generally very expensive and yield results somewhat less than satisfactory. In addition to the boron reinforcing fibers, attempts have been made to reinforce composite bodies with graphite and glass fibers. The graphite fibers are undesirable because of poor fiber-to-matrix adhesion which results in low shear strength of the composite article. The glass fibers have a disadvantage of a far lower modulus-to-density ratio than either boron or graphite fibers.

Thus, difficulties which are generally experienced when incorporating ceramic-type reinforcing elements into a matrix, include (1) undesirable reactivity of the ceramic material with the matrix material to thereby cause unwanted degradation of the reinforcing material and the matrix, (2) poor adhesion between the reinforcing fiber and the matrix material, and (3) relatively low strength of the resultant body.

Therefore, one object of this invention is to provide a novel reinforcing element for a composite body which has superior strength and is compatible with conventional matrix materials.

Another object of this invention is to provide a novel composite body.

A further object of this invention is to provide a novel composite body having a laminated structure.

According to one embodiment of this invention, a structural element is provided for a composite body which consists of a metal substrate which carries a coating of a solid solution metal carbonitride thereon. The element can be in the form of a thin sheet or a cylindrical filament, for example. The preferred metals of the substrate are selected from iron and titanium, and the preferred carbonitride coating is titanium carbonitride.

In another embodiment of this invention a composite structure is provided which comprises elements of said one embodiment encapsulated in a matrix which can include a metal such as aluminum or a polymer such as epoxy resin or polyimide.

According to a further embodiment of this invention, a composite laminated body is provided which comprises at least one sheet of a metal carrying a coating of metal carbonitride which is bonded to a second metal layer. Very high strength, light weight composite bodies are formed by bonding at least one element formed of a sheet-like substrate made of the material selected from iron and titanium coated with titanium carbonitride to at least one sheet of a metal selected from iron and titanium by diffusion bonding.

It has been found that the use of a recently developed solid solution carbonitride of a metal selected from silicon, boron, and the transition metals in Groups IVB, VB, and VIB of the Periodic Table as set forth on page B-2 of the Handbook of Chemistry and Physics, Chemical Rubber Company, 45th ed., (1964) on metallic elements such as steel and titanium results in a highly efficient, strong, and light weight reinforcing element which can be used in composite bodies which require both strength and light weight. In addition, these elements are highly resistant to extreme thermal and abrading conditions. The metal carbonitride coating has been found to be highly compatible with conventional matrix materials such as aluminum in that a very efficient bonding will occur between the filaments and the matrix, and such filaments are not reactive in the presence of the matrix material. Thus, a very strong, stiff, light weight composite body can be formed when utilizing the metal carbonitride coated elements as reinforcing members in a composite article. Furthermore, it has been found that the metal carbonitride coating, for example titanium carbonitride, is unusually compatible with iron and titanium, and particularly with steels and titanium alloys.

The solid solution layer of the metal carbonitride can be applied to a suitable substrate for the filament by the manner disclosed in copending U.S. Pat. application No. 769,356 now abandoned filed Oct. 21, 1968. This process includes the steps of heating the substrate to be coated to at least the decomposition temperature of the reactants (generally from about 400° C to about 1200° C) and then passing a gaseous stream containing the reactant over the substrate to thereby yield reactants at the temperature of the body to permit the reaction of the metal, carbon, and nitrogen, thereby forming a solid solution of the metal carbonitride on the body.

The reactants generally include a metal halide, e.g., titanium tetrachloride, molecular nitrogen and/or an easily decomposable nitrogen-containing compound, and easily decomposable carbon-containing compound (alternatively, an easily decomposable nitrogen and carbon-containing compound can be used), and molecular hydrogen as a reducing agent.

Suitable metal containing reactant compounds include metal halides. A preferred group of the metal halides is represented by the generic formula $Me(X)_n$ where n is a valence of Me, X is a halogen, e.g., florine, chlorine, bromine, and iodine, and Me is selected from silicon, boron, and transition metals in Groups IVB,

VB, and VIB of the Periodic Table as set forth on page B-2 of the Handbook of Chemistry & Physics, Chemical Rubber Company, 45th ed., (1964). Generally, the transition metal tetrahalides, such as titanium tetrachloride are most preferred. However, the transition metal dihalides and trihalides can be useful in some application, particularly, the higher temperature coating operations.

Suitable carbon-containing reactant compounds include cyclic and acyclic hydrocarbons having up to about 18 carbon atoms which readily decompose at the deposition temperature. Examples of suitable hydrocarbons include paraffins, such as methane, ethane, propane, butane, pentane, decane, pentadecane, octadecane, and aromatics such as benzene and halogen substituted derivatives thereof.

Suitable reactant compounds containing both carbon and nitrogen include aminoalkyenes, pyridenes, hydrazines, and alkylamines. Some specific examples include diaminethylene, diaminoethylene, pyridine, trimethylamine, triethylamine, hydrazine, methylhydrazine, and the like.

According to a preferred embodiment of this invention, a laminated composite body is formed, utilizing elements consisting of a metal sheet made of a material selected from iron and titanium, e.g., steel and titanium alloy which has been coated with a uniform layer of a metal carbonitride, preferably titanium carbonitride. The resulting element is then bound to at least one metal sheet of steel or titanium by diffusion bonding. For example, a multi-layer high strength, laminated body can be formed in accordance with this invention by bonding two metal sheets to each element. This body will in essence have a building block of titanium carbonitride coated element with a metal sheet bonded to either side thereof.

A typical method of forming a building block element of the preferred composite of this invention includes the initial formation of the reinforcing element by the vapor phase deposition of a solid solution layer of titanium carbonitride over both sides of a thin sheet of titanium or steel. For example, preferably the element would include a one-half to 2 mil titanium carbonitride coating over both sides of a 1 mil thick titanium or steel sheet. This will result in a three layer, reinforcing filament. Next, a one-half to 1 mil titanium or steel sheet is pressed against each of the one-half to 2 mil titanium carbonitride layers and diffusion bonded thereto. A typical bonding operation would include holding the two metal sheets against the titanium carbonitride layers at a pressure of from about 2000 to 4000 p.s.i., and heating the sheets to a temperature of from about 900° to about 1300° C from about one-half hour to one hour. This diffusion bonding operation will thereby result in a building block type element for a laminated body which consists of three layers of a metal (titanium or steel) separated by and held bound to a pair of titanium carbonitride layers. The stiffness of this composite material is from 2½ to 3 times the stiffness of the metal (titanium or steel) while the density is approximately the same as the metal.

The laminated body is built from the above described basic building block by next diffusion bonding titanium carbonitride coated metal layers to the two exposed metal layers on either side of the building block in a similar manner as described above. This novel laminated body can be utilized as a reinforcing element in a dissimilar matrix material, or can be used as a high strength, light weight article article. For example, very high strength, light weight turbine blades can be made in accordance with this invention by diffusion bonding the titanium carbonitride reinforcing elements and metal sheets while deformed within a mold or over a form in the shape of the desired turbine blade.

In addition to the above described use in a laminated composite body, the novel high strength reinforcing element of this invention can be utilized as a reinforcing element in a matrix of dissimilar material. For example, the reinforcing element of this invention can be formed into a suitable shape. For example, a thin strip or a filament (generally a very elongated cylindrical shape). Such filament can be utilized as a reinforcing element within a conventional matrix without unwanted reactivity toward the matrix and poor adhesion to the matrix. For example, the titanium carbonitride coated reinforcing elements of this invention can be incorporated within molten aluminum to increase the stiffness of a resulting composite body thereof. In this instance, the titanium carbonitride has been found to be nonreactive with the molten aluminum, and to bond excellently therewithin.

Alternatively, reinforcing elements of this invention can be incorporated into polymeric matrices such as epoxy resin and polyimided in a very satisfactory manner. By epoxy resin is meant commercially available materials known in the art which are usually derived from the reaction of the material selected from bisphenol A, biphenols, glycol, and glycerine, with epichlorohydrin. By polyimides it is meant the heat resistant aromatic polyimide resins made by reacting pyromellitic dianhydride with aromatic diamines. Thus, the reinforcing elements of this invention are highly compatible with the above-described high strength, temperature resistant matrix materials.

The reinforcing elements of this invention have been found not only to be non-reactive to conventional light weight, high strength matrix material, but also exhibit an unexpectedly high modulus of elasticity and tensile strength in relation to the comparatively low density. The titanium carbonitride coated reinforcing elements of this invention exhibit up to 1 percent of elastic character, which is about 10 times greater than conventional materials which usually fracture at 0.1 percent strain. In addition, the reinforcing elements possess a rather high tensile strength. For example, one-half mil titanium filament which has been uniformly coated with a solid solution layer of titanium carbonitride to yield a filament approximately 4 mils in diameter possesses a tensile strength of 600,000 p.s.i.

It has been found that the solid solution metal carbonitride layer can be used successfully as a coating on most conventional substrates to form a reinforcing element in accordance with this invention. For example, the metal carbonitride can be applied if desired, to tungsten, boron, molybdenum, aluminum and the like. However, it is preferred that the substrate of the reinforcing filament of this invention be selected from iron containing alloys including the various steels and titanium containing alloys including the various titanium alloys. The metal carbonitride, especially the titanium carbonitride, has been found to be highly compatible with most metals, particularly the steel and titanium in that it will adhere tightly thereto under temperature ex-

tremes, and furthermore, it will diffusion bond to most metals and not deleteriously react therewith.

While this invention has been described in relation to its preferred embodiments, it is to be understood that various modifications thereof will be apparent to one skilled in the art upon reading this specification, and it is intended to cover such modifications as fall within the scope of the appended claims.

I claim:

1. A laminated composite article comprising a first layer of a solid solution carbonitride of a metal selected from silicon, boron, and the transition metals in Groups IVB, VB and VIB of the Periodic Table integrally bonded between second and third metal layers.

2. The laminated composite article of claim **1** which is formed by vapor depositing said solid solution metal carbonitride first layer on said second layer to form an integral bond therebetween and said third layer is thereafter diffusion bonded to said solid solution carbonitride first layer to form an integral bond therebetween.

3. The laminated composite article of claim **2** wherein said metal layers are selected from iron and titanium.

4. The laminated composite article of claim **3** wherein said solid solution carbonitride comprises titanium carbonitride.

5. The composite article comprising at least one metal substrate coated with a solid solution layer of a carbonitride of a metal selected from silicon, boron and the transition metals in Groups IVB, VB and VIB, disposed within a matrix material.

6. The composite article of claim **5** wherein the said matrix material is selected from aluminum, epoxy resin and polyimide.

7. The composite article of claim **6** wherein said metal substrate is selected from iron and titanium.

8. The composite article of claim **7** wherein said solid solution carbonitride is titanium carbonitride.

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