



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁶ : C04B 38/00</p>	<p>A2</p>	<p>(11) International Publication Number: WO 98/43927</p> <p>(43) International Publication Date: 8 October 1998 (08.10.98)</p>
<p>(21) International Application Number: PCT/US98/06269</p> <p>(22) International Filing Date: 30 March 1998 (30.03.98)</p> <p>(30) Priority Data: 08/825,629 31 March 1997 (31.03.97) US</p> <p>(71) Applicant: PORVAIR CORPORATION [US/US]; 700 Shepherd Street, Hendersonville, NC 28792 (US).</p> <p>(72) Inventors: PICKRELL, Gary, R.; 21 Newport Drive, Travelers Rest, SC 29690 (US). BUTCHER, Kenneth, R.; 3561 Willow Creek Road, Hendersonville, MC 28793 (US).</p> <p>(74) Agents: SCHNEDLER, Steven, C. et al.; Carter & Schnedler, P.A., Suite 103, 56 Central Avenue, P.O. Box 2985, Asheville, NC 28802 (US).</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>Without international search report and to be republished upon receipt of that report.</i></p>
<p>(54) Title: POROUS CERAMIC ARTICLES AND METHOD FOR THE MANUFACTURE THEREOF</p>		
<p>The diagram illustrates a porous ceramic structure composed of numerous overlapping circular particles. Each particle is represented by a large outer circle (labeled 12) and a smaller inner circle (labeled 10). The inner circles are positioned such that they create a network of interconnected voids throughout the structure. The overall arrangement is dense and irregular, typical of a sintered porous material.</p>		
<p>(57) Abstract</p> <p>An improved porous ceramic article and a method for forming such porous ceramic article. A mixture of ceramic particles and pliable organic hollow spheres is prepared in a liquid, typically as a suspension. The article is formed by pressing, slip casting, extruding or injection molding the mixture. The article is dried to remove the liquid, and then is fired so that the ceramic particles are bonded such as by sintering, and the organic spheres are burned off, resulting in a strong porous ceramic article having uniformly spaced interconnected voids (10).</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

Porous Ceramic Articles and
Method for the Manufacture Thereof

Description

Technical Field

5 This invention relates to the formation of ceramic articles. The invention more particularly relates to the formation of porous ceramic articles.

Background Art

10 In the production of ceramic materials for use in refractory, kiln furniture, filtration, catalytic, bone implants and other applications, it is sometimes desired to reduce the overall density of the fabricated article by introducing porosity into the article during or after fabrication. The strategy employed for reducing the mass
15 of the article after fabrication usually involves removal of material from the article by means of grinding, drilling, routing or other mechanical methods to physically remove material from selected locations. This usually takes the form of drilling holes, routing channels, etc.
20 Reducing the mass of the material (per unit volume of space occupied by the fabricated article) during fabrication involves using a process which introduces porosity into the ceramic. This can be accomplished by various methods described in the literature.

25 Some of the basic patents assigned to Selee Corporation, an affiliate of the assignee of the present invention, disclose a method to produce a ceramic article with a high volume percent interconnected porosity by impregnating a reticulated polyurethane foam with a ceramic
30 slurry and heating to burn off the polymer and sinter the ceramic. This method can be used to produce various pore sizes and densities. The reported strengths for various ceramic materials fabricated in this manner lie in the 500 - 700 psi range.

Another method to produce low density ceramic kiln furniture is taught in U.S. Patent No. 4,812,424, whereby a porous aluminosilicate refractory aggregate is fired. The aluminum metal, alkali silicate and alkali aluminate chemical reaction producing a large volume of small gas bubbles is combined with a sodium silicate-sodium aluminate hydrogel setting reaction which traps the hydrogen gas bubbles in the ceramic. The strengths of this material are approximately in the 500 - 1000 psi range.

U.S. Patent Nos. 4,814,300, 4,846,906, 4,871,495, 4,878,947, 4,923,487, 4,963,515 and 4,976,760 are extensions of this basic technology to include membranes and are used in specific markets, such as diesel particulate traps and diesel filters.

European Patent Specification Publication No. EP 0 598 783 B1 discloses a method of preparing porous refractory articles by forming a dispersion comprising particles in a liquid carrier, introducing gas into the dispersion and removing the liquid carrier to provide a solid article having pores derived from the bubbles.

U.S. Patent No. 4,889,670 discloses a method to produce porous ceramic parts by combining a mixture of 60 - 90 weight percent of a particulate ceramic with 10 - 40 weight percent of a latex polymer, whereby the mixture is frothed by mechanical means, shaped, set and sintered to produce the porous article.

It is also well known that porosity can be introduced into a ceramic article by incorporating various types of organic particles into the ceramic body. Upon firing, these particles are oxidized and leave behind voids in the material.

Disclosure of Invention

In accordance with one form of this invention, there is provided a method for forming a porous ceramic article. A mixture of ceramic particles and pliable organic spheres is prepared in a liquid. Preferably, a suspension of the ceramic particles and pliable organic

spheres is formed. Preferably, the spheres are hollow and are made of a polymer, such as acrylic. The mixture is formed into a shaped article. The shaped article is dried. The shaped article is then fired so that the ceramic
5 particles are bonded such as by sintering, and the pliable organic spheres are burned off, resulting in voids in the shaped article.

In accordance with another form of this invention, there is provided another method for producing
10 porous ceramic articles. A suspension of ceramic articles and pliable organic hollow spheres are formed such that the ceramic articles and pliable hollow polymer spheres are simultaneously suspended in a liquid, preferably comprising water. A shaped article is formed after a sufficient
15 amount of water is added. A shaped article is formed by either slip casting, pressing, extrusion, or injection molding. The shaped article is dried to remove the water. The shaped article is then fired to allow bonding of the ceramic particles such as by sintering, and to burn off the
20 pliable organic hollow spheres, resulting in uniformly distributed voids in the shaped article.

A range of porosities of up to 95% void volume may be achieved using these methods. The size of the voids may be preselected by selecting the appropriate size
25 polymer spheres. The amount of porosity is easily controlled by the number of polymer spheres which are added. The size range of the pores can be closely controlled by controlling the size range of the polymer spheres which are used. The distribution of the pores in
30 the ceramic is highly uniform due to the fact that the polymer spheres in the ceramic particles are preferably simultaneously suspended by the addition of the appropriate suspending agent.

The article may be coated, for example with
35 another ceramic composition. It has been found that the coating will stay bonded to the article through a large number of thermal cycles. Similar coatings on other substrates do not adhere as well.

In accordance with another form of this invention, there is provided a porous ceramic article having a plurality of substantially spherical shaped voids. The voids are substantially uniformly dispersed throughout the article. The voids are interconnected with one another. For an article having a theoretical density in the range from 5% to 30%, the strength of the article is in the range from 700 psi to 4500 psi.

In another form of this invention, there is provided a porous ceramic article having a plurality of substantially spherical shaped voids therein. The voids are substantially uniformly dispersed throughout the article. The voids are interconnected with one another. A substantial number of the voids intersect with at least one adjacent void. A window is formed by the intersection. The window is substantially in the shape of a circle. The average diameter of the circle is in the range from approximately 11 microns to 22 microns.

In accordance with another form of this invention, there is provided a porous ceramic article having a plurality of substantially spherical shaped voids therein. The voids are substantially uniformly dispersed throughout the article. The voids are interconnected with one another. At least a portion of the article is coated. The coating may comprise a ceramic composition, such as zirconia. The coating will remain adhered to the article for at least ten thermal cycles. The preferred thermal cycle is from approximately room temperature to approximately 2200°F and back to approximately room temperature in approximately 2 hours.

Brief Description of the Drawings

The subject matter which is regarded as the invention is set forth in the appended claims. The invention itself, however, together with further objects and advantages thereof may be better understood in reference to the accompanying drawings in which:

FIGURE 1 is a sectional view of a portion of an article made in accordance with the subject invention, with the exposed side having been polished;

FIGURE 2 shows a portion of FIGURE 1, which has
5 been magnified.

Best Mode for Carrying Out the Invention

Porous ceramic articles were formed in accordance with the teaching of the invention as set forth in Examples 1-5 below.

10

EXAMPLE 1

A highly porous zirconia toughened alumina article was prepared by mixing 8.4 weight percent zirconia, 18.2 weight percent alumina with 16.1 weight percent water, 1.2 weight percent nitric acid, 4.3 weight percent starch,
15 1.1 weight percent petroleum jelly, and 0.8 weight percent pliable hollow polymer spheres. The average size of the spheres was 100 microns. These constituents were mixed in a Hobart mixer forming a paste with the consistency of bread dough. This mixture was then shaped by pressing in a
20 mold, removed, dried and fired to form the porous ceramic article. The fired article was composed of 72% void volume. The average void size was approximately 100 microns and the voids were very uniformly distributed across the article. Scanning electron microscopy of the
25 article revealed that the pores were highly connected. The average modulus of rupture of these articles with 72% void volume was approximately 4000 psi. Articles of this material have been cycled from room temperature to 2200°F and back to room temperature in 1.75 hours. The dimensions
30 of the article was approximately 3.25" x 2.5" x 0.25". After 100 of these thermal cycles, the average strength was still 4000 psi. This demonstrates the excellent thermal shock resistance of these materials. The ability of this material to be shaped in the green state by pressing in
35 molds allows the readily available automatic forming equipment to be used to fabricate the desired articles.

These automatic forming equipment not only allow parts to be molded in a short period of time, but also allow very economical production of the parts.

EXAMPLE 2

5 In another instance, the same procedure was used as in Example 1, except that the weight percent of pliable hollow polymer spheres which were used was increased. The resulting article was composed of 82% void volume with the result in the strength of approximately 2500 psi.

10 EXAMPLE 3

 In another instance, the same procedure was used as in Example 2, except that the weight percent of pliable hollow polymer spheres were increased. The resulting article was composed of 88% void volume with the result in
15 the strength of approximately 1500 psi.

EXAMPLE 4

 A highly porous zirconia toughened alumina article was prepared by mixing 8.8 weight percent zirconia, 72 weight percent alumina with 17 weight percent water, 1.3
20 weight percent nitric acid, and 0.84 weight percent pliable hollow polymer spheres, and 0.1 weight percent of a defoaming agent. Additional water was then added to produce a slurry suitable for slip casting in plaster of paris molds using traditional slip casting techniques.
25 Articles were formed by pouring the slip prepared as above in the plaster of paris molds and allowing suitable time for the molds to absorb the water. The cast parts were then taken from the mold, dried and fired. The average strength of these articles with 72% void volume was
30 approximately 4000 psi. In general, all the physical properties were the same as those described for the pressed material described in Example 1.

EXAMPLE 5

A highly porous zirconia toughened mullite article was prepared by mixing 38.4 weight percent zircon (zirconium silicate), 44.6 weight percent alumina with 15 weight percent water, 1 weight percent nitric acid, 1 weight percent pliable hollow polymer spheres, and 0.01 weight percent of a defoaming agent. The amount of water added was sufficient to produce a slurry suitable for slip casting in plaster of paris molds using traditional slip casting techniques. Articles were formed by pouring the slip prepared as above in the plaster of paris molds and allowing suitable time for the molds to absorb the water. The cast parts were then taken from the mold, dried and fired. The articles formed were composed of approximately 15 70% void volume space.

EXAMPLE 6

In another instance, solid substantially non-pliable polymer spheres of approximately the same average size as the pliable hollow polymer spheres mentioned in Examples 1-5 were used as a comparison. These solid spheres, which are very hard, were mixed in exactly the same manner as Example 1, except the solid spheres were substituted for the hollow spheres (equal volume percentages of solid spheres were substituted for the hollow spheres to maintain the same fired density). The bodies were dried and fired in exactly the same manner as in Example 1. The measured MOR (strengths) of the sintered body using the solid spheres was only 1350 psi. As a comparison, this is only about one-third to one-half of the strengths obtained when using the pliable hollow spheres. 30

EXAMPLE 7

In another instance, a commonly used organic filler material, walnut flour, was used in place of the pliable hollow spheres. The proper amount of the walnut flour was determined which would give the same fired density articles as obtained in Example 1. The procedure

followed was exactly the same as in Example 1, except the walnut flour was substituted for the pliable hollow spheres and additional water had to be added to make a body suitable for pressing. The articles made in this manner were dried and fired as in Example 1. The resulting articles underwent approximately 5 times the amount of shrinkage as those in Example 1 and were too weak to allow MOR testing to be performed.

The preferred range for the volume percent of the hollow pliable polymer sphere for a porous article is between 50% and 95% void volume.

The preferred range for the size of the pliable hollow polymer spheres is between 1 micron and 1000 microns.

As can be seen by comparing the articles which were obtained by Examples 6 and 7 to those of the invention set forth in Examples 1-5, it is clear that the invention produces far superior ceramic articles. It is believed that the ceramic articles produced by the invention are stronger primarily because cracks do not form during the drying process, which it is believed is due to the fact that the pliable hollow spheres deform when the ceramic matrix contracts during drying. This deformation does not occur when one uses hard solid substantially non-pliable spheres, as indicated in Example 6. It is believed that the strength of an article produced in accordance with this invention is in the range of 700 psi for a 5% theoretical density to 4500 psi for a 30% theoretical density. The strength is measured by supporting the article at the ends thereof and applying a force to the top of the article until the article breaks. Thus the ceramic articles produced by the invention have been shown to be much stronger than the prior art.

In addition, it is believed that the use of pliable hollow spheres enables paths between the resultant spherical voids to occur with more certainty because the adjacent hollow spheres do not have a mere single point of

contact, as do hard spheres, but have a substantial area of contact so that connections between the resultant voids are more likely when the adjacent spheres deform.

Referring more particularly to FIGURE 1, each
5 spherical void 10 includes at least one substantially circular window 12 formed by the intersection of an adjacent spherical void 10. The average diameter of the circular windows 12 is in the range from approximately 11 microns to 22 microns.

10 FIGURE 2 shows intersecting spherical voids 14 and 16 having windows 18 and 20, respectively. The windows formed by the intersection of spherical voids 14 and 16 are hidden from view.

The article may have a coating applied. A
15 coating is sometimes desirable for non-reactivity, hardness, impermeability, pore size control, and other characteristics. The coating may comprise a ceramic composition, such as zirconia. It has been found that a coating, when applied to the articles of the subject
20 invention, will remain adhered to the article over a large number of thermal cycles, compared to prior art articles which have been similarly coated. It has been found that the coating began to peel off prior art articles after less than ten thermal cycles from approximately room temperature
25 to approximately 2200°F and back to approximately room temperature in approximately 2 hours. On the other hand, it has been found that the coating on an article of the subject invention remained adhered to the article after
30 over 100 thermal cycles from approximately room temperature to approximately 2200°F and back to approximately room temperature in approximately 2 hours.

From the foregoing description of the preferred
embodiments of the invention, it will be apparent that many
modifications may be made therein. For example, porous
35 articles can be made using other ceramic compositions, such as oxides, carbides or nitrides of silicon, aluminum and zirconium, as well as mullite, cordierite or a mixture thereof. It will be understood, however, that the

embodiments of the invention are exemplifications of the invention only and that the invention is not limited thereto. It is to be understood, therefore, that it is intended in the appended claims to cover all modifications
5 as fall within the true spirit and scope of the invention.

Industrial Applicability

The way in which the invention is capable of being exploited and the way in which it can be made and used will be apparent from the foregoing.

Claims

1. A method for forming a porous ceramic article comprising the steps of:
preparing a mixture of ceramic particles and
5 pliable organic spheres in a liquid;
forming the mixture into a shaped article;
drying the shaped article;
firing the shaped article, wherein the
ceramic particles are bonded and the pliable organic
10 spheres are burned off, resulting in voids in the shaped article.
2. A method as set forth in Claim 1, wherein said liquid comprises water.
3. A method as set forth in Claim 1, further
15 including the step of suspending the ceramic particles and pliable organic spheres in the liquid.
4. A method as set forth in Claim 3, further including the step of adding a suspending agent for aiding in the formation of the suspension.
- 20 5. A method as set forth in Claim 1, wherein said shaped article is formed by slip casting.
6. A method as set forth in Claim 1, wherein said shaped article is formed by pressing.
7. A method as set forth in Claim 1, wherein
25 said shaped article is formed by extrusion.
8. A method as set forth in Claim 1, wherein said shaped article is formed by injection molding.

9. A method as set forth in Claim 1, wherein the void volume of the shaped article after firing is less than 95%.

10. A method as set forth in Claim 1, wherein
5 said pliable organic spheres are hollow.

11. A method as set forth in Claim 1, wherein said pliable organic spheres are made of acrylic.

12. A method as set forth in Claim 1, wherein the ceramic particles are selected from the group
10 consisting of oxides, carbides and nitrides of zirconium, silicon and aluminum, and mullite and cordierite, or mixtures thereof.

13. A method as set forth in Claim 12, wherein the ceramic particles comprise zirconia and alumina.

14. A method as set forth in Claim 1, wherein
15 said spheres range in diameter from 1 micron to 1000 microns.

15. A method as set forth in Claim 1, wherein said ceramic particles comprise a mixture of zirconium
20 silicate and alumina.

16. A method as set forth in Claim 1, further including the step of coating a portion of the article.

17. A method for forming a porous ceramic article comprising the steps of:
25 preparing a mixture of ceramic particles and pliable organic hollow spheres in a liquid;
forming the mixture into a shaped article;
drying the shaped article;
firing the shaped article, wherein the
30 ceramic particles are bonded and the pliable organic hollow

spheres are burned off, resulting in voids in the shaped article.

18. A method as set forth in Claim 17, wherein said fluid medium comprises water.

5 19. A method as set forth in Claim 17, further including the step of suspending the ceramic particles and pliable organic hollow spheres in the liquid.

20. A method as set forth in Claim 19, further including the step of adding a suspending agent for aiding
10 in the formation of the suspension.

21. A method as set forth in Claim 17, further including the step of adding an amount of water prior to drying; and wherein said shaped article is formed by slip casting.

15 22. A method as set forth in Claim 17, wherein said shaped article is formed by pressing.

23. A method as set forth in Claim 17, wherein the void volume of the shaped article after firing is less than 95%.

20 24. A method as set forth in Claim 17, wherein said pliable organic hollow spheres are made of acrylic.

25. A method as set forth in Claim 17, wherein said pliable organic hollow spheres range in diameter from 1 micron to 1000 microns.

25 26. A method as set forth in Claim 17, wherein a slurry containing the ceramic particles is formed first and then the pliable organic hollow spheres are added to the slurry.

27. A method as set forth in Claim 17, wherein the mixture is in the form of a paste having the consistency of bread dough.

28. A method as set forth in Claim 17, wherein
5 said ceramic particles and pliable organic hollow spheres are simultaneously suspended in the liquid.

29. A method as set forth in Claim 17, further including the step of coating at least a portion of the article.

10 30. A porous ceramic article comprising:
a ceramic article having a plurality of substantially spherical shaped voids therein; said voids being substantially uniformly dispersed throughout said article; said voids being interconnected with one another;
15 when the article has theoretical density in the range from 5% to 30%, the strength of the article is in the range from 700 psi to 4500 psi.

31. An article as set forth in Claim 30, wherein the ceramic constituents of said article comprise zirconia
20 and alumina.

32. An article as set forth in Claim 30, wherein said article is substantially free from cracks.

33. A porous ceramic article comprising:
a ceramic article having a plurality of
25 substantially spherical shaped voids therein; said voids being substantially uniformly dispersed throughout said article; said voids being interconnected with one another;
a substantial number of said voids intersecting with at least one adjacent void;
30 windows formed by said intersections; said windows being substantially in the shape of a circle;

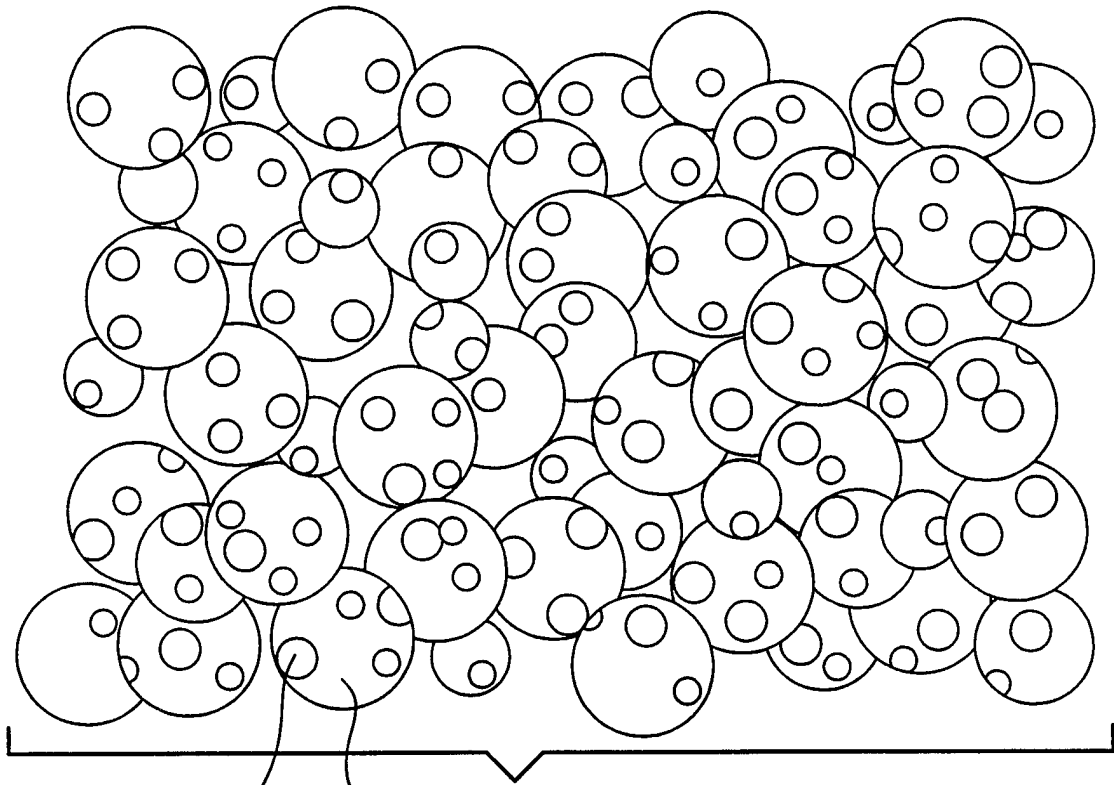
the average diameter of said circles being in the range from approximately 11 microns to 22 microns.

34. An article as set forth in Claim 33, wherein said article is substantially free from cracks.

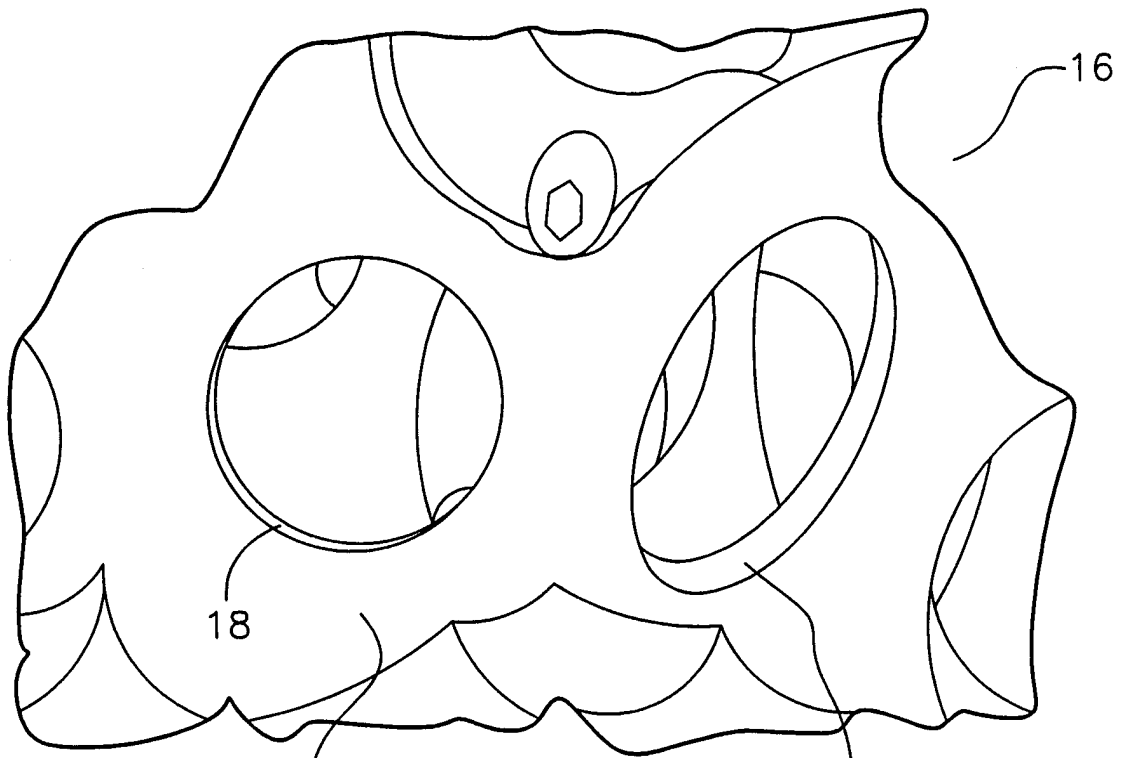
5 35. A porous ceramic article comprising:
a ceramic article having a plurality of substantially spherical shaped voids therein; said voids being substantially uniformly dispersed throughout said article; said voids being interconnected with one another;
10 at least a portion of said article having a coating, whereby said coating will remain adhered to said article for at least 10 thermal cycles.

36. An article as set forth in Claim 35, wherein said coating comprises a ceramic composition.

15 37. An article as set forth in Claim 35, wherein a thermal cycle is from approximately room temperature to approximately 2200°F and back to approximately room temperature in approximately 2 hours.



12 10 *Fig. 1*



14 18 16 20 *Fig. 2*