



- (51) International Patent Classification:

B22F 1/02 (2006.01)	B22F 5/00 (2006.01)
B22F 9/00 (2006.01)	E21B 33/12 (2006.01)
- (21) International Application Number: PCT/US2016/061179
- (22) International Filing Date: 9 November 2016 (09.11.2016)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 14/967,420 14 December 2015 (14.12.2015) US
- (71) Applicant: BAKER HUGHES INCORPORATED [US/US]; 17021 Aldine Westfield, Houston, Texas 77073 (US).
- (72) Inventors: SALINAS, Bobby J.; 17021 Aldine Westfield, Houston, Texas 77073 (US). XU, Zhiyue; 17021 Aldine Westfield, Houston, Texas 77073 (US).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,

HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

Published:

- with international search report (Art. 21(3))

(54) Title: METHODS OF MANUFACTURING DEGRADABLE TOOLS USING A GALVANIC CARRIER AND TOOLS MANUFACTURED THEREOF

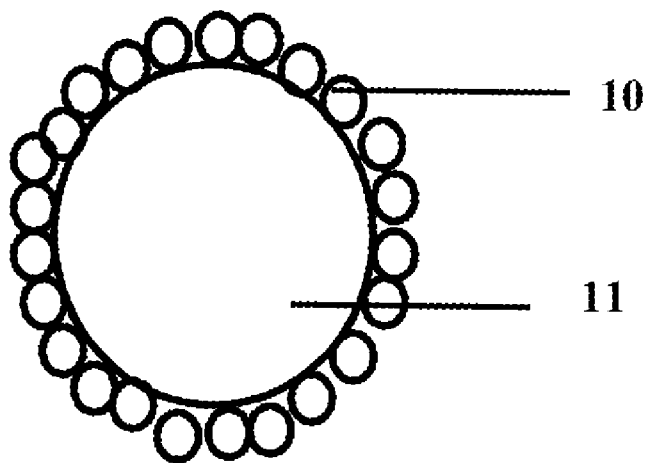


FIG. 1

(57) Abstract: A method of manufacturing a degradable article comprises: forming a mixture comprising composite particles dispersed in a metallic matrix material; the composite particles comprising a carrier and a disintegration agent coated on the carrier or embedded in the carrier, or a combination thereof and having a density that is about 0.2 to about 2.5 equivalents to that of the metallic matrix material when measured under the same testing conditions; and molding or casting the mixture to form a degradable article. The disintegration agent forms a plurality of galvanic cells with the metallic matrix material, or the carrier, or a combination thereof, in the degradable article.



METHODS OF MANUFACTURING DEGRADABLE TOOLS USING A GALVANIC CARRIER AND TOOLS MANUFACTURED THEREOF

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Application No. 14/967420, filed on December 14, 2015, which is incorporated herein by reference in its entirety.

BACKGROUND

[0002] The disclosure is directed to methods of manufacturing degradable tools, and in particular to methods of manufacturing degradable tools using a galvanic carrier. The disclosure also relates to the tools manufactured by the methods.

[0003] 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.

[0004] 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 degrade under downhole conditions.

[0005] Despite all the advances, the art is still receptive to alternative methods of manufacturing degradable tools, in particular methods that are effective to manufacture tools having uniform degradation rates.

BRIEF DESCRIPTION

[0006] In an embodiment, a method of manufacturing an article is provided. The method comprises forming a mixture comprising composite particles dispersed in a metallic matrix material; the composite particles comprising a carrier and a disintegration agent coated on the carrier or embedded in the carrier, or a combination thereof and having a density that is about 0.2 to about 2.5 equivalents to that of the metallic matrix material when measured under the same testing conditions; and molding or casting the mixture to form a degradable article; wherein the disintegration agent forms a plurality of galvanic cells with the metallic matrix material, or the carrier, or a combination thereof, in the degradable article.

[0007] Also disclosed is a degradable article produced by the method.

[0008] In another embodiment, a degradable article is provided. The article comprises: a metallic matrix comprising a plurality of grains formed from a metallic matrix material, a carrier, or a combination thereof; and a disintegration agent disposed on grain boundaries of the grains formed from the metallic matrix material, the carrier, or a combination thereof; the disintegration agent comprising particles having an aspect ratio greater than about 2; wherein the disintegration agent form a plurality of galvanic cells in the article with the metallic matrix material, the carrier, or a combination thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] Referring now to the drawings wherein like elements are numbered alike in the several Figures:

[0010] FIG. 1 illustrates a composite particle comprising a carrier coated with a disintegration agent;

[0011] FIG. 2 illustrates a composite particle comprising a carrier and a coating; where the coating comprising a disintegration agent;

[0012] FIG. 3 illustrates a composite particle comprising a carrier with a disintegration agent partially or fully embedded in the carrier; and

[0013] FIG. 4 illustrates a composite particle comprising a carrier with a disintegration agent embedded in the carrier as well as coated on the surface of the carrier.

DETAILED DESCRIPTION

[0014] Metals and metal alloys having a high activity on the saltwater galvanic series, such as a magnesium alloy, can be used as a matrix material to form degradable articles. A disintegration agent can be added to the matrix material to adjust the degradation rate. One method of forming the degradable article includes molding a solid-liquid mixture comprising solid disintegration agent particles dispersed in a molten matrix material. To form articles having controlled degradation rate, it is desirable to form a homogeneous solid liquid mixture. However, certain disintegration agents are much heavier than the matrix materials. Thus in the solid liquid mixture, these heavy disintegration agents have a tendency to precipitate in the light molten matrix material, which makes it challenging to achieve uniform distribution of the disintegration agents.

[0015] The inventors hereof have found that degradable articles having a controlled and uniform degradation rate can be made from a matrix material and composite particles comprising a carrier and a disintegration agent. In particular, the materials for the carrier and

the disintegration agent as well as the amounts of the carrier and the disintegration agent are selected such that the composite particles formed thereof have a density that is about 0.5 to about 1.5 equivalents to that of the metallic matrix material when measured under the same testing conditions. The disintegration agent is coated on the carrier or embedded in the carrier, or a combination thereof. When such composite particles are mixed with matrix materials, the composite particles can be uniformly distributed in the molten matrix material. Under the process conditions, the carrier can partially or completely melt releasing the disintegration agent. In the instance where the disintegration agent is coated on the carrier, upon the melting of the carrier (core), under agitation forces, the coating breaks into particles. Because the coating can have a thickness of only a few nanometers, the disintegration particles formed upon melting of the carrier can have a high aspect ratio. The high aspect ratio facilitates the maintenance of uniform distribution of the disintegration agent. Upon cooling, the uniformly distributed and released disintegration agent can be “frozen” in this place. Without wishing to be bound by theory, it is believed that the disintegration agent can then act as nucleation site for solidification of molten matrix material. As a further advantageous feature, the carrier forms galvanic cells with the disintegration agent allowing further control over the degradation rate of the article.

[0016] 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.

[0017] 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.

[0018] 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.

[0019] 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.

[0020] The composite particles comprise a carrier and a disintegration agent, wherein the disintegration agent is coated on the surface of the carrier, embed in the carrier, or a combination thereof. FIGS. 1-4 illustrate composite particles according to various embodiments of the disclosure. In FIG. 1, the composite particle comprises carrier 11 coated with disintegration particles 10. In FIG. 2, the disintegration agent forms a coating 20 on the surface of the carrier 21. In FIG. 3, the composite particle comprises carrier 31, disintegration particles 32 that are fully embedded in carrier 31 and disintegration particle 33 that are partially embedded in carrier 31. In FIG. 4, the composite particle comprises carrier 41, disintegration particles 42 that are fully embedded in carrier 41, disintegration particles 43 that are partially embedded in carrier 41 and disintegration particles 42 that are not embedded but disposed on the surface of carrier 41.

[0021] The disintegration agents 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 an embodiment, the disintegration agents also have a higher melting point than the carrier so that the carrier is at least partially melted during the process conditions. Exemplary disintegration agents 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. The disintegration agents can be in the form of a coating or particles embedded or disposed on a surface of the carrier. In the instance where the disintegration agents are particles, the particles can have an average particle size of about 50 nanometers to about 250 microns or about 1 to about 25 microns.

[0022] The carrier comprises one or more of the following: a magnesium-based alloy; an aluminum-based alloy; or a zinc-based alloy. The carrier can be same or different from the matrix material. The carrier comprises particles having an average particle size of about 1 micron to about 10 millimeters, or 50 microns to about 1 millimeter.

[0023] The composite particles have a density of about 0.2 to about 2.5 equivalents to that of the matrix material when tested under the same testing conditions. In another embodiment, the composite particles have a density of about 0.5 to about 1.5 equivalents to that of the matrix material when measured under the same testing conditions. The amount of the disintegration agent in the composite particles is about 0.01 wt% to about 50 wt%, or about 1 wt% to about 10 wt%, based on the total weight of the composite particles.

[0024] Methods of making the composite particles are not particularly limited. Suitable methods include physical vapor deposition, chemical deposition, milling, mechanical mixing or the like. Physical vapor deposition and vapor deposition are particularly suitable for making composite particles comprising disintegration agent coated on the carrier.

[0025] The disintegration agent, which has a lower reactivity relative to the metallic matrix material and the carrier, acts as a cathode, whereas the metallic matrix and the carrier, which are more reactive than the disintegration agents, are anodic relative to the disintegration agents. 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, the carrier, and the disintegration agent and the amounts of the disintegration agents relative to the sum of the weight of the metallic matrix and the carrier, the corrosion rate of the degradable article is adjusted.

[0026] The composite particles can be present in an amount of about 0.1 wt.% to about 50 wt.% or 0.1 wt.% to about 20 wt% based on the total weight of the mixture comprising the composite particles and metallic matrix material. The amount of the disintegration agents can vary depending on the specific materials used and desired corrosion rate. In an embodiment, the liquid-solid mixture comprises 0.001 to 10 wt.%, or 0.05 to 8 wt.%, or 0.1 to 6 wt.% of the disintegration agents, based on the total weight of the mixture comprising the composite particles and the metallic matrix material.

[0027] One way to form the liquid-solid mixture is to mix the metallic matrix material in a solid form with the composite particles to provide a blend; and heating the blend optionally 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 composite 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. The carrier can be at least partially melted. In an embodiment, the heating is to a temperature of about 450°C to about 850°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 disintegration agents dissolve under the process conditions.

[0028] Optionally an agitation force is applied to the metallic matrix material and the composite particles during the mixing and heating. 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 composite 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 composite 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 disintegration agents and thus agitating them during the mixing.

[0029] The homogeneous liquid-solid mixture can be molded or casted. The casting method is not limited and includes die casting. To mold the liquid-solid mixture, the mixture is first 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.

[0030] 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 90°C to about 450 °C or about 150°C to about 350 °C. Optionally 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.

[0031] 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 optionally applied to the molded product during the cooling process. The cooled article can be machined and used as is.

[0032] 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 250 °C to about 450 °C or about 320 °C to about 420 °C.

[0033] If necessary, the obtained articles can be further machined or shaped to form a bar, block, tubular, cylindrical billet, or toroid. Machining includes cutting, sawing, ablating, milling, facing, lathing, boring, and the like using, for example, a miller, saw, lathe, router, electric discharge machine, and the like.

[0034] The degradable article has a microstructure comprising a plurality of grains formed from the disintegration agent with the metallic matrix material, the carrier, or a combination of the metallic matrix material and the carrier. The grains have an average size of about 5 to about 300 microns. In an embodiment, the disintegration agents are disposed only on the grain boundaries. In another embodiment, the disintegration agents are disposed both on the grain boundaries and inside the grains.

[0035] When the composite particles comprise a carrier and a coating of the disintegration agent formed by methods such as chemical vapor deposition, the coating can have a thickness of 50 nanometers to 200 microns. During heating and/or mixing, the carrier at least partially melts. The unsupported coating breaks upon agitation into particles having a high aspect ratio. In an embodiment, the disintegration agent in the degradable article comprises particles having an aspect ratio greater than about 2, greater than about 4, or greater than about 6, or greater than about 10.

[0036] The degradable article thus has micron-sized or nano-sized galvanic cells where the metallic matrix material and/or the carrier are the anode and the disintegration agents are cathode. The degradable article has uniform dissolution rate. In an embodiment, the degradable 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).

[0037] Articles formed from the method disclosed herein are not particularly limited. Articles formed from the method disclosed herein are not particularly limited. Exemplary tools include flappers, hold down dogs and springs, screen protectors, seal bore protectors, electric submersible pump space out subs, full bore guns, chemical encapsulations, slips, dogs, springs and collet restraints, liner setting sleeves, timing actuation devices, emergency grapple release, chemical encapsulation containers, screen protectors, beaded screen protectors, whipstock lugs, whipstock coatings, pins, set screws, emergency release tools, gas generators, mandrels, release mechanisms, staging collars, C-rings, components of perforating gun systems, disintegrable whipstock for casing exit tools, shear pins, dissolvable body locking rings, mud motor stators, progressive cavity pump stators, or shear screws.

[0038] The article can be a downhole tool. In an embodiment, the tool is a single component. In another embodiment the tool inhibits flow. In yet another embodiment, the tool is pumpable within a subterranean environment.

[0039] Pumpable tools include plugs, direct connect plugs, bridge plugs, wiper plugs, frac plugs, components of frac plugs, drill in sand control beaded screen plugs, inflow control device plugs, polymeric plugs, disappearing wiper plugs, cementing plugs, balls, diverter balls, shifting and setting balls, swabbing element protectors, buoyant recorders, pumpable collets, float shoes, or darts.

[0040] The tools that inhibit flow include seals, high pressure beaded frac screen plugs, screen basepipe plugs, coatings for balls and seats, compression packing elements, expandable packing elements, O-rings, attached seals, bullet seals, sub-surface safety valve seals, sub-surface safety valve flapper seal, dynamic seals, V-rings, back up rings, drill bit seals, liner port plugs, atmospheric discs, atmospheric chamber discs, debris barriers, drill in stim liner plugs, inflow control device plugs, flappers, seats, ball seats, direct connect disks, drill-in linear disks, gas lift valve plug, fluid loss control flappers, electric submersible pump seals, shear out plugs, flapper valves, gaslift valves, or sleeves.

[0041] Methods to degrade an article comprises: exposing the polymer composition or the article to a fluid at a temperature of about 25°C to about 300°C, about 65°C to about 250°C, or about 65°C to about 150°C or about 175°C to about 250°C. The pressure can be about 100 psi to about 15,000 psi.

[0042] The fluid can comprises water, brine, or a combination comprising at least one of the foregoing. The brine can include NaCl, KCl, NaBr, MgCl₂, CaCl₂, CaBr₂, ZnBr₂, NH₄Cl, sodium formate, cesium formate, and the like.

[0043] Further included in this disclosure are the following specific embodiments, which do not necessarily limit the claims.

[0044] Embodiment 1. A method of manufacturing a degradable article, the method comprising:

forming a mixture comprising composite particles dispersed in a metallic matrix material; the composite particles comprising a carrier and a disintegration agent coated on the carrier or embedded in the carrier, or a combination thereof and having a density that is about 0.2 to about 2.5 equivalents to that of the metallic matrix material when measured under the same testing conditions; and

molding or casting the mixture to form a degradable article;

wherein the disintegration agent forms a plurality of galvanic cells with the metallic matrix material, with the carrier, or with a combination of the metallic matrix material and the carrier, in the degradable article.

[0045] Embodiment 2. The method of Embodiment 1 wherein the composite particles have a density that is about 0.5 to about 1.5 equivalents to that of the metallic matrix material when measured under the same testing conditions.

[0046] Embodiment 3. The method of Embodiment 1 or Embodiment 2, further comprising forming the composite particles by one or more of the following: physical vapor deposition; chemical vapor deposition; milling; or mechanical mixing.

[0047] Embodiment 4. The method of any one of Embodiments 1 to 3, wherein forming a mixture comprising composite particles dispersed in a metallic matrix material comprises:

mixing the metallic matrix material in a solid form with the composite particles to provide a blend; and

heating the blend to a temperature to selectively melt the metallic matrix material.

[0048] Embodiment 5. The method of Embodiment 4, wherein the carrier is at least partially melted at the temperature.

[0049] Embodiment 6. The method of any one of Embodiments 1 to 3, wherein forming a mixture comprising composite particles dispersed in a metallic matrix material comprises:

heating the metallic matrix material in a solid form to provide a molten metallic matrix material; and

introducing the composite particles to the molten matrix material.

[0050] Embodiment 7. The method of Embodiment 6, wherein heating the metallic matrix material is to a temperature of about 450°C to about 850°C.

[0051] Embodiment 8. The method of any one of Embodiments 1 to 7, wherein molding the mixture comprises pressure molding or vacuum molding.

[0052] Embodiment 9. The method of any one of Embodiments 1 to 8, wherein molding the mixture comprises applying a superatmospheric pressure of about 500 psi to about 30,000 psi to the mixture.

[0053] Embodiment 10. The method of any one of Embodiments 1 to 9, further comprising extruding the molded article.

[0054] Embodiment 11. The method of any one of Embodiments 1 to 10, wherein the carrier comprises one or more of the following: a magnesium-based alloy; an aluminum-based alloy; or a zinc-based alloy.

[0055] Embodiment 12. The method of any one of Embodiments 1 to 11, wherein the carrier comprises particles have an average particle size of about 1 micron to about 10 millimeters.

[0056] Embodiment 13. The method of any one of Embodiments 1 to 12, wherein the disintegration agent comprises 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.

[0057] Embodiment 14. The method of any one of Embodiments 1 to 13, wherein the disintegration agent comprises particles having an average particle size of about 200 nanometers to about 10 microns.

[0058] Embodiment 15. The method of any one of Embodiments 1 to 14, 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.

[0059] Embodiment 16. The method of any one of Embodiments 1 to 15, wherein the mixture comprises about 0.001 wt.% to about 10 wt.% of the disintegration agent, based on the total weight of the mixture.

[0060] Embodiment 17. A degradable article produced by the method of any one of Embodiments 1 to 16.

[0061] Embodiment 18. A degradable article comprising:
a metallic matrix comprising a plurality of grains formed from a metallic matrix material, a carrier, or a combination thereof; and
a disintegration agent disposed on grain boundaries of the grains formed from the metallic matrix material, the carrier, or a combination thereof; the disintegration agent comprising particles having an aspect ratio greater than about 2;

wherein the metallic matrix and the disintegration agent form a plurality of galvanic cells in the article.

[0062] Embodiment 19. The degradable article of Embodiment 18, wherein the disintegration agent comprises particles having an aspect ratio greater than about 5.

[0063] Embodiment 20. The degradable article of Embodiment 18 or Embodiment 19, wherein the disintegration agent is further disposed inside the grains formed from the metallic matrix material.

[0064] 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.” 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). 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.

[0065] All references cited herein are incorporated by reference in their entirety. 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.

CLAIMS

What is claimed is:

1. A method of manufacturing a degradable article, the method characterized by:
forming a mixture comprising composite particles dispersed in a metallic matrix material; the composite particles comprising a carrier (11, 21, 31, 41) and a disintegration agent coated on the carrier (11, 21, 31, 41) or embedded in the carrier (11, 21, 31, 41), or a combination thereof and having a density that is about 0.2 to about 2.5 equivalents to that of the metallic matrix material when measured under the same testing conditions; and
molding or casting the mixture to form a degradable article;
wherein the disintegration agent forms a plurality of galvanic cells with the metallic matrix material, with the carrier (11, 21, 31, 41), or with a combination of the metallic matrix material and the carrier (11, 21, 31, 41), in the degradable article.
2. The method of claim 1 wherein the composite particles have a density that is about 0.5 to about 1.5 equivalents to that of the metallic matrix material when measured under the same testing conditions.
3. The method of claim 1 or claim 2, further characterized by forming the composite particles by one or more of the following: physical vapor deposition; chemical vapor deposition; milling; or mechanical mixing.
4. The method of any one of claims 1 to 3, wherein forming a mixture comprising composite particles dispersed in a metallic matrix material comprises:
mixing the metallic matrix material in a solid form with the composite particles to provide a blend; and
heating the blend to a temperature to selectively melt the metallic matrix material.
5. The method of any one of claims 1 to 3, wherein forming a mixture comprising composite particles dispersed in a metallic matrix material comprises:
heating the metallic matrix material in a solid form to provide a molten metallic matrix material; and
introducing the composite particles to the molten matrix material.
6. The method of claim 6, wherein heating the metallic matrix material is to a temperature of about 450°C to about 850°C and a pressure of about 500 psi to about 30,000 psi to the mixture.
7. The method of any one of claims 1 to 6, further characterized by extruding the molded article.

8. The method of any one of claims 1 to 7, wherein the carrier comprises one or more of the following: a magnesium-based alloy; an aluminum-based alloy; or a zinc-based alloy.

9. The method of any one of claims 1 to 8, wherein the carrier comprises particles have an average particle size of about 1 micron to about 10 millimeters.

10. The method of any one of claims 1 to 9, wherein the disintegration agent comprises 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.

11. The method of any one of claims 1 to 10, 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.

12. The method of any one of claims 1 to 11, wherein the mixture comprises about 0.001 wt.% to about 10 wt.% of the disintegration agent, based on the total weight of the mixture.

13. A degradable article produced by the method of any one of claims 1 to 12.

14. A degradable article characterized by:
a metallic matrix comprising a plurality of grains formed from a metallic matrix material, a carrier, or a combination thereof; and
a disintegration agent disposed on grain boundaries of the grains formed from the metallic matrix material, the carrier, or a combination thereof; the disintegration agent comprising particles having an aspect ratio greater than about 2;

wherein the metallic matrix and the disintegration agent form a plurality of galvanic cells in the article,

wherein optionally the disintegration agent is further disposed inside the grains formed from the metallic matrix material.

15. The degradable article of claim 14, wherein the disintegration agent comprises particles having an aspect ratio greater than about 5.

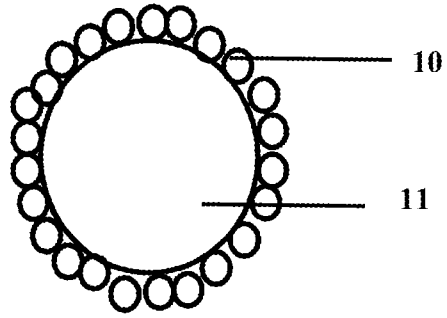


FIG. 1

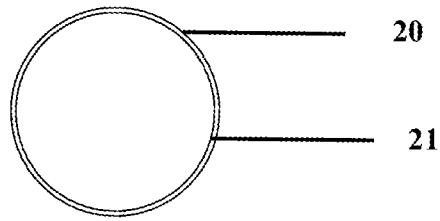


FIG. 2

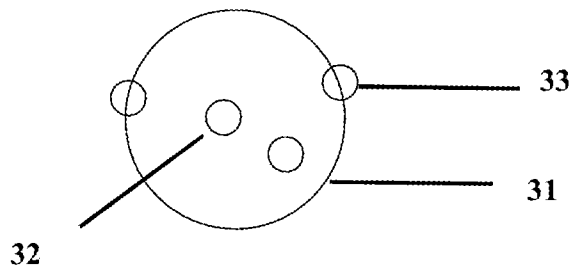


FIG. 3

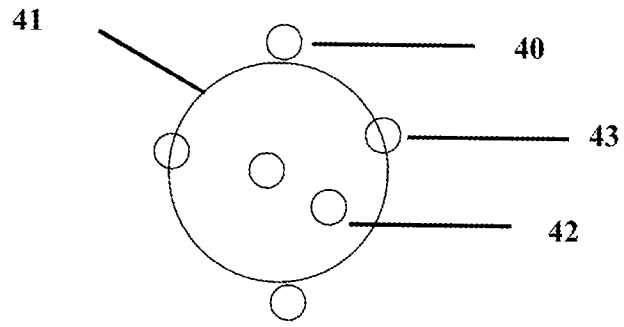


FIG. 4

A. CLASSIFICATION OF SUBJECT MATTER**B22F 1/02(2006.01)i, B22F 9/00(2006.01)i, B22F 5/00(2006.01)i, E21B 33/12(2006.01)i**

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)

B22F 1/02; B22F 3/10; E21B 34/06; C22C 49/04; E21B 33/12; E21B 41/00; B22D 21/04; C09K 8/58; E21B 34/08; B22F 9/00; B22F 5/00

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: downhole tool, degradable, dissolve, galvanic, cell, anode, cathode, metal, rate, control

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2015-0240337 A1 (TERVES, INC.) 27 August 2015 See paragraphs [0016], [0037]-[0048], [0057]-[0061]; and figures 1-3.	1-15
A	US 2014-0363692 A1 (SCHLUMBERGER TECHNOLOGY CORPORATION) 11 December 2014 See paragraphs [0062]-[0063], [0076], [0117]-[0120]; and figures 1A-1C, 2A-2B, 4, 13-16.	1-15
A	US 2010-0294510 A1 (HOLMES, KEVIN C.) 25 November 2010 See paragraphs [0013]-[0018]; and figures 1-3.	1-15
A	US 2014-0284063 A1 (HALLIBURTON ENERGY SERVICES, INC.) 25 September 2014 See paragraphs [0051]-[0061]; and figures 1-2.	1-15
A	WO 2013-184185 A1 (HALLIBURTON ENERGY SERVICES, INC.) 12 December 2013 See paragraphs [0029]-[0041]; and figures 1-4.	1-15

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

* Special categories of cited documents:

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

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

13 February 2017 (13.02.2017)

Date of mailing of the international search report

13 February 2017 (13.02.2017)

Name and mailing address of the ISA/KR

International Application Division

Korean Intellectual Property Office

189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea



Facsimile No. +82-42-481-8578

Authorized officer

BAE, Geun Tae

Telephone No. +82-42-481-3547



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2016/061179

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2015-0240337 A1	27/08/2015	CA 2936816 A1 CN 106029255 A GB 2537576 A WO 2015-127177 A1	27/08/2015 12/10/2016 19/10/2016 27/08/2015
US 2014-0363692 A1	11/12/2014	BR PI0700810 A CA 2573471 A1 GB 2435046 A GB 2435046 B NO 20070710 A US 2007-0181224 A1 US 2012-0080189 A1 US 8211247 B2 US 8663401 B2	13/11/2007 09/08/2007 15/08/2007 07/04/2010 10/08/2007 09/08/2007 05/04/2012 03/07/2012 04/03/2014
US 2010-0294510 A1	25/11/2010	AU 2010-249969 A1 AU 2010-249969 B2 BR PI1011062 A2 CA 2762070 A1 CA 2762070 C GB 2482621 A GB 2482621 B NO 20111603 A US 8413727 B2 WO 2010-135115 A2 WO 2010-135115 A3	03/11/2011 30/04/2015 05/04/2016 25/11/2010 18/02/2014 08/02/2012 02/10/2013 22/11/2011 09/04/2013 25/11/2010 24/03/2011
US 2014-0284063 A1	25/09/2014	US 9458692 B2 WO 2015-167640 A1	04/10/2016 05/11/2015
WO 2013-184185 A1	12/12/2013	AU 2013-272271 A1 AU 2013-272271 B2 AU 2014-385213 A1 AU 2014-385213 B2 CA 2868885 A1 EP 2825725 A1 EP 2825725 A4 MX 2014010920 A US 2013-0327540 A1 US 8905147 B2 WO 2015-108627 A1 WO 2015-134074 A1	18/09/2014 11/08/2016 11/09/2015 08/12/2016 12/12/2013 21/01/2015 29/06/2016 05/03/2015 12/12/2013 09/12/2014 23/07/2015 11/09/2015