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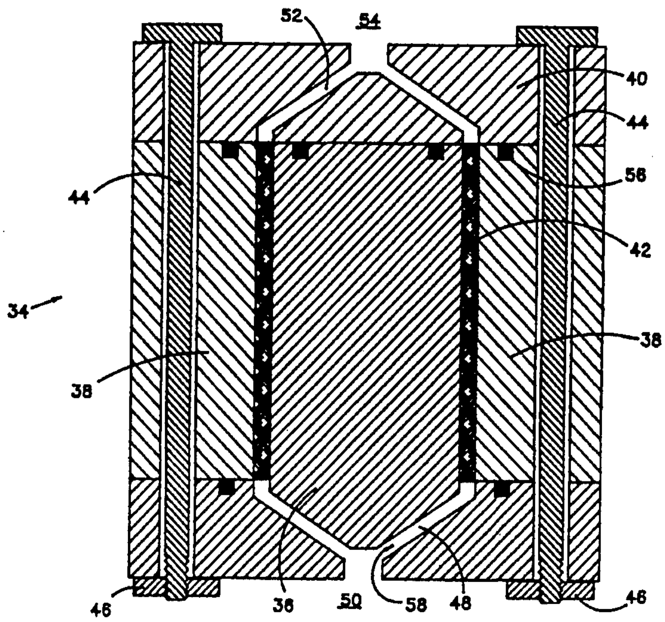

(57) Abstract

This invention relates to making cast metal parts with ceramic liners (12) for automobiles. The present invention solves over-exposure problems of metal parts subjected to increased temperatures and is embodied in a method of forming a ceramic (10) liner (12) for a part comprising the steps of, forming a liner of a ceramic material containing pores; filling the pores with a pre-ceramic polymer resin; and, firing the liner saturated with a pre-ceramic polymer resin at a temperature and for a time which converts the resin into a ceramic within the pores. The liner (12) can be mechanically attached, adhesively bonded, or a metal part can be cast onto the liner (12).

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"Ceramic Liner Infiltrated with Pre-Ceramic Polymer Resin"

TECHNICAL FIELD

This invention relates to the making of cast metal parts with ceramic liners for automobiles and, more particularly, to (1) a method of 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 (hereinafter used interchangeably with the term polymer-derived ceramic resin); firing the pre-ceramic polymer resin saturated liner at a temperature which converts the resin into a ceramic within the pores, and, attaching the ceramic liners to the mating surface of the metal part; (2) to methods for accomplishing the same result 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 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 the liner facing into a portion of the mold to be occupied by metal forming the part; and, filling the mold with molten metal to form the part with an integral, cast-in-place, ceramic insert; and, (3) to a method of forming fiber reinforced ceramic matrix composite (FRCMC) parts and liners comprising the steps of, forming a preform in the shape of the part from fibers of a generic fiber system (hereinafter used interchangeably with the term reinforcing fibers) 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 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 composite part.

BACKGROUND OF THE INVENTION

Operating temperatures of automobile and like internal combustion engines have increased for various reasons such as improved combustion efficiency and reduction of the fuel to air ratio (i.e. leaner burning engines) for the purposes of reducing emitted pollutants resulting from more complete burning of the fuel. Accordingly, there has been a corresponding need to protect metal parts subjected to these increased temperatures. An obvious approach tried with limited success in the prior art is to line the metal parts with ceramic. Thus, for example, we have an exhaust manifold 10 with a monolithic ceramic lining 12 as depicted in Figure 1 and a power head 14 with a ceramic lining 12 as depicted in Figure 2 being known in the prior art.

The problem of this prior art approach can be best understood with reference to Figure 3. As can be seen in the enlarged drawing, the monolithic ceramic material of the lining 12 as employed in the prior art is a porous material having a multitude of pores 16 throughout. Thus, the lining 12 of the prior art is fairly delicate, with nominal erosion resistance, and is easily broken if the part is dropped, struck, or otherwise subjected to a large force. if the lining 12 of the power head 14 breaks and a piece falls off inside the operating engine, the inside of the cylinder of the engine will most likely be heavily scored by the hard ceramic edges bouncing about. For both the power head 14 and the exhaust manifold 10, any gap or break in the ceramic liner will eventually result in damage to or the destruction of the unprotected underlying metal. A crack through the exhaust manifold 10 or through the power head 14 typically will require complete replacement of the part.

Also, the lining of a part with the monolithic ceramic material according to prior art techniques can be a delicate, costly, and time-consuming process.

Wherefore, it is an object of the present invention to provide a ceramic lining for an automotive internal combustion engine part or the like which is toughened to resist breakage and erosion.

It is another object of the present invention to provide a method for applying a ceramic lining to an automotive internal engine part or the like, which is simple, inexpensive, and can be rapidly assembled so as not to impact the high rate manufacturing schedule associated with automotive components.

It is still another object of the present invention to provide a method for applying a ceramic lining to an automotive internal engine part or the like, wherein the lining is cast into the part as part of the molding process.

It is yet another object of the present invention to provide a method for creating fiber reinforced ceramic matrix composite preforms for use in lining automotive internal engine parts and making automotive internal engine parts .

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.

DISCLOSURE OF THE INVENTION

The foregoing objects have been attained in a first aspect of the present invention by the 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 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 cementatious slurry into a liner-shaped 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 outgasssing. And, the step of filling the pores with a polymer-derived ceramic resin comprises placing the liner into a bath containing a liquid 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 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.

The foregoing objects have also been attained in a second aspect of the present invention by the method for forming a metal part 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 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 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 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 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 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 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.

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 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.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a simplified cross section of a prior art monolithic ceramic lined automobile exhaust manifold.

Figure 2 is a simplified cross section of a prior art monolithic ceramic lined automobile power head.

Figure 3 is an enlarged simplified drawing of the monolithic ceramic material employed in the prior art of Figures 1 and 2 depicting the pores contained therein.

Figure 4 is a simplified cross section of a first step in making a ceramic lined automobile part according to the present invention in a first approach.

Figure 5 is a simplified cross section of a second step in making a ceramic lined automobile part according to the present invention.

Figure 6 is a simplified cross section of a third step in making a ceramic lined automobile part according to the present invention.

Figure 7 is a simplified cross section of a third step in making a ceramic lined automobile part according to the present invention in a second approach.

Figure 8 is a simplified cross section of a forth step in making a ceramic lined automobile part according to the present invention in the second approach.

Figure 9 is a functional block diagram of the basic steps of making fiber reinforced ceramic matrix composite preforms for use in practicing the present invention in a preferred approach.

Figure 10 is a functional block diagram of the steps added to the preferred embodiment of the present invention.

Figure 11 is a detailed cross section of a mold used in the preferred embodiment of the present invention for making fiber reinforced ceramic matrix composite preform cylinder sleeves.

Figure 12 is a detailed cross section of a mold used in the preferred embodiment of the present invention for making fiber reinforced ceramic matrix composite preform pistons.

Figure 13 is a detailed cross section of a mold used in the preferred embodiment of the present invention for making fiber reinforced ceramic matrix composite preform cylinder head liners.

Figure 14 is a simplified cross section of a mold used in the preferred embodiment of the present invention for making one half of a fiber reinforced ceramic matrix composite manifold.

Figure 15 is a simplified cross section of a mold used in the preferred embodiment of the present invention for making the mating half of a fiber reinforced ceramic matrix composite manifold.

Figure 16 is a simplified cross section showing how the two halves of the manifold produced in Figures 14 and 15 are connected and fused together during firing.

Figure 17 is a simplified cross section of a mold used in the preferred embodiment of the present invention for making the mating half of a fiber reinforced ceramic matrix composite manifold when the first half and a ceramic foam core are used as part of the mold to reduce the necessary tooling.

BEST MODES FOR CARRYING OUT THE INVENTION

According to one aspect of the present invention, the typical prior art ceramic lining as described above is toughened against breakage by making it as a polymer-derived ceramic matrix composite (CMC) material. In a conventional polymer-derived CMC, a generic fiber system is disbursed throughout a pre-ceramic polymer resin. The mixture is then fired at a temperature and for a time as recommended by the material supplier in order to convert the resin into a ceramic material thereby forming the part of a fiber reinforced ceramic matrix composite (FRCMC) material. In this aspect of the present invention, low strength, porous ceramic material is substituted for the fiber system in the following manner.

One technique for lining a metal part with ceramic is to make a mold 18 having a mating surface 20 shaped to fit the metal part as depicted in Figure 4. After molding, the resultant liner 12 is then fit into the metal part in its intended position and mechanically held or bonded in place using commercially available high temperature adhesives or the like. To use this approach according to the present invention, the liner 12 is cast in the usual manner as depicted in Figure 4 using a cementatious slurry material such as, but not limited to, that commercially sold under the trade name Ceramacast by AREMCO. The cast liner 12 is fired in the usual manner as taught by the manufacturer to form the low strength ceramic liner 12'. According to the present invention, the ceramic liner 12' is then immersed in a vessel 22 containing a bath of a pre-ceramic polymer resin 24. The preferred resin 24 is a pre-ceramic polymer, silicon-carboxyl resin (sold by Allied Signal under the trade name Blackglas). The Blackglas resin has a viscosity substantially equal to water. Thus, it easily penetrates and fills the pores 16. Many liquid resin materials have a more honey-like viscosity. Such resins cannot fill the pores 16 and, therefore, will not attain the objects of the present invention. When the resin 24 has saturated the pores 16 of the ceramic liner 12', the liner 12' is again fired at a temperature and for a time as taught by the manufacturer of the resin, which converts the resin 24 into a ceramic within the pores 16, thereby creating the CMC liner 12". The CMC liner 12" can then be bonded into its mating part 26 as depicted in Figure 6.

In an alternate approach as depicted in Figures 7 and 8, the process is greatly simplified and the resultant interface between the liner 12" and its associated part 26 is strengthened by casting the metal part 26 directly onto/around the pre-existing toughened CMC liner 12'. The liner 12 is first cast as in Figure 4. After the steps described above with respect to Figure 5 of firing the liner 12 to form the liner 12', filling the pores 16 with resin 24, and firing the liner 12' to create the CMC liner 12", the CMC liner 12" is placed within a mold 30 compatible for casting metal 32 for the part 26 as depicted in Figure 7 facing into the space of the mold 30 to be occupied by the metal. The mold 30 is then filled with molten metal 32 as depicted in Figure 8 to form the part 26 with the liner 12" firmly held in place within the metal 32 when the metal 32 cools and hardens. Since the liner 12" is a toughened CMC, it is able to withstand the temperatures of the metal molding process without being damaged thereby.

Having thus described alternate methods for improving the strength of ceramic automotive parts liners and for casting liners directly into metal automotive parts, a preferred Resin Transfer Molding (RTM) method and apparatus for forming automotive parts or liners therefor of a ceramic matrix composite material according to a preferred embodiment of the present invention will now be described in detail. A functional block diagram of the steps of the basic RTM approach is depicted in Figure 9.

The first step is to form a shaped preform from the generic fiber system that is to be used. This is then inserted into a preform mold and the mold sealed. In the preferred approach, the generic fiber system occupies from 30% up to about 60% of the internal volume of the mold. As an alternative, but not preferred, approach, the mold can be filled with generic fiber chop to the same packing density by volume. A pre-ceramic polymer resin is then forced through the fibers to fill the remaining internal volume of the mold. The preferred resin is the previously described pre-ceramic polymer, silicon-carboxyl resin sold by Allied Signal under the trade name Blackglas This is because of its low viscosity which allows it to be forced through and saturate a high volume density of the generic fiber preform. The tighter the fiber density, the stronger the part will be. Thus, to use a resin of higher viscosity, the packing density of the fibers would have to be greatly reduced, resulting in a corresponding reduction in the strength of the part.

The resin impregnated preform within the mold is then heated to a level and for a time sufficient to polymerize the resin saturating the fiber preform. The preform is then like a bisque-ware in ceramics such that it does not have its full strength as yet, but can be handled. The polymer preform is removed from the mold and then fired at a temperature and for a time as set forth by the manufacturer of the resin so as to ceramitize the polymer. The part or liner in its basic form is thus formed as a ceramic matrix composite having preferably about 50-60% by volume of fiber content therein.

The firing process which turns the polymer to ceramic causes the formation of pores due to outgassing which takes place during the firing process. The resultant ceramic part is about 70% solid and 30% pores formed by outgassing. In this regard, it is much like the monolithic ceramics previously used to line automotive parts. The fiber reinforced ceramic matrix composite parts are, of course, much stronger than the monolithic parts because of the high fiber content. The same technique, however, can be used to make the parts even stronger. According to the preferred embodiment of the present invention, that is just what is done as depicted in Figure 10. The ceramic preform is immersed in liquid Blackglas resin (or an equivalent). The water-like viscosity of the resin causes it to fill the 30% pores in the part. The part is then fired once again for the time and at the temperature indicated by the manufacturer of the resin. This causes the resin within the 30% pores to be turned to ceramic. But, the firing process causes 30% of the 30% volume to be outgassed. So, the part is once again immersed in the liquid resin and fired for a third time. This process can be repeated until the pore removal has achieved a desired level. The resultant part is about 95%-98% ceramic and fibers with no outgassed pores to speak of. Thus, it is of maximum strength.

An RTM mold 34 for making fiber reinforced ceramic matrix composite cylinder sleeves according to the above-described process is depicted in Figure 11. The mold 34 includes a base/mandrel tool portion 36 that defines the bottom and cylindrical center of the mold. Two semi-cylindrical half-side portions 38 define the sleeve mold internal volume in combination with the base/mandrel tool portion 36. An upper cap tool 40 closes and seals the mold. The sleeve fiber preform 42 is slipped over the cylindrical center of the base/mandrel tool portion 36. The two half-side portions 38 are positioned around the preform 42 and the upper cap tool 40 put in its position. The entire mold 34 is then held together by the through bolts 44 and nuts 46.

The mold internal volume occupied by the preform 42 is connected by a series of feed bores 48 to a resin reservoir at 50. The upper cap tool 40 contains a series of drain bores 52 connecting the internal mold volume to a vacuum source at 54. Because of the water-like consistency of the resin, internal leakage between the components must be prevented by O-rings 56 as necessary.

With the mold 34 closed and sealed with the preform 42 in place, the vacuum source 54 is activated for creating a vacuum and the path to the resin reservoir 50 is opened. Resin 58 under pressure is forced into the mold 34 and through the preform 42 from the combined pressure and the vacuum from the vacuum source 54 until the preform 42 is totally saturated with the resin 58. The entire mold 34 is then heated to polymerize the resin 58. The mold 34 is then disassembled by reversing the above-described process to release the polymerized preform 42 from the mold 34.

Figure 12 depicts a mold 34′ employed to produce a piston which is all ceramic composite matrix material according to an RTM process. The preform 42′ is a piston-shape having cylindrical sidewalls and a closed top. The base/mandrel tool portion 36 has a modified central portion as shown which fits the internal shape of the piston preform 42′. Other than that, the mold 34′ and manner of using it are as described above for the mold 34 of Figure 11.

For a generally planar object such as a liner for a cylinder head, a mold 34" as depicted in Figure 13 can be used. In this case, the mandrel portion is unnecessary. Thus, the mold 34" comprises a base tool portion 36′ in combination with a cap tool portion 40′. Also, more bores 48 and 52 may be required to get full saturation of the preform 42".

A fully closed conduit type of part, such as a manifold, can be made according to the same RTM process of the present invention. Several aspects of the making of such a part are depicted in Figures 14-17. In Figures 14 and 15, we see two molds 34"′ each producing half of the manifold. The mold 34"′ of Figure 14 produces the top half and the mold 34"′ of Figure 15 produces the bottom half according to the above-described process. The two polymerized half-preforms 42"′ are then "snapped" together as depicted in Figure 16. When they are subsequently fired to ceramitize the resin, the two side joints are fused together thereby joining the two preforms 42"′ into a single ceramic part.

In the case of an exhaust manifold incorporating a ceramic foam 60 as a catalyst substrate, the shaped foam in combination with the bottom half preform 42"′ can be used as part of the mold 34"" thereby greatly simplifying the tooling of the mold cap 40" as well as the assembly process.

Having thus described the present invention in general terms, three specific examples of parts as built and tested by the inventors herein will now be described.

Example 1: Fabrication of a FRCMC Cylinder Sleeve

1. Fabricate or purchase a cylindrical preform of the requisite size (there are a number of U.S. vendors that weave fiber preforms for composite applications) from 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. The preform should be made so that when loaded in the mold tool, it takes up between 30% and 60% of the open volume within the closed tool. In the example, the preform was hand-constructed by the inventors.

2. The preform then had a fiber interface coating applied to it as per industry

best practices. 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 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 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 Synterials are commercial companies which will apply an interface coating as a purchased service. In the example, the interface coating was applied by the inventors as described in the above-referenced, co-pending application.

3. The cylindrical preform was then placed on the mandrel portion of the tool and the mold closed and sealed around it. It should be noted that in some instances such as with high fiber volume preforms, a hydraulic press or the like may be needed to close the mold.

4. The lower feed holes in the mold should be connected via flexible tubing with a valve to a container containing Blackglas resin. The upper vent hole was attached via flexible clear tubing with a valve to a vacuum source. Both valves were initially opened to allow the resin to be sucked up through the mold.

5. The container with the Blackglas resin was pressurized above 15 PSI, i.e. above atmospheric pressure, to create a positive pressure tending to force the resin through the mold. When the resin was flowing through the mold with no air bubbles present in the tubing on the vacuum (exit) side, both valves were closed.

6. The mold with the enclosed preform and resin mixture was then heated as per the 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

E) Cool at 1.2°/minute until temperature is below 140°F for part demolding.

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.

7. Upon cool-down of the mold, the mold was disassembled and the polymer composite component removed from the mold for pyrolysis.

NOTE: The previous seven steps identify a Resin Transfer Molding (RTM) approach to preparing the polymer composite component. Other applicable approaches to create the same part are Hand-Lay-up, Pultrusion, Filament Winding, Toe Placement, or Short Fiber Injection. These are all valid Polymer Composite Manufacturing Techniques to be included within the scope and spirit of the present invention and the claims appended hereto. These various techniques are not claimed to be inventive of the inventors herein in and of themselves and only the total method being described and claimed is novel to these inventors and this application.

8. The polymer composite component was then pyrolized. 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 example, the sleeve was placed in the box, the box placed in a standard furnace, stainless steel tubing was 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 was allowed to flow into the box, and out the top vent at a rate of 5-10 SCFH for the entire heat cycle, thus assuring the sleeve was

totally bathed in an argon environment. The furnace was 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

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.

9. Upon cooling, the sleeve was removed from the furnace and box and submerged in a bath of Blackglas resin for enough time to allow all air to be removed from the sleeve (typically 5 minutes or more). A vacuum infiltration step may also be used for this step.

10. Step 8 was repeated.

11. Step 9 was repeated.

12. Step 8 was repeated.

13. Step 9 was repeated.

14. Step 8 was repeated.

15. Step 9 was repeated.

16. Step 8 was repeated.

17. The sleeve was now ready for pre-wear coating application machining. The sleeve was honed (commercial grade diamond cutting stones recommended) to a inner diameter which was between 0.004" and .070" oversized that of the finished sleeve bore dimension. If the sleeve is intended for use in a 2-stroke engine, the intake and exhaust ports should be cut at this time using conventional machining practices (commercial grade diamond coated milling tools recommended). Upon the completion of

the machining processes, all sharp edges on the internal surface of the sleeve should be knocked down using diamond paper.

18. The sleeve was then placed in an oven for a time and at a temperature adequate to assure "burn off" of any of the cutting lubricants used in the machining process. (Typically 2 hours @700°F, but is lubricant dependent.)

19. The sleeve was now ready for the application of the wear coating as described in co-pending application serial number ______________________ filed on ________________ entitled REDUCING WEAR BETWEEN STRUCTURAL FIBER REINFORCED CERAMIC MATRIX COMPOSITE AUTOMOTIVE ENGINE PARTS IN SLIDING CONTACTING RELATIONSHIP In a first embodiment for coating the surface of the sleeve with a wear-resistant coating, a woven or non-woven cloth mat of fibers is employed. In this embodiment, the contacting surfaces of the structural fiber reinforced ceramic matrix composite component are covered with an erosion-resistant coating which bonds tightly to the wearing surface of the FRCMC structures. For this purpose, the erosion-resistant coating preferably comprises Mullite (i.e. alumina silicate Al_2Si_4), alumina (i.e. Al_2O_3), or equivalent, applied via a plasma spray generally according to techniques well known to those of ordinary skill in the art.

The erosion-resistant coating is applied as follows. Prior to the application of the erosion-resistant coating, all holes for spark plugs, valves, wrist pins, etc. are machined. Commercial grade diamond cutting tools are recommended for this purpose. Any other machining as described later is also done at this point. Upon the completion of the machining processes, if any, all sharp edges on the surface of the part are knocked down using diamond paper.

If the part has been machined, it is placed in an oven for a time and temperature adequate to assure "burn off" of any of the cutting lubricants used in the machining process. (Typically 2 hours A 700°F, but is lubricant dependent.)

The key is getting the erosion-resistant coating to bond to the FRCMC structure. If the surface of the FRCMC structure is not properly prepared, the erosion-resistant coating can simply flake off and provide no long-term protection. In the preferred approach, the surface of the FRCMC structure is lightly grit-blasted to form small divots within the ceramic matrix of the FRCMC structure. It is also believed that the light grit blasting exposes hairs or whiskers on the exposed fiber of the generic fiber system which the erosion-resistant coating can grip and adhere thereto. Typical grit blasting that has proved successful is 100 grit @ 20 PSI.

According to a second possible approach, the surface of the FRCMC structure can be provided with a series of thin, shallow, regularly-spaced grooves similar to fine "threads" of a nut or bolt, which the erosion-resistant coating can mechanical lock into. Essentially, the surface is scored to provide a roughened surface instead of a smooth surface. The depth, width, and spacing of the grooves is not critical and can be determined for each part or component without undue experimentation. In general, the grooves should be closely spaced so as to minimize any large smooth areas of the surface where there is a potential for the erosion-resistant coating to lose its adhesion and flake off. Thus, over-grooving would be preferable to under-grooving the surface with the exception that over-grooving requires the application of additional wear material to provide a smooth wear surface after final grinding. The grooves should be shallow so as to provide a mechanical locking area for the erosion-resistant coating without reducing the structural strength of the underlying FRCMC structure to any appreciable degree.

After surface preparation, the part is cleaned by using clean dry compressed air and then loaded in an appropriate holding fixture for the plasma spray process. Direct air blowers are used to cool the opposite side of the part during the application of the erosion-resistant coating.

The plasma sprayed erosion-resistant coating is then applied using a deposition rate set to 5 grams per minute or more. The holding fixture speed, plasma gun movement rate across the surface, and spray width are set to achieve a barber pole spray pattern with 50% overlap. The spray gun is set relative to the sprayed surface from 0.1 inches to 3 inches away. Particle sizes used for this process range from 170 to 400 mesh. Enough material is applied to allow for finish machining.

After the application of the erosion-resistant coating, the coated surface is smoothed out with diamond paper or an appropriate form tool (commercial grade diamond tools recommended) to achieve the final surface contour.

In an alternative embodiment, the erosion-resistant material in powder form may be dispersed within the matrix material (i.e. the resin) prior to forming the component for improved wear resistance. Alternatively, the plasma sprayed coating can be applied and then the part with the erosion-resistant coating attached can be further reinfiltrated with the pre-ceramic polymer resin and then converted to a ceramic state. The result is an additional toughening of the coating by essentially incorporating the coating into the mixed or combined ceramic matrix composite formed from the combination of the FRCMC and a ceramic matrix reinforced monolithic wear coating integrally bound together by the common ceramic matrix. The sleeve was grit-blasted using a grit and pressure adequate to remove any loose matrix material and expose the fibers within the CMC. (Typically 100 grit @ 20 PSI).

20. The sleeve was then cleaned by using clean dry compressed air.

21. The sleeve was then loaded in a rotation table fixture which rotated the sleeve around its centerline for the plasma spray process.

22. Direct air blowers were used to cool the outside of the sleeve while minimizing any air blowing through any of the porting where applicable.

23. The plasma sprayed wear coating was then applied using a deposition rate set to 5 grams per minute or more. The table rotation speed, plasma gun axial movement rate (in and out of the sleeve), and spray width were set to achieve a barber pole spray pattern with 50% overlap. The spray gun was set relative to the sprayed surface from 0.1 inches to 3 inches away. Particle sizes used for this process ranged from 170 to 400 mesh. Enough material was applied to achieve an undersized bore component.

24. After the application of the wear coating, the sleeve was honed (commercial

grade diamond stones recommended) to achieve the final sleeve bore. At this point, the sleeve was ready for installation into an engine block.

Example 2: Fabrication of a FRCMC Piston

1. A CMC piston was formed using RTM according to the same procedure as the cylinder sleeve of Example 1 for steps 1 through 16 thereof.

2. The component was now ready for pre-wear coating application machining. The piston was machined (commercial grade diamond cutting stones recommended) to a outer contour which was between 0.004" and .070" undersize that of the finished piston outer dimension. Upon the completion of the machining processes, all sharp edges on the surface of the piston were knocked down using diamond paper.

3. The piston was then be placed in an oven for a time and at a temperature adequate to assure "burn off" of any of the cutting lubricants used in the machining process. (Typically 2 hours @700°F, but is lubricant dependent.)

4. The piston was now ready for the application of the wear coating substantially as described in Example 1 with the exception that the sleeve was wear-coated on its inner surface, i.e. the one in sliding contact with the piston, while the piston was wear-coated on its exterior surface, i.e. the one in sliding contact with the sleeve. The exterior surface of the piston was grit-blasted using a grit and pressure adequate to remove any loose matrix material and expose the fibers within the CMC. (Typically 100 grit @ 20 PSI).

5. The piston was then cleaned by using clean dry compressed air.

6. The piston was then loaded in a rotation table fixture for the plasma spray process.

7. Direct air blowers were used to cool the inside of the piston.

8. The plasma sprayed wear coating was then applied using a deposition rate set to 5 grams per minute or more. The table rotation speed, plasma gun axial movement rate (up and down the piston), and spray width were set to achieve a barber pole spray

pattern with 50% overlap. The spray gun was set relative to the sprayed surface from 0.1 inches to 3 inches away. Particle sizes used for this process ranged from 170 to 400 mesh. Both the piston skirt and top were coated. Enough material was applied to achieve an oversized outside piston diameter.

9. After the application of the wear coating, the piston was turned (commercial grade diamond tools recommended) to achieve the final piston outer contour, ring grooves cut using a diamond cutting wheel, and any additional machining requirements as a function of the piston design. The completed piston was now ready for installation into an engine.

Example 3: Fabrication of a FRCMC Head/Headliner

1. A CMC cylinder head liner and a CMC cylinder head were formed using RTM according to the same procedure as the cylinder sleeve of Example 1 for steps 1 through 16 the thereof.

2. The components were now ready for pre-wear coating application machining. At this time and prior to the application of the wear coating, all holes (spark plug, valves etc.) were machined (commercial grade diamond cutting tools recommended). Upon the completion of the machining processes, all sharp edges on the surface of the head/headliner were knocked down using diamond paper.

3. The head/headliner were placed in an oven for a time and temperature adequate to assure "burn off" of any of the cutting lubricants used in the machining process. (Typically 2 hours @700°F, but is lubricant dependent)

4. The combustion chamber side of the head/headliner were grit-blasted using a grit and pressure adequate to remove any loose matrix material and expose the fibers within the CMC. (Typically 100 grit @ 20 PSI).

5. The head/headliner were cleaned by using clean dry compressed air.

6. The head/headliner were then loaded in a holding fixture for the plasma spray process.

7. Direct air blowers were used to cool the non-combustion chamber side of the head/headliner.

8. The plasma sprayed wear coating was then applied using a deposition rate set to 5 grams per minute or more. The holding fixture lateral speed, plasma gun vertical movement rate (up and down the surface), and spray width were set to achieve a barber pole spray pattern with 50% overlap. The spray gun was set relative to the sprayed surface from 0.1 inches to 3 inches away. Particle sizes used for this process ranged from 170 to 400 mesh. Enough material was applied to allow for finish machining.

9. After the application of the wear coating, the head/headliner combustion chamber area was smoothed out with diamond paper or an appropriate form tool (commercial grade diamond tools recommended) to achieve the final inner contour. In the case of the cylinder head, the block mating surface of the head was also machined flat at this point and was ready for use.

10. In the case of the headliner, the component was then bonded within it's metallic mate. It could, of course, also been cast into the metallic mate. After installation with it's mate, the block mating surface of the headliner was also machined flat. The ceramic-lined metal cylinder head was then ready for use.

WHAT IS CLAIMED IS:

1. A method of forming a breakage and erosion-resistant ceramic liner for a part comprising the steps of:

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

b) filling the pores with a pre-ceramic polymer resin; and

c) firing the liner filled with the pre-ceramic polymer resin for a time and at a temperature sufficient to convert the polymer resin to a ceramic within the pores thereby forming a reinforced ceramic composite.

2. The method of claim 1 wherein said step of forming the liner of a ceramic material containing pores comprises:

a) pouring a slurry cementatious ceramic material into a mold; and,

b) firing the slurry material for a time and at a temperature sufficient to sinter the slurry material into a porous ceramic liner.

3. The method of claim 1 wherein said step of filling the pores with a pre-ceramic polymer resin comprises:

placing the liner into a container containing a liquid pre-ceramic polymer resin having a viscosity substantially equal to water until the pores are saturated with the resin.

4. The method of claim 1 wherein said step of filling the pores with a pre-ceramic polymer resin comprises:

placing the liner into a bath containing silicon-carboxyl resin.

5. A method of forming a metal part having a breakage and erosion resistant ceramic liner comprising the steps of:

a) forming a metal part having a mating surface for receiving the liner;

b) forming a liner of a castable monolithic ceramic material containing pores;

c) filling the pores with a pre-ceramic polymer resin;

d) firing the liner saturated with the pre-ceramic polymer resin for a time and at a temperature sufficient to convert the resin to a ceramic within the pores thereby forming a reinforced ceramic composite; and,

e) bonding the ceramic liner to the mating surface of the metal part.

6. The method of claim 5 wherein said step of forming the liner of a ceramic material containing pores comprises:

a) pouring a cementations slurry material into a mold; and,

b) firing the slurry material for a time and at a temperature sufficient to sinter the slurry material into a porous ceramic liner.

7. The method of claim 5 wherein said step of filling the pores with a pre-ceramic polymer resin comprises:

placing the liner into a container containing a liquid pre-ceramic polymer resin having a viscosity substantially equal to water until the pores are saturated with the resin.

8. The method of claim 5 wherein said step of filling the pores with a pre-ceramic polymer resin comprises: placing the liner into a container containing silicon-carboxyl resin.

9. A method of forming a metal part having a breakage resistant ceramic liner

comprising the steps of:

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

b) filling the pores with a pre-ceramic polymer resin;

c) firing the liner saturated with the pre-ceramic polymer resin for a time and at a temperature sufficient to convert the polymer resin to a ceramic within the pores thereby forming a reinforced ceramic composite;

d) positioning the liner within a mold for the metal part with the mating surface of the liner facing into a portion of the mold to be occupied by metal forming the part; and,

e) filling the mold with molten metal to form the part in combination with the liner.

10. The method of claim 9 wherein said step of forming the liner of a ceramic material containing pores comprises:

a) pouring a cementatious ceramic slurry material into a mold, and,

b) firing the slurry material for a time and at a temperature sufficient to sinter the slurry material into a porous ceramic liner.

11. The method of claim 9 wherein said step of filling the pores with a pre-ceramic polymer resin comprises:

placing the liner into a bath containing a liquid pre-ceramic polymer resin having a viscosity substantially equal to water until the pores are saturated with the resin.

12. The method of claim 9 wherein said step of filling the pores with a pre-ceramic polymer resin comprises:

placing the liner into a bath containing silicon-carboxyl resin.

13. A heat resistant, erosion resistant, non-fragile ceramic-lined exhaust manifold for an internal combustion engine comprising:

a) a metal manifold defining an exhaust gas-conducting conduit having inner walls; and,

b) said inner walls of said conduit being lined with a ceramic material having pores wherein said pores contain a pre-ceramic polymer resin in a ceramic state.

14. The heat-resistant, erosion resistant, non-fragile ceramic-lined exhaust manifold of claim 13 wherein:

said pre-ceramic polymer resin comprises silicon-carboxyl resin in its ceramic state.

15. A heat-resistant, erosion resistant, non-fragile ceramic-lined power head for an internal combustion engine comprising:

a) a metal power head having a cylinder-facing surface; and,

b) said cylinder-facing surface of said power head being lined with a ceramic material having pores wherein said pores contain a pre-ceramic polymer resin in a ceramic state.

16. The heat-resistant, erosion resistant, non-fragile ceramic-lined power head of claim 15 wherein:

said pre-ceramic polymer resin comprises silicon-carboxyl resin in its ceramic state.

17. A fiber reinforced ceramic matrix composite automotive part derived by:

a) forming a fiber preform in the shape of the part from reinforcing fibers employable in fiber reinforced ceramic matrix composites;

b) placing the preform in a cavity of a mold having the shape of the part;

c) forcing a liquid pre-ceramic polymer resin through the cavity to fill the cavity and saturate the preform;

d) heating the mold for a time and at a temperature sufficient to transform the preform saturated with the liquid pre-ceramic polymer resin to a polymer composite part;

e) removing the polymer composite part from the mold; and,

f) firing the polymer composite part in an inert atmosphere for a time and at a temperature sufficient to transform the pre-ceramic polymer resin to a ceramic whereby the polymer composite part is transformed into a fiber reinforced ceramic matrix composite part.

18. The automotive part of claim 17 and after step (f) thereof additionally derived by:

g) immersing the fiber reinforced ceramic matrix composite part containing pores formed by outgassing during firing into a bath of the liquid pre-ceramic polymer resin to fill the pores with the liquid pre-ceramic polymer resin;

h) firing the fiber reinforced ceramic matrix composite part in an inert atmosphere for a time and at a temperature sufficient to transform the pre-ceramic polymer resin in the pores to a ceramic; and,

i) repeating steps (g) and (h) until the pore density within the final fiber reinforced ceramic matrix composite part is less than a preestablished percentage affording maximum strength to the part.

19. A fiber reinforced ceramic matrix composite engine manifold derived by:

a) forming a first preform in a shape of a lower portion of the manifold from reinforcing fibers employable in fiber reinforced ceramic matrix composites;

b) placing the first preform in a cavity of a first mold having the shape of the lower portion of the manifold;

c) forcing a liquid pre-ceramic polymer resin through the cavity to fill the cavity and saturate the first preform;

d) heating the first mold for a time and at a temperature sufficient to transform the first preform saturated with the liquid pre-ceramic polymer resin to a first polymer composite part;

e) removing the first polymer composite part from the mold;

f) forming a second preform in a shape of an upper portion of the manifold from the reinforcing fibers;

g) placing the second preform in a cavity of a second mold having the shape of the upper portion of the manifold;

h) forcing the liquid pre-ceramic polymer resin through the cavity to fill the cavity and saturate the second preform;

i) heating the second mold for a time and at a temperature sufficient to transform the second preform saturated with the liquid pre-ceramic polymer resin to a second polymer composite part;

j) removing the second polymer composite part from the mold;

k) 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,

i) firing the polymer composite manifold in an inert atmosphere for a time and at a temperature sufficient to transform the pre-ceramic polymer resin to 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.

20. The engine manifold of claim 19 and after step (l) thereof additionally derived by:

m) immersing the fiber reinforced ceramic matrix composite manifold containing pores formed by outgassing during firing into a bath of the liquid pre-ceramic polymer resin to fill the pores with the liquid pre-ceramic polymer resin;

n) firing the fiber reinforced ceramic matrix composite manifold in an inert atmosphere for a time and at a temperature sufficient to transform the pre-ceramic polymer resin in the pores to a ceramic; and,

o) repeating steps (m) and (n) until the pore density within the final fiber reinforced ceramic matrix composite manifold is less than a pre-established percentage affording maximum strength to the part.

21. A method of making a fiber reinforced ceramic matrix composite engine manifold comprising the steps of:

a) forming a first preform in a shape of a lower portion of the manifold from reinforcing fibers employable in fiber reinforced ceramic matrix composites;

b) placing the first preform in a cavity of a first mold having the shape of the lower portion of the manifold;

c) forcing a liquid pre-ceramic polymer resin through the cavity to fill the cavity and saturate the first preform;

d) heating the first mold for a time and at a temperature sufficient to transform the first preform saturated with the liquid pre-ceramic polymer resin to a first polymer composite part;

e) removing the first polymer composite part from the mold;

f) forming a second preform in a shape of an upper portion of the manifold from the reinforcing fibers;

g) placing the second preform in a cavity of a second mold having the shape of the upper portion of the manifold;

h) forcing the liquid pre-ceramic polymer resin through the cavity to fill the cavity and saturate the second preform;

i) heating the second mold for a time and at a temperature sufficient to transform the second preform saturated with the liquid pre-ceramic polymer resin to a second polymer composite part;

j) removing the second polymer composite part from the mold;

k) 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;

i) firing the polymer composite manifold in an inert atmosphere for a time and at a temperature sufficient to transform the pre-ceramic polymer resin to 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;

wherein the manifold is an exhaust manifold internally filled with a ceramic foam catalyst substrate structure and prior to said step (g) 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:

f1) placing the first preform as part of a cavity-defining wall of the second mold; and,

f2) 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.

AMENDED CLAIMS

[received by the International Bureau on 8 November 1996 (08.11.96); original claims 1, 5, 9, 15, and 16 amended; remaining claims unchanged (8 pages)]

1. A method of forming a breakage and erosion-resistant ceramic liner for a part comprising the steps of:

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

b) filling the pores with a pre-ceramic polymer resin; and

c) firing the liner filled with the pre-ceramic polymer resin for a time and at a temperature sufficient to convert the polymer resin to a ceramic within the pores thereby forming a reinforced ceramic composite.

2. The method of claim 1 wherein said step of forming the liner of a ceramic material containing pores comprises:

a) pouring a slurry cementatious ceramic material into a mold; and,

b) firing the slurry material for a time and at a temperature sufficient to sinter the slurry material into a porous ceramic liner.

3. The method of claim 1 wherein said step of filling the pores with a pre-ceramic polymer resin comprises:

placing the liner into a container containing a liquid pre-ceramic polymer resin having a viscosity substantially equal to water until the pores are saturated with the resin.

4. The method of claim 1 wherein said step of filling the pores with a pre-ceramic polymer resin comprises:

placing the liner into a bath containing silicon-carboxyl resin.

5. A method of forming a metal part having a breakage and erosion resistant ceramic liner comprising the steps of:

a) forming a metal part having a mating surface for receiving the liner;

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

c) filling the pores with a pre-ceramic polymer resin;

d) firing the liner saturated with the pre-ceramic polymer resin for a time and at a temperature sufficient to convert the resin to a ceramic within the pores thereby forming a reinforced ceramic composite; and,

e) bonding the ceramic liner to the mating surface of the metal part.

6. The method of claim 5 wherein said step of forming the liner of a ceramic material containing pores comprises:

a) pouring a cementations slurry material into a mold; and,

b) firing the slurry material for a time and at a temperature sufficient to sinter the slurry material into a porous ceramic liner.

7. The method of claim 5 wherein said step of filling the pores with a pre-ceramic polymer resin comprises:

placing the liner into a container containing a liquid pre-ceramic polymer resin having a viscosity substantially equal to water until the pores are saturated with the resin.

8. The method of claim 5 wherein said step of filling the pores with a pre-ceramic polymer resin comprises: placing the liner into a container containing silicon-carboxyl resin.

9. A method of forming a metal part having a breakage resistant ceramic liner comprising the steps of:

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

b) filling the pores with a pre-ceramic polymer resin;

c) firing the liner saturated with the pre-ceramic polymer resin for a time and at a temperature sufficient to convert the polymer resin to a ceramic within the pores thereby forming a reinforced ceramic composite;

d) positioning the liner within a mold for the metal part with the mating surface of the liner facing into a portion of the mold to be occupied by metal forming the part; and,

e) filling the mold with molten metal to form the part in combination with the liner.

10. The method of claim 9 wherein said step of forming the liner of a ceramic material containing pores comprises:

a) pouring a cementatious ceramic slurry material into a mold, and,

b) firing the slurry material for a time and at a temperature sufficient to sinter the slurry material into a porous ceramic liner.

11. The method of claim 9 wherein said step of filling the pores with a pre-ceramic polymer resin comprises:

placing the liner into a bath containing a liquid pre-ceramic polymer resin having a viscosity substantially equal to water until the pores are saturated with the resin.

12. The method of claim 9 wherein said step of filling the pores with a pre-ceramic polymer resin comprises:

AMENDED SHEET (ARTICLE 19)

placing the liner into a bath containing silicon-carboxyl resin.

13. A heat resistant, erosion resistant, non-fragile ceramic-lined exhaust manifold for an internal combustion engine comprising:

a) a metal manifold defining an exhaust gas-conducting conduit having inner walls; and,

b) said inner walls of said conduit being lined with a ceramic material having pores wherein said pores contain a pre-ceramic polymer resin in a ceramic state.

14. The heat-resistant, erosion resistant, non-fragile ceramic-lined exhaust manifold of claim 13 wherein:

said pre-ceramic polymer resin comprises silicon-carboxyl resin in its ceramic state.

15. A heat-resistant, erosion resistant, non-fragile ceramic-lined cylinder head for an internal combustion engine comprising:

a) a metal cylinder head having a cylinder-facing surface; and,

b) said cylinder-facing surface of said cylinder head being lined with a ceramic material having pores wherein said pores contain a pre-ceramic polymer resin in a ceramic state.

16. The heat-resistant, erosion resistant, non-fragile ceramic-lined cylinder head of claim 15 wherein:

said pre-ceramic polymer resin comprises silicon-carboxyl resin in its ceramic state.

17. A fiber reinforced ceramic matrix composite automotive part derived by:

a) forming a fiber preform in the shape of the part from reinforcing fibers employable in fiber reinforced ceramic matrix composites;

b) placing the preform in a cavity of a mold having the shape of the part;

c) forcing a liquid pre-ceramic polymer resin through the cavity to fill the cavity and saturate the preform;

d) heating the mold for a time and at a temperature sufficient to transform the preform saturated with the liquid pre-ceramic polymer resin to a polymer composite part;

e) removing the polymer composite part from the mold; and,

f) firing the polymer composite part in an inert atmosphere for a time and at a temperature sufficient to transform the pre-ceramic polymer resin to a ceramic whereby the polymer composite part is transformed into a fiber reinforced ceramic matrix composite part.

18. The automotive part of claim 17 and after step (f) thereof additionally derived by:

g) immersing the fiber reinforced ceramic matrix composite part containing pores formed by outgassing during firing into a bath of the liquid pre-ceramic polymer resin to fill the pores with the liquid pre-ceramic polymer resin;

h) firing the fiber reinforced ceramic matrix composite part in an inert atmosphere for a time and at a temperature sufficient to transform the pre-ceramic polymer resin in the pores to a ceramic; and,

i) repeating steps (g) and (h) until the pore density within the final fiber reinforced ceramic matrix composite part is less than a preestablished percentage affording maximum strength to the part.

19. A fiber reinforced ceramic matrix composite engine manifold derived by:

a) forming a first preform in a shape of a lower portion of the manifold from reinforcing fibers employable in fiber reinforced ceramic matrix composites;

b) placing the first preform in a cavity of a first mold having the shape of the lower portion of the manifold;

c) forcing a liquid pre-ceramic polymer resin through the cavity to fill the cavity and saturate the first preform;

d) heating the first mold for a time and at a temperature sufficient to transform the first preform saturated with the liquid pre-ceramic polymer resin to a first polymer composite part;

e) removing the first polymer composite part from the mold;

f) forming a second preform in a shape of an upper portion of the manifold from the reinforcing fibers;

g) placing the second preform in a cavity of a second mold having the shape of the upper portion of the manifold;

h) forcing the liquid pre-ceramic polymer resin through the cavity to fill the cavity and saturate the second preform;

i) heating the second mold for a time and at a temperature sufficient to transform the second preform saturated with the liquid pre-ceramic polymer resin to a second polymer composite part;

j) removing the second polymer composite part from the mold;

k) 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,

l) firing the polymer composite manifold in an inert atmosphere for a time and at a temperature sufficient to transform the pre-ceramic polymer resin to 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.

20. The engine manifold of claim 19 and after step (l) thereof additionally derived by:

m) immersing the fiber reinforced ceramic matrix composite manifold containing pores formed by outgassing during firing into a bath of the liquid pre-ceramic polymer resin to fill the pores with the liquid pre-ceramic polymer resin;

n) firing the fiber reinforced ceramic matrix composite manifold in an inert atmosphere for a time and at a temperature sufficient to transform the pre-ceramic polymer resin in the pores to a ceramic; and,

o) repeating steps (m) and (n) until the pore density within the final fiber reinforced ceramic matrix composite manifold is less than a pre-established percentage affording maximum strength to the part.

21. A method of making a fiber reinforced ceramic matrix composite engine manifold comprising the steps of:

a) forming a first preform in a shape of a lower portion of the manifold from reinforcing fibers employable in fiber reinforced ceramic matrix composites;

b) placing the first preform in a cavity of a first mold having the shape of the lower portion of the manifold;

c) forcing a liquid pre-ceramic polymer resin through the cavity to fill the cavity and saturate the first preform;

d) heating the first mold for a time and at a temperature sufficient to transform the first preform saturated with the liquid pre-ceramic polymer resin to a first polymer composite part;

e) removing the first polymer composite part from the mold;

f) forming a second preform in a shape of an upper portion of the manifold from the reinforcing fibers;

g) placing the second preform in a cavity of a second mold having the shape of the upper portion of the manifold;

h) forcing the liquid pre-ceramic polymer resin through the cavity to fill the cavity and saturate the second preform;

i) heating the second mold for a time and at a temperature sufficient to transform the second preform saturated with the liquid pre-ceramic polymer resin to a second polymer composite part;

j) removing the second polymer composite part from the mold;

k) 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;

l) firing the polymer composite manifold in an inert atmosphere for a time and at a temperature sufficient to transform the pre-ceramic polymer resin to 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;

wherein the manifold is an exhaust manifold internally filled with a ceramic foam catalyst substrate structure and prior to said step (g) 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:

f1) placing the first preform as part of a cavity-defining wall of the second mold; and,

f2) 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.

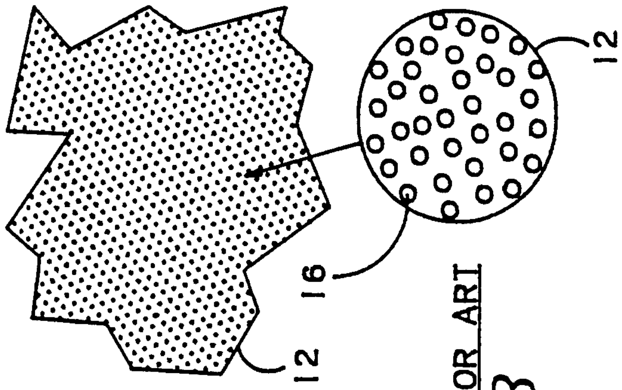

FIG. 3
PRIOR ART

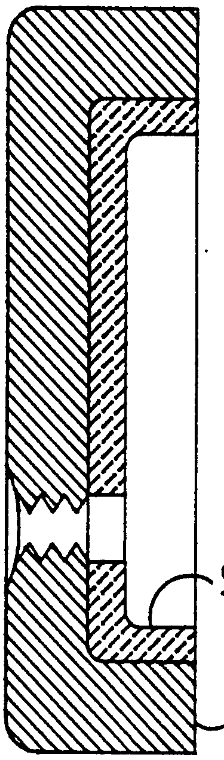

FIG. 2
PRIOR ART

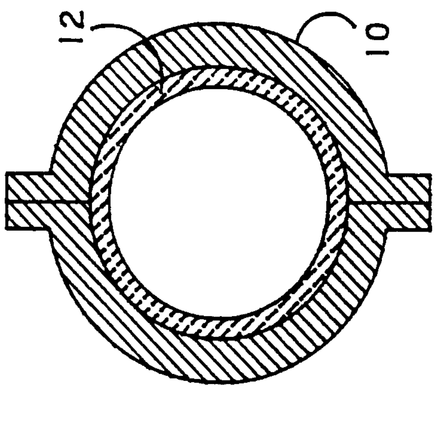

FIG. 1
PRIOR ART

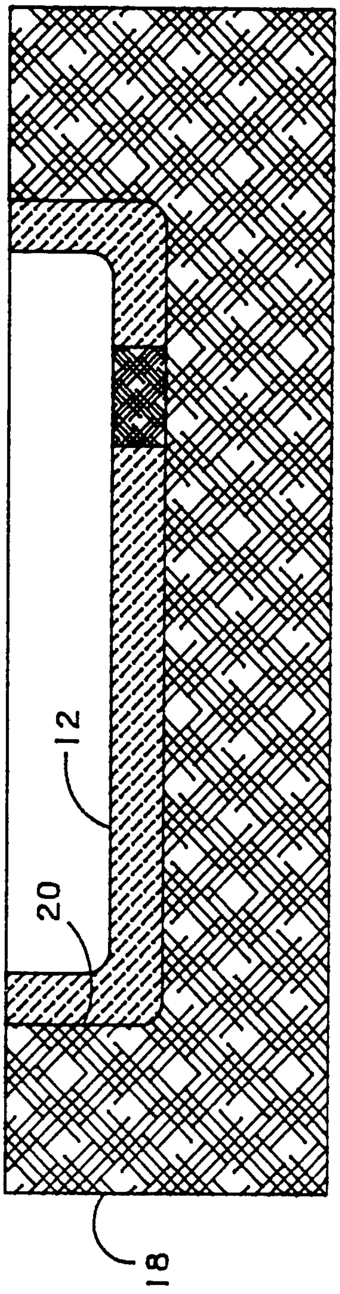

FIG. 4

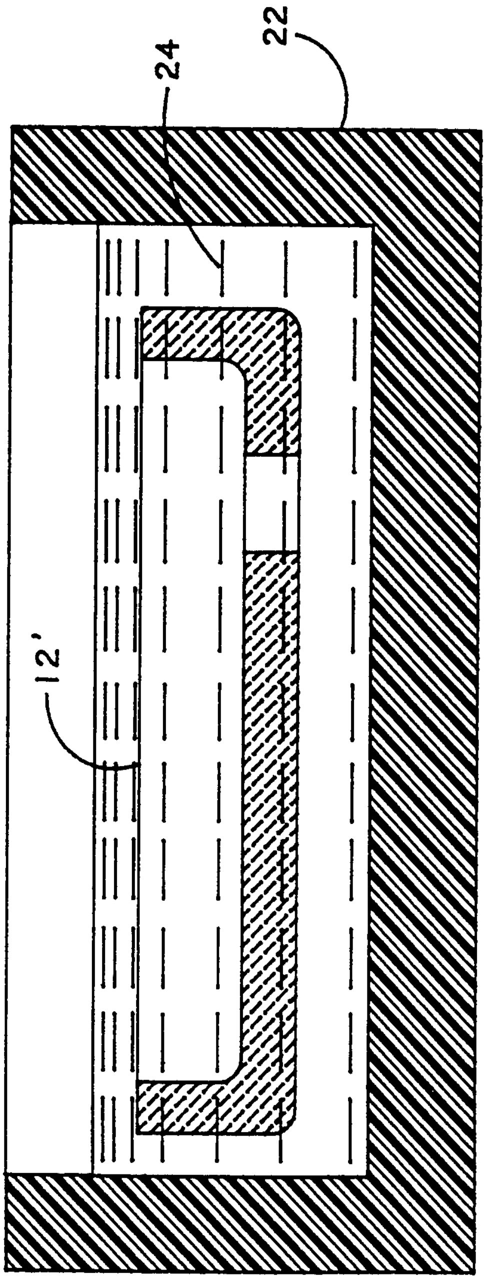

FIG. 5

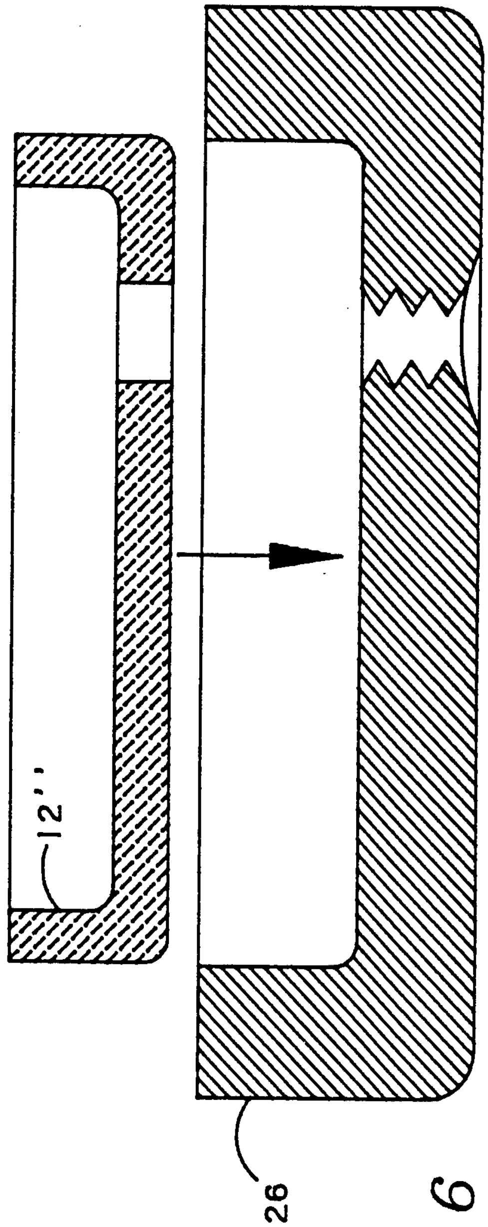

FIG. 6

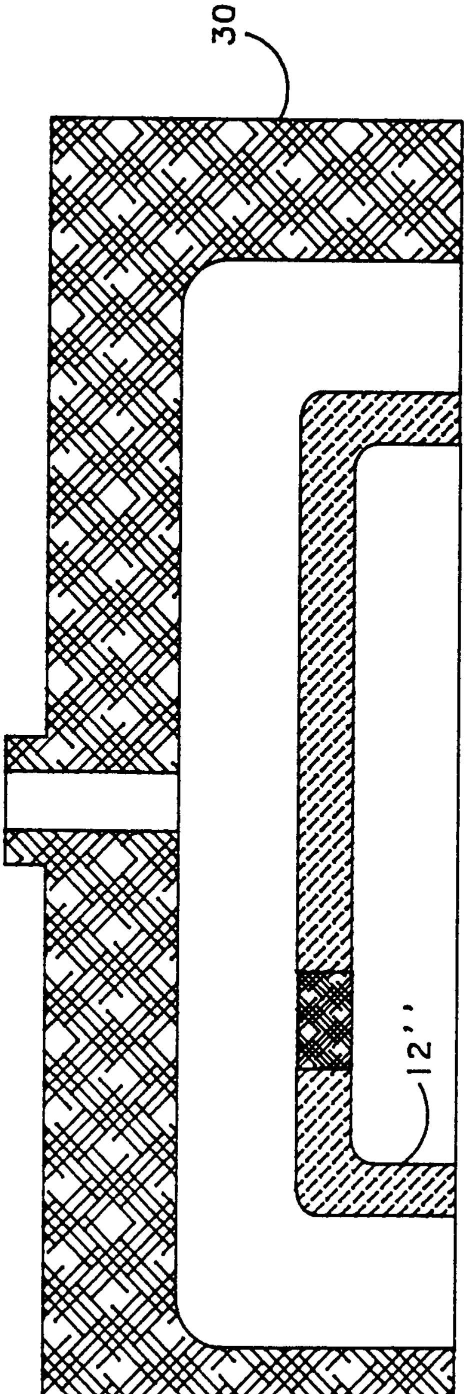

FIG. 7

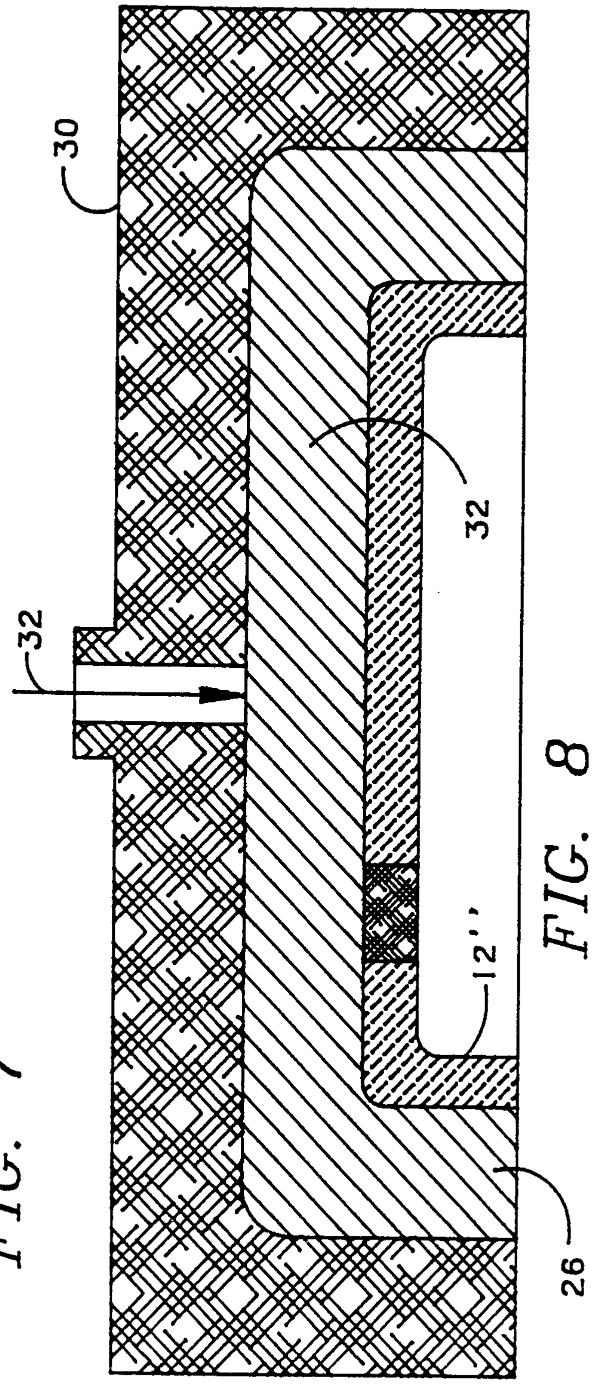

FIG. 8

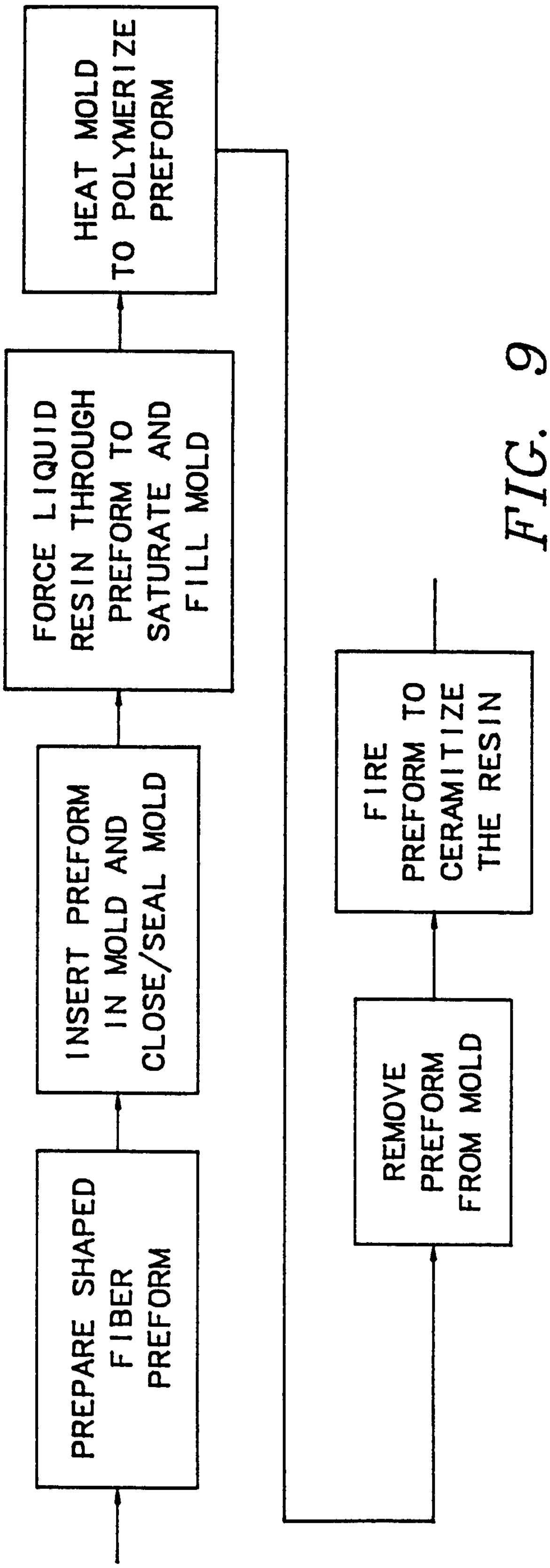
PREPARE SHAPED FIBER PREFORM
INSERT PREFORM IN MOLD AND CLOSE/SEAL MOLD
FORCE LIQUID RESIN THROUGH PREFORM TO SATURATE AND FILL MOLD
HEAT MOLD TO POLYMERIZE PREFORM
REMOVE PREFORM FROM MOLD
FIRE PREFORM TO CERAMITIZE THE RESIN

FIG. 9

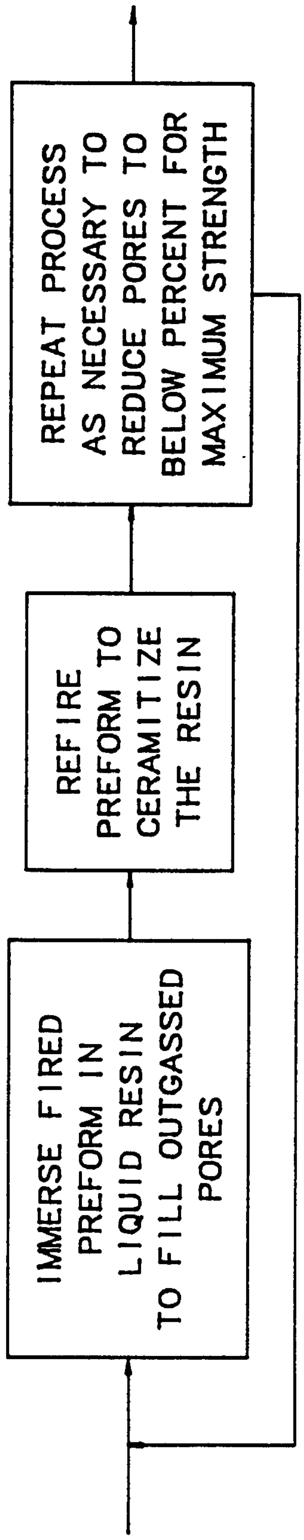
IMMERSE FIRED PREFORM IN LIQUID RESIN TO FILL OUTGASSED PORES
REFIRE PREFORM TO CERAMITIZE THE RESIN
REPEAT PROCESS AS NECESSARY TO REDUCE PORES TO BELOW PERCENT FOR MAXIMUM STRENGTH

FIG. 10

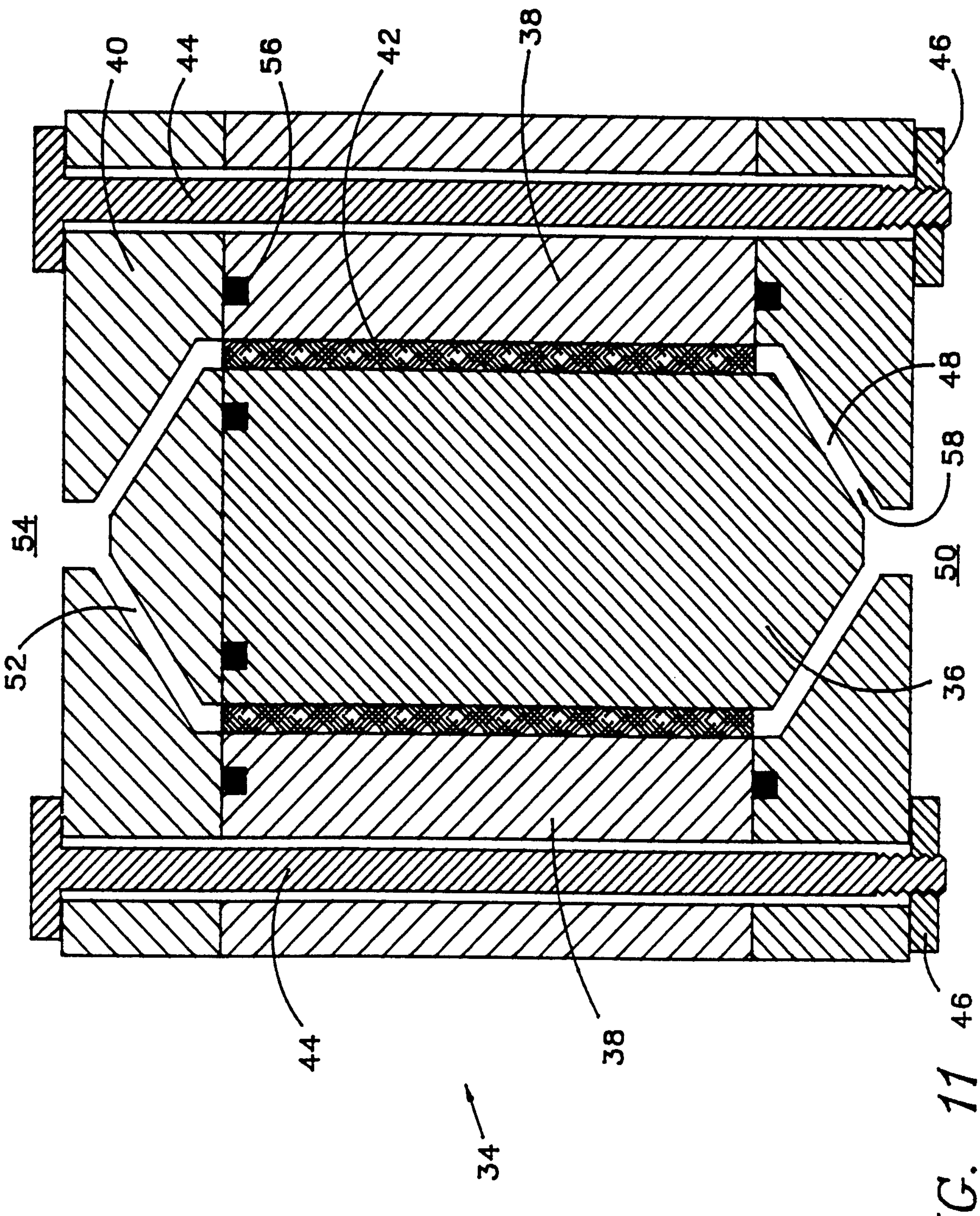

FIG. 11

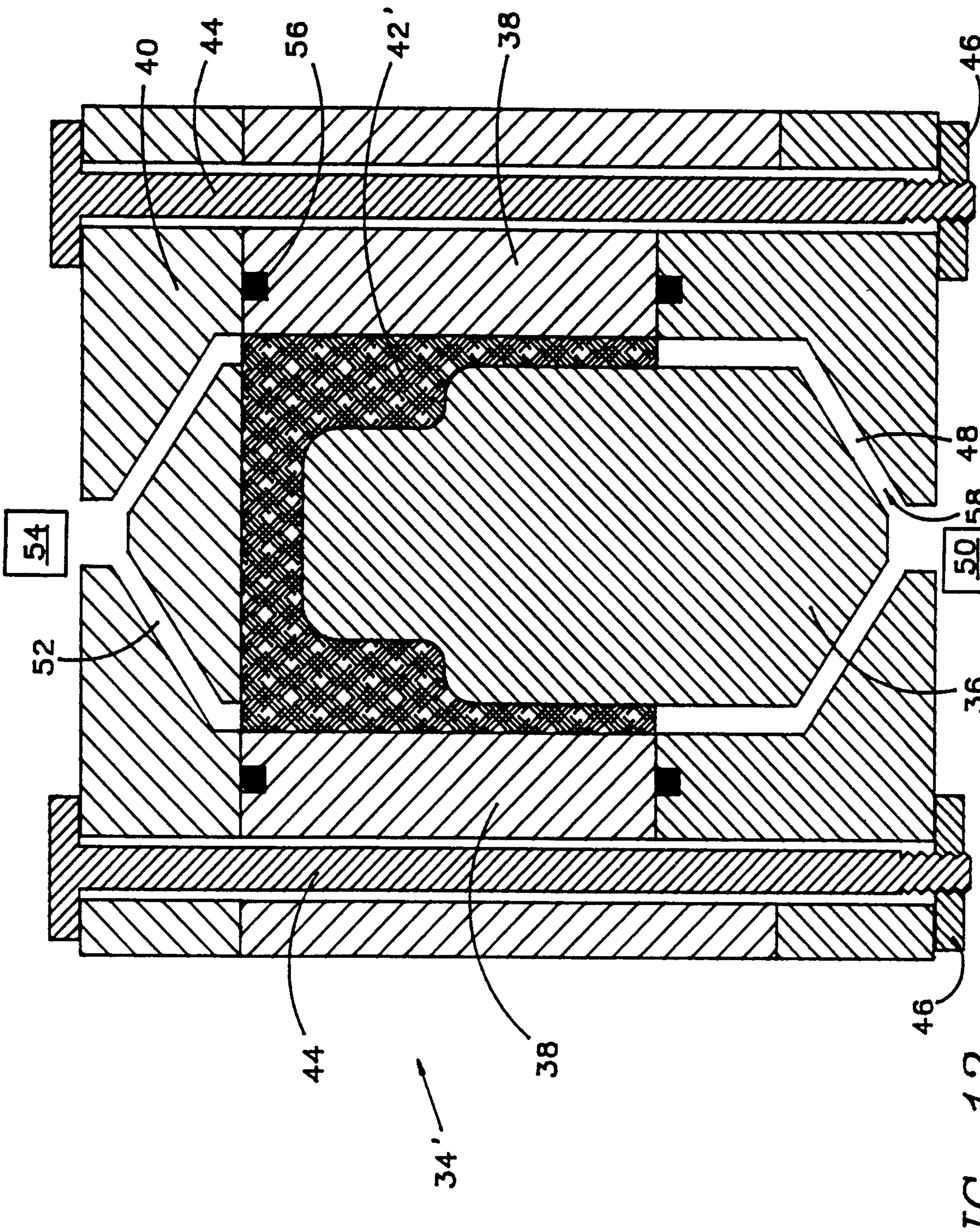

FIG. 12

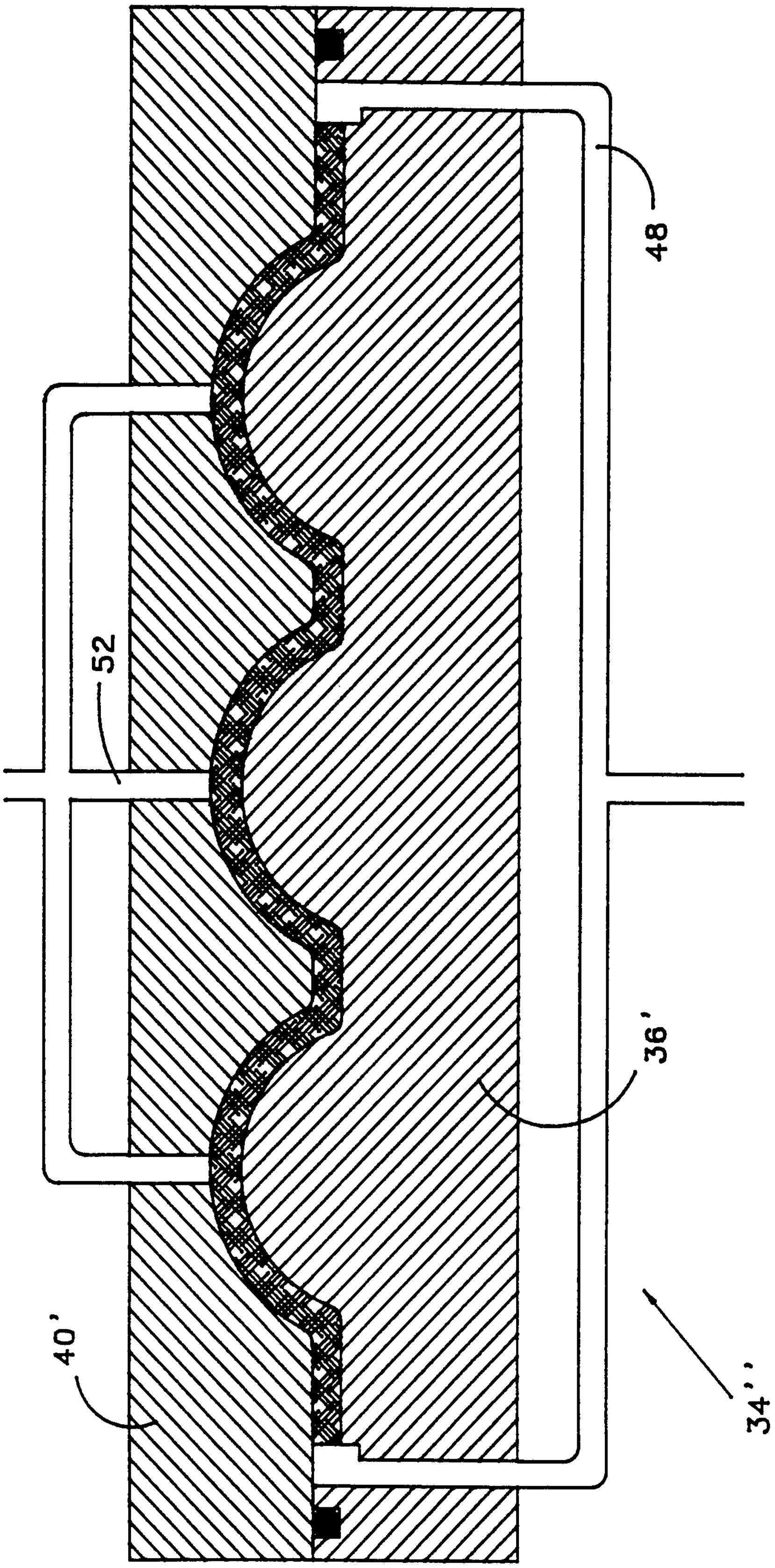

FIG. 13

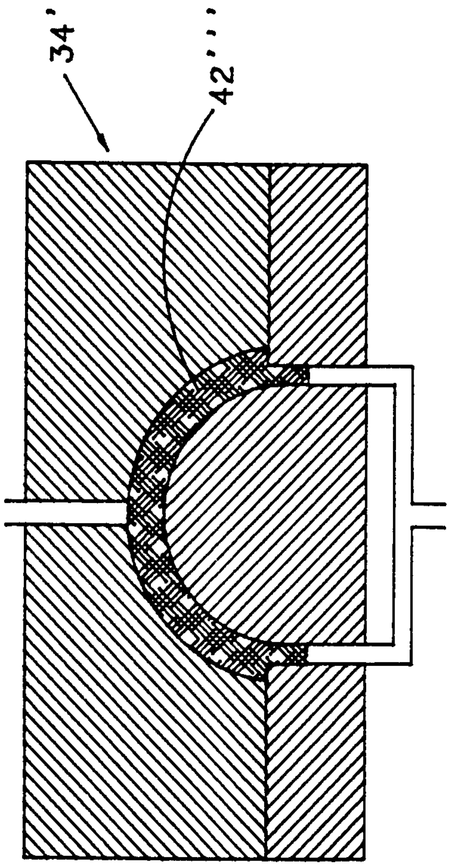

FIG. 14

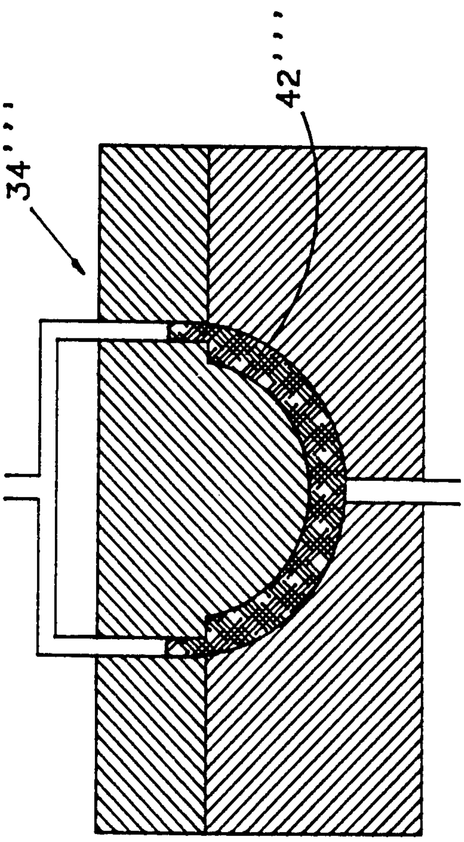

FIG. 15

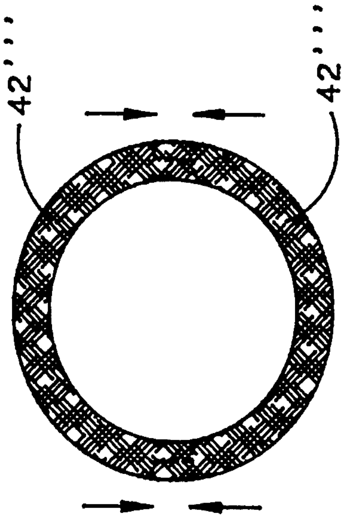

FIG. 16

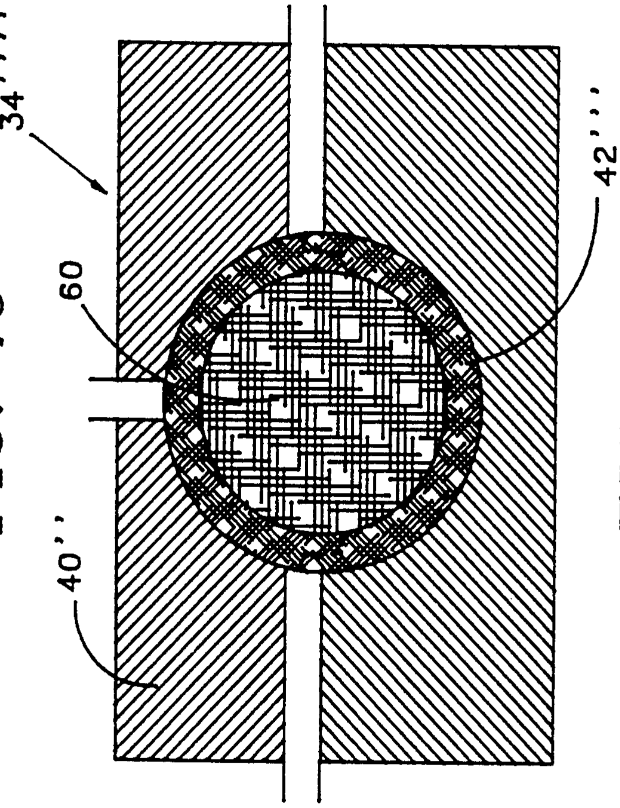

FIG. 17

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/11772

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B22D 19/00
US CL :164/97, 98; 60/282, 302, 323; 428/312.4, 312.6, 307.7, 313.9
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; 60/282, 302, 323; 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

APS

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 3,173,451 (Slayter) 16 March 1965, Col. 1, Lines 39-47	1-14 and 17-21
Y	US, A, 3,488,723 (Veazie) 06 January 1970, figure 8, col. 1, lines 37-47, col. 4, lines 45-51.	1-14 and 17-21
Y	US, A, 4,206,598 (Rao et al.) 10 June 1980, abstract, col. 1, lines 6+.	1-14 and 17-21
A	US, A, 4,245,611 (Mitchell et al.) 20 January 1981	1-14 and 17-21
A	US, A, 4,341,826 (Prewo et al.) 27 July 1982, abstract, col. 1, lines 29-30 and 62-68, col. 2, lines 62-68.	1-14 and 17-21

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document published on or after the international filing date

"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)

"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

"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

"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

"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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 AUGUST 1996	16 SEP 1996

Name and mailing address of the ISA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	RANDOLPH S. HERRICK Sheila Veney Paralegal Specialist Group 3200
Facsimile No. (703) 305-3230	Telephone No. (703) 308-2687

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/11772

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, 4,657,951 (TAKARADA ET AL.) 14 April 1987, abstract, col. 2, lines 5-23 and 60-68.	1-14 and 17-21
A	US, A, 4,818,732 (FOX ET AL.) 04 April 1989, abstract.	1-14 and 17-21
A	US, A, 4,884,400 (TANAKA ET AL.) 05 December 1989, abstract, col. 2, lines 6-9, 17-33 and 47-54.	1-14 and 17-21
Y	US, A, 4,928,645 (BERNEBURG ET AL.) 29 May 1990, col. 4, lines 19-67.	1-14 and 17-21
Y	US, A, 4,972,674 (YAMADA ET AL.) 27 November 1990, abstract, col. 2, lines 5+.	1-14 and 17-21
A	US, A, 5,018,661 (CYB) 28 May 1991.	
Y	US, A, 5,066,626 (FUKAO ET AL.) 19 November 1991, abstract, figure 3, col. 1, lines 12-16, col. 2, lines 23-35.	5-12
A	US, A, 5,139,979 (ANDERSON ET AL.) 18 August 1992.	
A	US, A, 5,167,271 (LANGE ET AL.) 01 December 1992.	
A	US, A, 5,225,283 (LEUNG ET AL.) 06 July 1993, abstract	1-14 and 17-21
Y	US, A, 5,231,059 (LEUNG ET AL.) 27 July 1993, abstract, col. 6, lines 12-13, 33-38 and 46-50.	1-14 and 17-21
Y	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 lines 28-36, col. 6, lines 24-26, 51-53, 63 and 67-68, col. 7, lines 59-63, col. 8 lines 29-37 and col. 9, lines 53-55.	1-14 and 17-21
Y	JP, 61-215415 (HINO) 25 September 1986, abstract.	1-14 and 17-21
Y	JP, 60-187712 (TAZAKI) 25 September 1985, abstract.	1-14 and 17-21
Y	JP, 60-81420 (TAZAKI) 05 September 1985, abstract.	1-14 and 17-21

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/11772

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 15-16
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

The term powerhead is unclear and there is a lack of structure to properly identify the feature

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest
☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.