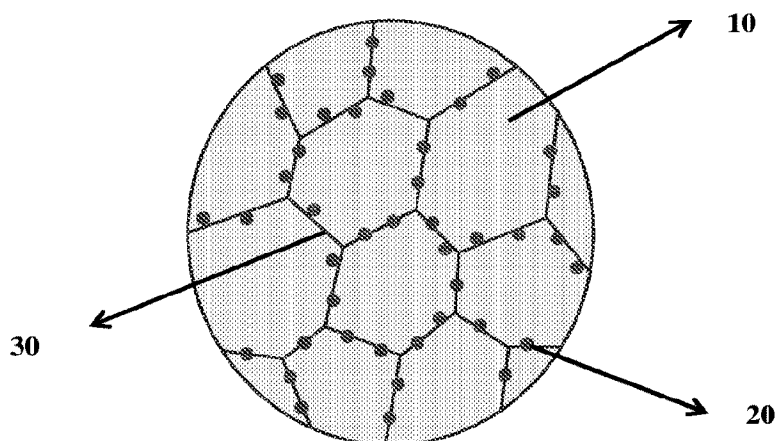




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(54) Titre : PROCEDES DE FABRICATION D'OUTILS SOLUBLES PAR L'INTERMEDIAIRE D'UN MOULAGE A L'ETAT LIQUIDE-SOLIDE
(54) Title: METHODS OF MANUFACTURING DISSOLVABLE TOOLS VIA LIQUID-SOLID STATE MOLDING



(57) Abrégé/Abstract:

A method of manufacturing a dissolvable article comprises forming a liquid-solid mixture comprising secondary particles homogeneously dispersed in a molten metallic matrix material; disposing the liquid-solid mixture in a mold; agitating the liquid-solid mixture in the mold; and molding the liquid-solid mixture under agitation to form a dissolvable article, wherein the secondary particles and the metallic matrix material form a plurality of micro- or nano-sized galvanic cells in the dissolvable article.

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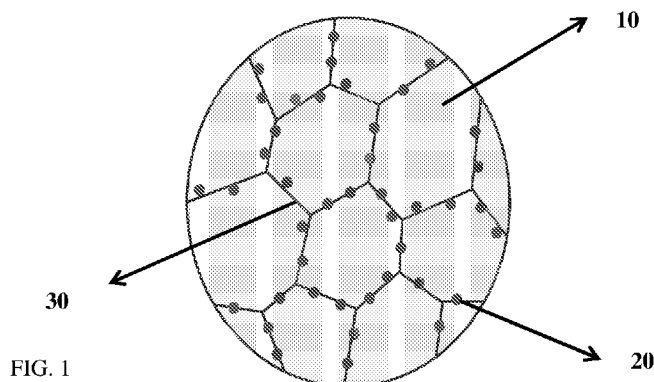


FIG. 1

(57) Abstract: A method of manufacturing a dissolvable article comprises forming a liquid-solid mixture comprising secondary particles homogeneously dispersed in a molten metallic matrix material; disposing the liquid-solid mixture in a mold; agitating the liquid-solid mixture in the mold; and molding the liquid-solid mixture under agitation to form a dissolvable article, wherein the secondary particles and the metallic matrix material form a plurality of micro- or nano-sized galvanic cells in the dissolvable article.

METHODS OF MANUFACTURING DISSOLVABLE TOOLS VIA LIQUID-SOLID STATE MOLDING

BACKGROUND

[0001] The disclosure is directed to methods of manufacturing dissolvable tools, and in particular to liquid-solid state molding methods of manufacturing dissolvable tools.

[0002] Oil and natural gas, or carbon dioxide sequestration wells often utilize wellbore components or tools that, due to their function, are only required to have limited service lives that are considerably less than the service life of the well. After a component or tool service function is complete, it must be removed or disposed of in order to recover the original size of the fluid pathway for use, including hydrocarbon production, CO₂ sequestration, etc.

[0003] To facilitate removal, such tools or components may be formed of a corrodible material so that they need not be physically removed by, for example, a mechanical operation, but may instead corrode or dissolve under downhole conditions.

[0004] Despite all the advances, the art is still receptive to alternative methods of manufacturing dissolvable tools, in particular methods having increased manufacturing capacity and reduced material cost.

BRIEF DESCRIPTION

[0005] A method of manufacturing a dissolvable article comprises: forming a liquid-solid mixture comprising secondary particles homogeneously dispersed in a molten metallic matrix material; disposing the liquid-solid mixture in a mold; agitating the liquid-solid mixture in the mold; and molding the liquid-solid mixture under agitation to form a dissolvable article, wherein the secondary particles and the metallic matrix material form a plurality of micro- or nano-sized galvanic cells in the dissolvable article.

[0006] Also disclosed is a dissolvable article comprising a metallic matrix comprising a plurality of grains formed from a metallic matrix material; the grains having a size of about 5 microns to about 300 microns; and secondary particles disposed on grain boundaries of the grains formed from the metallic matrix material; the secondary particles having a size of about 0.1 micron to about 2 microns; wherein the secondary particles and the metallic matrix material form a plurality of micro- or nano-sized galvanic cells in the dissolvable article.

[0007] Also disclosed is a method of manufacturing a dissolvable article, the method comprising: forming a liquid-solid mixture comprising secondary particles dispersed in a

molten metallic matrix material; disposing the liquid-solid mixture in a mold; agitating the liquid-solid mixture in the mold; molding the liquid-solid mixture under agitation to form a molded dissolvable article, wherein molding the liquid-solid mixture comprises applying a superatmospheric pressure of about 500 psi to about 30,000 psi to the liquid-solid mixture under agitation; cooling the molded dissolvable article; and applying an agitating force to the molded dissolvable article during cooling thus forming the dissolvable article, wherein the secondary particles have an original shape and an original composition before being dispersed in the molten metallic matrix material, and greater than 90 wt. % of the secondary particles remain in the original shape and the original composition in the dissolvable article, and wherein the secondary particles and the metallic matrix material form a plurality of micro- or nano-sized galvanic cells in the dissolvable article.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] Referring now to the drawings wherein like elements are numbered alike in the several Figures:

[0009] FIG. 1 illustrates the microstructure of an article according to an embodiment of the disclosure;

[0010] FIG. 2 illustrates the microstructure of an article according to another embodiment of the disclosure; and

[0011] FIG. 3 illustrates the electrons' flowing directions during the dissolution of the article.

DETAILED DESCRIPTION

[0012] The inventors hereof have found that dissolvable tools can be made by liquid-solid state molding. The method increases the manufacture capacity as the size of the tools made from the method is almost unlimited. Moreover, the method has reduced material cost. As a further advantageous feature, the dissolvable tools made from the method have adjustable and uniform dissolution rates.

[0013] The method comprises forming a liquid-solid mixture comprising secondary particles homogeneously dispersed in a molten metallic matrix material; disposing the liquid-solid mixture in a mold; agitating the liquid-solid mixture in the mold; and molding the liquid-solid mixture under agitation to form the dissolvable article.

[0014] The matrix material comprises one or more of the following: a magnesium-based alloy; an aluminum-based alloy; or a zinc-based alloy. As used herein, the term "metal-based alloy" means a metal alloy wherein the weight percentage of the specified metal in the alloy is greater than the weight percentage of any other component of the alloy, based on the total weight of the alloy.

[0015] Magnesium-based alloys suitable for use include alloys of magnesium with aluminum (Al), cadmium (Cd), calcium (Ca), cobalt (Co), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), silicon (Si), silver (Ag), strontium (Sr), thorium (Th), tungsten (W), zinc (Zn), zirconium (Zr), or a combination comprising at least one of these elements. Alloying or trace elements can be included in varying amounts to adjust the corrosion rate of the magnesium. Exemplary commercial magnesium-based alloys which include different

combinations of the above alloying elements to achieve different degrees of corrosion resistance include but are not limited to, for example, those alloyed with aluminum, strontium, and manganese such as AJ62, AJ50x, AJ51x, and AJ52x alloys, and those alloyed with aluminum, zinc, and manganese such as AZ91A-E alloys. Other exemplary magnesium-based alloys include MgZrZn, MgAlZn, AlCuZnMn, and AlMgZnSiMn.

[0016] Aluminum-based alloys include all alloys that have aluminum as an alloy constituent. Exemplary aluminum alloys include Al-Cu alloy, Al-Mn alloy, Al-Si alloy, Al-Mg alloy, Al-Mg-Si alloy, Al-Zn alloy, Al-Li alloy, Al-Cu-Mg-X alloy, Al-Zn-Mg-Cu-X, where X represents alloying elements including Zn, Mn, Si, Cr, Fe, Ni, Ti, V, Cu, Pb, Bi, and Zr.

[0017] Zinc-based alloys include alloys of zinc with Al, Cu, Mg, Pb, Cd, Sn, Fe, Ni, Si, or a combination of the above elements. In a specific embodiment, the metallic matrix material is a magnesium alloy.

[0018] The metallic matrix material used to prepare the dissolvable article is in a particular form. The matrix particles have an initial average particle size from about 0.1 μm to about 500 μm , in an embodiment 0.5 μm to about 250 μm . The shape of the matrix particles may be regular or irregular. In an embodiment, the matrix particles may be, for example, spherical or oblong. Useful metallic matrix material has a corrosion rate of about 0.1 to about 200 $\text{mg}/\text{cm}^2/\text{hour}$, specifically about 1 to about 150 $\text{mg}/\text{cm}^2/\text{hour}$ using aqueous 3 wt% KCl solution at 200°F (93°C).

[0019] The secondary particles, which have a lower reactivity relative to the metallic matrix material, acts as a cathode, whereas the metallic matrix, made of an alloy such as magnesium-based alloy which is more reactive than the secondary particles, is anodic relative to the secondary particles. A galvanic discharge cycle (e.g., corrosion) occurs between the relatively anodic and relatively cathodic materials in the presence of an electrolyte. By adjusting the compositions of the metallic matrix material and the secondary particles and the amount of the secondary particles relative to the metallic matrix, the corrosion rate of the dissolvable article is adjusted.

[0020] The secondary particles have a higher melting point as compared to the metallic matrix material so that the metallic matrix material can be selectively melted during the manufacturing process. In addition, the secondary particles and the metallic matrix material are selected such that they form micro- or nano-sized galvanic cells under the process conditions to make the dissolvable article. In particular, the secondary particles and

the metallic matrix material are selected such that they do not form intermetallic compounds or a solid solution phase or only forms a solid solution phase with very small solubility under the process conditions so that all or a large portion (for example, greater than 90 wt.%, greater than about 95 wt.%, or greater than about 98 wt.%) of the secondary particles remain in their original composition and shape in the article. In an embodiment, less than about 10 wt. %, less than about 5 wt. %, or less than about 2 wt. % of secondary particles dissolve or form a solid solution phase or form an intermetallic compound with the metallic matrix material. Without wishing to be bound by theory, it is believed that if secondary particles react with the matrix material forming an intermetallic compound or solid solution and are fully consumed during the material processing, then the manufactured articles may not have galvanic cells thus are not dissolvable. Further without wishing to be bound by theory, it is believed that if less than 10 wt.% of secondary particles form a solid solution or intermetallic compound with the metallic matrix material during the process to prepare the dissolvable article, based on the total weight of the secondary particles, the articles prepared from such metallic matrix materials and secondary particles keep high chemical potential difference between the matrix and the secondary particles thus providing an article having a high dissolution rate.

[0021] Exemplary secondary particles include one or more of the following: a metal; an oxide of the metal; a nitride of the metal; or a cermet of the metal; wherein the metal is one or more of the following: W; Co; Cu; Ni; or Fe.

[0022] The amount of the secondary particles can vary depending on the specific materials used and desired corrosion rate. In an embodiment, the liquid-solid mixture comprises 0.01 to 10 wt.%, or 0.05 to 8 wt.%, or 0.1 to 6 wt.% of the secondary particles, based on the total weight of the liquid-solid mixture. In another embodiment, the weight ratio of the metallic matrix material relative to the secondary particles is about 99:1 to about 9:1 in the liquid-solid mixture.

[0023] One way to form the liquid-solid mixture is to mix the metallic matrix material in a solid form with the secondary particles to provide a blend; and heating the blend under agitation to selectively melt the metallic matrix material. Alternatively, the liquid solid mixture is made by heating the metallic matrix material in a solid form to provide a molten metallic matrix material; and introducing the secondary particles to the molten matrix material under agitation. Heating the blend and heating the metallic matrix material can be conducted at a temperature above the melting point of the metallic matrix material but below the melting point of the secondary particles. In an embodiment, the heating is to a

temperature of about 600°C to about 800°C. The heating can be conducted at atmospheric pressure in the presence or absence of an inert atmosphere. In another embodiment, less than about 10 wt. %, less than about 5 wt. %, less than about 2 wt. %, or less than about 1 wt% of the secondary particles dissolve under the process conditions.

[0024] To form a homogeneous liquid-solid mixture, an agitation force is applied to the metallic matrix material and the secondary particles. The agitation force can be generated by mechanical means, electromagnetic means, acoustic means, or a combination comprising at least one of the foregoing. For example, the metallic matrix material and the secondary particles can be mechanically stirred in a crucible or a furnace. A magnetic field can also be applied to the metallic matrix material and the secondary particles. By randomly changing the field direction, the magnitude, and the frequency of the field, an agitation force is generated. Alternatively or in addition to mechanical and electromagnetic forces, an acoustic generator such as a megasonic energy source imparts wave energy to the metallic matrix material and the secondary particles and thus agitating them during the mixing.

[0025] The homogeneous liquid-solid mixture is then disposed in a mold. The method of disposing is not particularly limited. For example, the homogeneous liquid-solid mixture can be poured into the mold, pushed into the mold under a superatmospheric pressure, or drawn to the mold under a subatmospheric pressure.

[0026] The molding can be a pressure molding or a vacuum molding. In an embodiment the molding is conducted at a pressure of about 500 psi to about 30,000 psi or about 1000 psi to about 5000 psi. The pressure can be a superatmospheric pressure or a subatmospheric pressure. In an embodiment, the mold is not heated. In another embodiment, the mold is heated to a temperature of about 200°F to about 800°F or about 300°F to about 600°F.

[0027] During the molding, an agitation force is applied to the mixture by mechanical means, electromagnetic means, acoustic means, or a combination comprising at least one of the foregoing. Without wishing to be bound by theory, it is believed that without agitation, the secondary particles may separate out from the metallic matrix material. As a result, the secondary particles may not be uniformly distributed throughout the molded product; and the dissolvable article would not have a uniform dissolution rate.

[0028] The mold product is allowed to cool down to room temperature when the mold is still under pressure. In the instance where the molded product is subjected to a subsequent extrusion operation, the molded product can be cooled to a temperature above the room

temperature. An agitation force is also applied to the molded product during the cooling process. The cooled article can be machined and used as is.

[0029] For applications requiring higher strength, the molded article is further extruded. During extrusion, the pores inside the molded product are fully closed to provide a condensed article having high tensile strength, high shear strength, and high compression strength. In addition, the extruded product dissolves more uniformly. The extrusion temperature is about 600°F to about 800°F.

[0030] The dissolvable article has a microstructure comprising a plurality of grains formed from the metallic matrix material. The grains have an average size of about 5 to about 300 microns. The size of the secondary particles is about 0.1 micron to about 2 microns. The variation of the average particle size of the secondary particles in the final dissolvable article and the average particle size of the secondary particles used to make the dissolvable article is less than about 10%, less than about 5% or less than about 2% based on the initial average particle size of the secondary particles. In an embodiment, the secondary particles are disposed only on the grain boundaries. In another embodiment, the secondary particles are disposed both on the grain boundaries and inside the grains.

[0031] The dissolvable article thus has micron-sized or nano-sized galvanic cells where the metallic matrix is the anode and the secondary particles are cathode. The dissolvable article has uniform dissolution rate. In an embodiment, the dissolvable article has a corrosion rate of about 1 to about 300 mg/cm²/hour, specifically about 10 to about 200 mg/cm²/hour using aqueous 3 wt% KCl solution at 200°F (93°C).

[0032] FIGs. 1 and 2 illustrate the microstructures of articles according to some embodiments of the disclosure. The dissolvable article has a plurality of grains 10 formed from a metallic matrix material. The grains form grain boundaries 30. In FIG. 1, the secondary particles 20 are only disposed on grain boundaries. In FIG. 2, the secondary particles 20 are disposed on the grain boundaries as well inside the grains.

[0033] FIG. 3 shows a grain 10 and secondary particles 20 disposed in the grain. Because the metallic matrix material is more reactive than the secondary particles, the matrix material loses electrons and forms a cation. The electrons move from the metallic matrix material to the secondary particles. The direction of the electron movement is shown as 60 in FIG. 3. The cations formed from the matrix material dissolves in the electrolyte shown as 50 in FIG. 3. The presence of multiple micron-sized or nano-sized galvanic cells ensures that the reaction is conducted in a controllable manner.

[0034] Articles formed from the method disclosed herein are not particularly limited. Exemplary dissolvable articles include downhole articles such as a ball, a ball seat, a fracture plug, a bridge plug, a wiper plug, shear out plugs, a debris barrier, an atmospheric chamber disc, a swabbing element protector, a sealbore protector, a screen protector, a beaded screen protector, a screen basepipe plugs, a drill in stim liner plugs, ICD plugs, a flapper valve, a gaslift valve, a transmatic CEM plug, float shoes, darts, diverter balls, shifting/setting balls, ball seats, sleeves, teleperf disks, direct connect disks, drill-in liner disks, fluid loss control flappers, shear pins or screws, cementing plugs, teleperf plugs, drill in sand control beaded screen plugs, HP beaded frac screen plugs, hold down dogs and springs, a seal bore protector, a stimcoat screen protector, or a liner port plug.

[0035] All ranges disclosed herein are inclusive of the endpoints, and the endpoints are independently combinable with each other. As used herein, “combination” is inclusive of blends, mixtures, alloys, reaction products, and the like.

[0036] The use of the terms “a” and “an” and “the” and similar referents in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. “Or” means “and/or.” Further, it should further be noted that the terms “first,” “second,” and the like herein do not denote any order, quantity (such that more than one, two, or more than two of an element can be present), or importance, but rather are used to distinguish one element from another. The modifier “about” used in connection with a quantity is inclusive of the stated value and has the meaning dictated by the context (e.g., it includes the degree of error associated with measurement of the particular quantity). Unless defined otherwise, technical and scientific terms used herein have the same meaning as is commonly understood by one of skill in the art to which this invention belongs. As used herein, the size or average size of the particles refers to the largest dimension of the particles and can be determined by high resolution electron or atomic force microscope technology.

[0037] While typical embodiments have been set forth for the purpose of illustration, the foregoing descriptions should not be deemed to be a limitation on the scope herein. Accordingly, various modifications, adaptations, and alternatives can occur to one skilled in the art without departing from the spirit and scope herein.

What is claimed is:

1. A method of manufacturing a dissolvable article, the method comprising:
forming a liquid-solid mixture comprising secondary particles dispersed in a molten metallic matrix material;
disposing the liquid-solid mixture in a mold;
agitating the liquid-solid mixture in the mold;
molding the liquid-solid mixture under agitation to form a molded dissolvable article, wherein molding the liquid-solid mixture comprises applying a superatmospheric pressure of about 500 psi to about 30,000 psi to the liquid-solid mixture under agitation;
cooling the molded dissolvable article; and
applying an agitating force to the molded dissolvable article during cooling thus forming the dissolvable article,
wherein the secondary particles have an original shape and an original composition before being dispersed in the molten metallic matrix material, and greater than 90 wt. % of the secondary particles remain in the original shape and the original composition in the dissolvable article, and
wherein the secondary particles and the metallic matrix material form a plurality of micro- or nano-sized galvanic cells in the dissolvable article.
2. The method of claim 1, wherein less than 10 wt. % of the secondary particles form a solid solution, an intermetallic compound, or a combination thereof with the metallic matrix material, based on the total weight of the secondary particles.
3. The method of claim 1 or 2, wherein forming the liquid-solid mixture comprises:
mixing the metallic matrix material in a solid form with the secondary particles to provide a blend; and
heating the blend under agitation to selectively melt the metallic matrix material.
4. The method of claim 1 or 2, wherein forming the liquid-solid mixture comprises:
heating the metallic matrix material in a solid form to provide a molten metallic matrix material; and
introducing the secondary particles to the molten matrix material under agitation.

5. The method of claim 4, wherein heating the metallic matrix material is to a temperature of about 600°C to about 700°C.
6. The method of any one of claims 1 to 5, wherein agitating the liquid-solid mixture comprises applying an agitation force to the mixture by mechanical means, electromagnetic means, acoustic means, or a combination comprising at least one of the foregoing.
7. The method of any one of claims 1 to 6, wherein the metallic matrix material comprises one or more of the following: a magnesium-based alloy; an aluminum-based alloy; or a zinc-based alloy.
8. The method of any one of claims 1 to 7, wherein the secondary particles comprise one or more of the following: a metal; an oxide of the metal; a nitride of the metal; or a cermet of the metal; wherein the metal is one or more of the following: W; Co; Cu; Ni; or Fe.
9. The method of any one of claims 1 to 8, wherein the liquid-solid mixture comprises about 1 wt % to about 10 wt % of secondary particles, based on the total weight of the liquid solid mixture.
10. The method of any one of claims 1 to 9, wherein the dissolvable article has a microstructure comprising a plurality of grains formed from the metallic matrix material.
11. The method of claim 10, wherein the secondary particles are disposed on grain boundaries of the grains formed from the metallic matrix material.
12. The method of claim 11, wherein the secondary particles are further disposed inside the grains.
13. The method of any one of claims 3 to 12, when not dependent on claim 2, wherein less than 10 wt. % of the secondary particles form an intermetallic compound with the metallic matrix material, based on the total weight of the secondary particles.

14. The method of any one of claims 3 to 12, when not dependent on claim 2, wherein less than 5 wt. % of the secondary particles form an intermetallic compound with the metallic matrix material, based on the total weight of the secondary particles.
15. The method of any one of claims 1 to 7, wherein the secondary particles comprise one or more of the following: a metal; an oxide of the metal; a nitride of the metal; or a cermet of the metal; and the metal is W, Co, or a combination thereof.
16. The method of any one of claims 1 to 15, wherein greater than 95 wt. % of the secondary particles remain in the original shape and the original composition in the dissolvable article.
17. The method of any one of claims 1 to 7, wherein greater than 98 wt. % of the secondary particles remain in the original shape and the original composition in the dissolvable article.
18. The method of any one of claims 1 to 7, wherein the secondary particles are at least one of: a metal, an oxide of said metal, a nitride of said metal, and a cermet of said metal, wherein the metal is W, Co or a combination thereof.
19. The method of claim 1, wherein the liquid-solid mixture comprises 0.1 to 6 wt. % of secondary particles homogeneously dispersed in the molten metallic matrix material based on the total weight of the liquid-solid mixture.
20. The method of claim 19, wherein the metallic matrix material comprises one or more of the following: a magnesium-based alloy; an aluminum-based alloy; or a zinc-based alloy, and the secondary particles comprising a metal; an oxide of the metal; a nitride of the metal; or a cermet of the metal; wherein the metal is one or more of the following: W; Co; Cu; Ni; or Fe.
21. The method of claim 19 or 20, wherein molding the liquid-solid mixture comprises applying a superatmospheric pressure of about 1,000 psi to about 5,000 psi to the liquid solid mixture under agitation.

22. The method of any one of claims 19 to 21, wherein greater than 98 wt. % of the secondary particles remain in the original shape and the original composition in the dissolvable article.
23. The method of any one of claims 19 to 22, wherein the secondary particles are at least one of: a metal, an oxide of said metal, a nitride of said metal, and a cermet of said metal, wherein the metal is W, Co or a combination thereof.
24. A method of manufacturing a condensed dissolvable article, the method comprising:
subjecting the dissolvable article of any one of claims 1 to 23 to an extrusion operation to yield the condensed dissolvable article.

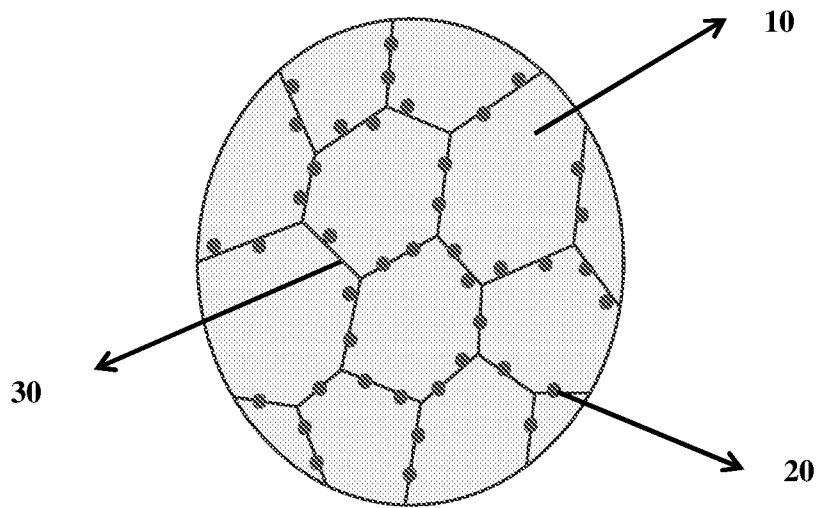


FIG. 1

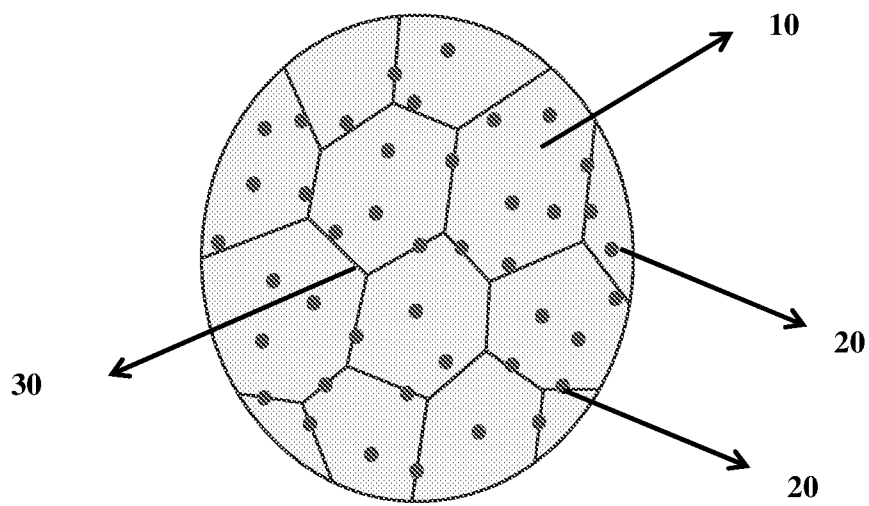


FIG. 2

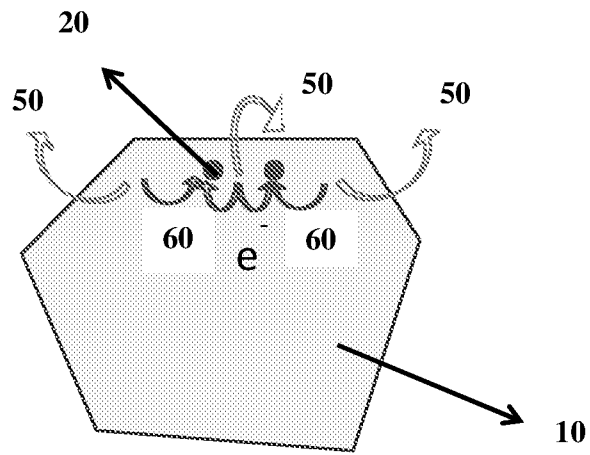


FIG. 3

