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REINFORCED CARBONACEOUS BODIES

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6 Claims

ABSTRACT OF THE DISCLOSURE

Process for making reinforced carbonaceous bodies comprising mixing parapolypheylene and carbon diffusion resistant metal coated, or uncoated fibers of tantalum, boron, titanium, tungsten, or molybdenum, pressing the mixture and pyrolyzing the pressed mixture.

CROSS-REFERENCES TO RELATED APPLICATIONS

This invention is related to that described in the co-pending U.S. patent application Ser. No. 492,315, which describes a pyrolyzable aromatic compound, parapolypheylene.

BACKGROUND OF THE INVENTION

This invention pertains to a process for making reinforced carbonaceous bodies. In the prior art, reinforced carbonaceous bodies were formed using a pyrolyzable matrix such as tar or pitch mixed with particulate carbon and graphite surrounding reinforcing materials such as carbon and graphite fibers. The composite was pyrolyzed, forming a graphitic structure containing the reinforcing materials.

The prior art processes have the disadvantage of utilizing matrix materials which become plastic at or below pyrolyzation temperatures. Consequently, complicated mold formation is required to control dimensional stability.

In a co-pending application, the use of parapolypheylene as a starting material for graphic structures has been described. The property of parapolypheylene which permits it to be compacted into a coherent mass and then pyrolyzed into a coherent crystalline graphitic structure was there described. Moreover, the resulting material is harder than graphite and has other distinguishing characteristics. The material can usually be used wherever graphite is normally used, such as in insulation structures, brush stock, and projector carbon, to mention a few.

It has been found that the graphitic-like material resulting from the pyrolysis of parapolypheylene is unsuitable for some applications, due to its high elastic modulus below about 1500° C. This high elastic modulus naturally indicates a brittle material. This brittleness frequently results in structural failure of the part due to incidental mechanical shock. Additionally, if the part is connected to a substrate material with a high coefficient of thermal expansion, thermal cycling can induce mechanical stresses in the graphitic-like part, causing structural failure. However, at temperatures above about 1500° C. carbon has sufficient plasticity to resist minor stresses and mechanical shocks. Consequently, the problem of shock and strain resistance is not so critical at temperature above about 1500° C.

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PRIOR ART

One solution to the described structural failure is to reinforce the carbonaceous structures. However, common reinforcing materials, such as glass fibers, glass cloth and steel wires, are unsatisfactory either because they react with carbon, as in the case of glass and steel, or because they do not have sufficient mechanical strength themselves in temperature regimes as high as 1500° C. The normal requirements for reinforcing fiber, e.g., strength, high modulus stability, fabricability, etc., are still required.

It is an object of this invention to provide an improved process for the production of reinforced carbonaceous bodies.

It is a further object of this invention to provide processes for the formation of reinforced carbonaceous bodies that do not require complicated mold structures.

It is a further object of this invention to provide graphite bodies reinforced with materials other than carbon or graphite reinforcements.

Further advantages and objects of this invention will become apparent from the following description.

SUMMARY OF THE INVENTION

The process of the instant invention comprises disposing in a die a compound selected from the group consisting of parapolypheylene, mixtures of parapolypheylene and graphite, mixtures of parapolypheylene and carbon and mixtures of parapolypheylene, carbon and graphite with carbon diffusion resistant metal coated or uncoated reinforcing fibers selected from the group consisting of boron, tantalum, titanium, tungsten, and molybdenum, compressively forming the mixture at pressures of between 100 and 120,000 p.s.i., and pyrolyzing the formed mixtures at a temperature of between 650° C. and 2500° C. for between 0.1 and 4 hours. One hour is preferred. It has been unexpectedly found that the carbon diffusion resistant metal coated or uncoated reinforcing material selected from the group consisting of boron, tantalum, titanium, tungsten and molybdenum are satisfactory for reinforcing the carbonaceous bodies of the instant invention. For parts that are going to be subjected to temperatures of from about 900–1400° C., materials selected from the group consisting of tantalum, titanium, tungsten and molybdenum are satisfactory. However, above about 1400° C., these materials are less satisfactory as some degree of carburization weakens these fibers. Consequently, above these temperatures it is preferred that the fibers be coated with a carbon diffusion resistant metallic coating. These metals suitable for this purpose known to the art generally fall into the class known as Group VIII metals, excluding iron, but additionally including rhenium. These metals do not readily form carbides and under most conditions do not form carbides at all. However, some of these metals exhibit this diffusion resistant property to a greater extent. The best metals in the group are rhenium, rhodium and iridium and of this preferred group, the favored member is rhenium.

It is preferred that the reinforcing materials be in the form of wires or fibers with an aspect ratio, that is, ratio of length to diameter, of between 10 and 1,000. These fibers can be randomly aligned in the graphitic structure or they may be in an orderly arrangement whereby additional strength is given the reinforced bodies in selected directions. In general, the reinforcing

fibers should comprise between 5 and 80 percent by volume of the graphitic structure. The fibers are included in the polymer mixture by simple mixing if no alignment is desired. If a particular alignment is desired, the fibers can be disposed by manual means.

The material parapolymethylene and its method of manufacture is well known. The polymer may be characterized as infusible, consisting of benzene rings linked through the para positions. If unsubstituted, it contains carbon and hydrogen in a weight ratio of about 18:1. The hydrogen of the parapolymethylene can be substituted with halogens, e.g., chlorine. Also, the parapolymethylene can be polynuclear. This polynuclear state is indicated by an increase in the carbon to hydrogen ratio. In addition to being infusible, the polymer is chemically inert, with a high degree of thermal stability. Thus, this material is termed intractable. The polymer as obtained from the process of its manufacture is a fluffy brown powder having a very high surface area. The polymers of the invention are pressed at pressures of at least 1000 p.s.i. Pressures as high as 120,000 p.s.i. have been utilized. It is obvious that the pressure utilized for the pressing of the powder will affect the denseness of the final compacted mass. However, it is to be pointed out that solid masses capable of being pyrolyzed are obtainable over the entire range stated. For various given applications, more compacted masses or, in other words, higher pressures become desirable. The pressing can transpire by utilization of any conventional techniques involving mechanical or isostatic methods which in themselves form no part of the invention. The compaction can transpire at room temperature and gives a strong dense body over the given ranges. Alternatively, pressure can occur at elevated temperatures. Compacted material has considerable lubricity so that the mold release is quite easy. The parapolymethylene, for example, in the pressed green state exhibits a strength of up to 2000 p.s.i. Additionally, x-ray diffraction studies show a high degree of anisotropy.

The compacted powder containing reinforcing fibers is then placed in a furnace whereby the compact mass is pyrolyzed. During pyrolysis the hydrogen and atoms other than the carbon present in the parapolymethylene are driven off as volatiles, leaving a carbonaceous mass containing reinforcing fibers. The material is left in the furnace at the pyrolyzation temperature for time sufficient for pyrolysis of the entire mass to occur. The furnace can be operated at a partial vacuum, or with an inert atmosphere. In any case, the atmosphere in the furnace should not be reactive with the parapolymethylene. Pyrolysis temperatures can vary in the range of 650 to 2500° C. The soak or residence time of the compacted mass in the temperature environment will vary according to the temperature. However, for practical purposes, it has been found that a residence time of one hour in the temperature ranges set forth is sufficient for pyrolysis to occur.

In the fabrication of the reinforced carbonaceous articles, some problem may be encountered with distortion of the article upon cooling. This distortion is caused by shrinkage of the parapolymethylene compressively loading the fibers. To overcome this, powdered graphite or carbon can be added to the parapolymethylene mixture, thereby reducing pyrolysis shrinkage and hence compressive loading. The preferred mixture utilizes 65% carbon or graphite by weight. However, a range of from 30% to 80% has been found to be suitable.

After formation and pyrolysis, the article can be machined to any desired shape. Ordinary machining techniques can be used, using techniques known in the art to form graphitic materials.

The process and compositions of the instant invention are illustrated by the following examples:

EXAMPLE I

A fibrous reinforced body was formed with 5-mil

boron fibers. These fibers are a deposit of boron on a fine tungsten wire having an aspect ratio of about 100. They were chopped into short lengths, ca. 1/2-inch and 5 weight percent of them was mixed with parapolymethylene and pressed to 1/2-inch diameter disc at 100,000 p.s.i. The disc was then pyrolyzed at 1000° C. for one hour in argon. Subsequently, the specimen was sectioned and examined microscopically; the boron fibers were found to have remained intact and to be lying flat and normal to the pressing direction.

EXAMPLE II

A superior strength reinforced carbonaceous object resistant to thermal and mechanical shock is made by mixing 50 volume percent by weight rhenium coated tantalum fibers having an aspect ratio of about 500 with parapolymethylene, pressing the mixture at 50,000 p.s.i., and pyrolyzing the pressed mixture for 45 minutes at 2000° C. in a vacuum.

EXAMPLE III

A reinforced carbonaceous body is made by mixing 75 volume percent titanium fibers having an aspect ratio of 750 and parapolymethylene, pressing at 20,000 p.s.i., and pyrolyzing at 800° C. for three hours in a helium atmosphere.

EXAMPLE IV

A reinforced carbonaceous body is made by mixing 25 volume percent osmium coated molybdenum fibers having an aspect ratio of 20 with parapolymethylene, pressing at 110,000 p.s.i. and pyrolyzing for four hours at 2200° C. in argon.

EXAMPLE V

A reinforced carbonaceous body is made by mixing 20 volume percent iridium coated titanium fibers having an aspect ratio of 200 with a mixture of 65 percent by weight graphite and 35 percent by weight parapolymethylene, pressing at 30,000 p.s.i., and pyrolyzing for two hours at 1700° C. in an argon atmosphere.

EXAMPLE VI

A body is made by the same procedure as described in Example V, using the same constituents, except the body, in addition to fibers, comprises 25 weight percent graphite, 20 weight percent carbon, and 55 weight percent parapolymethylene.

EXAMPLE VII

A body is made by the same procedure as described in Example V, using the same constituents, except the body, in addition to fibers, comprises 75 weight percent carbon and 25 weight percent parapolymethylene.

Since it is obvious that many changes and modifications can be made in the above described details without departing from the nature and spirit of the invention, it is to be understood that the invention is not to be limited thereto except as set forth in the appended claims.

I claim:

1. The process of fabricating reinforced carbonaceous bodies comprising:

disposing in a die a compound selected from the group consisting of parapolymethylene, mixtures of parapolymethylene and graphite, mixtures of parapolymethylene and carbon and mixtures of parapolymethylene, carbon and graphite, with carbon diffusion resistant metal coated or uncoated reinforcing fibers selected from the group consisting of boron, tantalum, titanium, tungsten and molybdenum,

compressively forming the mixture at pressures of between 1000 and 120,000 p.s.i., and pyrolyzing the formed mixtures at a temperature of between 650° C. and 2500° C.

2. The process of claim 1 wherein the fibers have an aspect ratio of between 10 and 1000.

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3. The process of claim 1 wherein the pyrolysis takes place for between 0.1 and 4.0 hours.

4. The process of claim 1 wherein the fibers are uncoated and selected from the group consisting of titanium, tungsten, tantalum, and boron.

5. A reinforced carbonaceous body comprising:
carbon and carbon diffusion resistant metal, coated or
uncoated fibers selected from the group consisting
of boron, tantalum, titanium, tungsten, and molyb-
denum, having an aspect ratio of between 10 and
1000 produced by pyrolyzing a formed mixture com-
prising parapolyphenylene.

6. The material of claim 5 wherein the fibers are un-

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coated and selected from the group consisting of titanium, tungsten, tantalum, and boron.

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