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(54) Title: METHOD FOR MANUFACTURING A POROUS FOAM SUPPORT, AND POROUS FOAM SUPPORTS FOR CATALYTIC REACTORS, ADSORPTION PROCESSES AND ENERGY STORAGE

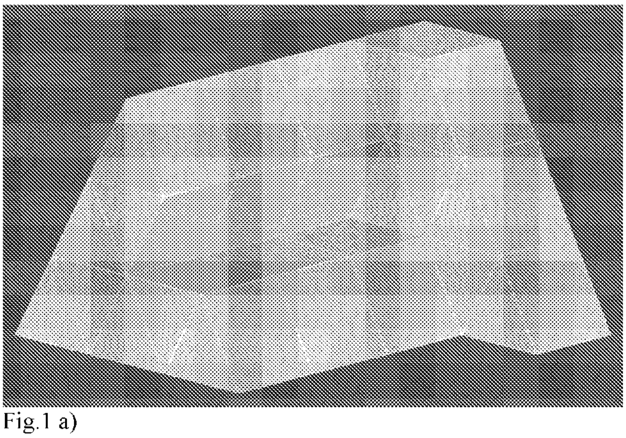

Fig.1 a)

(57) **Abstract:** It is described a method for manufacturing of a porous foam support comprising a number of cells, the method comprising: - producing a 3D tessellation of space with polyhedrons, wherein the arrangement of the polyhedrons provides a complete space filled with a solid structure representing the cells of the porous foam support, - subtracting polyhedrons and n-sided prisms to generate cell porosity and interconnectivity and control flow properties. The resulting porous foam support may be manufactured by additive manufacturing or 3D printing.

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Method for manufacturing a porous foam support, and porous foam supports for catalytic reactors, adsorption processes and energy storage

INTRODUCTION

The project leading to this application has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 680414.

The present invention provides a methodology to produce iso-reticular cellular foam structures to be used as catalysts, catalysts supports, adsorbent materials and gas storage. The methodology used for production may be applicable to any material, for example, polymers, ceramics and metals, and combinations of them, but not exclusive to these categories. This methodology is particularly suited to be used for production of foam-structures using additive manufacturing, but is not restrictive to this manufacturing technique. Other methods of preparation like injection moulding or casting can be used.

Nowadays, there are a wide diversity catalysts and adsorbents that are produced as honeycombs or foams (Fiedler, 1957; Ross et al., 2012; Twigg and Sengelow, 1989; Del-Gallo et al., 2011; Naruse et al., 2011; Lipton and Lipton, 2015). Honeycomb monoliths are quite widespread in the market, being the most common application the abatement of nitrogen oxides in vehicles (Kato, 2008). They are also used for other purposes like selective adsorption of gas contaminants and water (Kendall, 2000; Baker, 2008). The main advantage of honeycomb monoliths is the low pressure drop they provide when compared to packed beds of particulates (extrudates or pellets). However, since the flow in each parallel channels is laminar, mixing and thermal transfer are limited. The mixing of the gas in each channel is mainly driven by molecular diffusion.

Inventions related to catalyst particles and structured catalysts preparation by additive manufacturing have already been reported (Williams, 2012; Coupland, 2015; Li et al., 2016). These inventions relate either to the patenting of the composition of the material to be used in the additive manufacturing process

(Williams, 2012) or considering only catalysts particles or monoliths (Coupland, 2015) or membrane-type structures (Li et al., 2016).

Foam-like materials have the potential to improve mass and heat transfer limitations. They are cellular materials; each of the cells is formed by a combination of windows and struts (walls). Foams combine high porosity and also high degree of interconnectivity (Twigg and Richardson, 2007). The high porosity results in low pressure drop, and the interconnectivity favours the radial mixing improving mass transfer significantly (by convection). The radial mixing also contributes to promote fast heat transfer to the surroundings. For these reasons, catalytic foams have an enormous potential to be used as next-generation structured catalysts (Twigg and Richardson, 2007). Foam-like structures have been much less used for adsorption processes (Hu et al., 2009).

The utilization of foams is not limited to chemical processes. Closed-cell foams are nowadays used as space fillers for isolation (Cook and Capotosto, 2015). Open-cell foams are also used to build resistant structures with important material savings in several areas ranging from bridge construction to windmills and implants (Garg et al., 2001; Luscher, 2016). Although our methodology is applicable to all these areas, we are only restricting its field of application to the chemical industry and energy storage, namely to catalytic reactors and separation processes as well as energy carrier (gas or liquid for example) storage driven by selective adsorption.

Nowadays, open-cell foams made of different materials have different production methods. Polymeric and ceramic foams are mostly produced using polyurethane expansion. In the case of ceramic foams, the polyurethane foam is loaded with a ceramic material as slurry and then the polyurethane is removed at high temperatures. Metallic foams (sometimes termed as metal sponges) are produced by several methods including gas or foaming agent in molten metal, casting or more recently additive manufacturing (Furman, et al., 2010; Kashani-Shirazi et al., 2012; Medina et al., 2014; García-Moreno, 2016, Selvam et al., 2016).

The traditional techniques for manufacturing open-cell foams result in random cells with also variable strut dimensions. It has been confirmed by 3D tomography that there can be wide distributions of cell size, shape, strut width and distribution in a single foam (Montminy et al., 2004; Jang et al., 2008). Indeed, complex numerical geometrical descriptions of these foams can be used for detailed modelling based on tomography data (Storm et al., 2013; Siegkas et al., 2014; Liebscher et al., 2015).

In that sense, both controlled casting and additive manufacturing have proved that they can bring advantages over traditional routes enabling uniform cell structure, shape and distribution. Casting of metals using the Kelvin cell model with circular windows has already been performed by casting, although the technique is limited to relatively large cell size (> 10 mm diameter).

The random distribution of cells, windows and strut width has a serious impact in catalytic and adsorption properties and result in several complications using these materials in reactors and adsorbers. For example, when multiple or consecutive reactions take place, a distribution of cell size results in lower selectivity towards the desired component in reactors and in wide mass transfer zones for adsorption processes. For this reason, materials and/or support materials with uniform properties are much desired since they will allow better control of selectivity and of flow conditions.

SUMMARY OF THE INVENTION

In a first aspect the invention provides a method for manufacturing a porous foam support comprising a number of cells, the method comprising producing a 3D tessellation of space with polyhedrons, wherein the arrangement of the polyhedrons provides a complete space filled with a solid structure representing the cells of the porous foam support.

The polyhedrons may be space filling polyhedrons, or a combination of space filling polyhedrons and non-space filling solids. The cells are obtained by generating a first polyhedron representing a unitary cell of the solid structure, and subtracting a second polyhedron from the first polyhedron, wherein the second polyhedron is an internal polyhedron of the first polyhedron and being similar to the first polyhedron. The solid structure may be generated by generating each polyhedron at a time until the structure is filled with polyhedrons. The method may further include *n*-sided prisms to generate interconnection between the cells. The polyhedrons may have an m-modal structure, where m is the number of solids used for the 3D tessellation of space representing the porous foam support. The cells may have an iso-reticular structure. Independent control of porosity and flow properties may be obtained using different space-filling solids and by designing at least one of the following:

- a relative rotation between the space-filling solids, and/or
- a cell aperture by adjusting the number and size of the *n*-sided prisms.

The complete space may be Euclidian or curved. The method may further comprise fabricating the porous foam support by additive manufacturing. The porous foam support may be fabricated by 3D printing.

The porous foam support may have a porosity ranging from 0.04 to 0.995, preferably from 0.35 to 0.97 and more preferable from 0.7 to 0.90. The porous foam support may be an iso-reticular cellular catalytic foam.

The porous foam support may be an iso-reticular cellular foamed adsorbent materials. The iso-reticular cellular foamed adsorbent material may have a porosity ranging from 0.04 to 0.995, preferably from 0.35 to 0.97 and more preferable from 0.25 to 0.55.

The porous foam support may be an iso-reticular cellular adsorbent for gas storage. The iso-reticular cellular adsorbent for gas storage may have a porosity ranging from 0.04 to 0.995, preferably from 0.05 to 0.40 and more preferable from 0.08 to 0.20.

In a further aspect the invention provides an iso-reticular cellular catalytic foam manufactured by the process as described above.

In an even further aspect the invention provides an iso-reticular cellular foamed adsorbent material manufactured by a process as described above.
In an even further aspect the invention provides an iso-reticular cellular adsorbent for gas storage manufactured by a process as described above.

BRIEF DESCRIPTION OF DRAWINGS

Example embodiments of the invention will now be described with reference to the followings drawings, where:
Figure 1. Space tessellation by: (a) hexagonal prisms as example of space-filling solids; (b) combination of two non-space filling solids (octahedrons and tetrahedrons).
Figure 2. Different steps of the methodology to construct one iso-reticular cell.
Figure 3. Iso-reticular foam structure constructed with cubes as unitary cells.
Figure 4. Iso-reticular foam structure constructed with cubes and rotated 45° already prepared to be fitted in a cylindrical tube.
Figure 5. Cell structure constructed with 6 pyramids that fit within a cube. The structure presents the same porosity than the one constructed with cubes and shown in Figure 2 but different strut width.

DETAILED DESCRIPTION

Our major aim is to provide a methodology to manufacture iso-reticular open-cell foams with uniform properties that can be used for chemicals production and energy (gas) carriers. The major advantage of our approach is that the foams can be produced with custom-made tunability of several process parameters: it is possible to independently control porosity and strut dimension (important for diffusion-limited processes) and also tailor flow conditions. As mentioned before, we envision additive manufacturing as the preferred manufacturing route for such foams.

Our methodology targets the production of digital files (typically stl, cad or obv files) that can be used for fabrication of the foams. The production of such iso-reticular foam structures is based on a series of mathematical procedures that will render different products with different and tunable properties, that will be used as foam support, foam catalyst, foam-type adsorbent (for separation or for gas storage). With this methodology is possible to obtain a library of solids that can provide a framework for selection the appropriate structure instead of a more comprehensive and time-consuming structure optimization.

The methodology starts by producing a 3D tessellation of space with polyhedrons. The arrangement of such polyhedrons should be such that the complete Euclidean space considered is filled with one solid that will be the final shape of the foam. This can be achieved with space-filling polyhedrons or with combinations of non-space-filling solids that result in a perfect tessellation of 3D Euclidean space (tetrahedron and octahedrons for example). Examples of the initial solid tessellation are shown in Figure 1 for the case of space-filling solids (a) and combination of non-space-filling solids (b).

Each of the polyhedrons used for generating the structure represents the structure of the unitary cells of the structure. So, for a tessellation of space by space-filling solids, the cell arrangement can be completely iso-reticular. For space tessellations composed of two or more types of solids, the cells will have bi- or more generically, *k*-modal structures, being *k* the number of solids used for the tessellation of space. Traditionally, chemical structures constitute examples of *k*-modal structures (Engel, 1986).

There are several space-filling polyhedrons. The most well-known examples are: cube (only Platonic solid that is space-filling solid), triangular prism, hexagonal prism (typical honeycomb structure), truncated octahedron, rhombic dodecahedron, several tetradecahedra (including the Kelvin cell), gyrobifastigium, etc.

In total there are over 200 space-filling solids (Engel, 1986). An equal number of iso-reticular foams with unimodal cell distribution can be generated. The combination of non-space-filling solids to render a space tessellation is relatively high and then a significant number of other structures can be obtained. In this case, although the overall structure of the foam can be considered as homogeneous, the structure of the cells will not be unimodal but *k*-modal depending on the number of polyhedrons used. A *k*-modal distribution can be disadvantageous to control selectivity in some reaction systems, but may be favourable to facilitate fluid transport in adsorption cases related to energy storage.

A simple way to visualize the mathematical procedure required to generate the stl file, the following mathematical operations should be considered. Assuming a cell (termed as A) centered at the point (0,0,0) in the Euclidean space. If we draw the same cell shape centered at the same point but with a smaller unit size termed as B, it is possible to obtain a closed-cell foam unit cell termed as C by performing: C = A-B. Closed cell foams are used in several markets, most dominantly as isolation materials. Closed cell foams might retain floatability which makes them interesting for life-protection materials and recreation.

For opening the connections between the different cells the same number of polyhedral as the cell sides is defined and subtracted to the closed-cell foam (C). For such, it is defined a polyhedron consisting of *n*-sided prism corresponding to the number of vertices of the face to be removed and by placing them in the right position, they can be subtracted to the original structure. Such mathematical operations should be performed for as many cells as required in the *x, y, z* directions (or other coordinates if found more proper). A representation of the different steps for the case of open cell foams where the unitary cell is composed by cubes is shown in Figure 2.

There are other mathematical operations to reach the same type of results. Another mathematical operation that can be used is by "pilling" 3D solids (the struts of the foam-like materials) in order to build a similar structure as the one obtained by the previously presented methodology.

The major advantage of creating such structures is that there exist several options to tune the foam properties. For example, by modifying the size of the internal polyhedron, it is possible to obtain cells with the same overall shape, but resulting with a different porosity.

It should be noted however that increasing the strut width can result in diffusion-limited processes (both in catalytic reactors and in adsorption processes). Instead of the *n*-sided prisms used for window creation, other structures can be used being possible to tailor the mixing of fluids in the individual cells of the foam. By tuning the number and location of *n*-sided prisms it is also possible to tailor the surface area of the foams which might be useful for some applications.

Another possibility to tailor foam properties is to control the inlet – outlet of each cell in order to control and tailor the radial mixing. In this regard, there are two different possibilities of achieving flow control. The first one is to control the shape, size and/or position of the polyhedrons that had to be subtracted to generate the windows of the cells. The second strategy is to tune the relative rotation of the foam cells with the reactor/adsorber column where it will be used. The first strategy will have a simultaneous impact in the flow conditions and in the overall porosity, while controlling rotation, only the flow conditions (radial and axial mixing and eventually pressure drop) are modified but porosity is kept constant.

Generating a library of different solids with iso-reticular cells, it is possible to tailor foam porosity by using different sets of polyhedrons that constitutes each cell. All the space-filling solids have different number of vertices (V), edges (E) and faces (F). As will be shown in the examples, using different polyhedrons, it is possible to change the overall porosity value but keeping the strut width. This means that by selecting different polyhedrons (a design parameter), we can produce foams or foam supports with independent control of porosity and strut width. This is a major innovation in the development of foams that together with the possibility of having iso-reticular unimodal cells, can provide control of selectivity of the process.

Using the methodology presented here, it is possible to independently control the porosity, the size, shape and distribution of solids, as well as the content of the catalyst which can be part of the structure used in the generation of the foam or placed afterwards. Moreover, to control the flow distribution in the structure, window size as well as distribution and rotation of the shapes can be applied.

The methodology that supports the fabrication of the foams presented here is used to generate an electronic file that is used for the production of the desired foam material. Different mathematical approaches can be used to reach similar conclusions, like "pilling" of 3D solids to conform similar unimodal cell structures. Many tools to design such foams can be obtained from crystallography studies where *k*-modal structures are available (with *k* corresponding to the different number of molecules). The different shapes required to construct the foam generating file can be drawn in many available software and after producing it, the final shape can be exported as an electronic file, stl or obj for example, to be manufactured using 3D printing machines preferentially. Other files can be used in different machines of fabrication.

The following examples aim to demonstrate the application of the methodology for generation of some foam structures.

Example 1

The procedure of generating one iso-reticular foam support or catalytic/adsorbent/energy gas carrier foam with cubes is described. The operation on a cell level is similar to the one shown in Figure 2. Define Function "A" as a tessellation of space with desired number of cubes of side L in *x, y, z* coordinates. Define Function "B" an array of cubes such that are centered at the same position of all existing cubes as in Function A, but they have a dimension P, provided that P < L. Function C will be defined as the subtraction of both functions: C = A – B. Function C represents the structure of a closed-cell foam with uniform walls of size (L-P). Porosity of this closed foam is defined as: $\epsilon = P^3/L^3$. A function "D" should be defined as a sum of parallelepipeds (with two sides smaller than P and one side being very small termed as □L) that will be placed in each of the existing walls of each cube such that it covers every connection between the cells. By performing the mathematical operation G = C-D, we obtain the open-cell foam. Stages of the different stages reported in this example are listed in Figure 2. The number of cells multiplied by the dimension of the cell "L" will define the total size of the foam while the amount of substrate will be defined by the L-P value. An example of a foam with (5x5x4) cells in (*x, y, z*) position is shown in Figure 3. The porosity of this foam is given by:

$$\varepsilon_f = \frac{[3(L-P)P^2 + P^3]}{L^3}$$

An alternative methodology to generate this foam is to define a cube with desired dimensions in *x, y, z* and subtract function B first and then function D. Additionally, this example is not limited to the generation of cubic foams but any arrangements of cubes distributed in the three dimensions are possible.

Example 2.

The structure provided in the previous example is not optimal for radial mixing of fluids. For that purpose it is possible to rotate the whole foam structure to be fitted in a pre-specified shape, like a cylindrical column. With 45° rotation, radial mixing is maximized. An example of such foam is shown in Figure 4. Such approach is suitable also for textural rotations of the whole foam to be fitted into structures with non-standard shapes. Rotation in two dimensions is also possible and may improve further radial mixing.

Example 3.

The previous examples considered tessellation of space with cubes. We have control of mixing by the rotation and control of porosity by defining the internal polyhedra. However, for diffusion limited reactions for example it might be interesting to control independently the amount of substrate and its porosity. In the previous cases, the representative dimension of the struts (for diffusion purposes) is (L-P).

An independent control of strut width and porosity can be obtained by using different sets of polyhedra. Using pyramids is also possible to replicate the same approach as in example 1. An example of the unitary cell is shown in Figure 5. In this case, the porosity is the same as the one in the previous examples but the strut width is approx. (L-P)/2. This allows a decrease in P, decreasing the porosity but keeping the strut width under control.

Example 4.

Other combinations of space-filling solids with external dimensions L (or a) and internal dimensions P (or b) render different porosities. A list of different possibilities is listed in the following Table indicating that using different polyhedrons is possible to obtain foams with different porosities, flow control, strut width and mixing control (by controlling number of walls in each cell).

Shape	Porosity	Strut width
Cubic cell	$\varepsilon_f = \frac{[3(L-P)P^2 + P^3]}{L^3}$	$(L-P)$
Cubic cell with pyramids	$\varepsilon_f = \frac{[3(L-P)P^2 - 2P^3]}{L^3}$	$\sim \frac{(L-P)}{2}$
Truncated octahedron	$\varepsilon_f = \frac{b^3}{a^3} + \frac{2}{3}\sqrt{\frac{3}{2}}\frac{b^2(a-b)}{a^3}$	$(L-P)$
Elongated dodecahedron	$\varepsilon_f = \frac{b^3}{a^3} + \left[\frac{3\sqrt{3} + 4\sin(80^\circ)}{6}\right]\frac{b^2(a-b)}{a^3}$	$(L-P)$

Rhombic dodecahedron	$\varepsilon_f = \frac{b^3}{a^3} + \left[\frac{63\sin(70^\circ)}{16\sqrt{3}}\right]\frac{b^2(a-b)}{a^3}$	$(L-P)$
Hexagonal prisms (fully interconnected)	$\varepsilon_f = \frac{b^3}{a^3} + \left[\frac{2(\sqrt{3}+1)}{\sqrt{3}}\right]\frac{b^2(a-b)}{a^3}$	$(L-P)$
Hexagonal prisms (partially interconnected)	$\varepsilon_f = \frac{b^3}{a^3} + \left[\frac{(\sqrt{3}+1)}{\sqrt{3}}\right]\frac{b^2(a-b)}{a^3}$	$(L-P)$

Having described preferred embodiments of the invention it will be apparent to those skilled in the art that other embodiments incorporating the concepts may be used. These and other examples of the invention illustrated above are intended by way of example only and the actual scope of the invention is to be determined from the following claims.

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PATENT CLAIMS

1. Method for manufacturing a porous foam support comprising a number of cells, the method comprising:
- producing a 3D tessellation of space with polyhedrons, wherein the arrangement of the polyhedrons provides a complete space filled with a solid structure representing the cells of the porous foam support.

2. Method according to claim 1, wherein the polyhedrons are space filling polyhedrons, or a combination of space filling polyhedrons and non-space filling solids.

3. Method according to claim 1 or claim 2, wherein each of the polyhedrons is obtained by:
- generating a first polyhedron representing a unitary cell of the solid structure, and
- subtracting a second polyhedron from the first polyhedron, wherein the second polyhedron is an internal polyhedron of the first polyhedron and being similar to the first polyhedron.

4. Method according to claim 3, further comprising generating the solid structure by generating each polyhedron at a time until the structure is filled with polyhedrons.

5. Method according to claim one of claims 1-4, further comprising using n-sided prisms to generate interconnection between the cells.

6. Method according to claim one of claims 1-5, wherein the polyhedrons have an m-modal structure, where m is the number of solids used for the 3D tessellation of space representing the porous foam support.

7. Method according to one of claims 1-6, wherein the cells have an iso-reticular structure.

8. Method according to one of claims 1-7, wherein independent control of porosity and flow control is obtained using different space-filling solids and by designing at least one of:
- a relative rotation between the space-filling solids, and
- a cell aperture by adjusting the number and size of the n-sided prisms.

9. Method according to one of claims 1-8, wherein the complete space is Euclidian or curved.

10. Method according to one of claims 1-9, wherein the porous foam support have a porosity ranging from 0.04 to 0.995, preferably from 0.35 to 0.97 and more preferable from 0.7 to 0.90.

11. Method according to one of claims 1-10, further comprising fabricating the porous foam support by additive manufacturing.

12. Method according to one of claims 1-10, further comprising fabricating the porous foam support by 3D printing.

13. Method according to at least one of claims 1-12, wherein the porous foam support is an iso-reticular cellular catalytic foam.

14. Method according to at least one of claims 1-12, wherein the porous foam support is an iso-reticular cellular foamed adsorbent materials.

15. Method according to claim 14, wherein the iso-reticular cellular foamed adsorbent material has a porosity ranging from 0.04 to 0.995, preferably from 0.35 to 0.97 and more preferable from 0.25 to 0.55.

16. Method according to at least one of claims 1-12, wherein the porous foam support is an iso-reticular cellular adsorbent for gas storage.

17. Method according to claim 16, wherein the iso-reticular cellular adsorbent for gas storage has a porosity ranging from 0.04 to 0.995, preferably from 0.05 to 0.40 and more preferable from 0.08 to 0.20.

18. Iso-reticular cellular catalytic foam manufactured by the process according to at least one of claims 1-12.

19. Iso-reticular cellular foamed adsorbent material manufactured by a process according to at least one of claims 1-12.

20. Iso-reticular cellular adsorbent for gas storage manufactured by a process according to at least one of claims 1-12.

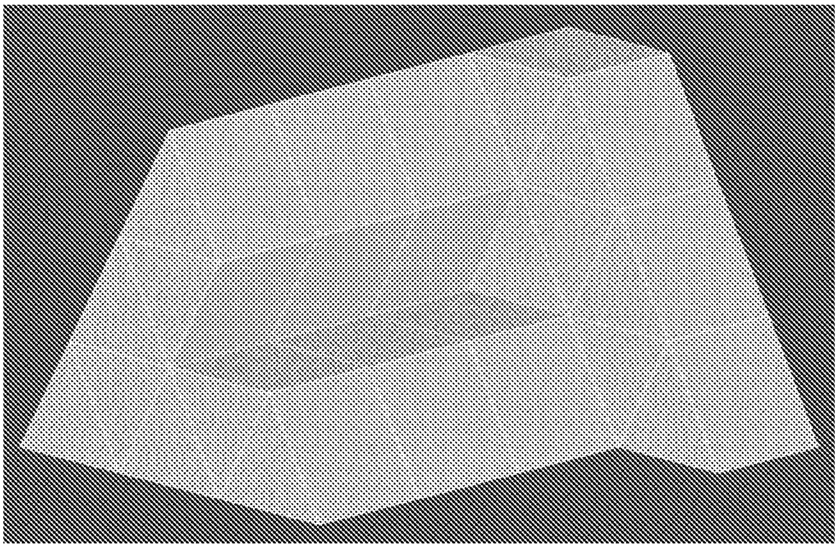

Fig.1 a)

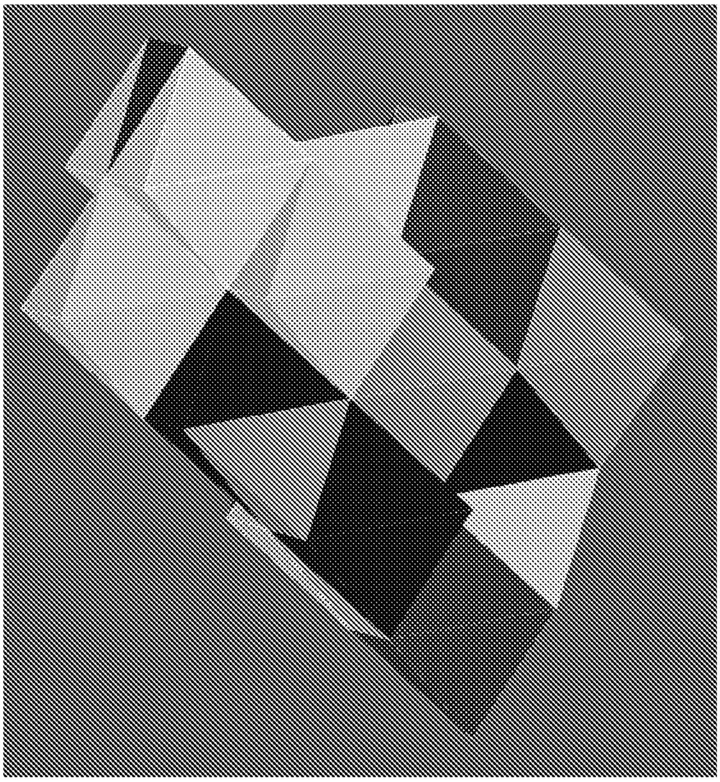

Fig. 1b)

Figure 1. Space tessellation by: (a) hexagonal prisms as example of space-filling solids; (b) combination of two non-space filling solids (octahedrons and tetrahedrons).

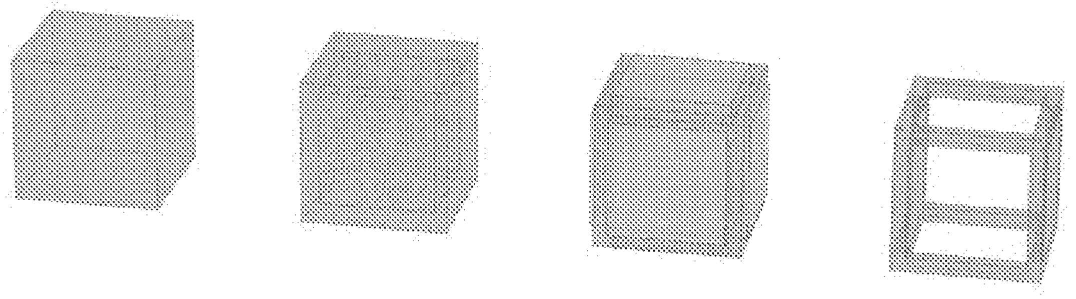

Figure 2. Different steps of the methodology to construct one iso-reticular cell.

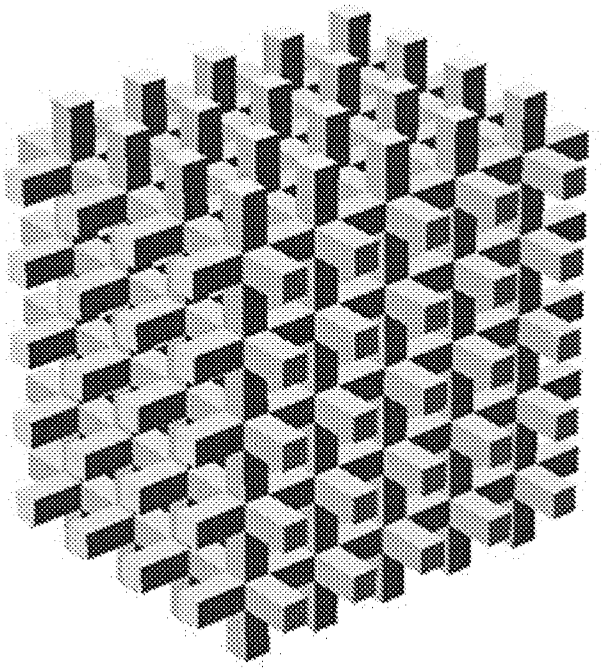

Figure 3. Iso-reticular foam structure constructed with cubes as unitary cells.

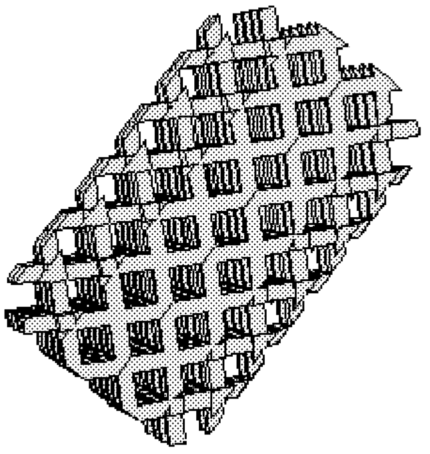

Figure 4. Iso-reticular foam structure constructed with cubes and rotated 45° already prepared to be fitted in a cylindrical tube.

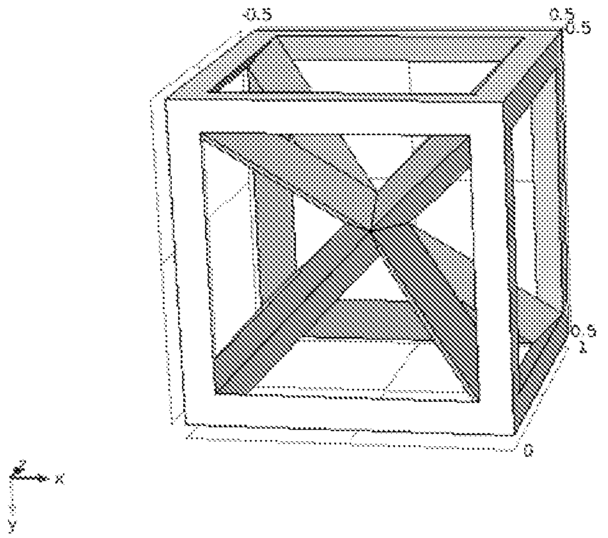

Figure 5. Cell structure constructed with 6 pyramids that fit within a cube. The structure presents the same porosity than the one constructed with cubes and shown in Figure 2 but different strut width.

INTERNATIONAL SEARCH REPORT

International application No
PCT/NO2017/050104

A. CLASSIFICATION OF SUBJECT MATTER
INV. G06F17/50 G06T17/00
ADD.

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)
G06F G06T

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

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

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y A	CHUA C K ET AL: "DEVELOPMENT OF A TISSUE ENGINEERING SCAFFOLD STRUCTURE LIBRARY FOR RAPID PROTOTYPING. PART 2: PARAMETRIC LIBRARY AND ASSEMBLY PROGRAM", THE INTERNATIONAL JOURNAL OF ADVANCED MANUFACTURING TECHNOLOGY, SPRINGER, LONDON, vol. 21, no. 4, January 2003 (2003-01), pages 302-312, XP008047637, ISSN: 0268-3768, DOI: 10.1007/S001700300035 abstract figures 1-5, 7-9; table 2 page 302, right-hand column, lines 20-34 section 2 (first paragraph) and 2.1 (second paragraph); page 303, left-hand column section 2.3: Assembling the unit cells; pages 303-304	1-7,9-17 8 18-20

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

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Date of the actual completion of the international search 8 September 2017	Date of mailing of the international search report 18/09/2017
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Alexe, Mihai

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	section 2.4.3: Porosity; page 308 sections 3 and 3.1; page 308, right-hand column section 4: scaffold fabrication through SLS; page 309, right-hand column, lines 1-4 section 5: Automatic scaffold assembly; page 311, right-hand column, paragraph 1-2 the whole document -----	
X	VIKAS KUMAR ET AL: "DESIGN OF PERIODIC CELLULAR STRUCTURES FOR HEAT EXCHANGER APPLICATIONS", 20TH ANNUAL INTERNATIONAL SOLID FREEFORM FABRICATION SYMPOSIUM, 5 August 2009 (2009-08-05), pages 738-748, XP055404434,	18-20
Y	abstract; figures 2, 3, 4, 5, 8, 9; table	8
A	1 page 739, paragraph 2 page 744, paragraph 1 the whole document -----	1-7,9-17
X	CHI-MUN CHEAH ET AL: "Automatic Algorithm for Generating Complex Polyhedral Scaffold Structures for Tissue Engineering", TISSUE ENGINEERING, LARCHMONT, NY, US, vol. 10, no. 3/4, January 2004 (2004-01), pages 595-610, XP002691483, ISSN: 1076-3279, DOI: 10.1089/107632704323061951	1-7,9-17
Y	abstract	8
A	figures 4, 5, 8, 10 Critical design parameters: porosity and pore size; page 599, right-hand column - page 600, left-hand column CAD modeling and RP fabrication of complex (multi-modal) assemblies; page 606, left-hand column; figure 6 the whole document -----	18-20

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Anonymous: "Metal foam - Wikipedia", , 11 April 2016 (2016-04-11), pages 1-9, XP055404580, Retrieved from the Internet: URL:https://en.wikipedia.org/w/index.php?title=Metal_foam&oldid=714757497 [retrieved on 2017-09-07]	18-20
A	Page 1: Regular foamed aluminium; Page 4: Regular foams gallery Heat transfer and catalytic applications in automobiles; page 6, lines 3-6 the whole document -----	1-17
X	BANHART J: "MANUFACTURE, CHARACTERISATION AND APPLICATION OF CELLULAR METALS AND METAL FOAMS", PROGRESS IN MATERIALS SCIE, PERGAMON PRESS, GB, vol. 46, 2001, pages 559-632, XP008031000, ISSN: 0079-6425, DOI: 10.1016/S0079-6425(00)00002-5	18-20
A	section 2.1.4.2; page 582 sections 4.3.2-4.3.5; pages 618-619 the whole document -----	1-17