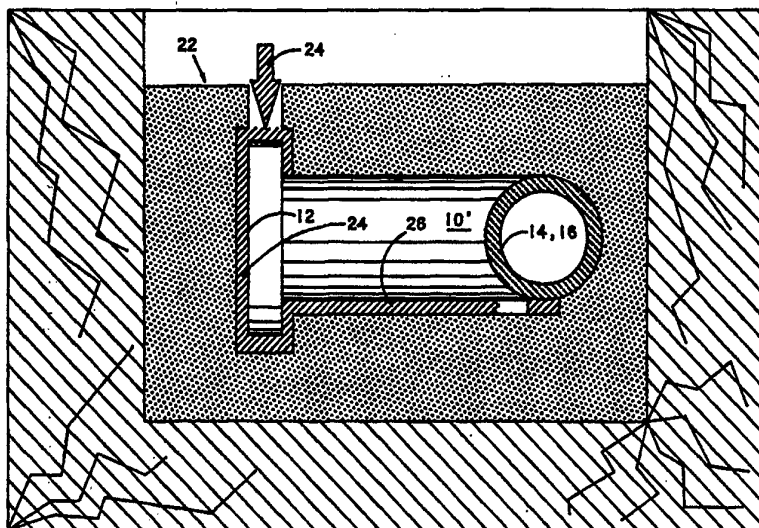




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(54) Title: METAL COATED, CERAMIC, FIBER REINFORCED CERAMIC MANIFOLD



(57) Abstract

This invention relates to parts of an internal combustion engine or the like and, more particularly, to a reinforced ceramic matrix composite exhaust manifold (10) for internal combustion engine applications. The present invention solves the problems of failure due to thermal shock, damage from minor impacts, erosion, engine weight, and the like. A method of making the exhaust manifold (10) comprises the steps of forming a liner of a castable monolithic ceramic material containing pores, filling the pores with a pre-ceramic polymer resin, coating reinforcing fibers with an interface material, forming a mixture of a pre-ceramic polymer resin and reinforcing fibers coated with the interface material, forming an exhaust manifold shaped structure from the mixture by placing the mixture on at least a portion of the castable material, and firing the structure, thereby forming a reinforced ceramic composite.

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Metal Coated, Ceramic, Fiber Reinforced Ceramic Manifold

TECHNICAL FIELD

5 This invention relates to parts of an internal combustion engine or the like and, more particularly, to apparatus for ducting the exhaust emissions of an internal combustion engine comprising; a plurality of header pipes connected to and receiving exhaust gases from the plurality of the exhaust ports of the engine; and an outlet therefrom connected to an exhaust pipe. More specifically, the invention relates to a
10 breakage resistant, high temperature resistant, corrosion resistant, low heat rejection, structural fiber reinforced ceramic matrix composite exhaust manifold for internal combustion engine applications.

BACKGROUND OF THE INVENTION

15 For many years, the exhaust systems of internal combustion engines have remained substantially unchanged. There is a metal exhaust manifold, typically cast iron or steel, or tubular steel, that collects the exhaust gases emitted from the exhaust ports of the engine and outputs them into a single exhaust pipe. Typically, a muffler, and/or a catalytic converter device is disposed in-line with the exhaust pipe to reduce noise and
20 pollutants associated with engine operation. A typical prior art exhaust manifold design is depicted in simplified form in Figure 1 where it is generally indicated as 10. There are a plurality of flanges 12 which are bolted or clamped over the exhaust ports (not shown) of the engine (also not shown). The flanges connect individual header pipes 14 to a common outlet pipe 16 which leads and is connected to the exhaust system (not shown)
25 at 18. Since good (minimal restriction) exhaust gas flow is important in overall engine performance, the curves of the pipes, the interior smoothness, and the like, are factors considered by designers thereof. Such factors are somewhat relevant to the novelty of the present invention but will not be addressed herein in favor of simplified drawings which clearly point out the true novelty in a manner easily understood by those of

ordinary skill in the art.

Most early and present prior art exhaust manifolds were totally of metal as indicated in Figure 2. Commercial manifolds were/are generally of cast iron or cast steel while specialty manifolds for high performance engines and the like were/are of welded
5 steel or stainless steel pipe so as to provide a "tuned" exhaust as known to those skilled in the art. Engine designers continue to have difficulties with current exhaust manifolds of metal design in two distinct arenas. First, during heavy load engine operation exhaust gases can be in excess of 1400°F while the engine block that it is mechanically connected to is held to a maximum of 300°F by the water cooling system. If a cast iron
10 exhaust manifold is allowed to get too hot, the manifold can warp or even crack due to the large loads introduced into it from the large differences in thermal expansion between the two mechanically connected parts. This is due to its higher temperature. The manifold wants to thermally grow to a much larger size than the mechanical connection to the block will allow. This failure allows raw exhaust gases into the engine
15 compartment. This occurrence typically requires replacement of, or removal and repair of the manifold. Although this is not a well known problem, those skilled in the art of engine design will agree that it is a continuing dilemma.

Current technology approaches to alleviating the problem are to utilize a much higher cost stainless steel, which has a substantially lower coefficient of thermal
20 expansion than cast iron, or to reduce the overall temperature of the exhaust manifold by increasing the heat rejected back to the block at the mounting flanges, or to segment the exhaust manifold into sections that slide inside one another so as to provide the manifold with the ability to grow. The segmented exhaust manifolds, however, tend to leak at the joints over time. The second major arena of difficulty for engine designers
25 comes primarily in the marine industry. Here, regulatory requirements dictate maximum allowable engine compartment temperatures and engine "touch" temperatures for in-board marine applications. This typically requires the use of water cooled exhaust manifolds to achieve the regulatory constraints. The main problem associated with this

approach is corrosion of the metal manifold. As a result, water-cooled cast iron manifolds must be replaced much more often than desirable; or, the manifolds must be manufactured of a much more costly stainless steel material.

More recently, for use with engines having higher operating temperatures, the addition of a ceramic liner 20, as shown in Figure 3, has been suggested. For this, the prior art suggests only the use of a monolithic ceramic material. See, for example, the 1995 patent of Ford Motor Company to Hartsock (5,404,721).

Wherefore, it is the object of the present invention to provide such an exhaust manifold made entirely of a structural fiber reinforced ceramic matrix composite (FRCMC) material.

Other objects and benefits of this invention will become apparent from the description which follows hereinafter when read in conjunction with the drawing figures which accompany it.

15 DISCLOSURE OF THE INVENTION

The foregoing objects have been achieved in an exhaust manifold for an internal combustion engine having a plurality of header pipes to be connected to and receiving exhaust gases from respective ones of a plurality of exhaust ports of the engine and a single outlet to be connected to an exhaust pipe or system wherein the exhaust manifold is of a structural fiber reinforced ceramic matrix composite material comprising fibers of a generic fiber system that have been coated with a generic interface material disposed throughout a ceramic matrix.

The preferred resin to create the ceramic matrix is either of the two polymer-derived ceramic resins comprising silicon-carboxyl and alumina silicate or a cementitious resin that has been modified to emulate the processing methods of typical structural polymer composite systems such as monoaluminum phosphate (also known as monoaluminum phosphate) resin. The preferred generic fiber system comprises alumina, Altex, Nextel 312, Nextel 440, Nextel 510, Nextel 550, silicon nitride, silicon carbide,

HPZ, graphite, carbon and peat. The preferred generic interface material comprises carbon, silicon nitride, silicon carboxyl, silicon carbide or boron nitride or a layered combination of one or more of the above interfacial materials.

In another co-pending application entitled METHODS AND APPARATUS FOR
5 MAKING CERAMIC MATRIX COMPOSITE LINED AUTOMOTIVE PARTS AND FIBER
REINFORCED CERAMIC MATRIX COMPOSITE AUTOMOTIVE PARTS by the inventors
herein serial number _____, filed on even date herewith, an improved structural
fiber reinforced ceramic matrix composite (FRCMC) material is disclosed for lining
metal parts such as exhaust manifolds which does not suffer from the problems of failure
10 due to thermal shock, damage from minor impacts, or erosion of a monolithic ceramic
liner. A first aspect is a method for forming a metal part having a breakage resistant
ceramic liner comprising the steps of, forming a metal part having a mating surface for
receiving the liner; forming a liner of a ceramic material containing pores; filling the pores
with a pre-ceramic polymer resin; firing the pre-ceramic polymer resin saturated liner at
15 a temperature and for a time (designated by the resin manufacturer) which converts the
resin into a ceramic within the pores; and, bonding the ceramic liner to the mating
surface of the metal part.

In one embodiment, the step of forming the liner of a ceramic material containing
pores comprises pouring an inexpensive castable cementitious slurry into a liner-shaped
20 mold, firing the molded slurry material for a time and at a temperate which converts it
into a handleable pre-ceramic form, removing the pre-ceramic form from the mold, and
firing the pre-ceramic form for a time and at a temperate which converts it into a ceramic
form containing pores formed by out-gassing. And, the step of filling the pores with a
polymer-derived ceramic resin comprises placing the liner into a bath containing a liquid
25 pre-ceramic polymer resin until the pores are saturated with the resin. Preferably, the
resin is silicon-carboxyl resin (sold by Allied-Signal under the trade name Blackglas).

In a second embodiment, the step of forming the liner of a ceramic material
containing pores comprises positioning a fiber preform into a liner-shaped mold to occupy

30% to 60% of the volume of the mold, forcing a liquid pre-ceramic polymer resin through the preform to fill the remaining volume of the mold with the liquid pre-ceramic polymer resin, firing the mold for a time and at a temperate which converts it into a handleable pre-ceramic form, removing the pre-ceramic form from the mold, and firing
5 the pre-ceramic form for a time and at a temperate which converts the liquid pre-ceramic polymer resin into a ceramic matrix composite form containing pores formed by outgassing. Preferably, the liquid pre-ceramic polymer resin is silicon-carboxyl resin, e.g. Blackglas.

A second aspect of the present invention is a method for forming a metal part
10 having a breakage resistant ceramic liner comprising the steps of, forming a liner of a ceramic material containing pores; filling the pores with a pre-ceramic polymer resin; firing the pre-ceramic polymer resin saturated liner at a temperature and for a time (as designated by the resin manufacturer), which converts the resin into a ceramic within the pores; positioning the liner within a mold for the metal part with the mating surface of
15 the liner facing into a portion of the mold to be occupied by the metal forming the part; and, filling the mold with molten metal to form the part.

As with the first aspect, the step of forming the liner of a ceramic material containing pores can comprise either approach described above. And, the step of filling the pores with a polymer-derived ceramic resin again comprises placing the liner into a
20 bath containing a liquid pre-ceramic polymer resin until the pores are saturated with the resin; firing the pre-ceramic polymer resin saturated liner at a temperature and for a time which converts the resin into a ceramic within the pores.

In all cases where the pores formed by outgassing are filled, it is preferred to repeat the pore-filling and re-heating process several times to virtually totally remove the
25 pores from the final product.

In another aspect of the present invention, a method of making a fiber reinforced ceramic matrix composite automotive part is disclosed comprising the steps of, forming a preform in the shape of the part from fibers of a generic fiber system employable in

fiber reinforced ceramic matrix composites; placing the preform in a cavity of a mold having the shape of the part; forcing a liquid polymer-derived ceramic resin through the cavity to fill the cavity and saturate the preform; heating the mold at a temperature and for a time associated with the polymer-derived ceramic resin which transforms the liquid
5 polymer-derived ceramic resin-saturated preform into a polymer composite part; removing the polymer composite part from the mold; and, firing the polymer composite part in an inert atmosphere at a temperature and for a time associated with the polymer-derived ceramic resin which transforms the polymer-derived ceramic resin into a ceramic whereby the polymer composite part is transformed into a fiber reinforced ceramic matrix
10 composite part.

Preferably, the method also includes the steps of, immersing the fiber reinforced ceramic matrix composite part containing pores formed by outgassing during firing into a bath of the liquid polymer-derived ceramic resin to fill the pores with the liquid polymer-derived ceramic resin; firing the fiber reinforced ceramic matrix composite part
15 in an inert atmosphere at a temperature and for a time associated with the polymer-derived ceramic resin which transforms the polymer-derived ceramic resin in the pores into a ceramic; and, repeating this process until the pore density within the final fiber reinforced ceramic matrix composite part is less than a pre-established percentage affording maximum strength to the part.

20 The preferred method is also adaptable to forming hollow parts such as engine manifolds by employing the steps of, forming a first preform in the shape of a lower portion of the manifold from fibers of a generic fiber system employable in fiber reinforced ceramic matrix composites; placing the first preform in a cavity of a first mold having the shape of the lower portion of the manifold; forcing a liquid polymer-derived
25 ceramic resin through the cavity to fill the cavity and saturate the first preform; heating the first mold at a temperature and for a time associated with the polymer-derived ceramic resin which transforms the liquid polymer-derived ceramic resin-saturated first preform into a first polymer composite part; removing the first polymer composite part

from the mold; forming a second preform in the shape of an upper portion of the manifold from fibers of the generic fiber system; placing the second preform in a cavity of a second mold having the shape of the upper portion of the manifold; forcing the liquid polymer-derived ceramic resin through the cavity to fill the cavity and saturate the second preform; heating the second mold at a temperature and for a time associated with the polymer-derived ceramic resin which transforms the liquid polymer-derived ceramic resin-saturated second preform into a second polymer composite part; removing the second polymer composite part from the mold; fitting the first polymer composite part and the second polymer composite part together along mating edges to form the manifold as a hollow conduit-shaped part; and, firing the polymer composite manifold in an inert atmosphere at a temperature and for a time associated with the polymer-derived ceramic resin which transforms the polymer-derived ceramic resin into a ceramic whereby the polymer composite manifold is transformed into a fiber reinforced ceramic matrix composite manifold and the upper portion and the lower portion are fused together along the mating edges. Pores formed by outgassing are preferably sealed in the manner described above to give maximum strength to the resultant manifold and seal any leakage that may exist along the mating edges.

Where the manifold is an exhaust manifold to be internally filled with a ceramic foam catalyst substrate structure the process and required tooling can be greatly simplified by prior to the step of placing the second preform in a cavity of a second mold having the shape of the upper portion of the manifold additionally including the steps of, placing the first preform as part of a cavity-defining wall of the second mold; and, placing the ceramic foam catalyst substrate structure in the first preform whereby the first preform and the ceramic foam catalyst substrate structure in combination form part of the cavity of the second wall.

Thus, in the interest of engine weight, and the like, an exhaust manifold entirely of a ceramic material would be highly desirable.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a simplified plan view of a typical exhaust manifold structure.

Figure 2 is a cross section through the exhaust manifold of Figure 1 in the plane II/III/IV-II/III/IV when the manifold is a prior art metal manifold.

5 Figure 3 is a cross section through the exhaust manifold of Figure 1 in the plane II/III/IV-II/III/IV when the manifold is a prior art metal manifold having a monolithic ceramic liner on the inner walls thereof.

Figure 4 is a cross section through the exhaust manifold of Figure 1 in the plane II/III/IV-II/III/IV when the manifold is an all FRCMC manifold according to the present
10 invention.

Figure 5 is a partially cutaway drawing of a mold showing how the all FRCMC manifold of the present invention can have additional structural metal members attached thereto by molding them in place.

15 BEST MODE FOR CARRYING OUT THE INVENTION

According to the present invention and as also employed in the engine mentioned above, the exhaust manifold 10' of Figure 4 is made entirely from a FRCMC structure that eliminates the strain intolerance and notch sensitivity of conventional prior art monolithic ceramic structures. The FRCMC of this invention employs any of several
20 polymer-derived ceramic resins (hereinafter used interchangeably with the term pre-ceramic polymer resin) commercially available such as silicon-carboxyl resin (sold by Allied-Signal under the trade name Blackglas), alumina-silicate resin (sold by Applied Poceramics under the trade name C02) or cementitious systems that have been modified to emulate the processing methods of typical structural polymer composite systems such
25 as monoaluminum phosphate (aka monoaluminophosphate) resin combined with a generic fiber system (hereinafter used interchangeably with the term reinforcing fibers) such as, but not limited to, alumina, Altex, Nextel 312, Nextel 440, Nextel 510, Nextel 550, silicon nitride, silicon carbide, HPZ, graphite, carbon, and peat. To accomplish the

objectives of the present invention, the fiber system is first coated to 0.1 to 5.0 microns thickness with an interface material such as, but not limited to, carbon, silicon nitride, silicon carboxyl, silicon carbide, or boron nitride. The interface material prevents the resin from adhering directly to the fibers of the fiber system. Thus, when the resin has been
5 converted to a ceramic, there is a weak disbond layer between the ceramic and fibers imparting the desired more ductile qualities to the final FRCMC.

Thus, according to the present invention, the steps of constructing a breakage resistant, heat resistant, corrosion resistant, low heat rejection, ceramic exhaust manifold comprise applying the interface material on the fiber system as per best industry
10 standards, mixing the interface-coated fiber system with the resin, forming the manifold as per best industry practices used in the fabrication of structural polymer composite hardware, and firing the resultant part at a high temperature per material supplier specifications to convert the resin into a ceramic.

There are a number of distinct advantages offered by a FRCMC internal
15 combustion engine exhaust manifold over current metal and potential monolithic ceramic manifolds, they are as follows:

- 1) Being that the manifold is a ceramic, it inherently has a better insulating capability than it's metallic counterpart, thus reducing engine compartment heat load.
- 2) Being that the manifold is a ceramic, it has a substantially lower coefficient
20 of thermal expansion than it's metallic counterpart, thus reducing the thermally induced loads on the manifold from top extreme temperature differential between the engine block and the manifold.
- 3) Being that the manifold is a ceramic, it is inherently corrosion resistant.
- 4) Being that the manifold is a ceramic, it inherently is more temperature
25 resistant than it's metallic counterpart.
- 5) Being that the manifold is a ceramic, it inherently is substantially lighter than it's metallic counterpart (FRCMC is lower density than aluminum, i.e. approximately 0.08 pounds/cubic inch).

6) Being that the manifold is a fiber reinforced composite with a fiber interface coating, it is substantially more strain tolerant (ductile) than it's monolithic ceramic counterpart.

7) Being that the manifold is a fiber reinforced composite with a fiber interface
5 coating, it is substantially less notch sensitive than it's monolithic ceramic counterpart.

8) Being that the manifold is a fiber reinforced composite with a fiber interface coating, it is substantially more breakage resistant than it's monolithic ceramic counterpart.

9) Being that the manifold is a fiber reinforced composite with a fiber interface
10 coating, it's strength characteristics can be tailored via choice of fiber, interface coating, and fiber orientation.

10) Being that the manifold is a fiber reinforced composite with a fiber interface coating, it's coefficient of thermal expansion can be tailored to better match that of the engine block via selection of fiber system.

15 11) Being that the manifold is a fiber reinforced ceramic matrix composite with a fiber interface coating, it's material properties do not degrade as a function of temperature in the manifold operating temperature range as does it's metallic counterpart.

12) Being that the manifold is a fiber reinforced ceramic matrix composite with
20 a fiber interface coating, it is more resistant to damage resulting from thermal shock than it's monolithic ceramic counterpart.

Example: Fabrication of a FRCMC Exhaust Manifold

1. Lay-up either a pair of half-manifolds (upper and lower halves) to be joined
25 at a later step or a total manifold from woven cloth matting of fibers, such as, but not limited to, alumina, Altex, Nextel 312, Nextel 440, Nextel 510, Nextel 550, silicon nitride, silicon carbide, HPZ, graphite, carbon, and peat.

2. The half manifolds or total manifold fiber preform then have a fiber interface

coating applied as per industry best practices. The fiber could have been coated prior to forming the fiber manifold shapes. The assignee of this application, Northrop Corporation, currently has a number of patents on the application of interface coatings, including, U.S. Patent No. 5,034,181, entitled APPARATUS FOR METHOD OF
5 MANUFACTURING PREFORMS; U.S. Patent No. 5,110,771, entitled METHOD OF FORMING A PRECRACKED FIBER COATING FOR TOUGHENING CERAMIC FIBER-MATRIX COMPOSITES; U.S. Patent No. 5,275,984, entitled FIBER COATING OF UNBONDED MULTI-LAYERS FOR TOUGHENING CERAMIC FIBER-MATRIX COMPOSITES; U.S. Patent No. 5,162,271, entitled METHOD OF FORMING A DUCTILE FIBER COATING
10 FOR TOUGHENING NON-OXIDE CERAMIC MATRIX COMPOSITES; and U.S. Patent No. 5,221,578, entitled WEAK FRANGIBLE FIBER COATING WITH UNFILLED PORES FOR TOUGHENING CERAMIC FIBER-MATRIX COMPOSITES, the teachings of which are incorporated herein by reference. Also, Allied-Signal or Sinterials are commercial companies which will apply an interface coating as a purchased service.

15 3. The half-manifolds or total manifold are then saturated with the resin, in this example being Blackglas resin. This step may also include squeezing the mixture of polymer-derived ceramic resin and interface material-coated fibers of a generic fiber system under pressure into a mold to form the manifold shaped structure.

 4. The resin-saturated half-manifolds or total manifold is then heated as per the
20 following cycle:

- A) Ramp from ambient to 150°F at 2.7°/minute
- B) Hold at 150°F for 30 minutes
- C) Ramp at 1.7°/minute to 300°F
- D) Hold at 300°F for 60 minutes
- 25 E) Cool at 1.2°/minute until temperature is below 140°F.

It should be noted that there are a variety of heat-up cycle definitions which will create usable product and the foregoing is by way of one example only and not intended to be exclusive.

5. If half-manifolds were made, they are snapped or fitted together along mating edges at this point to form a total manifold. The two pieces now fitted together are dipped in Blackglas resin for a minimum of five minutes. The part is then removed from the resin and heated as per the previous ramp-up rate to hold the edges together.

5 6. The polymer composite manifold is then pyrolyzed. In this regard, fabrication of a sealable container, such as a stainless steel box, capable of withstanding 1900°F is required for the pyrolysis cycle in a standard furnace. In the alternative, an inert gas furnace could be used if available. The box should have two tubing connections, one on the bottom and one on the top to allow the box to be flooded with an inert gas. In this
10 example, the manifold is placed in the box, the box placed in a standard furnace, stainless steel tubing is connected to the lower connector on the box and to a supply of high purity argon. Any equivalent inert gas could, of course, be used. The argon is allowed to flow into the box, and out the top vent at a rate of 5-10 standard cubic feet per hour for the entire heat cycle, thus assuring the manifold is totally enveloped in an
15 inert environment. The furnace is closed and fired on the following basis:

- A) Ramp to 300°F at 223°/hour
- B) Ramp to 900°F at 43°/hour
- C) Ramp to 1400°F at 20°/hour
- D) Ramp to 1600°F at 50°/hour
- 20 E) Hold at 1600°F for 4 hours
- F) Ramp to 77°F at -125°/hour

Again, there are a variety of heating schedules other than this one, given by way of example only, which will yield usable hardware.

7. Upon cooling, the manifold is removed from the furnace and box and
25 submerged in a bath of Blackglas resin for enough time to allow all air to be removed from the manifold (typically 5 minutes or more). A vacuum infiltration step may also be used for this step. This fills any pores caused by outgassing or shrinkage of the matrix in the FRCMC manifold with the resin.

8. Steps 6 and 7 are then repeated until the level of porosity is below a desired level which imparts the maximum strength to the final FRCMC manifold. Typically, it is preferred that this cycle be repeated five times. The manifold is then ready for use.

Figure 5 depicts an alternate aspect of the present invention which can be employed, if desired, to augment the strength of the resultant manifold. Being a ceramic material, the manifold 10' can be subjected to molten metal without damage. Thus, one can make a basic manifold 10' as described above which does not have completed flanges 12, for example. As depicted in Figure 5, the basic manifold 10' is then positioned within a mold 22. Molten metal 24 is then poured into the mold 22. The metal 24 flows around the encased portions of the FRCMC manifold 10' capturing them within the metal as it hardens thus forming the flanges 12 and/or, if desired, a strong-back system 26 which can be bolted to the automobile to support the manifold 10' against excessive bending forces from the exhaust system and the like.

WHAT IS CLAIMED IS:

1. A method of making a high temperature resistant fiber reinforced ceramic matrix composite exhaust manifold for an engine comprising the steps of:

- 5 a) forming a liner of a castable monolithic ceramic material containing pores;
b) filling the pores of the castable monolithic ceramic material with a pre-ceramic polymer resin;
c) coating reinforcing fibers with an interface material to prevent a pre-ceramic polymer resin from adhering strongly to the reinforcing fibers;
10 d) forming a mixture of a pre-ceramic polymer resin and reinforcing fibers coated with the interface material;
e) forming an exhaust manifold shaped structure from the mixture of the pre-ceramic polymer resin and the reinforcing fibers coated with the interface material by placing the mixture on at least a portion of the castable monolithic ceramic material;
15 and,
f) firing the exhaust component shaped structure at a temperature and a time sufficient to convert the pre-ceramic polymer resin to a ceramic thereby forming a reinforced ceramic composite.

20 2. The method of claim 1 wherein said step of coating reinforcing fibers with an interface material comprises:

coating the reinforcing fibers with 0.1 to 5.0 microns thickness of at least one layer of the interface material of at least one of carbon, silicon nitride, silicon carbide, silicon carboxide, or boron nitride.

25

3. The method of claim 1 wherein said step of coating reinforcing fibers with an interface material comprises:

coating reinforcing fibers of at least one of alumina, Altex, Nextel 312,

Nextel 440, Nextel 510, Nextel 550, silicon nitride, silicon carbide, carbon, or peat with the interface material.

4. The method of claim 1 wherein said step of forming a mixture of the pre-ceramic polymer resin and the reinforcing fibers coated with the interface material comprises:

mixing the reinforcing fibers coated with the interface material with a material chosen from the group consisting of pre-ceramic polymer resins commercially available such as silicon-carboxyl resin, alumina-silicate resin or monoaluminum phosphate resin.

5. The method of claim 1 wherein said step of forming an exhaust manifold shaped structure from the mixture of the pre-ceramic polymer resin and reinforcing fibers coated with the interface material comprises:

squeezing the mixture of the pre-ceramic polymer resin and the reinforcing fibers coated with the interface material under pressure into a mold to form the manifold shaped structure prior to firing.

6. The method of claim 1 and, after said step (d) thereof of firing additionally comprising the steps of:

a) positioning the ceramic manifold in a mold; and,
b) pouring molten metal into the mold around portions of the ceramic manifold to add additional structural components of metal to the ceramic manifold.

7. A method of making a high temperature resistant fiber reinforced ceramic matrix composite exhaust manifold for an engine comprising the steps of:

a) forming a liner of a castable monolithic ceramic material containing pores;
b) filling the pores of the castable monolithic ceramic material with a pre-

ceramic polymer resin;

c) coating reinforcing fibers with an interface material to prevent a pre-ceramic polymer resin from adhering directly to the reinforcing fibers, the reinforcing fibers comprising fibers of at least one of alumina, Nextel 312, Nextel 440, Nextel 510, 5 Nextel 550, silicon nitride, silicon carbide, HPZ, graphite, carbon, or peat, the interface material comprising a few microns thickness of at least one of carbon, silicon nitride, silicon carbide, silicon carboxide, or boron nitride;

d) forming a mixture of a pre-ceramic polymer resin chosen from the group consisting of silicon-carboxyl resin, monoaluminum phosphate resin, or alumina silicate 10 resin and the reinforcing fibers coated with the interface material;

e) forming an exhaust manifold shaped structure from the mixture of the pre-ceramic polymer resin and the reinforcing fibers coated with the interface material by placing the mixture on at least a portion of the castable monolithic ceramic material; and,

15 f) firing the exhaust manifold shaped structure at a temperature and for a time sufficient to convert the pre-ceramic polymer resin to a ceramic thereby forming a reinforced ceramic composite.

8. The method of claim 7 wherein said step of forming a mixture of a pre-ceramic polymer resin and reinforcing fibers coated with the interface material comprises: 20 saturating a woven cloth matting of the reinforcing fibers coated with the interface material and the pre-ceramic polymer resin.

9. The method of claim 8 wherein said step of forming an exhaust manifold 25 shaped structure from the mixture of the pre-ceramic polymer resin and the reinforcing fibers coated with the interface material additionally includes the step of:

squeezing the woven cloth matting of the reinforcing fibers coated with the interface material and saturated with the pre-ceramic polymer resin in a mold under

pressure prior to firing.

10. The method of claim 7 and, after said step (d) of firing additionally comprising the steps of:

- 5 a) positioning the manifold in a mold; and,
 b) pouring molten metal into the mold around portions of the manifold to add additional structural metal components to the manifold.

11. A method of making a high temperature resistant fiber reinforced ceramic
10 matrix composite exhaust manifold for an engine comprising the steps of:

- a) forming a liner of a castable monolithic ceramic material containing pores;
 b) filling the pores of the castable monolithic ceramic material with a pre-ceramic polymer resin;
 c) coating reinforcing fibers with an interface material to prevent a pre-
15 ceramic polymer resin from adhering directly to the reinforcing fibers, the reinforcing fibers comprising fibers of at least one of alumina, Nextel 312, Nextel 440, Nextel 510, Nextel 550, silicon nitride, silicon carbide, HPZ, graphite, carbon, or peat, the interface material comprising 0.1 to 5.0 microns thickness of at least one of carbon, silicon nitride, silicon carbide, silicon carboxide, or boron nitride;
20 d) forming a mixture of silicon-carboxyl resin and the reinforcing fibers coated with the interface material;
 e) forming an exhaust manifold shaped structure from the mixture of the silicon-carboxyl resin and the reinforcing fibers coated with the interface material by placing the mixture on at least a portion of the castable monolithic ceramic material; and,
25 f) firing the exhaust manifold shaped structure at a temperature and for a time sufficient to convert the silicon-carboxyl to a ceramic.

12. The method of claim 11 wherein said step of forming a mixture of silicon-

carboxyl resin and reinforcing fibers coated with the interface material comprises:

saturating a woven cloth matting of the reinforcing fibers coated with the interface material with the silicon-carboxyl resin.

5 13. The method of claim 12 wherein said step of forming an exhaust manifold shaped structure from the mixture of the silicon-carboxyl resin and reinforcing fibers coated with the interface material additionally includes the step of:

squeezing the woven cloth matting of the reinforcing fibers coated with the interface material and saturated with the silicon-carboxyl resin in a mold under pressure
10 prior to firing.

14. The method of claim 11 and, after said step (d) of firing additionally comprising the steps of:

a) immersing the fired manifold into a bath of silicon-carboxyl resin to fill
15 pores formed by outgassing therein with the silicon-carboxyl resin;

b) refiring the manifold at a temperature and for a time sufficient to convert the silicon-carboxyl to a ceramic; and,

c) repeating steps (a) and (b) until the remaining volume of pores formed by outgassing is below an amount which maximizes the strength of the manifold.
20

15. The method of claim 11 and, after said step (d) of firing additionally comprising the steps of:

a) positioning the manifold in a mold; and,

b) pouring molten metal into the mold around portions of the manifold
25 to add additional structural metal components to the manifold.

16. The method of claim 15 and, after said step (c) additionally comprising the steps of:

- a) positioning the manifold in a mold; and,
- b) pouring molten metal into the mold around portions of the manifold to add additional structural metal components to the manifold.

5 17. The method of claim 1 wherein said step of coating reinforcing fibers with an interface material comprises:

coating reinforcing fibers with the interface material, wherein said reinforcing fibers comprises ceramic fibers capable of withstanding high processing temperatures associated with converting the pre-ceramic polymer resin to a ceramic
10 matrix in an inert environment.

18. The method of claim 4 wherein said step of forming a mixture of pre-ceramic polymer resin and the reinforcing fibers coated with the interface material comprises:

15 mixing the reinforcing fibers coated with the interface material with a modified cementitious pre-ceramic polymer resin emulating the processing methods of structural polymer composite systems.

19. The method of claim 1 wherein the step of forming an exhaust manifold
20 comprises:

forming an exhaust manifold shaped structure from the mixture of the pre-ceramic polymer resin and the reinforcing fibers coated with the interface material by placing the mixture on an inside portion of the castable monolithic ceramic material.

25 20. The method of claim 1 wherein the step of forming an exhaust manifold comprises:

forming an exhaust manifold shaped structure from the mixture of the pre-ceramic polymer resin and the reinforcing fibers coated with the interface material by placing the

mixture on an outside portion of the castable monolithic ceramic material.

21. The method of claim 1 wherein the step of forming an exhaust manifold comprises:

- 5 forming an exhaust manifold shaped structure from the mixture of the pre-ceramic polymer resin and the reinforcing fibers coated with the interface material by placing the mixture around the castable monolithic ceramic material.

10 22. The method of claim 7 wherein the step of forming an exhaust manifold comprises:

forming an exhaust manifold shaped structure from the mixture of the pre-ceramic polymer resin and the reinforcing fibers coated with the interface material by placing the mixture on an inside portion of the castable monolithic ceramic material.

15 23. The method of claim 7 wherein the step of forming an exhaust manifold comprises:

forming an exhaust manifold shaped structure from the mixture of the pre-ceramic polymer resin and the reinforcing fibers coated with the interface material by placing the mixture on an outside portion of the castable monolithic ceramic material.

20

24. The method of claim 7 wherein the step of forming an exhaust manifold comprises:

forming an exhaust manifold shaped structure from the mixture of the pre-ceramic polymer resin and the reinforcing fibers coated with the interface material by placing the
25 mixture around the castable monolithic ceramic material.

25. The method of claim 11 wherein the step of forming an exhaust manifold comprises:

forming an exhaust manifold shaped structure from the mixture of the pre-ceramic polymer resin and the reinforcing fibers coated with the interface material by placing the mixture on an inside portion of the castable monolithic ceramic material.

5 26. The method of claim 11 wherein the step of forming an exhaust manifold comprises:

forming an exhaust manifold shaped structure from the mixture of the pre-ceramic polymer resin and the reinforcing fibers coated with the interface material by placing the mixture on an outside portion of the castable monolithic ceramic material.

10

27. The method of claim 11 wherein the step of forming an exhaust manifold comprises:

forming an exhaust manifold shaped structure from the mixture of the pre-ceramic polymer resin and the reinforcing fibers coated with the interface material by placing the
15 mixture around the castable monolithic ceramic material.

28. A high temperature resistant fiber reinforced ceramic matrix composite exhaust manifold for an engine comprising:

a castable monolithic ceramic liner containing pores saturated with a pre-
20 ceramic polymer resin in a ceramic state;

reinforcing fibers coated with an interface material for preventing a pre-ceramic polymer resin from adhering strongly to the reinforcing fibers;

an exhaust manifold shaped structure formed from a mixture comprising a pre-ceramic polymer resin and the reinforcing fibers coated with the interface material;

25 and

wherein the mixture is disposed on at least a portion of the castable monolithic ceramic material.

AMENDED CLAIMS

[received by the International Bureau on 11 November 1996 (11.11.96);
original claims 1,3,6-7,10,11,14-16 and 18-28 amended;
remaining claims unchanged (9 pages)]

1. A method of making a high temperature resistant fiber reinforced ceramic matrix composite exhaust manifold for an engine comprising the steps of:

5 a) forming a liner of a cast monolithic ceramic material containing pores;
b) filling the pores of the cast monolithic ceramic material with a pre-ceramic polymer resin;

c) coating reinforcing fibers with an interface material to prevent a pre-ceramic polymer resin from adhering strongly to the reinforcing fibers;

10 d) forming a mixture of a pre-ceramic polymer resin and reinforcing fibers coated with the interface material;

e) forming an exhaust manifold shaped structure from the mixture of the pre-ceramic polymer resin and the reinforcing fibers coated with the interface material by placing the mixture on at least a portion of the cast monolithic ceramic
15 material; and,

f) firing the exhaust component shaped structure at a temperature and a time sufficient to convert the pre-ceramic polymer resin to a ceramic thereby forming a reinforced ceramic composite.

20 2. The method of claim 1 wherein said step of coating reinforcing fibers with an interface material comprises:

coating the reinforcing fibers with 0.1 to 5.0 microns thickness of at least one layer of the interface material of at least one of carbon, silicon nitride, silicon carbide, silicon carboxide, or boron nitride.

25

3. The method of claim 1 wherein said step of coating reinforcing fibers with an interface material comprises:

coating reinforcing fibers of at least one of alumina, high purity alumina, alumina boro silicate, mullite, alumina silicate, silicon nitride, silicon carbide, carbon, or peat with the interface material.

5 4. The method of claim 1 wherein said step of forming a mixture of the pre-ceramic polymer resin and the reinforcing fibers coated with the interface material comprises:

 mixing the reinforcing fibers coated with the interface material with a material chosen from the group consisting of pre-ceramic polymer resins commercially
10 available such as silicon-carboxyl resin, alumina-silicate resin or monoaluminum phosphate resin.

 5. The method of claim 1 wherein said step of forming an exhaust manifold shaped structure from the mixture of the pre-ceramic polymer resin and reinforcing
15 fibers coated with the interface material comprises:

 squeezing the mixture of the pre-ceramic polymer resin and the reinforcing fibers coated with the interface material under pressure into a mold to form the manifold shaped structure prior to firing.

20 6. The method of claim 1 and, after said step (f) thereof of firing additionally comprising the steps of:

- a) positioning the ceramic manifold in a mold; and,
- b) pouring molten metal into the mold around portions of the ceramic manifold to add additional structural components of metal to the ceramic manifold.

25

7. A method of making a high temperature resistant fiber reinforced ceramic matrix composite exhaust manifold for an engine comprising the steps of:

a) forming a liner of a cast monolithic ceramic material containing pores;

b) filling the pores of the cast monolithic ceramic material with a pre-
5 ceramic polymer resin;

c) coating reinforcing fibers with an interface material to prevent a pre-ceramic polymer resin from adhering directly to the reinforcing fibers, the reinforcing fibers comprising fibers of at least one of alumina, high purity alumina, alumina boro silicate, mullite, alumina silicate, silicon nitride, silicon carbide, HPZ, graphite, carbon,
10 or peat, the interface material comprising a few microns thickness of at least one of carbon, silicon nitride, silicon carbide, silicon carboxide, or boron nitride;

d) forming a mixture of a pre-ceramic polymer resin chosen from the group consisting of silicon-carboxyl resin, monoaluminum phosphate resin, or alumina silicate resin and the reinforcing fibers coated with the interface material;

15 e) forming an exhaust manifold shaped structure from the mixture of the pre-ceramic polymer resin and the reinforcing fibers coated with the interface material by placing the mixture on at least a portion of the cast monolithic ceramic material; and,

f) firing the exhaust manifold shaped structure at a temperature and for a
20 time sufficient to convert the pre-ceramic polymer resin to a ceramic thereby forming a reinforced ceramic composite.

8. The method of claim 7 wherein said step of forming a mixture of a pre-ceramic polymer resin and reinforcing fibers coated with the interface material

25 comprises:

 saturating a woven cloth matting of the reinforcing fibers coated with the interface material and the pre-ceramic polymer resin.

9. The method of claim 8 wherein said step of forming an exhaust manifold shaped structure from the mixture of the pre-ceramic polymer resin and the reinforcing fibers coated with the interface material additionally includes the step of:
squeezing the woven cloth matting of the reinforcing fibers coated with
5 the interface material and saturated with the pre-ceramic polymer resin in a mold under pressure prior to firing.

10. The method of claim 7 and, after said step (f) of firing additionally comprising the steps of:
10 a) positioning the manifold in a mold; and,
b) pouring molten metal into the mold around portions of the manifold to add additional structural metal components to the manifold.

11. A method of making a high temperature resistant fiber reinforced ceramic
15 matrix composite exhaust manifold for an engine comprising the steps of:
a) forming a liner of a cast monolithic ceramic material containing pores;
b) filling the pores of the cast monolithic ceramic material with a pre-ceramic polymer resin;
c) coating reinforcing fibers with an interface material to prevent a pre-
20 ceramic polymer resin from adhering directly to the reinforcing fibers, the reinforcing fibers comprising fibers of at least one of alumina, high purity alumina, alumina boro silicate, mullite, alumina silicate, silicon nitride, silicon carbide, HPZ, graphite, carbon, or peat, the interface material comprising 0.1 to 5.0 microns thickness of at least one of carbon, silicon nitride, silicon carbide, silicon carboxide, or boron nitride;
25 d) forming a mixture of silicon-carboxyl resin and the reinforcing fibers coated with the interface material;

e) forming an exhaust manifold shaped structure from the mixture of the silicon-carboxyl resin and the reinforcing fibers coated with the interface material by placing the mixture on at least a portion of the cast monolithic ceramic material; and,
f) firing the exhaust manifold shaped structure at a temperature and for a
5 time sufficient to convert the silicon-carboxyl to a ceramic.

12. The method of claim 11 wherein said step of forming a mixture of silicon-carboxyl resin and reinforcing fibers coated with the interface material comprises:

10 saturating a woven cloth matting of the reinforcing fibers coated with the interface material with the silicon-carboxyl resin.

13. The method of claim 12 wherein said step of forming an exhaust manifold shaped structure from the mixture of the silicon-carboxyl resin and
15 reinforcing fibers coated with the interface material additionally includes the step of:
squeezing the woven cloth matting of the reinforcing fibers coated with the interface material and saturated with the silicon-carboxyl resin in a mold under pressure prior to firing.

20 14. The method of claim 11 and, after said step (f) of firing additionally comprising the steps of:

a) immersing the fired manifold into a bath of silicon-carboxyl resin to fill pores formed by outgassing therein with the silicon-carboxyl resin;
b) refiring the manifold at a temperature and for a time sufficient to
25 convert the silicon-carboxyl to a ceramic; and,
c) repeating steps (a) and (b) until the remaining volume of pores formed by outgassing is below an amount which maximizes the strength of the manifold.

15. The method of claim 11 and, after said step (f) of firing additionally comprising the steps of:

- a) positioning the manifold in a mold; and,
 - b) pouring molten metal into the mold around portions of the
- 5 manifold to add additional structural metal components to the manifold.

16. The method of claim 15 and, after said step (e) additionally comprising the steps of:

- a) positioning the manifold in a mold; and,
 - b) pouring molten metal into the mold around portions of the
- 10 manifold to add additional structural metal components to the manifold.

17. The method of claim 1 wherein said step of coating reinforcing fibers with an interface material comprises:

- 15 coating reinforcing fibers with the interface material, wherein said reinforcing fibers comprises ceramic fibers capable of withstanding high processing temperatures associated with converting the pre-ceramic polymer resin to a ceramic matrix in an inert environment.

20 18. The method of claim 4 wherein said step of forming a mixture of pre-ceramic polymer resin and the reinforcing fibers coated with the interface material comprises:

mixing the reinforcing fibers coated with the interface material with a modified cementitious pre-ceramic polymer resin.

25

19. The method of claim 1 wherein the step of forming an exhaust manifold comprises:

forming an exhaust manifold shaped structure from the mixture of the pre-ceramic polymer resin and the reinforcing fibers coated with the interface material by
5 placing the mixture on an inside portion of the cast monolithic ceramic material.

20. The method of claim 1 wherein the step of forming an exhaust manifold comprises:

forming an exhaust manifold shaped structure from the mixture of the pre-
10 ceramic polymer resin and the reinforcing fibers coated with the interface material by placing the mixture on an outside portion of the cast monolithic ceramic material.

21. The method of claim 1 wherein the step of forming an exhaust manifold comprises:

15 forming an exhaust manifold shaped structure from the mixture of the pre-ceramic polymer resin and the reinforcing fibers coated with the interface material by placing the mixture around the cast monolithic ceramic material.

22. The method of claim 7 wherein the step of forming an exhaust manifold
20 comprises:

forming an exhaust manifold shaped structure from the mixture of the pre-ceramic polymer resin and the reinforcing fibers coated with the interface material by placing the mixture on an inside portion of the cast monolithic ceramic material.

23. The method of claim 7 wherein the step of forming an exhaust manifold
25 comprises:

forming an exhaust manifold shaped structure from the mixture of the pre-ceramic polymer resin and the reinforcing fibers coated with the interface material by placing the mixture on an outside portion of the cast monolithic ceramic material.

5 24. The method of claim 7 wherein the step of forming an exhaust manifold comprises:

forming an exhaust manifold shaped structure from the mixture of the pre-ceramic polymer resin and the reinforcing fibers coated with the interface material by placing the mixture around the cast monolithic ceramic material.

10

25. The method of claim 11 wherein the step of forming an exhaust manifold comprises:

forming an exhaust manifold shaped structure from the mixture of the pre-ceramic polymer resin and the reinforcing fibers coated with the interface material by
15 placing the mixture on an inside portion of the cast monolithic ceramic material.

26. The method of claim 11 wherein the step of forming an exhaust manifold comprises:

forming an exhaust manifold shaped structure from the mixture of the pre-ceramic polymer resin and the reinforcing fibers coated with the interface material by
20 placing the mixture on an outside portion of the cast monolithic ceramic material.

27. The method of claim 11 wherein the step of forming an exhaust manifold comprises:

25 forming an exhaust manifold shaped structure from the mixture of the pre-ceramic polymer resin and the reinforcing fibers coated with the interface material by placing the mixture around the cast monolithic ceramic material.

28. A high temperature resistant fiber reinforced ceramic matrix composite exhaust manifold for an engine comprising:

a cast monolithic ceramic liner containing pores saturated with a pre-ceramic polymer resin in a ceramic state;

5 reinforcing fibers coated with an interface material for preventing a pre-ceramic polymer resin from adhering strongly to the reinforcing fibers;

an exhaust manifold shaped structure formed from a mixture comprising a pre-ceramic polymer resin and the reinforcing fibers coated with the interface material; and

10 wherein the mixture is disposed on at least a portion of the cast monolithic ceramic material.

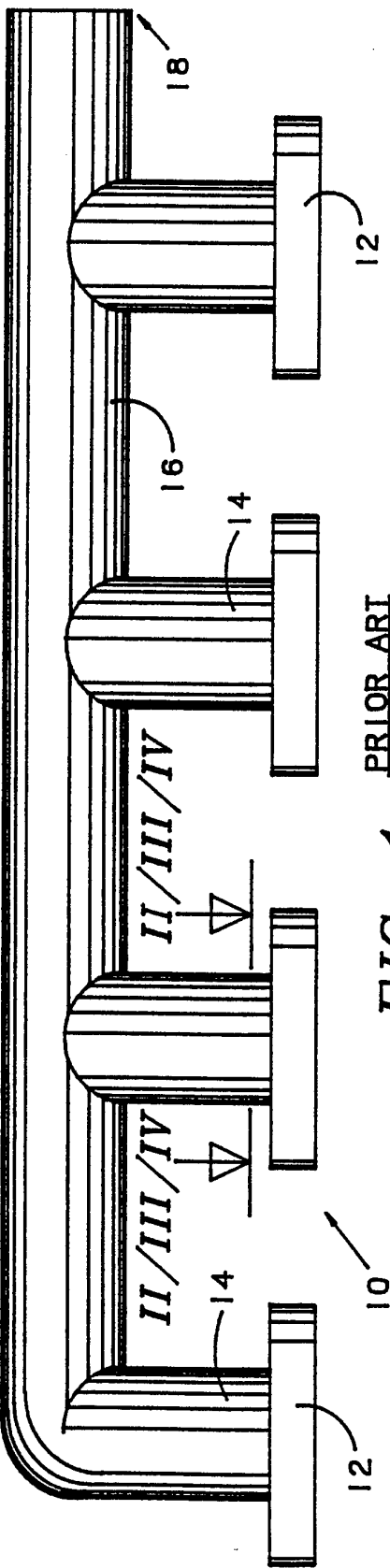


FIG. 1 PRIOR ART

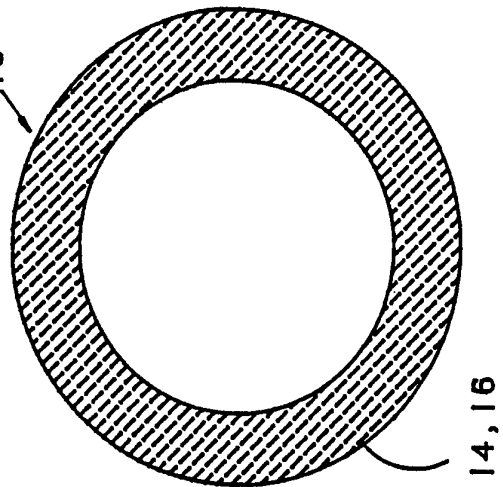
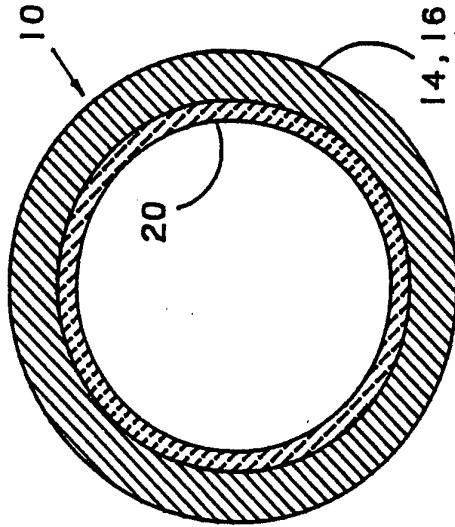
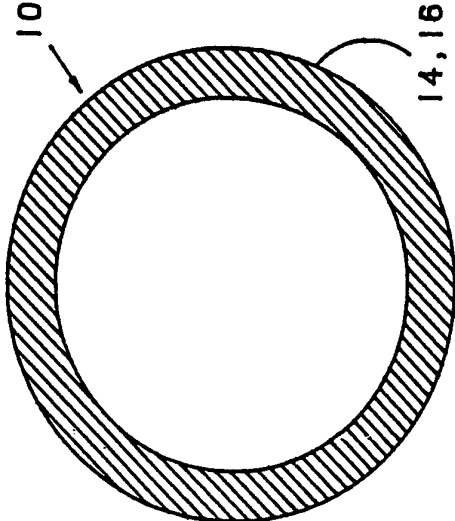


FIG. 4



PRIOR ART

FIG. 3



PRIOR ART

FIG. 2

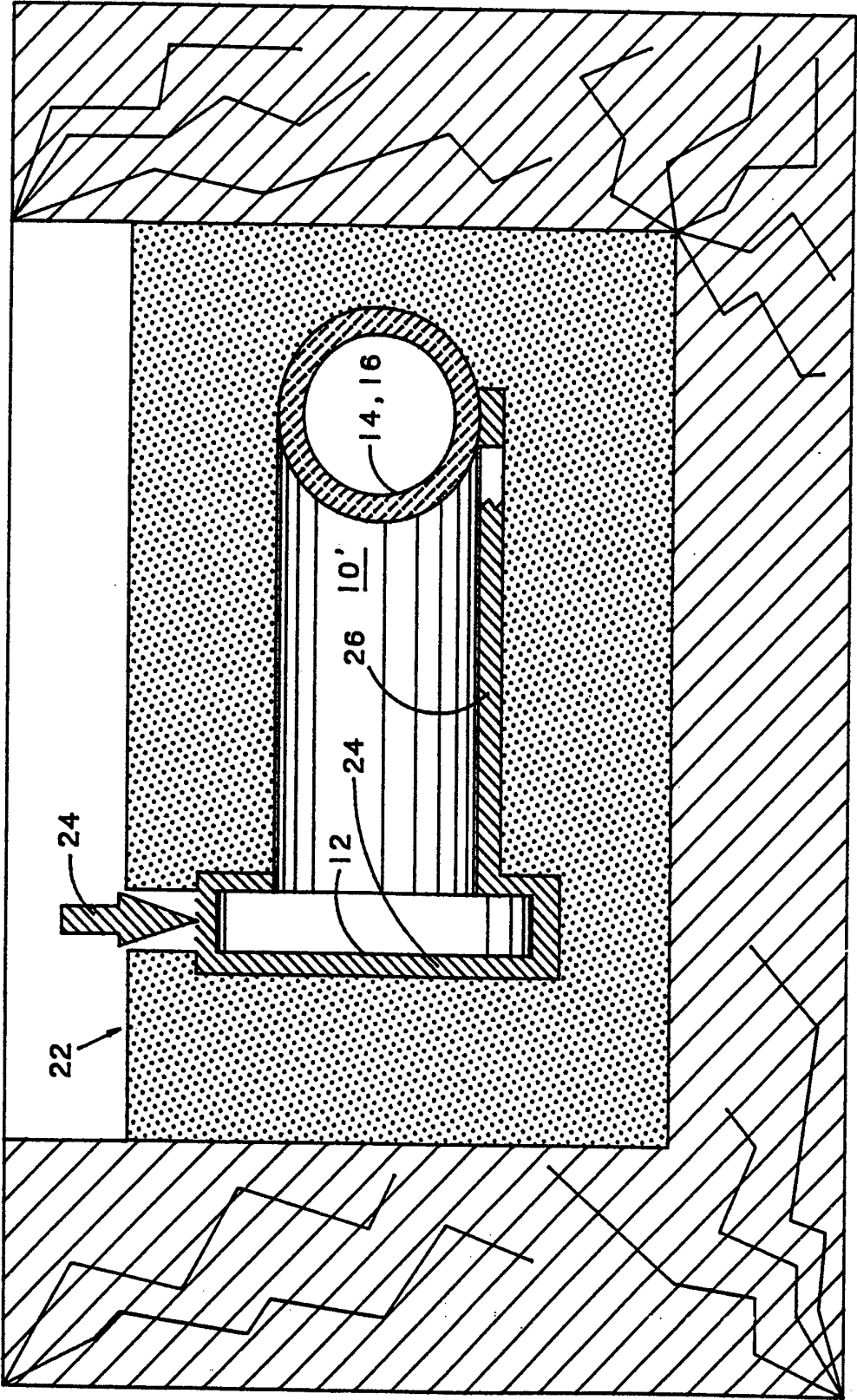


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/11794

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C04B 35/76, 37/00

US CL : 164/97, 98; 264/60; 427/266

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 164/97, 98; 264/60; 427/266, 299, 407.1, 385.1; 428/312.4, 312.6, 307.7, 313.9

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 3,173,451 (Slayter) 16 March 1965, col. 1, lines 39-47.	1-27
A	US, A, 3,488,723 (Veazie) 06 January 1970, figure 8, col. 1, lines 37-47, col. 4, lines 45-51.	1-28
A	US, A, 3,714,971 (Venable, Jr.) 25 January 1971, col. 1, lines 33-41 and 54-72.	1-28
A	US, A, 3,749,591 (Hider et al.) 31 July 1973.	1-28
A	US, A, 3,956,531 (Church et al.) 11 May 1976, see entire document.	1-28
A	US, A, 4,210,617 (Bowman) 01 July 1980, abstract.	1-28

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 06 SEPTEMBER 1996	Date of mailing of the international search report 27 SEP 1996
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer FR RANDOLPH S. HERRICK Telephone No. (703) 308-2687 <i>Sheila Vene</i> Paralegal Specialist Group 5200

INTERNATIONAL SEARCH REPORT

 International application No.
 PCT/US96/11794

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,511,612 (Huther et al.) 16 April 1985, abstract, col. 1, lines 19-40.	1-28
A	US, A, 4,206,598 (Rao et al.) 10 June 1980, abstract, col. 1, lines 6+.	1-28
A	US, A, 4,245,611 (Mitchell et al.) 20 January 1981.	1-28
A	US, A, 4,341,826 (Prewo et al.) 27 July 1982, abstract, col. 1, lines 29-30 and 62-65, col. 2, lines 62-68.	1-28
A	US, A, 4,657,951 (Takarada et al.) 14 April 1987, abstract, col. 2, lines 6-9, 17-33 and 47-54.	1-28
A	US, A, 4,818,732 (Fox et al.) 04 April 1989, abstract.	1-28
A	US, A, 4,884,400 (Tanaka et al.) 05 December 1989, abstract, col. 2, lines 6-9, 17-33 and 47-54.	1-28
A	US, A, 4,928,645 (Berneburg et al.) 29 May 1990, col. 4, lines 19-67.	1-28
A	US, A, 4,972,674 (Yamada et al.) 27 November 1990, abstract, col. 2, lines 5+.	1-28
A	US, A, 5,018,661 (Cyb) 28 May 1991, see entire document.	1-28
A	US, A, 5,066,626 (Fukao et al.) 19 November 1991, abstract, figure 3, col. 1, lines 12-16, col. 2, lines 23-35.	1-28
A	US, A, 5,139,717 (Peuckert et al.) 18 August 1992, col. 1, lines 20-23 and 33-39.	1-28
A	US, A, 5,167,271 (Lange et al.) 01 December 1992, see entire document.	1-28
A	US, A, 5,223,064 (Gadkaree) 29 June 1993, see entire document.	1-28
A	US, A, 5,225,283 (Leung et al.) 06 July 1993, abstract.	1-28
A	US, A, 5,230,924 (Li) 27 July 1993, see entire document.	1-28
A	US, A, 5,231,059 (Leung et al.) 27 July 1993, abstract, col. 6, lines 12-13, 33-38 and 46-50.	1-28

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/11794

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 5,258,084 (Leung et al.) 02 November 1993, abstract, col. 1, lines 28-36, col. 3, lines 24-30, col. 4, lines 4-11, col. 5, line 19, col. 6, lines 24-26, 51-53 and 67-68, col. 7, lines 59-63, col. 8 lines 53-55.	1-28
A	US, A, 5,382,453 (Mason) 17 January 1995, abstract.	1-28