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CERAMIC HEAT EXCHANGER STRUCTURES

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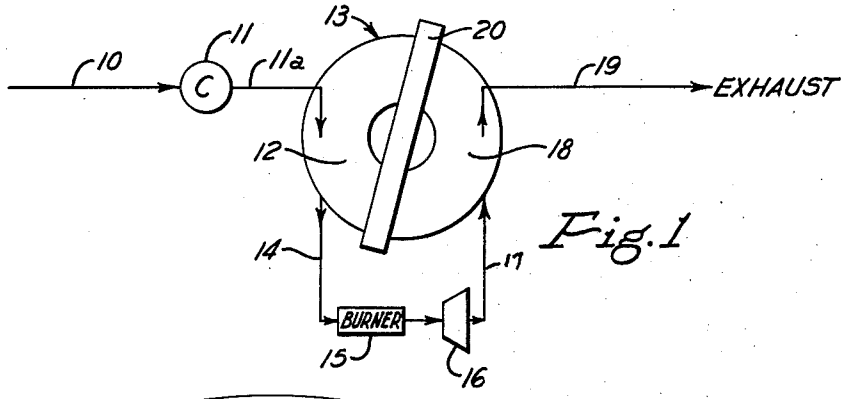


Fig. 1

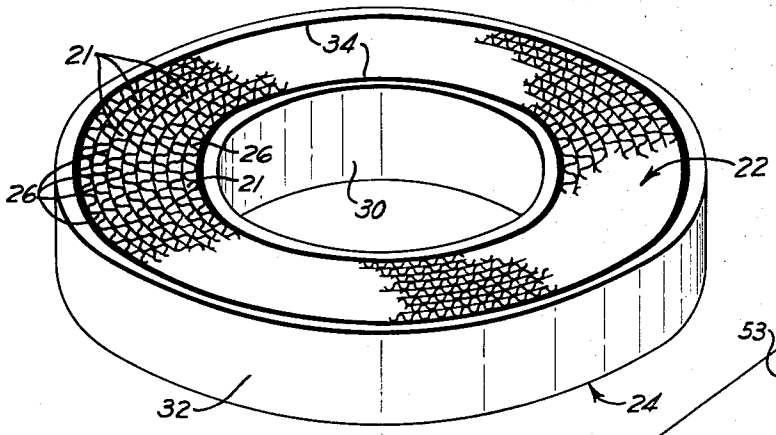


Fig. 2

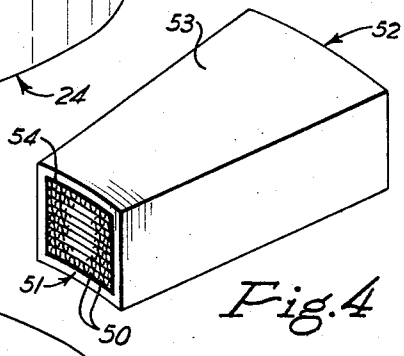


Fig. 4

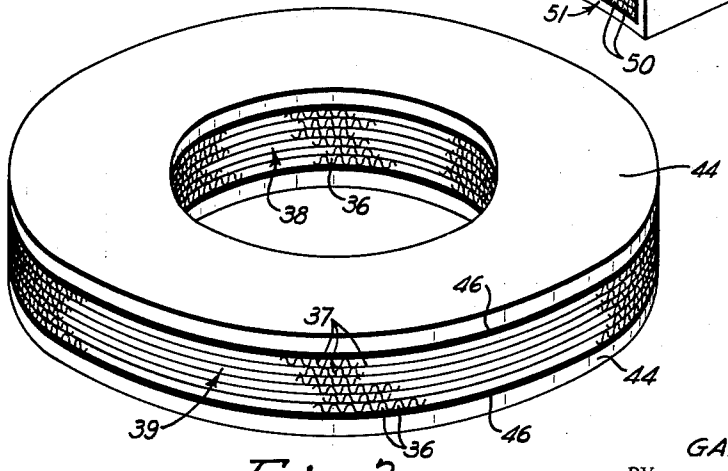


Fig. 3

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CERAMIC HEAT EXCHANGER STRUCTURES

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This invention relates to heat exchangers and in particular it concerns regenerative heat exchanger bodies particularly useful for application with gas turbines.

It is the primary object of the present invention to provide heat exchanger bodies composed of thin walled ceramic material, that are lightweight, are inexpensive, are characterized by a low coefficient of thermal expansion, and are chemically and thermally durable.

These and other objects are attained in accordance with this invention in which a thin walled ceramic honeycomb is formed from ceramic materials hereinafter described in detail, and is provided with a protective covering cemented to several of its surfaces. The honeycomb body is characterized by a plurality of unobstructed gas flow paths extending through it to a pair of opposed, substantially parallel surfaces. The term unobstructed as used in this application means that the flow paths have no internal structure that, for example, would stop gas flow. The unobstructed flow paths can be characterized as desired and may be linear, tortuous or the like. These gas paths are separated from one another by thin walls of the ceramic material. The specific design of the structure coupled with the character of the ceramic materials in the completed product result in a body uniquely suited as a regenerative heat exchanger for application at high and rapidly changing temperatures such as are encountered in gas turbine operation.

The invention will be most readily understood upon considering its detailed description in conjunction with the attached drawing in which:

FIG. 1 is a schematic representation of a heat exchanger and auxiliary equipment showing the flow of gas therethrough;

FIG. 2 is a perspective view of a heat exchange body of the invention in which the channels are arranged for axial flow;

FIG. 3 is a perspective view of a second embodiment of the heat exchange body in which the channels are arranged for radial flow; and

FIG. 4 is a perspective view of a honeycomb segment that can be used in making a radial flow heat exchanger.

Referring now to FIG. 1, fresh intake gas is fed by a line **10** to a compressor **11** wherein its temperature and pressure are raised. The gas from compressor **11** then is passed through line **11***a* into a first portion **12** of a heat exchanger body **13** heated to a high temperature as hereinafter described. In that portion of the heat exchanger **13**, the gas is heated by the heat in the ceramic walls defining the gas flow paths and emerges at the opposite surface through line **14** at a higher temperature. The highly heated gas is then passed to a burner **15** where its temperature is further raised by combustion. The hot gas from the burner is then expanded through a turbine **16** where part of its energy is converted to work. The exhaust gas from the turbine is conducted through line **17** into a relatively cool portion **18** of the heat exchanger body **13** where it gives up a substantial portion of its heat. Gas from this portion of the heat exchanger body is exhausted through a line **19**. It is to be noted that the heat exchanger body **13** is rotated in use; accordingly, after one portion of it has been heated from the gases exhausted by the turbine, that heated portion rotates to the compressor inlet where the gas fed from the compressor can recover the heat. The two portions

12 and **18** are divided from one another by the stationary seal **20** extending across the top and bottom surfaces of the heat exchanger body.

Heat exchanger bodies for a system such as is shown in FIG. 1 are generally cylindrical or annular in shape. Such a body for an axial flow system is shown in FIG. 2.

Referring now to FIG. 2, the heat exchanger body for the axial flow system comprises a honeycomb having a plurality of unobstructed gas channels **21** extending from its top surface **22** through to its bottom surface **24** and generally parallel to the central axis of the body. These gas channels are defined and separated from one another by thin walls of ceramic material **26**. At its hub or axial bore and along its outside surface, the honeycomb body is covered with, respectively, a hub wall **30** and a rim wall **32**. The hub and rim walls or members **30** and **32** are cemented to the honeycomb body by a cement **34** that is foamed in place. The heat exchanger body of FIG. 2 can be rotated by means, not shown, bearing on the hub, on the rim or on both.

For a radial flow heat exchanger, the gas channels extend radially of the central axis of the cylindrical or annular shaped honeycomb body such as is shown in FIG. 3. The honeycomb is characterized by a plurality of unobstructed gas flow paths **36** separated from one another by thin ceramic walls **37** and extending from the central wall **38** outwardly and terminating in the outer surface **39**. Where the honeycomb of a radial flow heat exchanger body is essentially one piece, the top and bottom surfaces are covered with rim members **44** that are cemented to the honeycomb structure by a foamed ceramic cement **46**. Rotation of the radial flow heat exchanger body is achieved by use of members, not shown, that may apply rotational force on the rims.

For some purposes it is desirable to have the radial flow heat exchanger body made of a plurality of segments. For example, if a part of the body should be damaged, a segmented honeycomb body can be readily repaired by simple replacement of the damaged segment. A segment of the type from which such a honeycomb body can be assembled is shown in FIG. 4. In the embodiment of FIG. 4, the segment comprises a truncated pyramidal body having channels **50** extending between two of its parallel surfaces **51** and **52**. The other external surfaces are covered with a rim member **53** that, as before, is cemented to the honeycomb body by a foamed cement **54**. The annular structure for the heat exchanger is made from the segments by binding the required number of segments to one another as by applying steel straps along the top and bottom of the collective surfaces **52** of the segments. This result could also be achieved by using covering members, such as those shown at **44** in FIG. 3, cemented to the assembled segments.

Ceramic honeycomb bodies that are useful in accordance with the teachings of this invention can be prepared by several processes. For example, a pulverized ceramic material can be admixed with a suitable binder and then extruded to a ribbon form. The resulting ribbon can be further shaped if desired, and assembled, either by itself or with other ribbons of this material to the desired honeycomb shape. The resulting assembly is then sintered to a unitary structure. Preferably, however, the ceramic honeycomb body is prepared by coating a suitable carrier with a mixture of a pulverized ceramic and a binder, crimping the resulting coated carrier and then assembling it to the desired shape alone or with another coated carrier that need not be crimped. The assembled body is then heated to a temperature sufficient to sinter it to a unitary structure as more fully detailed hereinafter. This latter procedure is, generally, the process set forth in the copending application of Robert Z. Hollenbach, Serial

Number 759,706, filed September 8, 1958, and now Patent Number 3,112,184 granted November 26, 1963.

The purpose of the binder is to bond the unfired ceramic material to the carrier, to impart green strength to the coated carrier and to retain the formed unfired article in the desired shape after forming and prior to sintering. In order that the resultant article be essentially all ceramic material having a low coefficient of thermal expansion, it is preferred to use an organic binder, especially those that are heat curable or thermosetting, that can be removed by decomposition and/or volatilization when the article is fired. Among the many materials having the requisite, well known characteristics of binders, that can be used in the process are such natural materials as gum arabic, colophony and shellac and such synthetic organic resins as acrylate resins, methacrylate resins, alkyd resins, cellulose derivatives, coumarone indene resin, phenolic resins, polyamides, polyesters, resorcinol resins, styrene resins, terpene resins, urea resins, vinyl resins, chlorinated paraffins and melamine resins.

The purpose of the carrier is to provide support for the unfired coating to allow it to be formed to the desired shape prior to sintering the ceramic coating. Tea bag paper is a preferred carrier and a list of other suitable materials is disclosed in the aforementioned Hollenbach patent application, to which reference can be made. Tea bag paper, as well as other organic film materials, substantially decompose upon firing and thus result in an article consisting almost entirely of ceramic material.

In order to produce a structure in accordance with the present invention having characteristics suitable for a heat exchanger body, it is essential that ceramic materials be used that have a low coefficient of thermal expansion in the fired state on the order of about minus 10 to plus 10 times $10^{-7}/°$ C. over an extended temperature range. Suitable ceramic materials for this purpose include lithium aluminosilicates such as, for example, glass or crystalline petalite and beta spodumene, glass-ceramics having a lithium aluminosilicate base and especially those made in accordance with Example 1 of United States patent to Stookey, Number 2,920,971, as well as mixtures of any of the foregoing materials. Petalite glass-ceramic mixtures generally include about 10 to 40 weight percent of the glass-ceramic and the remainder petalite. Beta spodumene-petalite mixtures usually contain about 1 to 4 parts of petalite for each 4 to 1 parts of beta spodumene. These materials normally are used in a particle size of about minus 200 mesh (Tyler) or finer, depending on the wall thickness desired in the resulting article.

Structures are assembled from ceramic coated carriers in a variety of ways, and the resulting structures are called honeycombs, a term which in this specification means a unitary body having a multitude of unobstructed gas paths of any predetermined size and shape, each such gas path being defined by ceramic walls and extending to opposed essentially parallel surfaces. These structures can be assembled from multiple layers of film corrugated with the same pattern with alternate layers laterally disposed a distance equal to half of the width of the individual pattern so that layers do not nest with each other. The honeycomb structure can also be formed from rolling alternate layers of crimped and uncrimped coated carriers until the desired shape is formed. A structure can also be formed by assembling to a stack alternate crimped and uncrimped coated carriers until the desired dimensions are attained. Other ways of assembling these honeycombs will be apparent to those skilled in the art.

The firing of the green structure or matrix, however formed, is accomplished in the normal manner for ceramic firing by placing the article in a furnace and heating it at a rate slow enough to prevent breakage due to thermal shock to a temperature high enough to cause the ceramic particles to sinter. While the firing schedule, including heating rates and sintering temperatures, will vary depending upon the ceramic material utilized, the size and shape of the article formed, and the atmosphere used, the details of such schedules are not critical and suitable conditions are readily determinable by one skilled in the art of firing ceramic articles.

As noted hereinbefore, the surfaces of the honeycomb body other than those where the gas flow paths terminate are covered. These covering members, sometimes termed rims or hubs, can be formed in any desired manner. A preferred method of preparation involves forming a slip, suitably of the same composition as the ceramic used in the honeycomb body or of a glass such as the borosilicate glasses disclosed in the United States patent to Hood et al. Number 2,106,744, and slip casting to the desired shape. Another suitable procedure involves heat sagging strips composed, for example, of the aforementioned borosilicate glass, to arcuate sections. Then several, e.g. four or more, arcuate sections are assembled to the desired shape and the abutting ends are joined by heat sealing.

The rim and hub or other cover members are attached to the honeycomb body by use of a ceramic cement that will foam and readily bond those members and that has a low coefficient of thermal expansion in the foamed state. Cement for this purpose has a composition, by weight, of 1 to 16 percent of lead oxide, 1 to 15 percent of a flux, 1 to 6 percent of silicon carbide, 1 to 6 percent of SO_3, and substantially all of the remainder, and at least about 70 percent of the total cement composition, a lithium-aluminosilicate ceramic such as glassy or cystalline petalite, a glassy ceramic having such a base composition or any combination of the foregoing. Glass petalite is the preferred ceramic. Typical flux materials include the fluorides and oxides of magnesium, calcium, strontium, barium, zinc, cadmium, lead, lithium, sodium and pottassium. Suitably a mixture of oxide and fluoride fluxes is used. The SO_3 content of the batch is provided by, for example, a compound such as calcium sulfate, barium sulfate, strontium sulfate or lithium sulfate. It will be apparent that the use of any of these compounds provides both the SO_3 and an oxide flux. Lead sulfate, which also may be used, provides the essential lead oxide and SO_3. The cement is used by pouring it into the spaces between the parts to be joined and then firing the unit to a temperature of about 1050° to 1150° C. until foaming and sintering are complete. Thereafter, the unit is cooled to handling temperature.

The invention will be described further in conjunction with the following example in which the details are given by way of illustration and not by way of limitation.

In this example, a ceramic composition is made of 75 parts by weight of petalite and 25 parts by weight of a glass-ceramic having the following approximate composition by oxide analysis in weight percent: 70 percent SiO_2, 18 percent Al_2O_3, 5 percent TiO_2, 3 percent Li_2O, 3 percent MgO and 1 percent ZnO. The composition is ball-milled to a minus 200 mesh (Tyler) particle size. A solution of the following composition is added to 2160 grams of the ceramic material in the ball mill:

640 cc. of isopropanol
860 cc. of ethyl-acetate
180 cc. of Versamid 115
480 cc. Hysol 6111

Versamid 115 is the trade name of a thermoplastic polymer supplied by General Mills, Inc. It is prepared by condensation of polymerized unsaturated fatty acids, such as dilinoleic acid, with aliphatic amines such as ethylene diamine.

The ceramic material and the binder are further ball-milled for about three hours to produce a uniform suspension. A porous natural cellulose paper, commonly known as 3½ pound tea bag paper, cut to a width of 4 inches is then dipped into the suspension and dried by heating to 120° C. for 2 minutes. The dried, coated paper is then heated to 180° C. and crimped to produce a pattern, taken in cross-section, in the shape of an isosceles triangle

with legs about 0.07 inch long and an open base about 0.1 inch wide. The crimped, unfired, coated paper is rolled up simultaneously with a sheet of tea bag paper of the same width, which has been coated in the same manner but not crimped, upon a 2-inch diameter reel until an annular cylinder with an outside diameter of about 23 inches is obtained. Preferably, the uncrimped coated paper is not dried prior to the roll-up operation, but this paper is dried by forcing air heated to about 120° C. through the channels of the annular cylinder as they are formed during the roll-up operation.

The unfired matrix body is then placed in a sealed furnace chamber and heated in accordance with the following schedule:

Temperature range:	Firing rate
Room temp. to 700° C.	350° C./hr.
Hold at 700° C.	1 hour.
700° C. to 1220° C.	Furnace rate.
Hold at 1220° C.	30 minutes.
Cool to room temp.	Furnace rate.
Refire to 1240° C.	300° C./hr.
Hold at 1240° C.	7 hours.

The sintered article is then cooled to handling temperature and removed from the furnace.

Rim and hub members are made for the foregoing honeycomb from a slip of the glass-ceramic used in preparing the honeycomb. The slip is cast in annular molds of a size to fit the honeycomb with about one-eighth inch clearance. After drying, the molds are removed and the cast structures are fired at about 1250° C.

The rim, hub and honeycomb are assembled. Then a cement having the following composition by weight is used to join these members: 9.23 percent of zinc fluoride, 1.28 percent of calcium fluoride, 3.42 percent of silicon carbide, and the remainder petalite that had been fused with lead sulfate in an amount such that it contained 8 percent of lead oxide and 2.87 percent of SO_3. A batch of this cement composition is dispersed in a mixture containing 75 weight percent of butyl alcohol and 25 weight percent of toluene and is wet ball-milled to thoroughly mix the batch. This cement is poured in the annular spaces in the assembly. The resulting assembly is then placed in a furnace and raised to 100° C. at a rate of 2° C./min. After 2 hours at 100° C., the temperature is raised at 5° C/minute to 1100° C. and is held at 1100° C. for one hour and 15 minutes to permit the foaming action to be completed. It is then furnace cooled at a rate of 5° C./min. to handling temperature.

Honeycomb bodies formed to heat exchanger members as just detailed are characterized by an extremely large number of gas channels per unit of surface area. Quite commonly, a square foot of the surface of the honeycomb will have over 57,000 channels. As is evident, therefore, most of the cross section is void and the resulting units are relatively lightweight, having a density on the order of about 30 pounds per cubic foot. These bodies made with the ceramic materials hereinbefore specified have a low coefficient of thermal expansion of about minus 10 to about plus 10×10^{-7}/° C. over a range up to about 300° C., and may actually be zero. It is accordingly, evident that these bodies can be subjected to tremendous thermal shock as by repeated thermal cycling to over 1000° C., a temperature beyond usual gas turbine operating temperatures, without adverse effect. The excellent chemical durability of the structure allows its extended use despite the corrosive conditions experienced in the application contemplated.

From the foregoing discussion and description, it is evident that the present invention provides a heat exchanger body of excellent utility in that it is physically and chemically durable yet inexpensive, it is characterized by a low coefficient of thermal expansion and therefore can readily be produced to fixed dimensions and used, as by rotating it, without concern about developing a poor fit. The invention is further advantageous in that these unique results are achieved with readily available and inexpensive raw materials while applying skills available to artisans in the ceramic arts. Unless otherwise stated or apparent, all percentages and parts given in the foregoing description are by weight.

In accordance with the provisions of the patent statutes, I have explained the principles of my invention and have illustrated and described what I now considered to be its best embodiment. However, I desire to have it understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically illustrated and described.

I claim:

1. A rotatable, annular-shaped heat exchanger body comprising a thin walled ceramic honeycomb having two pairs of substantially parallel opposing surfaces and a plurality of unobstructed gas passages extending between and terminating in a first pair of said opposing substantially parallel surfaces, said gas passages being defined by thin walls of said ceramic, rigid covering members on each of the other pair of opposing surfaces, and a foamed ceramic cement joining said covering members to said honeycomb, said covering members, ceramic honeycomb and foamed ceramic cement all having a low and essentially similar coefficient of thermal expansion.

2. A heat exchanger body in accordance with claim 1 in which said unobstructed gas passages are essentially parallel to the central axis of said heat exchanger body.

3. A heat exchanger body in accordance with claim 1 in which said unobstructed gas passages are essentially radial to the central axis of said heat exchanger body.

4. A rotatable, annular-shaped heat exchanger body formed of a plurality of ceramic honeycomb segments each having a rectangular base pyramidal shape truncated parallel to its base and a plurality of unobstructed gas passages extending between the base and its parallel surface, said segments being assembled to an annular shaped body with the collected bases thereof constituting the external wall, a ceramic covering member on each of the surfaces of each segment other than its base and the surface parallel thereto, a foamed ceramic cement joining said ceramic covering members to said honeycomb segments, and means retaining said assembled segments in position relative to one another, said ceramic honeycomb segments, said covering members and said foamed ceramic cement all having a low and essentially similar coefficient of thermal expansion.

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