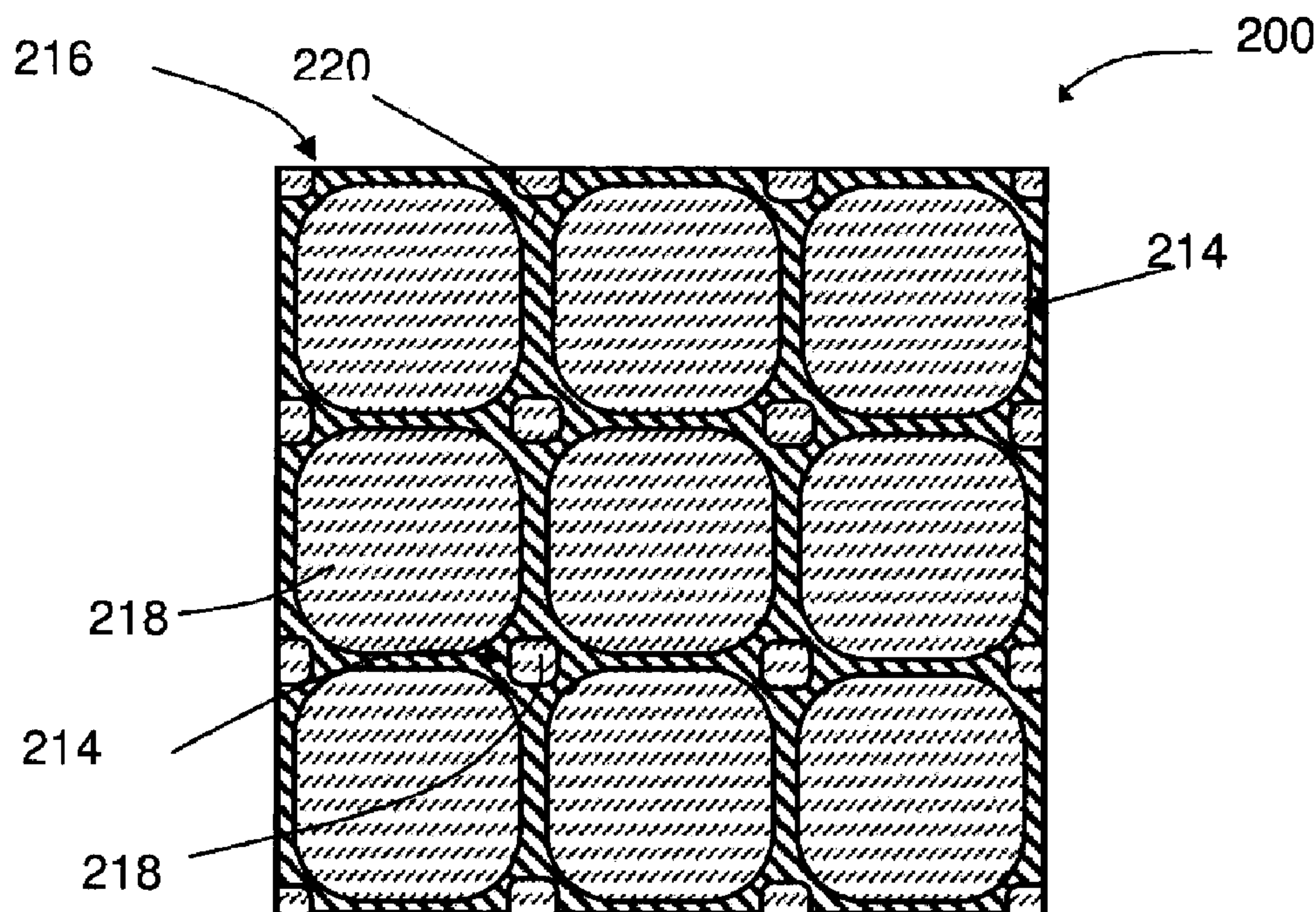




(86) Date de dépôt PCT/PCT Filing Date: 2011/10/27
(87) Date publication PCT/PCT Publication Date: 2012/05/03
(45) Date de délivrance/Issue Date: 2015/09/08
(85) Entrée phase nationale/National Entry: 2013/04/23
(86) N° demande PCT/PCT Application No.: US 2011/058105
(87) N° publication PCT/PCT Publication No.: 2012/058436
(30) Priorité/Priority: 2010/10/27 (US12/913,310)

(51) Cl.Int./Int.Cl. *C01B 31/02* (2006.01),
C04B 35/52 (2006.01), *C09K 3/14* (2006.01),
C09K 8/02 (2006.01)
(72) Inventeurs/Inventors:
XU, ZHIYUE, US;
CHAKRABORTY, SOMA, US;
AGRAWAL, GAURAV, US
(73) Propriétaire/Owner:
BAKER HUGHES INCORPORATED, US
(74) Agent: SIM & MCBURNEY

(54) Titre : COMPOSITE DE CARBONE NANOMATRICIEL
(54) Title: NANOMATRIX CARBON COMPOSITE



(57) Abrégé/Abstract:

A nanomatrix carbon composite is disclosed. The nanomatrix carbon composite includes a substantially-continuous, cellular nanomatrix comprising a nanomatrix material. The composite also includes a plurality of dispersed particles comprising a particle core material that comprises an allotrope of carbon dispersed in the nanomatrix and a bond layer extending throughout the nanomatrix between the dispersed particles. The nanomatrix carbon composites are uniquely lightweight, high-strength, high thermal conductivity materials that also provide uniquely selectable and controllable corrosion properties, including very rapid corrosion rates, useful for making a wide variety of degradable or disposable articles, including various downhole tools and components.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property

Organization

International Bureau

(43) International Publication Date

3 May 2012 (03.05.2012)



(10) International Publication Number

WO 2012/058436 A3

(51) International Patent Classification:

C01B 31/02 (2006.01) C09K 8/02 (2006.01)
C09K 3/14 (2006.01) C04B 35/52 (2006.01)

(21) International Application Number:

PCT/US2011/058105

(22) International Filing Date:

27 October 2011 (27.10.2011)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

12/913,310 27 October 2010 (27.10.2010) US

(71) Applicant (for all designated States except US): **BAKER HUGHES INCORPORATED** [US/US]; P.O. Box 4740, Houston, Texas 77210-4740 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **XU, Zhiyue** [US/US]; 18709 N. Bee Cave Springs Circle, Cypress, Texas 77433 (US). **CHAKRABORTY, Soma** [IN/US]; 10919 West Road #718, Houston, Texas 77064 (US). **AGRAWAL, Gaurav** [US/US]; 18231 E. Peakview Pl., Aurora, Colorado 80016 (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, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, 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, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, 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, 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))

[Continued on next page]

(54) Title: NANOMATRIX CARBON COMPOSITE

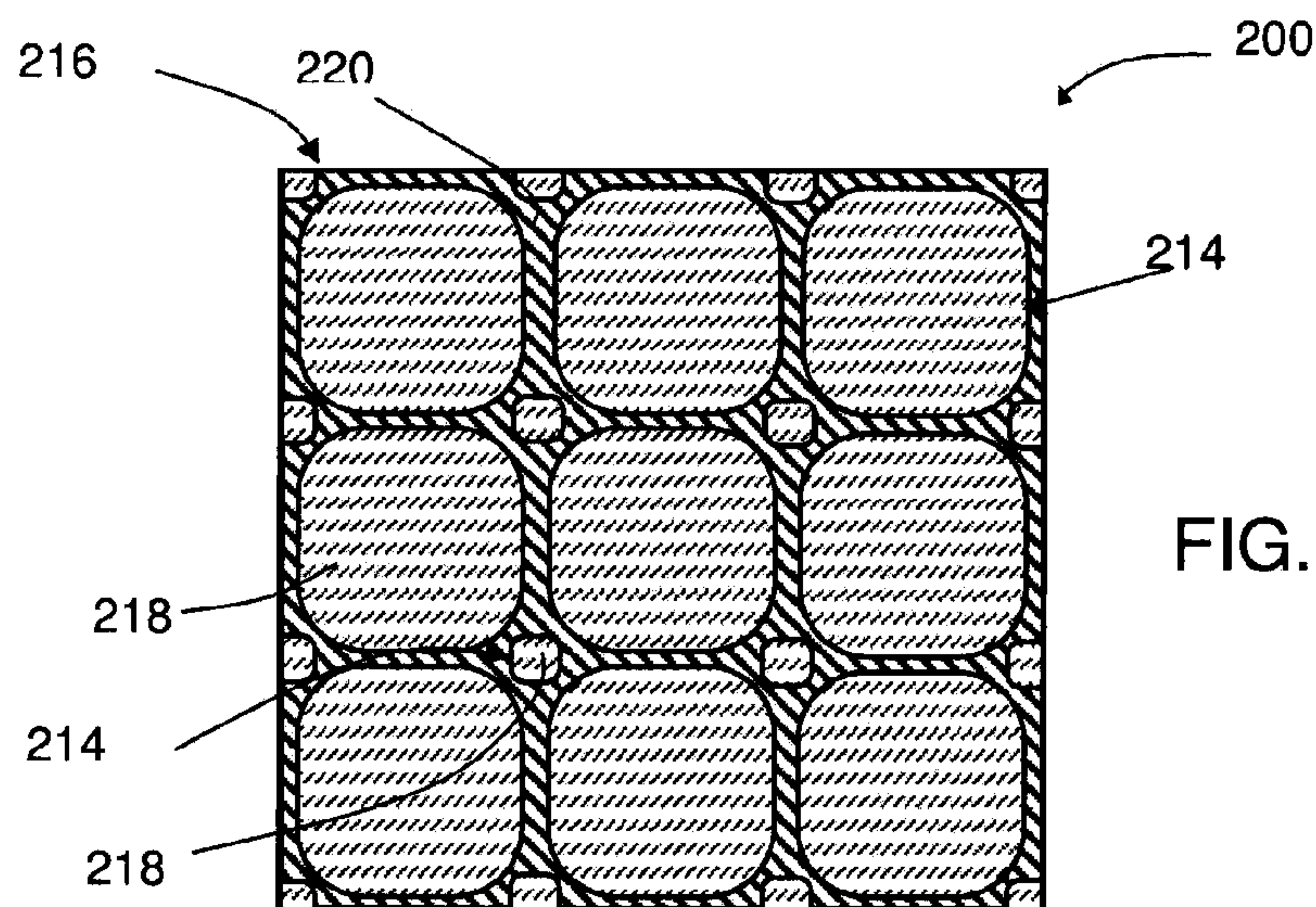


FIG. 10

(57) Abstract: A nanomatrix carbon composite is disclosed. The nanomatrix carbon composite includes a substantially-continuous, cellular nanomatrix comprising a nanomatrix material. The composite also includes a plurality of dispersed particles comprising a particle core material that comprises an allotrope of carbon dispersed in the nanomatrix and a bond layer extending throughout the nanomatrix between the dispersed particles. The nanomatrix carbon composites are uniquely lightweight, high-strength, high thermal conductivity materials that also provide uniquely selectable and controllable corrosion properties, including very rapid corrosion rates, useful for making a wide variety of degradable or disposable articles, including various downhole tools and components.

WO 2012/058436 A3



-
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))* (88) **Date of publication of the international search report:**
5 July 2012

NANOMATRIX CARBON COMPOSITE**BACKGROUND**

[0001] Downhole operations, including well production or completion, particularly for oil and natural gas wells, utilize components and tools, particularly rotatable components and tools, which must maintain a high abrasion resistance and a low coefficient of sliding friction under extreme conditions, such as, high temperatures and high pressures for their efficient operation. These include many types of rotatable rotors, shafts, bushings, bearings, sleeves and the like. The high temperatures can be elevated further by heat generated by the components and tools themselves. The materials used to fabricate these downhole components and tools are carefully selected to provide the properties described under these extreme operating conditions.

[0002] Additionally, in some applications, these components and tools are designed to have limited service lives and are configured to be removed or disposed of in order to recover the original size of the fluid pathway for use, including hydrocarbon production, CO₂ sequestration, etc. In order to eliminate the need for milling or drilling operations for removal or disposal, the removal of components and tools formed of a nanomatrix powder metal compact by rapid, controlled dissolution has been described in the following patent documents: U.S. Patent Application Publication Nos. 2011/0132143; 2011/0135953; 2011/0136707; 2011/0135530; U.S. Patent Nos. 8,297,364; 8,403,037; 8,327,931; and 8,528,633 that were all filed on December 8, 2009; and U.S. Patent No. 8,425,651 that was filed on July 30, 2010, which are assigned to the same assignee as this application, Baker Hughes Incorporated of Houston, Texas.

[0003] In order to maintain a high abrasion resistance, a low coefficient of sliding friction or a high thermal conductivity, or a combination of these properties, these downhole components and tools frequently employ surface coatings, internal layers or other features to provide these characteristics. These features must also be compatible with the overall material systems used to manufacture these components and tools, such as, for example, material systems comprising nanomatrix powder metal compacts.

[0004] Therefore, the development of materials having the desired combination of high abrasion resistance, low coefficient of sliding friction, or high thermal conductivity, or a combination of these properties, for use in downhole components and tools, particularly those that include nanomatrix powder metal compacts, is very desirable.

SUMMARY

[0005] An exemplary embodiment of a nanomatrix carbon composite is disclosed. The nanomatrix carbon composite includes a substantially-continuous, cellular nanomatrix comprising a nanomatrix material. The composite also includes a plurality of dispersed particles comprising a particle core material that comprises an allotrope of carbon dispersed in the cellular nanomatrix and a bond layer extending throughout the cellular nanomatrix between the dispersed particles.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] Referring now to the drawings wherein like elements are numbered alike in the several Figures:

[0007] FIG. 1 is a schematic illustration of an exemplary embodiment of a powder as disclosed herein having a uni-modal distribution of particle sizes;

[0008] FIG. 2 is a schematic illustration of an exemplary embodiment of a powder particle 12 as it would appear in an exemplary section view represented by section 2-2 of FIG. 1;

[0009] FIG. 3 is a schematic illustration of a second exemplary embodiment of a powder particle 12 as it would appear in a second exemplary section view represented by section 2-2 of FIG. 1;

[0010] FIG. 4 is a schematic illustration of a third exemplary embodiment of a powder particle 12 as it would appear in a third exemplary section view represented by section 2-2 of FIG. 1;

[0011] FIG. 5 is a schematic illustration of a fourth exemplary embodiment of a powder particle 12 as it would appear in a fourth exemplary section view represented by section 2-2 of FIG. 1;

[0012] FIG. 6 is a schematic illustration of a second exemplary embodiment of a powder as disclosed herein having a multi-modal distribution of particle sizes;

[0013] FIG. 7 is a schematic illustration of a third exemplary embodiment of a powder as disclosed herein having a multi-modal distribution of particle sizes;

[0014] FIG. 8 is a flow chart of an exemplary embodiment of a method of making a powder as disclosed herein;

[0015] FIG. 9 is a schematic of illustration of an exemplary embodiment of adjacent first and second powder particles of a powder composite made using a powder mixture having single-layer coated powder particles;

[0016] FIG. 10 is a schematic illustration of an exemplary embodiment of a powder composite as disclosed herein formed from a first powder and a second powder and having a homogenous multi-modal distribution of particle sizes;

[0017] FIG. 11 is a schematic illustration of an exemplary embodiment of a powder composite as disclosed herein formed from a first powder and a second powder and having a non-homogeneous multi-modal distribution of particle sizes.

[0018] FIG. 12 is a schematic of illustration of another exemplary embodiment of adjacent first and second powder particles of a powder composite of made using a powder mixture having multilayer coated powder particles;

[0019] FIG. 13 is a schematic illustration of an exemplary embodiment of a powder composite as disclosed herein formed from a first and second uncoated powder and having a homogeneous multimodal distribution of particle sizes;

[0020] FIG. 14 is a schematic illustration of an exemplary embodiment of a powder composite as disclosed herein formed from a first and second uncoated powder and having a non-homogeneous multimodal distribution of particle sizes;

[0021] FIG. 15 is a schematic cross-sectional illustration of an exemplary embodiment of a precursor powder composite; and

[0022] FIG. 16 is a flowchart of an exemplary method of making a powder composite as disclosed herein.

DETAILED DESCRIPTION

[0023] Lightweight, high-strength metallic materials are disclosed that may be used in a wide variety of applications and application environments, including use in various wellbore environments to make various selectably and controllably disposable or degradable lightweight, high-strength downhole tools or other downhole components, as well as many other applications for use in both durable and disposable or degradable articles. These materials may be used to make various downhole tools and components and may also be used to provide various surface coatings, internal layers, inserts or other features or aspects of these devices. These lightweight, high-strength and selectably and controllably degradable

materials include fully-dense, sintered powder composites formed from coated powder materials that include various carbon nanoparticle cores having various single layer and multilayer nanoscale metallic coatings. These powder composites are made from metal coated carbon nanoparticle powders that include various carbon nanoparticle cores, such as various graphene, fullerene or nanodiamond nanoparticles, or combinations thereof, that are dispersed within a cellular nanomatrix formed from various nanoscale metallic coating layers of metallic coating materials, particularly electrochemically-active (e.g., having relatively higher standard oxidation potentials) lightweight, metals, and are particularly useful in wellbore applications. These powder composites provide a unique and advantageous combination of properties, including a high compression and shear strength, low density, high abrasion resistance, low coefficient of sliding friction, high thermal conductivity, high thermal conductivity or selectable and controllable corrosion properties, particularly rapid and controlled dissolution in various wellbore fluids, or a combination of these properties. For example, these powder composites may be used provide surface coatings to lower the coefficient of sliding friction and enhance the tribological properties of various downhole tools and components. In another example, these powder composites may be used to enhance the thermal conductivity of various downhole tools and components, either as a surface coating, internal layer, insert or other feature.

[0024] Referring to FIGS. 1-5, a metallic powder 10 includes a plurality of metallic, coated powder particles 12. Powder particles 12 may be formed to provide a powder 10, including free-flowing powder, that may be poured or otherwise disposed in all manner of forms or molds (not shown) having all manner of shapes and sizes and that may be used to fashion precursor powder composites 100 (FIG. 15) and powder composites 200 (FIGS. 9-14), as described herein, that may be used as, or for use in manufacturing, various articles of manufacture, including various wellbore tools and components.

[0025] Each of the metallic, coated powder particles 12 of powder 10 includes a particle core 14 and a metallic coating layer 16 disposed on the particle core 14. The particle core 14 includes a core material 18. The core material 18 may include any suitable allotrope of carbon for forming the particle core 14 that provides powder particle 12 that can be sintered to form a lightweight, high-strength, high thermal conductivity powder composite 200 having selectable and controllable dissolution characteristics. Suitable allotropes include diamond; including microparticle/micron diamond or nanoparticle diamond (nanodiamond); graphite, including various graphenes; fullerenes, including various buckyballs, buckyball clusters, nanobuds or nanotubes, including single-wall or multi-wall nanotubes; amorphous

carbon; glassy carbon; carbon nanofoam; lonsdaleite; or chaoite, or a combination thereof. Particle core 14 may have any suitable shape or size, including various microparticle shapes, and more particularly, many nanoparticle shapes. As used herein, microparticles include various regular and irregular particle shapes, including planar, spheroidal, ellipsoidal and tubular or cylindrical shapes, having at least one particle dimension greater than about 0.1 μm to about 700 μm , and more particularly about 0.3 μm to about 300 μm , and more particularly about 0.7 μm to about 100 μm . As used herein, nanoparticles include various regular and irregular particle shapes, including planar, spheroidal, ellipsoidal and tubular or cylindrical shapes, having at least one particle dimension of about 100 nm or less, and more particularly at least one particle dimension that is between about 0.1 nm to about 100 nm, and more particularly about 1.0 nm to about 100 nm. Suitable core materials include various carbon nanoparticles, including various graphenes; fullerenes or nanodiamonds, or a combination thereof. Suitable fullerenes may include buckyballs, buckyball clusters, buckypapers, nanobuds or nanotubes, including single-wall nanotubes and multi-wall nanotubes. Fullerenes also include three-dimensional polymers of any of the above. Suitable fullerenes may also include metallofullerenes, or those which encompass various metals or metal ions.

[0026] Fullerenes in the form of substantially spheroidal hollow polyhedrons or buckyballs, as disclosed herein, may include any of the known cage-like hollow allotropic forms of carbon possessing a polyhedral structure. Buckyballs may include, for example, from about 20 to about 100 carbon atoms. For example, C_{60} is a fullerene having 60 carbon atoms and high symmetry (D_{5h}), and is a relatively common, commercially available fullerene. Exemplary fullerenes include, for example, C_{30} , C_{32} , C_{34} , C_{38} , C_{40} , C_{42} , C_{44} , C_{46} , C_{48} , C_{50} , C_{52} , C_{60} , C_{70} , C_{76} , C_{84} and the like. Buckyballs or buckyball clusters may include any suitable ball size or diameter, including substantially spheroidal configurations having any number of carbon atoms.

[0027] Nanotubes are carbon based, tubular or cylindrical fullerene structures having open or closed ends, which may be inorganic or made entirely or partially of carbon, and may include also other elements such as metals or metalloids. Both single-wall and multi-wall nanotubes are substantially cylindrical may have any predetermined tube length or tube diameter, or combination thereof. Multi-wall nanotubes may have any predetermined number of walls.

[0028] Nanographite is a cluster of plate-like sheets of graphite, in which a stacked structure of one or more layers of the graphite, which has a plate-like two dimensional

structure of fused hexagonal rings with an extended delocalized π -electron system, layered and weakly bonded to one another through π - π stacking interaction. Graphene in general, and including nanographene, may be a single sheet or several sheets of graphite having nano-scale dimensions, such as an average particle size of (average largest dimension) of less than about, for example, 500nm, or in other embodiments may have an average largest dimension greater than about 1 μ m. Nanographene may be prepared by exfoliation of nanographite or by catalytic bond-breaking of a series of carbon-carbon bonds in a carbon nanotube to form a nanographene ribbon by an “unzipping” process, followed by derivatization of the nanographene to prepare, for example, nanographene oxide. Graphene nanoparticles may be of any suitable predetermined planar size, including any predetermined length or predetermined width, and thus may include any predetermined number of carbon atoms.

[0029] The nanodiamonds used herein may be from a naturally occurring source, such as a by-product of milling or other processing of natural diamonds, or may be synthetic, prepared by any suitable commercial method such as, but not limited to, high-pressure high-temperature (HPHT), explosive shock (also referred to as detonation, abbreviated DTD), chemical vapor deposition (CVD), physical vapor deposition (PVD), ultrasonic cavitation, and the like. Nanodiamonds may be used as received, or may be sorted and cleaned by various methods to remove contaminants and non-diamond carbon phases that may be present, such as residues of amorphous carbon or graphite. Nanodiamonds may be monocrystalline or polycrystalline. Nanodiamonds may include various regular and irregular shapes, including substantially spheroidal shapes. The nanodiamonds may be monodisperse, where all particles are of the same size with little variation, or polydisperse, where the particles have a range of sizes and are averaged. Generally, polydisperse nanodiamonds are used. Nanodiamonds of different average particle size may be used, and in this way, the particle size distribution of the nanodiamonds may be unimodal (exhibiting a single distribution), bimodal exhibiting two distributions, or multi-modal, exhibiting more than one particle size distribution, as described herein.

[0030] Core material 18, including the type of carbon nanoparticle, or combination of types of carbon nanoparticles, may be selected to provide a high dissolution rate in a predetermined wellbore fluid, but may also be selected to provide a relatively low dissolution rate, including zero dissolution, where dissolution of the nanomatrix material causes the particle core 14 to be rapidly undermined and liberated from the particle composite at the interface with the wellbore fluid, such that the effective rate of dissolution of particle

composites made using particle cores 14 of these core materials 18 is high, even though core material 18 itself may have a low dissolution rate, including core materials 18 that may be substantially insoluble in the wellbore fluid.

[0031] Particle core 14 and core material 18 have a melting temperature (T_P). As used herein, T_P includes the lowest temperature at which incipient melting or liquation or other forms of partial melting occur within core material 18, regardless of whether core material 18 comprises a pure metal, an alloy with multiple phases having different melting temperatures or a composite of materials having different melting temperatures.

[0032] Particle cores 14 may have any suitable particle size or range of particle sizes or distribution of particle sizes. For example, the particle cores 14 may be selected to provide an average particle size that is represented by a normal or Gaussian type unimodal distribution around an average or mean, as illustrated generally in FIG. 1. In another example, particle cores 14 may be selected or mixed to provide a multimodal distribution of particle sizes, including a plurality of average particle core sizes, such as, for example, a homogeneous bimodal distribution of average particle sizes, as illustrated generally and schematically in FIG. 6. The selection of the distribution of particle core size may be used to determine, for example, the particle size and interparticle spacing 15 of the particles 12 of powder 10.

[0033] Particle cores 14 may have any suitable particle shape, including any regular or irregular geometric shape, or combination thereof, associated with the carbon nanoparticle or nanoparticles selected. In an exemplary embodiment, particle cores 14 may comprise graphenes, and include various flat or curved planar structures. In another, exemplary embodiment, particle cores 14 may include various fullerenes, and include substantially spheroidal shapes (e.g., buckyballs or buckyball clusters) or substantially tubular shapes (e.g., single-wall or multi-wall nanotubes). In yet another, exemplary embodiment, particle cores 14 may include various nanodiamonds, and include substantially spheroidal shapes (e.g., nanodiamonds or nanodiamond clusters). In other embodiments, various combinations of these carbon nanoparticles and their respective shapes may be employed.

[0034] Each of the metallic, coated powder particles 12 of powder 10 also includes a metallic coating layer 16 that is disposed on particle core 14. Metallic coating layer 16 includes a metallic coating material 20. Metallic coating material 20 gives the powder particles 12 and powder 10 its metallic nature. Metallic coating layer 16 may be any suitable thickness, including a nanoscale coating layer. In an exemplary embodiment, metallic coating layer 16 may have a thickness of about 25nm to about 2500nm. The thickness of

metallic coating layer 16 may vary over the surface of particle core 14, but will preferably have a substantially uniform thickness over the surface of particle core 14. Metallic coating layer 16 may include a single layer, as illustrated in FIG. 2, or a plurality of layers as a multilayer coating structure, as illustrated in FIGS. 3-5 for up to four layers. In a single layer coating, or in each of the layers of a multilayer coating, the metallic coating layer 16 may include a single constituent chemical element or compound, or may include a plurality of chemical elements or compounds. Where a layer includes a plurality of chemical constituents or compounds, they may have all manner of homogeneous or heterogeneous distributions, including a homogeneous or heterogeneous distribution of metallurgical phases. This may include a graded distribution where the relative amounts of the chemical constituents or compounds vary according to respective constituent profiles across the thickness of the layer. In both single layer and multilayer coatings 16, each of the respective layers, or combinations of them, may be used to provide a predetermined property to the powder particle 12 or a sintered powder composite formed therefrom. For example, the predetermined property may include the bond strength of the metallurgical bond between the particle core 14 and the coating material 20; the interdiffusion characteristics between the particle core 14 and metallic coating layer 16, including any interdiffusion between the layers of a multilayer coating layer 16; the interdiffusion characteristics between the various layers of a multilayer coating layer 16; the interdiffusion characteristics between the metallic coating layer 16 of one powder particle and that of an adjacent powder particle 12; the bond strength of the metallurgical bond between the metallic coating layers of adjacent sintered powder particles 12, including the outermost layers of multilayer coating layers; and the electrochemical activity of the coating layer 16.

[0035] Metallic coating layer 16 and coating material 20 have a melting temperature (T_C). As used herein, T_C includes the lowest temperature at which incipient melting or liquation or other forms of partial melting occur within coating material 20, regardless of whether coating material 20 comprises a pure metal, an alloy with multiple phases each having different melting temperatures or a composite, including a composite comprising a plurality of coating material layers having different melting temperatures.

[0036] Metallic coating material 20 may include any suitable metallic coating material 20 that provides a sinterable outer surface 21 that is configured to be sintered to an adjacent powder particle 12 that also has a metallic coating layer 16 and sinterable outer surface 21. In powders 10 that also include second or additional (coated or uncoated) particles 32, as described herein, the sinterable outer surface 21 of metallic coating layer 16 is

also configured to be sintered to a sinterable outer surface 21 of second particles 32. In an exemplary embodiment, the powder particles 12 are sinterable at a predetermined sintering temperature (T_S) that is a function of the core material 18 and coating material 20, such that sintering of powder composite 200 is accomplished entirely in the solid state and where T_S is less than T_P and T_C . Sintering in the solid state limits particle core 14/metallic coating layer 16 interactions to solid state diffusion processes and metallurgical transport phenomena and limits growth of and provides control over the resultant interface between them. In contrast, for example, the introduction of liquid phase sintering would provide for rapid interdiffusion of the particle core 14/metallic coating layer 16 materials and make it difficult to limit the growth of and provide control over the resultant interface between them, and thus interfere with the formation of the desirable microstructure of particle composite 200 as described herein.

[0037] In an exemplary embodiment, core material 18 will be selected to provide a core chemical composition and the coating material 20 will be selected to provide a coating chemical composition and these chemical compositions will also be selected to differ from one another. In another exemplary embodiment, the core material 18 will be selected to provide a core chemical composition and the coating material 20 will be selected to provide a coating chemical composition and these chemical compositions will also be selected to differ from one another at their interface. Differences in the chemical compositions of coating material 20 and core material 18 may be selected to provide different dissolution rates and selectable and controllable dissolution of powder composites 200 that incorporate them making them selectably and controllably dissolvable. This includes dissolution rates that differ in response to a changed condition in the wellbore, including an indirect or direct change in a wellbore fluid. In an exemplary embodiment, a powder composite 200 formed from powder 10 having chemical compositions of core material 18 and coating material 20 that make composite 200 is selectably dissolvable in a wellbore fluid in response to a changed wellbore condition that includes a change in temperature, change in pressure, change in flow rate, change in pH or change in chemical composition of the wellbore fluid, or a combination thereof. The selectable dissolution response to the changed condition may result from actual chemical reactions or processes that promote different rates of dissolution, but also encompass changes in the dissolution response that are associated with physical reactions or processes, such as changes in wellbore fluid pressure or flow rate.

[0038] In an exemplary embodiment of a powder 10, particle core 14 includes a carbon microparticle or nanoparticle, or a combination thereof, as core material 18, and more

particularly may include a graphene, fullerene or nanodiamond nanoparticle, or a combination thereof, and metallic coating layer 16 includes Al, Zn, Mn, Mg, Mo, W, Cu, Fe, Si, Ca, Co, Ta, Re, or Ni, or an oxide, nitride or a carbide thereof, or a combination of any of the aforementioned materials as coating material 20. More particularly, metallic coating layer 16 may include electrochemically active metals having a standard oxidation potential greater than or equal to that of Zn, including Mg, Al, Mn or Zn, or a combination thereof. These electrochemically active metals are very reactive with a number of common wellbore fluids, including any number of ionic fluids or highly polar fluids, such as those that contain various chlorides, and provide very high dissolution rates in these fluids. Examples include fluids comprising potassium chloride (KCl), hydrochloric acid (HCl), calcium chloride (CaCl_2), calcium bromide (CaBr_2) or zinc bromide (ZnBr_2).

[0039] With regard to the electrochemically active metals as core materials 18, including Mg, Al, Mn or Zn, these metals may be used as pure metals or in any combination with one another, including various alloy combinations of these materials, including binary, tertiary, or quaternary alloys of these materials. These combinations may also include composites of these materials. Further, in addition to combinations with one another, the Mg, Al, Mn or Zn core materials 18 may also include other constituents, including various alloying additions, to alter one or more properties of the particle cores 14, such as by improving the strength, lowering the density or altering the dissolution characteristics of the core material 18.

[0040] Among the electrochemically active metals, Mg, either as a pure metal or an alloy or a composite material, is particularly useful, because of its low density and ability to form high-strength alloys, as well as its high degree of electrochemical activity, since it has a standard oxidation potential higher than Al, Mn or Zn. Mg alloys include all alloys that have Mg as an alloy constituent. Mg alloys that combine other electrochemically active metals, as described herein, as alloy constituents are particularly useful, including binary Mg-Zn, Mg-Al and Mg-Mn alloys, as well as tertiary Mg-Zn-Y and Mg-Al-X alloys, where X includes Zn, Mn, Si, Ca or Y, or a combination thereof. These Mg-Al-X alloys may include, by weight, up to about 85% Mg, up to about 15% Al and up to about 5% X. Particle core 14 and core material 18, and particularly electrochemically active metals including Mg, Al, Mn or Zn, or combinations thereof, may also include a rare earth element or combination of rare earth elements. As used herein, rare earth elements include Sc, Y, La, Ce, Pr, Nd or Er, or a combination of rare earth elements. Where present, a rare earth element or combinations of rare earth elements may be present, by weight, in an amount of about 5% or less.

[0041] In another exemplary embodiment of powder 10, particle core 14 includes a carbon microparticle or nanoparticle, or a combination thereof, as core material 18, and more particularly may include a graphene, fullerene or nanodiamond nanoparticle, or a combination thereof, and metallic coating layer 16 includes a single layer of Mg, Al or Ni, or a combination thereof, as coating material 20, as illustrated in FIG. 2. Where metallic coating layer 16 includes a combination of two or more constituents, such as, for example Mg and Al, or Al and Ni, the combination may include various graded or co-deposited structures of these materials where the amount of each constituent, and hence the composition of the layer, varies across the thickness of the layer, as also illustrated in FIG. 2.

[0042] In yet another exemplary embodiment, particle core 14 includes a carbon microparticle or nanoparticle, or a combination thereof, as core material 18, and more particularly may include a graphene, fullerene or nanodiamond nanoparticle, or a combination thereof, and coating layer 16 includes two layers as core material 20, as illustrated in FIG. 3. The first layer 22 is disposed on the surface of particle core 14 and includes Mg, Al or Ni, or a combination thereof, as described herein. The second layer 24 is disposed on the surface of the first layer and includes Al, Zn, Mg, Mo, W, Cu, Fe, Si, Ca, Co, Ta, Re or Ni, or a combination thereof, and the first layer has a chemical composition that is different than the chemical composition of the second layer. In general, first layer 22 will be selected to provide a strong metallurgical bond to particle core 14 and to limit interdiffusion between the particle core 14 and coating layer 16, particularly first layer 22. Second layer 24 may be selected to increase the strength of the metallic coating layer 16, or to provide a strong metallurgical bond and promote sintering with the second layer 24 of adjacent powder particles 12, or both. In an exemplary embodiment, the respective layers of metallic coating layer 16 may be selected to promote the selective and controllable dissolution of the coating layer 16 in response to a change in a property of the wellbore, including the wellbore fluid, as described herein. However, this is only exemplary and it will be appreciated that other selection criteria for the various layers may also be employed. For example, any of the respective layers may be selected to promote the selective and controllable dissolution of the coating layer 16 in response to a change in a property of the wellbore, including the wellbore fluid, as described herein. Exemplary embodiments of a two-layer metallic coating layers 16 for use on particles cores 14 include first/second layer combinations comprising Al/Ni and Al/W.

[0043] In still another embodiment, particle core 14 includes a carbon microparticle or nanoparticle, or a combination thereof, as core material 18, and more particularly may

include a graphene, fullerene or nanodiamond nanoparticle, or a combination thereof, and coating layer 16 includes three layers, as illustrated in FIG. 4. The first layer 22 is disposed on particle core 14 and may include Mg, Al or Ni, or a combination thereof. The second layer 24 is disposed on first layer 22 and may include Al, Zn, Mg, Mo, W, Cu, Fe, Si, Ca, Co, Ta, Re or Ni, or an oxide, nitride or a carbide thereof, or a combination of any of the aforementioned second layer materials. The third layer 26 is disposed on the second layer 24 and may include Al, Mn, Fe, Co, Ni or a combination thereof. In a three-layer configuration, the composition of adjacent layers is different, such that the first layer has a chemical composition that is different than the second layer, and the second layer has a chemical composition that is different than the third layer. In an exemplary embodiment, first layer 22 may be selected to provide a strong metallurgical bond to particle core 14 and to limit interdiffusion between the particle core 14 and coating layer 16, particularly first layer 22. Second layer 24 may be selected to increase the strength of the metallic coating layer 16, or to limit interdiffusion between particle core 14 or first layer 22 and outer or third layer 26, or to promote adhesion and a strong metallurgical bond between third layer 26 and first layer 22, or any combination of them. Third layer 26 may be selected to provide a strong metallurgical bond and promote sintering with the third layer 26 of adjacent powder particles 12. However, this is only exemplary and it will be appreciated that other selection criteria for the various layers may also be employed. For example, any of the respective layers may be selected to promote the selective and controllable dissolution of the coating layer 16 in response to a change in a property of the wellbore, including the wellbore fluid, as described herein. An exemplary embodiment of a three-layer coating layer for use on particles cores comprising Mg include first/second/third layer combinations comprising Al/Al₂O₃/Al.

[0044] In still another embodiment, particle core 14 includes a carbon microparticle or nanoparticle, or a combination thereof, as core material 18, and more particularly may include a graphene, fullerene or nanodiamond nanoparticle, or a combination thereof, and coating layer 16 includes four layers, as illustrated in FIG. 5. In the four layer configuration, the first layer 22 may include Al or Ni, or a combination thereof, as described herein. The second layer 24 may include Al, Zn, Mg, Mo, W, Cu, Fe, Si, Ca, Co, Ta, Re or Ni or an oxide, nitride, carbide thereof, or a combination of the aforementioned second layer materials. The third layer 26 may also include Al, Zn, Mg, Mo, W, Cu, Fe, Si, Ca, Co, Ta, Re or Ni, or an oxide, nitride or carbide thereof, or a combination of any of the aforementioned third layer materials. The fourth layer 28 may include Al, Mn, Fe, Co, Ni or a combination thereof. In the four layer configuration, the chemical composition of adjacent

layers is different, such that the chemical composition of first layer 22 is different than the chemical composition of second layer 24, the chemical composition is of second layer 24 different than the chemical composition of third layer 26, and the chemical composition of third layer 26 is different than the chemical composition of fourth layer 28. In an exemplary embodiment, the selection of the various layers will be similar to that described for the three-layer configuration above with regard to the inner (first) and outer (fourth) layers, with the second and third layers available for providing enhanced interlayer adhesion, strength of the overall metallic coating layer 16, limited interlayer diffusion or selectable and controllable dissolution, or a combination thereof. However, this is only exemplary and it will be appreciated that other selection criteria for the various layers may also be employed. For example, any of the respective layers may be selected to promote the selective and controllable dissolution of the coating layer 16 in response to a change in a property of the wellbore, including the wellbore fluid, as described herein

[0045] The thickness of the various layers in multi-layer configurations may be apportioned between the various layers in any manner so long as the sum of the layer thicknesses provide a nanoscale coating layer 16, including layer thicknesses as described herein. In one embodiment, the first layer 22 and outer layer (24, 26, or 28 depending on the number of layers) may be thicker than other layers, where present, due to the desire to provide sufficient material to promote the desired bonding of first layer 22 with the particle core 14, or the bonding of the outer layers of adjacent powder particles 12, during sintering of powder composite 200.

[0046] Powder 10 may also include an additional or second powder 30 interspersed in the plurality of powder particles 12, as illustrated in FIG. 7. In an exemplary embodiment, the second powder 30 includes a plurality of second powder particles 32. These second powder particles 32 may be selected to change a physical, chemical, mechanical or other property of a powder particle composite 200 formed from powder 10 and second powder 30, or a combination of such properties. In an exemplary embodiment, the property change may include an increase in the compressive strength of powder composite 200 formed from powder 10 and second powder 30. In another exemplary embodiment, the second powder 30 may be selected to promote the selective and controllable dissolution of in particle composite 200 formed from powder 10 and second powder 30 in response to a change in a property of the wellbore, including the wellbore fluid, as described herein. Second powder particles 32 may be uncoated or coated with a metallic coating layer 36. When coated, including single layer or multilayer coatings, the coating layer 36 of second powder particles 32 may comprise

the same coating material 40 as coating material 20 of powder particles 12, or the coating material 40 may be different. The second powder particles 32 (uncoated) or particle cores 34 may include any suitable material to provide the desired benefit, including many metals. In an exemplary embodiment, when coated powder particles 12 comprising Mg, Al, Mn or Zn, or a combination thereof are employed, suitable second powder particles 32 may include Ni, W, Cu, Co or Fe, or a combination thereof. In another exemplary embodiment, suitable second powder particles 32 may include a metal, ceramic, glass, including hollow glass microspheres, or carbon, including carbon nanoparticles, or a combination thereof. Since second powder particles 32 will also be configured for solid state sintering to powder particles 12 at the predetermined sintering temperature (T_S), particle cores 34 will have a melting temperature T_{AP} and any coating layers 36 will have a second melting temperature T_{AC} , where T_S is less than T_{AP} and T_{AC} . It will also be appreciated that second powder 30 is not limited to one additional powder particle 32 type (i.e., a second powder particle), but may include a plurality of additional powder particles 32 (i.e., second, third, fourth, etc. types of additional powder particles 32) in any number.

[0047] Referring to FIG. 8, an exemplary embodiment of a method 300 of making a metallic powder 10 is disclosed. Method 300 includes forming 310 a plurality of particle cores 14 as described herein. Method 300 also includes depositing 320 a metallic coating layer 16 on each of the plurality of particle cores 14. Depositing 320 is the process by which coating layer 16 is disposed on particle core 14 as described herein.

[0048] Forming 310 of particle cores 14 may be performed by any suitable method for forming a plurality of particle cores 14 of the desired core material 18, which essentially comprise methods of forming a powder of core material 18. Suitable powder forming methods include various arc discharge, flame synthesis; laser ablation, chemical vapor deposition (CVD) and super-growth CVD methods.

[0049] Depositing 320 of metallic coating layers 16 on the plurality of particle cores 14 may be performed using any suitable deposition method, including various thin film deposition methods, such as, for example, chemical vapor deposition and physical vapor deposition methods. In an exemplary embodiment, depositing 320 of metallic coating layers 16 may be performed using fluidized bed chemical vapor deposition (FBCVD). Depositing 320 of the metallic coating layers 16 by FBCVD includes flowing a reactive fluid as a coating medium that includes the desired metallic coating material 20 through a bed of particle cores 14 fluidized in a reactor vessel under suitable conditions, including temperature, pressure and flow rate conditions and the like, sufficient to induce a chemical reaction of the coating

medium to produce the desired metallic coating material 20 and induce its deposition upon the surface of particle cores 14 to form coated powder particles 12. The reactive fluid selected will depend upon the metallic coating material 20 desired, and will typically comprise an organometallic compound that includes the metallic material to be deposited, such as nickel tetracarbonyl ($\text{Ni}(\text{CO})_4$), tungsten hexafluoride (WF_6), and triethyl aluminum ($\text{C}_6\text{H}_{15}\text{Al}$), that is transported in a carrier fluid, such as helium or argon gas. The reactive fluid, including carrier fluid, causes at least a portion of the plurality of particle cores 14 to be suspended in the fluid, thereby enabling the entire surface of the suspended particle cores 14 to be exposed to the reactive fluid, including, for example, a desired organometallic constituent, and enabling deposition of metallic coating material 20 and coating layer 16 over the entire surfaces of particle cores 14 such that they each become enclosed forming coated particles 12 having metallic coating layers 16, as described herein. As also described herein, each metallic coating layer 16 may include a plurality of coating layers. Coating material 20 may be deposited in multiple layers to form a multilayer metallic coating layer 16 by repeating the step of depositing 320 described above and changing 330 the reactive fluid to provide the desired metallic coating material 20 for each subsequent layer, where each subsequent layer is deposited on the outer surface of particle cores 14 that already include any previously deposited coating layer or layers that make up metallic coating layer 16. The metallic coating materials 20 of the respective layers (e.g., 22, 24, 26, 28, etc.) may be different from one another, and the differences may be provided by utilization of different reactive media that are configured to produce the desired metallic coating layers 16 on the particle cores 14 in the fluidize bed reactor.

[0050] As illustrated in FIGS. 1 and 8, particle core 14 and core material 18 and metallic coating layer 16 and coating material 20 may be selected to provide powder particles 12 and a powder 10 that is configured for compaction and sintering to provide a powder composite 200 that is lightweight (i.e., having a relatively low density), high-strength and is selectably and controllably removable from a wellbore in response to a change in a wellbore property, including being selectably and controllably dissolvable in an appropriate wellbore fluid, including various wellbore fluids as disclosed herein. Powder composite 200 includes a substantially-continuous, cellular nanomatrix 216 of a nanomatrix material 220 having a plurality of dispersed particles 214 dispersed throughout the cellular nanomatrix 216. The substantially-continuous cellular nanomatrix 216 and nanomatrix material 220 formed of sintered metallic coating layers 16 is formed by the compaction and sintering of the plurality of metallic coating layers 16 of the plurality of powder particles 12. The chemical

composition of nanomatrix material 220 may be different than that of coating material 20 due to diffusion effects associated with the sintering as described herein. Nanomatrix carbon composite 200 also includes a plurality of dispersed particles 214 that comprise particle core material 218. Dispersed particle cores 214 and core material 218 correspond to and are formed from the plurality of particle cores 14 and core material 18 of the plurality of powder particles 12 as the metallic coating layers 16 are sintered together to form nanomatrix 216. The chemical composition of core material 218 may be different than that of core material 18 due to diffusion effects associated with sintering as described herein.

[0051] As used herein, the use of the term substantially-continuous cellular nanomatrix 216 does not necessarily connote the major constituent of the powder composite, but rather may refer to the minority constituent or constituents, whether by weight or by volume. This is distinguished from many matrix composite materials where the matrix comprises the majority constituent by weight or volume. The use of the term substantially-continuous, cellular nanomatrix is intended to describe the extensive, regular, continuous and interconnected nature of the distribution of nanomatrix material 220 within powder composite 200. As used herein, "substantially-continuous" describes the extension of the nanomatrix material throughout powder composite 200 such that it extends between and envelopes substantially all of the dispersed particles 214. Substantially-continuous is used to indicate that complete continuity and regular order of the nanomatrix around each dispersed particle 214 is not required. For example, defects in the coating layer 16 over particle core 14 on some powder particles 12 may cause bridging of the particle cores 14 during sintering of the powder composite 200, thereby causing localized discontinuities to result within the cellular nanomatrix 216, even though in the other portions of the powder composite the nanomatrix is substantially continuous and exhibits the structure described herein. As used herein, "cellular" is used to indicate that the nanomatrix defines a network of generally repeating, interconnected, compartments or cells of nanomatrix material 220 that encompass and also interconnect the dispersed particles 214. As used herein, "nanomatrix" is used to describe the size or scale of the matrix, particularly the thickness of the matrix between adjacent dispersed particles 214. The metallic coating layers that are sintered together to form the nanomatrix are themselves nanoscale thickness coating layers. Since the nanomatrix at most locations, other than the intersection of more than two dispersed particles 214, generally comprises the interdiffusion and bonding of two coating layers 16 from adjacent powder particles 12 having nanoscale thicknesses, the matrix formed also has a nanoscale thickness (e.g., approximately two times the coating layer thickness as described

herein) and is thus described as a nanomatrix. Further, the use of the term dispersed particles 214 does not necessarily connote the minor constituent of powder composite 200, but rather may refer to the majority constituent or constituents, whether by weight or by volume. The use of the term dispersed particle is intended to convey the discontinuous and discrete distribution of particle core material 218 within powder composite 200.

[0052] Powder composite 200 may have any desired shape or size, including that of a cylindrical billet or bar that may be machined or otherwise used to form useful articles of manufacture, including various wellbore tools and components. The pressing used to form precursor powder composite 100 and sintering and pressing processes used to form powder composite 200 and deform the powder particles 12, including particle cores 14 and coating layers 16, to provide the full density and desired macroscopic shape and size of powder composite 200 as well as its microstructure. The microstructure of powder composite 200 may include an equiaxed configuration of dispersed particles 214 that are dispersed throughout and embedded within the substantially-continuous, cellular nanomatrix 216 of sintered coating layers, particularly in the case of substantially spherical carbon nanoparticles, including various substantially spherical fullerenes, such as buckyballs and buckyball clusters, and nanodiamonds. This microstructure is somewhat analogous to an equiaxed grain microstructure with a continuous grain boundary phase, except that it does not require the use of alloy constituents having thermodynamic phase equilibria properties that are capable of producing such a structure. Rather, this equiaxed dispersed particle structure and cellular nanomatrix 216 of sintered metallic coating layers 16 may be produced using constituents where thermodynamic phase equilibrium conditions would not produce an equiaxed structure. The equiaxed morphology of the dispersed particles 214 and cellular network 216 of particle layers results from sintering and deformation of the powder particles 12 as they are compacted and interdiffuse and deform to fill the interparticle spaces 15 (FIG. 1). The sintering temperatures and pressures may be selected to ensure that the density of powder composite 200 achieves substantially full theoretical density.

[0053] In an exemplary embodiment as illustrated in FIGS. 1, dispersed particles 214 are formed from particle cores 14 dispersed in the cellular nanomatrix 216 of sintered metallic coating layers 16, and the nanomatrix 216 includes a metallurgical bond 217, such as a solid-state metallurgical bond, or bond layer 219, as illustrated schematically in FIG. 9, extending between the dispersed particles 214 throughout the cellular nanomatrix 216 that is formed at a sintering temperature (T_S), where T_S is less than T_C and T_P . As indicated, metallurgical bond 217 is formed by controlled interdiffusion between the coating layers 16

of adjacent powder particles 12 that are compressed into touching contact during the compaction and sintering processes used to form powder compact 200, as described herein. In one embodiment, this may include a solid-state metallurgical bond 217 formed in the solid state by solid-state interdiffusion between the coating layers 16 of adjacent powder particles 12 that are compressed into touching contact during the compaction and sintering processes used to form powder composite 200, as described herein. As such, sintered coating layers 16 of cellular nanomatrix 216 include a bond layer 219 that has a thickness (t) defined by the extent of the interdiffusion of the coating materials 20 of the metallic coating layers 16, which will in turn be defined by the nature of the coating layers 16, including whether they are single or multilayer coating layers, whether they have been selected to promote or limit such interdiffusion, and other factors, as described herein, as well as the sintering and compaction conditions, including the sintering time, temperature and pressure used to form powder composite 200.

[0054] As nanomatrix 216 is formed, including bond 217 and bond layer 219, the chemical composition or phase distribution, or both, of metallic coating layers 16 may change. Nanomatrix 216 also has a melting temperature (T_M). As used herein, T_M includes the lowest temperature at which incipient melting or liquation or other forms of partial melting will occur within nanomatrix 216, regardless of whether nanomatrix material 220 comprises a pure metal, an alloy with multiple phases each having different melting temperatures or a composite, including a composite comprising a plurality of layers of various coating materials having different melting temperatures, or a combination thereof, or otherwise. As dispersed particles 214 and particle core materials 218 are formed in conjunction with nanomatrix 216, diffusion of constituents of metallic coating layers 16 into the particle cores 14 is also possible, which may result in changes in the chemical composition or phase distribution, or both, of particle cores 14. As a result, dispersed particles 214 and particle core materials 218 may have a melting temperature (T_{DP}) that is different than T_P . As used herein, T_{DP} includes the lowest temperature at which incipient melting or liquation or other forms of partial melting will occur within dispersed particles 214. In one exemplary embodiment, powder composite 200 is formed at a sintering temperature (T_S), where T_S is less than T_C , T_P , T_M and T_{DP} , and the sintering is performed entirely in the solid-state resulting in a solid-state bond layer. In another exemplary embodiment, powder compact 200 is formed at a sintering temperature (T_S), where T_S is greater than or equal to one or more of T_C , T_P , T_M or T_{DP} and the sintering includes limited or partial melting within the powder compact 200 as described herein, and further may include

liquid-state or liquid-phase sintering resulting in a bond layer that is at least partially melted and resolidified. In this embodiment, the combination of a predetermined T_s and a predetermined sintering time (t_s) will be selected to preserve the desired microstructure that includes the cellular nanomatrix 216 and dispersed particles 214. For example, localized liquation or melting may be permitted to occur, for example, within all or a portion of nanomatrix 216 so long as the cellular nanomatrix 216/dispersed particle 214 morphology is preserved, such as by selecting particle cores 14, T_s and t_s that do not provide for complete melting of particle cores. Similarly, localized liquation may be permitted to occur, for example, within all or a portion of dispersed particles 214 so long as the cellular nanomatrix 216/dispersed particle 214 morphology is preserved, such as by selecting metallic coating layers 16, T_s and t_s that do not provide for complete melting of the coating layer or layers 16. Melting of metallic coating layers 16 may, for example, occur during sintering along the metallic layer 16 /particle core 14 interface, or along the interface between adjacent layers of multi-layer coating layers 16. It will be appreciated that combinations of T_s and t_s that exceed the predetermined values may result in other microstructures, such as an equilibrium melt/resolidification microstructure if, for example, both the nanomatrix 216 (i.e., combination of metallic coating layers 16) and dispersed particles 214 (i.e., the particle cores 14) are melted, thereby allowing rapid interdiffusion of these materials.

[0055] Dispersed particles 214 of powder composite 200 may have any suitable particle size, including the average particle sizes described herein for particle cores 14.

[0056] Dispersed particles 214 may have any suitable shape depending on the shape selected for particle cores 14 and powder particles 12, as well as the method used to sinter and composite powder 10. In an exemplary embodiment, powder particles 12 may be spheroidal or substantially spheroidal and dispersed particles 214 may include an equiaxed particle configuration as described herein.

[0057] The nature of the dispersion of dispersed particles 214 may be affected by the selection of the powder 10 or powders 10 used to make particle composite 200. In one exemplary embodiment, a powder 10 having a unimodal distribution of powder particle 12 sizes may be selected to form powder composite 200 and will produce a substantially homogeneous unimodal dispersion of particle sizes of dispersed particles 214 within cellular nanomatrix 216. In another exemplary embodiment, a plurality of powders 10 having a plurality of powder particles with particle cores 14 that have the same core materials 18 and different core sizes and the same coating material 20 may be selected and uniformly mixed as described herein to provide a powder 10 having a homogenous, multimodal distribution of

powder particle 12 sizes, and may be used to form powder composite 200 having a homogeneous, multimodal dispersion of particle sizes of dispersed particles 214 within cellular nanomatrix 216, as illustrated schematically in FIGS. 6 and 10. Similarly, in yet another exemplary embodiment, a plurality of powders 10 having a plurality of particle cores 14 that may have the same core materials 18 and different core sizes and the same coating material 20 may be selected and distributed in a non-uniform manner to provide a non-homogeneous, multimodal distribution of powder particle sizes, and may be used to form powder composite 200 having a non-homogeneous, multimodal dispersion of particle sizes of dispersed particles 214 within cellular nanomatrix 216, as illustrated schematically in FIG. 11. The selection of the distribution of particle core size may be used to determine, for example, the particle size and interparticle spacing of the dispersed particles 214 within the cellular nanomatrix 216 of powder composites 200 made from powder 10.

[0058] As illustrated generally in FIGS. 7 and 13, nanomatrix carbon composite 200 may also be formed using coated metallic powder 10 and an additional or second powder 30, as described herein. The use of an additional powder 30 provides a powder composite 200 that also includes a plurality of dispersed second particles 234, as described herein, that are dispersed within the nanomatrix 216 and are also dispersed with respect to the dispersed particles 214. Dispersed second particles 234 may be formed from coated or uncoated second powder particles 32, as described herein. In an exemplary embodiment, coated second powder particles 32 may be coated with a coating layer 36 that is the same as coating layer 16 of powder particles 12, such that coating layers 36 also contribute to the nanomatrix 216. In another exemplary embodiment, the second powder particles 232 may be uncoated such that dispersed second particles 234 are embedded within nanomatrix 216. As disclosed herein, powder 10 and additional powder 30 may be mixed to form a homogeneous dispersion of dispersed particles 214 and dispersed second particles 234, as illustrated in FIG. 13, or to form a non-homogeneous dispersion of these particles, as illustrated in FIG. 14. The dispersed second particles 234 may be formed from any suitable additional powder 30 that is different from powder 10, either due to a compositional difference in the particle core 34, or coating layer 36, or both of them, and may include any of the materials disclosed herein for use as second powder 30 that are different from the powder 10 that is selected to form powder composite 200. In an exemplary embodiment, dispersed second particles 234 may include Fe, Ni, Co or Cu, or oxides, nitrides or carbides thereof, or a combination of any of the aforementioned materials.

[0059] Nanomatrix 216 is a substantially-continuous, cellular network of metallic coating layers 16 that are sintered to one another. The thickness of nanomatrix 216 will depend on the nature of the powder 10 or powders 10 used to form powder composite 200, as well as the incorporation of any second powder 30, particularly the thicknesses of the coating layers associated with these particles. In an exemplary embodiment, the thickness of nanomatrix 216 is substantially uniform throughout the microstructure of powder composite 200 and comprises about two times the thickness of the coating layers 16 of powder particles 12. In another exemplary embodiment, the cellular network 216 has a substantially uniform average thickness between dispersed particles 214 of about 50nm to about 5000nm.

[0060] Nanomatrix 216 is formed by sintering metallic coating layers 16 of adjacent particles to one another by interdiffusion and creation of bond layer 219 as described herein. Metallic coating layers 16 may be single layer or multilayer structures, and they may be selected to promote or inhibit diffusion, or both, within the layer or between the layers of metallic coating layer 16, or between the metallic coating layer 16 and particle core 14, or between the metallic coating layer 16 and the metallic coating layer 16 of an adjacent powder particle, the extent of interdiffusion of metallic coating layers 16 during sintering may be limited or extensive depending on the coating thicknesses, coating material or materials selected, the sintering conditions and other factors. Given the potential complexity of the interdiffusion and interaction of the constituents, description of the resulting chemical composition of nanomatrix 216 and nanomatrix material 220 may be simply understood to be a combination of the constituents of coating layers 16 that may also include one or more constituents of dispersed particles 214, depending on the extent of interdiffusion, if any, that occurs between the dispersed particles 214 and the nanomatrix 216. Similarly, the chemical composition of dispersed particles 214 and particle core material 218 may be simply understood to be a combination of the constituents of particle core 14 that may also include one or more constituents of nanomatrix 216 and nanomatrix material 220, depending on the extent of interdiffusion, if any, that occurs between the dispersed particles 214 and the nanomatrix 216.

[0061] In an exemplary embodiment, the nanomatrix material 220 has a chemical composition and the particle core material 218 has a chemical composition that is different from that of nanomatrix material 220, and the differences in the chemical compositions may be configured to provide a selectable and controllable dissolution rate, including a selectable transition from a very low dissolution rate to a very rapid dissolution rate, in response to a controlled change in a property or condition of the wellbore proximate the composite 200,

including a property change in a wellbore fluid that is in contact with the powder composite 200, as described herein. Nanomatrix 216 may be formed from powder particles 12 having single layer and multilayer coating layers 16. This design flexibility provides a large number of material combinations, particularly in the case of multilayer coating layers 16, that can be utilized to tailor the cellular nanomatrix 216 and composition of nanomatrix material 220 by controlling the interaction of the coating layer constituents, both within a given layer, as well as between a coating layer 16 and the particle core 14 with which it is associated or a coating layer 16 of an adjacent powder particle 12. Several exemplary embodiments that demonstrate this flexibility are provided below.

[0062] As illustrated in FIG. 9, in an exemplary embodiment, powder composite 200 is formed from powder particles 12 where the coating layer 16 comprises a single layer, and the resulting nanomatrix 216 between adjacent ones of the plurality of dispersed particles 214 comprises the single metallic coating layer 16 of one powder particle 12, a bond layer 219 and the single coating layer 16 of another one of the adjacent powder particles 12. The thickness (t) of bond layer 219 is determined by the extent of the interdiffusion between the single metallic coating layers 16, and may encompass the entire thickness of nanomatrix 216 or only a portion thereof. In one exemplary embodiment of powder composite 200 formed using a single layer powder 10, powder composite 200 may include dispersed particles 214 comprising Mg, Al, Zn or Mn, or a combination thereof, as described herein, and nanomatrix 216 may include Al, Zn, Mn, Mg, Mo, W, Cu, Fe, Si, Ca, Co, Ta, Re or Ni, or an oxide, carbide or nitride thereof, or a combination of any of the aforementioned materials, including combinations where the nanomatrix material 220 of cellular nanomatrix 216, including bond layer 219, has a chemical composition and the core material 218 of dispersed particles 214 has a chemical composition that is different than the chemical composition of nanomatrix material 216. The difference in the chemical composition of the nanomatrix material 220 and the core material 218 may be used to provide selectable and controllable dissolution in response to a change in a property of a wellbore, including a wellbore fluid, as described herein. In a further exemplary embodiment of a powder composite 200 formed from a powder 10 having a single coating layer configuration, dispersed particles 214 include Mg, Al, Zn or Mn, or a combination thereof, and the cellular nanomatrix 216 includes Al or Ni, or a combination thereof.

[0063] As illustrated in FIG. 12, in another exemplary embodiment, powder composite 200 is formed from powder particles 12 where the coating layer 16 comprises a multilayer coating layer 16 having a plurality of coating layers, and the resulting nanomatrix

216 between adjacent ones of the plurality of dispersed particles 214 comprises the plurality of layers (t) comprising the coating layer 16 of one particle 12, a bond layer 219, and the plurality of layers comprising the coating layer 16 of another one of powder particles 12. In FIG. 12, this is illustrated with a two-layer metallic coating layer 16, but it will be understood that the plurality of layers of multi-layer metallic coating layer 16 may include any desired number of layers. The thickness (t) of the bond layer 219 is again determined by the extent of the interdiffusion between the plurality of layers of the respective coating layers 16, and may encompass the entire thickness of nanomatrix 216 or only a portion thereof. In this embodiment, the plurality of layers comprising each coating layer 16 may be used to control interdiffusion and formation of bond layer 219 and thickness (t).

[0064] In one exemplary embodiment of a powder composite 200 made using powder particles 12 with multilayer coating layers 16, the composite includes dispersed particles 214 comprising Mg, Al, Zn or Mn, or a combination thereof, as described herein, and nanomatrix 216 comprises a cellular network of sintered two-layer coating layers 16, as shown in FIG. 3, comprising first layers 22 that are disposed on the dispersed particles 214 and a second layers 24 that are disposed on the first layers 22. First layers 22 include Al or Ni, or a combination thereof, and second layers 24 include Al, Zn, Mn, Mg, Mo, W, Cu, Fe, Si, Ca, Co, Ta, Re or Ni, or a combination thereof. In these configurations, materials of dispersed particles 214 and multilayer coating layer 16 used to form nanomatrix 216 are selected so that the chemical compositions of adjacent materials are different (e.g. dispersed particle/first layer and first layer/second layer).

[0065] In another exemplary embodiment of a powder composite 200 made using powder particles 12 with multilayer coating layers 16, the composite includes dispersed particles 214 comprising Mg, Al, Zn or Mn, or a combination thereof, as described herein, and nanomatrix 216 comprises a cellular network of sintered three-layer metallic coating layers 16, as shown in FIG. 4, comprising first layers 22 that are disposed on the dispersed particles 214, second layers 24 that are disposed on the first layers 22 and third layers 26 that are disposed on the second layers 24. First layers 22 include Al or Ni, or a combination thereof; second layers 24 include Al, Zn, Mn, Mg, Mo, W, Cu, Fe, Si, Ca, Co, Ta, Re or Ni, or an oxide, nitride or carbide thereof, or a combination of any of the aforementioned second layer materials; and the third layers include Al, Zn, Mn, Mg, Mo, W, Cu, Fe, Si, Ca, Co, Ta, Re or Ni, or a combination thereof. The selection of materials is analogous to the selection considerations described herein for powder composite 200 made using two-layer coating

layer powders, but must also be extended to include the material used for the third coating layer.

[0066] In yet another exemplary embodiment of a powder composite 200 made using powder particles 12 with multilayer coating layers 16, the composite includes dispersed particles 214 comprising Mg, Al, Zn or Mn, or a combination thereof, as described herein, and nanomatrix 216 comprise a cellular network of sintered four-layer coating layers 16 comprising first layers 22 that are disposed on the dispersed particles 214; second layers 24 that are disposed on the first layers 22; third layers 26 that are disposed on the second layers 24 and fourth layers 28 that are disposed on the third layers 26. First layers 22 include Al or Ni, or a combination thereof; second layers 24 include Al, Zn, Mn, Mg, Mo, W, Cu, Fe, Si, Ca, Co, Ta, Re or Ni, or an oxide, nitride or carbide thereof, or a combination of any of the aforementioned second layer materials; third layers include Al, Zn, Mn, Mg, Mo, W, Cu, Fe, Si, Ca, Co, Ta, Re or Ni, or an oxide, nitride or carbide thereof, or a combination of any of the aforementioned third layer materials; and fourth layers include Al, Mn, Fe, Co or Ni, or a combination thereof. The selection of materials is analogous to the selection considerations described herein for powder composites 200 made using two-layer coating layer powders, but must also be extended to include the material used for the third and fourth coating layers.

[0067] In another exemplary embodiment of a powder composite 200, dispersed particles 214 comprise a metal having a standard oxidation potential less than Zn or a non-metallic material, or a combination thereof, as described herein, and nanomatrix 216 comprises a cellular network of sintered metallic coating layers 16. Suitable non-metallic materials include various ceramics, glasses or forms of carbon, or a combination thereof. Further, in powder composites 200 that include dispersed particles 214 comprising these metals or non-metallic materials, nanomatrix 216 may include Al, Zn, Mn, Mg, Mo, W, Cu, Fe, Si, Ca, Co, Ta, Re or Ni, or an oxide, carbide or nitride thereof, or a combination of any of the aforementioned materials as nanomatrix material 220.

[0068] Referring to FIG. 15, sintered powder composite 200 may comprise a sintered precursor powder composite 100 that includes a plurality of deformed, mechanically bonded powder particles as described herein. Precursor powder composite 100 may be formed by compaction of powder 10 to the point that powder particles 12 are pressed into one another, thereby deforming them and forming interparticle mechanical or other bonds 110 associated with this deformation sufficient to cause the deformed powder particles 12 to adhere to one another and form a green-state powder composite having a green density that is less than the theoretical density of a fully-dense composite of powder 10, due in part to interparticle spaces

15. Compaction may be performed, for example, by isostatically pressing powder 10 at room temperature to provide the deformation and interparticle bonding of powder particles 12 necessary to form precursor powder composite 100.

[0069] Referring to FIG. 16, a method 400 of making a powder composite 200. Method 400 includes forming 410 a coated metallic powder 10 comprising powder particles 12 having particle cores 14 with nanoscale metallic coating layers 16 disposed thereon, wherein the metallic coating layers 16 have a chemical composition and the particle cores 14 have a chemical composition that is different than the chemical composition of the metallic coating material 16. Method 400 also includes forming 420 a powder composite by applying a predetermined temperature and a predetermined pressure to the coated powder particles sufficient to sinter them by solid-phase or liquid-phase sintering of the coated layers of the plurality of the coated particle powders 12 to form a substantially-continuous, cellular nanomatrix 216 of a nanomatrix material 220 and a plurality of dispersed particles 214 dispersed within nanomatrix 216 as described herein. Forming 410 of coated metallic powder 10 comprising powder particles 12 having particle cores 14 with nanoscale metallic coating layers 16 disposed thereon may be performed by any suitable method. In an exemplary embodiment, forming 410 includes applying the metallic coating layers 16, as described herein, to the particle cores 14, as described herein, using fluidized bed chemical vapor deposition (FBCVD) as described herein. Applying the metallic coating layers 16 may include applying single-layer metallic coating layers 16 or multilayer metallic coating layers 16 as described herein. Applying the metallic coating layers 16 may also include controlling the thickness of the individual layers as they are being applied, as well as controlling the overall thickness of metallic coating layers 16. Particle cores 14 may be formed as described herein. Forming 420 of the powder composite 200 may include any suitable method of forming a fully-dense composite of powder 10. In an exemplary embodiment, forming 420 includes dynamic forging of a green-density precursor powder composite 100 to apply a predetermined temperature and a predetermined pressure sufficient to sinter and deform the powder particles and form a fully-dense nanomatrix 216 and dispersed particles 214 as described herein. Dynamic forging as used herein means dynamic application of a load at temperature and for a time sufficient to promote sintering of the metallic coating layers 16 of adjacent powder particles 12, and may preferably include application of a dynamic forging load at a predetermined loading rate for a time and at a temperature sufficient to form a sintered and fully-dense powder composite 200. In an exemplary embodiment, dynamic forging included: 1) heating a precursor or green-state powder composite 100 to a

predetermined sintering temperature, such as, for example, a temperature sufficient to promote interdiffusion between metallic coating layers 16 of adjacent powder particles 12; 2) holding the precursor powder composite 100 at the sintering temperature for a predetermined hold time, such as, for example, a time sufficient to ensure substantial uniformity of the sintering temperature throughout the precursor composite 100; 3) forging the precursor powder composite 100 to full density, such as, for example, by applying a predetermined forging pressure according to a predetermined pressure schedule or ramp rate sufficient to rapidly achieve full density while holding the composite at the predetermined sintering temperature; and 4) cooling the composite to room temperature. The predetermined pressure and predetermined temperature applied during forming 420 will include a sintering temperature, T_S , and forging pressure, P_F , as described herein that will ensure sintering, such as solid-state sintering, and deformation of the powder particles 12 to form fully-dense powder composite 200, including bond 217, such as a solid-state bond, and bond layer 219. The steps of heating to and holding the precursor powder composite 100 at the predetermined sintering temperature for the predetermined time may include any suitable combination of temperature and time, and will depend, for example, on the powder 10 selected, including the materials used for particle core 14 and metallic coating layer 16, the size of the precursor powder composite 100, the heating method used and other factors that influence the time needed to achieve the desired temperature and temperature uniformity within precursor powder composite 100. In the step of forging, the predetermined pressure may include any suitable pressure and pressure application schedule or pressure ramp rate sufficient to achieve a fully-dense powder composite 200, and will depend, for example, on the material properties of the powder particles 12 selected, including temperature dependent stress/strain characteristics (e.g., stress/strain rate characteristics), interdiffusion and metallurgical thermodynamic and phase equilibria characteristics, dislocation dynamics and other material properties. For example, the maximum forging pressure of dynamic forging and the forging schedule (i.e., the pressure ramp rates that correspond to strain rates employed) may be used to tailor the mechanical strength and toughness of the powder composite. The maximum forging pressure and forging ramp rate (i.e., strain rate) is the pressure just below the composite cracking pressure, i.e., where dynamic recovery processes are unable to relieve strain energy in the composite microstructure without the formation of a crack in the composite. For example, for applications that require a powder composite that has relatively higher strength and lower toughness, relatively higher forging pressures and ramp rates may be used. If relatively higher toughness of the powder composite is needed, relatively lower

forging pressures and ramp rates may be used. The short duration of the forging cycle is a significant advantage as it limits interdiffusion, including interdiffusion within a given metallic coating layer 16, interdiffusion between adjacent metallic coating layers 16 and interdiffusion between metallic coating layers 16 and particle cores 14, to that needed to form metallurgical bond 217 and bond layer 219, while also maintaining the desirable equiaxed dispersed particle 214 shape with the integrity of cellular nano matrix 216 strengthening phase. The duration of the dynamic forging cycle is much shorter than the forming cycles and sintering times required for conventional powder composite forming processes, such as hot isostatic pressing (HIP), pressure assisted sintering or diffusion sintering.

[0070] Forming 420 of the powder composite 200 may also include other methods of forming a fully-dense composite of powder 10, such as methods by which a surface coating of powder composite 200 may be formed, including thermal spraying, plasma spraying, or laser fusion or cladding.

[0071] Method 400 may also optionally include forming 430 a precursor powder composite by compacting the plurality of coated powder particles 12 sufficiently to deform the particles and form interparticle bonds to one another and form the precursor powder composite 100 prior to forming 420 the powder composite. Compacting may include pressing, such as isostatic pressing, of the plurality of powder particles 12 at room temperature to form precursor powder composite 100. Compacting 430 may be performed at room temperature.

[0072] Method 400 may optionally also include intermixing 440 a second powder 30 into powder 10 as described herein prior to the forming 420 the powder composite, or forming 430 the precursor powder composite.

[0073] While one or more embodiments have been shown and described, modifications and substitutions may be made thereto without departing from the scope of the invention as defined by the claims appended thereto. Accordingly, it is to be understood that the present invention has been described by way of illustrations and not limitation.

What is claimed is:

1. A nanomatrix carbon composite comprising:
a substantially-continuous, cellular nanomatrix comprising a nanomatrix material;
a plurality of dispersed particles comprising a particle core material that comprises an allotrope of carbon dispersed in the cellular nanomatrix; and
a bond layer extending throughout the cellular nanomatrix between the dispersed particles.
2. The nanomatrix carbon composite of claim 1, wherein the bond layer comprises a solid-state bond layer.
3. The nanomatrix carbon composite of claim 2, wherein the nanomatrix material has a melting temperature (T_M), and the particle core material has a melting temperature (T_{DP}) and wherein the composite is sinterable in a solid-state at a sintering temperature (T_S), and T_S is less than T_M and T_{AP} .
4. The nanomatrix carbon composite of claim 1, wherein the bond layer comprises a partially melted and resolidified bond layer.
5. The nanomatrix carbon composite of claim 1 or 2, wherein the particle core material comprises a carbon microparticle or nanoparticle, or a combination thereof.
6. The nanomatrix carbon composite of claim 5, wherein the core material comprises a graphene, fullerene or nanodiamond nanoparticle, or a combination thereof
7. The nanomatrix carbon composite of claim 6, wherein the core material comprises a fullerene, and the fullerene comprises a single-wall nanotube, multi-wall nanotube, buckyball or buckyball cluster, or a combination thereof.
8. The nanomatrix carbon composite of any one of claims 1 to 7, wherein the dispersed particles have an average particle size of about 0.1nm to about 700 μ m.

9. The nanomatrix carbon composite of any one of claims 1 to 8, wherein the dispersion of dispersed particles comprises a substantially homogeneous dispersion within the cellular nanomatrix.
10. The nanomatrix carbon composite of any one of claims 1 to 8, wherein the dispersion of dispersed particles comprises a multi-modal distribution of particle sizes within the cellular nanomatrix.
11. The nanomatrix carbon composite of any one of claims 1 to 8, wherein the dispersed particles have an equiaxed particle shape.
12. The nanomatrix carbon composite of any one of claims 1 to 11, further comprising a plurality of dispersed second particles, wherein the dispersed second particles are also dispersed within the cellular nanomatrix and with respect to the dispersed particles.
13. The nanomatrix carbon composite of claim 12, wherein the dispersed second particles comprise Fe, Ni, Co or Cu, or oxides, nitrides or carbides thereof, or a combination of any of the aforementioned materials.
14. The nanomatrix carbon composite of claim 1, wherein the nanomatrix material comprises Al, Zn, Mn, Mg, Mo, W, Cu, Fe, Si, Ca, Co, Ta, Re or Ni, or an oxide, carbide or nitride thereof, or a combination of any of the aforementioned materials.
15. The nanomatrix carbon composite of any one of claims 1 to 14, wherein the cellular nanomatrix has an average thickness of about 50nm to 5000nm.
16. The nanomatrix carbon composite of claim 1, wherein the composite is formed from a sintered powder comprising a plurality of powder particles, each powder particle having a particle core that upon sintering comprises a dispersed particle and a single metallic coating layer disposed thereon, and wherein the cellular nanomatrix between adjacent ones of the plurality of dispersed particles comprises the single metallic coating layer of one powder particle, the bond layer and the single metallic coating layer of another of the powder particles.

17. The nanomatrix carbon composite of claim 16, wherein the dispersed particles comprise a graphene, fullerene or nanodiamond nanoparticle, or a combination thereof, and the cellular nanomatrix comprises Mg, Al, or Ni, or a combination thereof.

18. The nanomatrix carbon composite of claim 1, wherein the composite is formed from a sintered powder comprising a plurality of powder particles, each powder particle having a particle core that upon sintering comprises a dispersed particle and a plurality of metallic coating layers disposed thereon, and wherein the cellular nanomatrix between adjacent ones of the plurality of dispersed particles comprises the plurality of metallic coating layers of one powder particle, the bond layer and plurality of metallic coating layers of another of the powder particles, and wherein adjacent ones of the plurality of metallic coating layers have different chemical compositions.

19. The nanomatrix carbon composite of claim 18, wherein the plurality of layers comprises a first layer that is disposed on the particle core and a second layer that is disposed on the first layer.

20. The nanomatrix carbon composite of claim 19, wherein the dispersed particles comprise a graphene, fullerene or nanodiamond nanoparticle, or a combination thereof, and the first layer comprises Mg, Al or Ni, or a combination thereof, and the second layer comprises Al, Zn, Mn, Mg, Mo, W, Cu, Fe, Si, Ca, Co, Ta, Re or Ni, or a combination thereof, wherein the first layer has a chemical composition that is different than a chemical composition of the second layer.

21. The nanomatrix carbon composite of claim 20, further comprising a third layer that is disposed on the second layer.

22. The nanomatrix carbon composite of claim 21, wherein the first layer comprises Mg, Al or Ni, or a combination thereof, the second layer comprises Al, Zn, Mn, Mg, Mo, W, Cu, Fe, Si, Ca, Co, Ta, Re or Ni, or an oxide, nitride or carbide thereof, or a combination of any of the aforementioned second layer materials, and the third layer comprises Al, Zn, Mn, Mg, Mo, W, Cu, Fe, Si, Ca, Co, Ta, Re or Ni, or a combination thereof, wherein the second layer has a chemical composition that is different than a chemical composition of the third layer.

23. The nanomatrix carbon composite of claim 22, further comprising a fourth layer that is disposed on the third layer.

24. The nanomatrix carbon composite of claim 23, wherein the first layer comprises Mg, Al or Ni, or a combination thereof, the second layer comprises Al, Zn, Mn, Mg, Mo, W, Cu, Fe, Si, Ca, Co, Ta, Re or Ni, or an oxide, nitride or carbide thereof, or a combination of any of the aforementioned second layer materials, the third layer comprises Al, Zn, Mn, Mg, Mo, W, Cu, Fe, Si, Ca, Co, Ta, Re or Ni, or an oxide, nitride or carbide thereof, or a combination of any of the aforementioned third layer materials, and the fourth layer comprises Al, Mn, Fe, Co or Ni, or a combination thereof, wherein the second layer has a chemical composition that is different than a chemical composition of the third layer and the third layer has a chemical composition that is different than a chemical composition of the fourth layer.

1/7

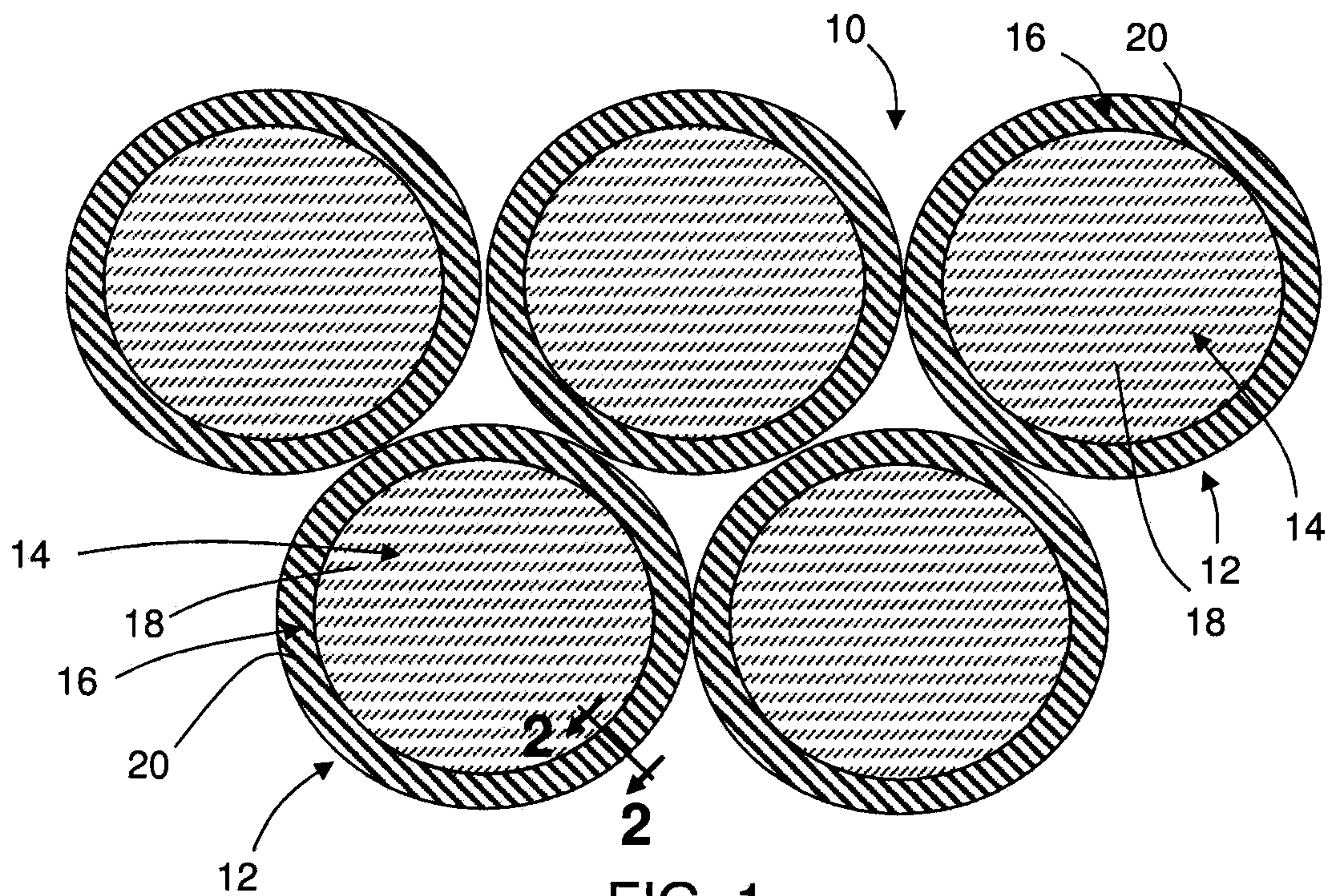


FIG. 1

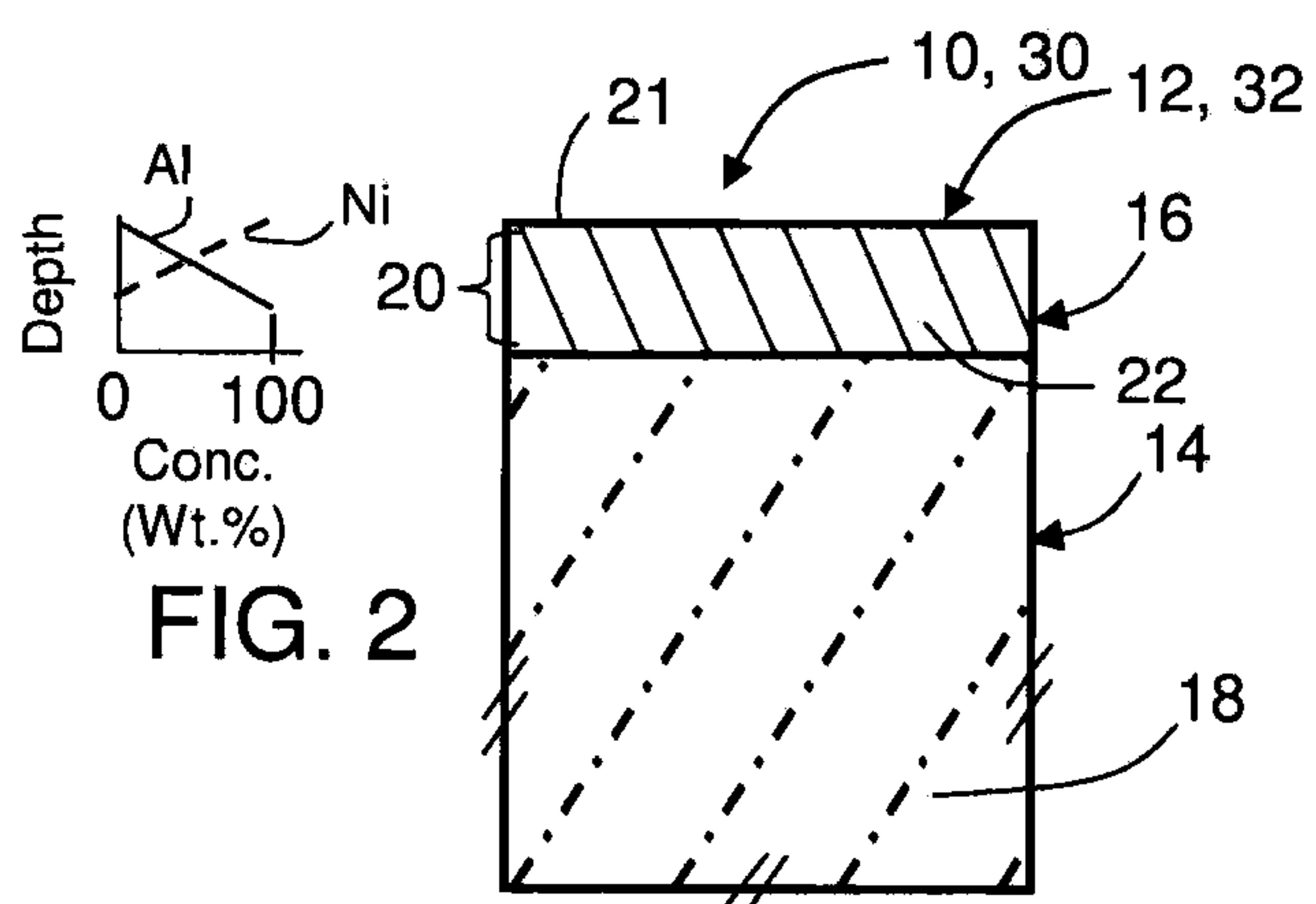


FIG. 2

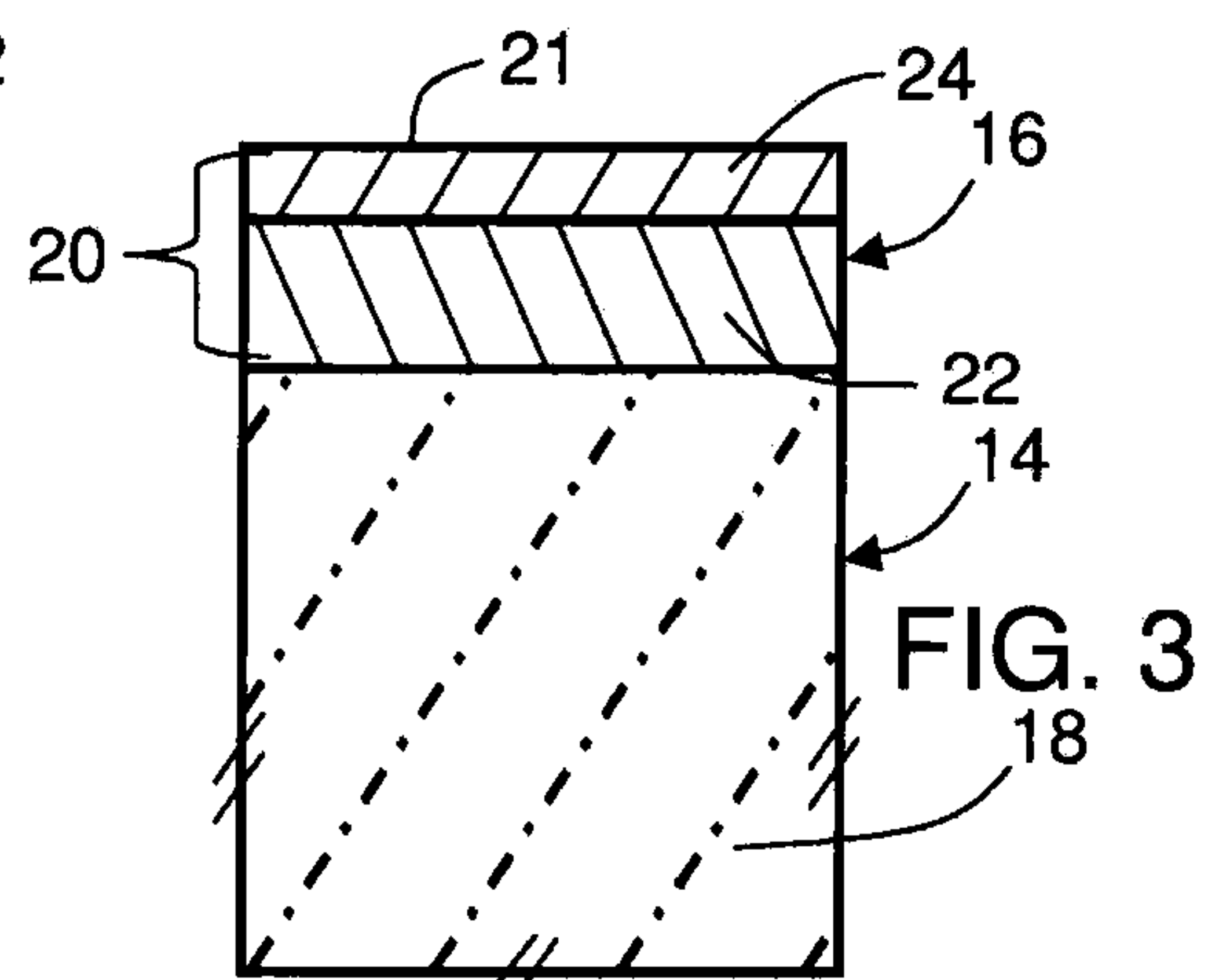


FIG. 3

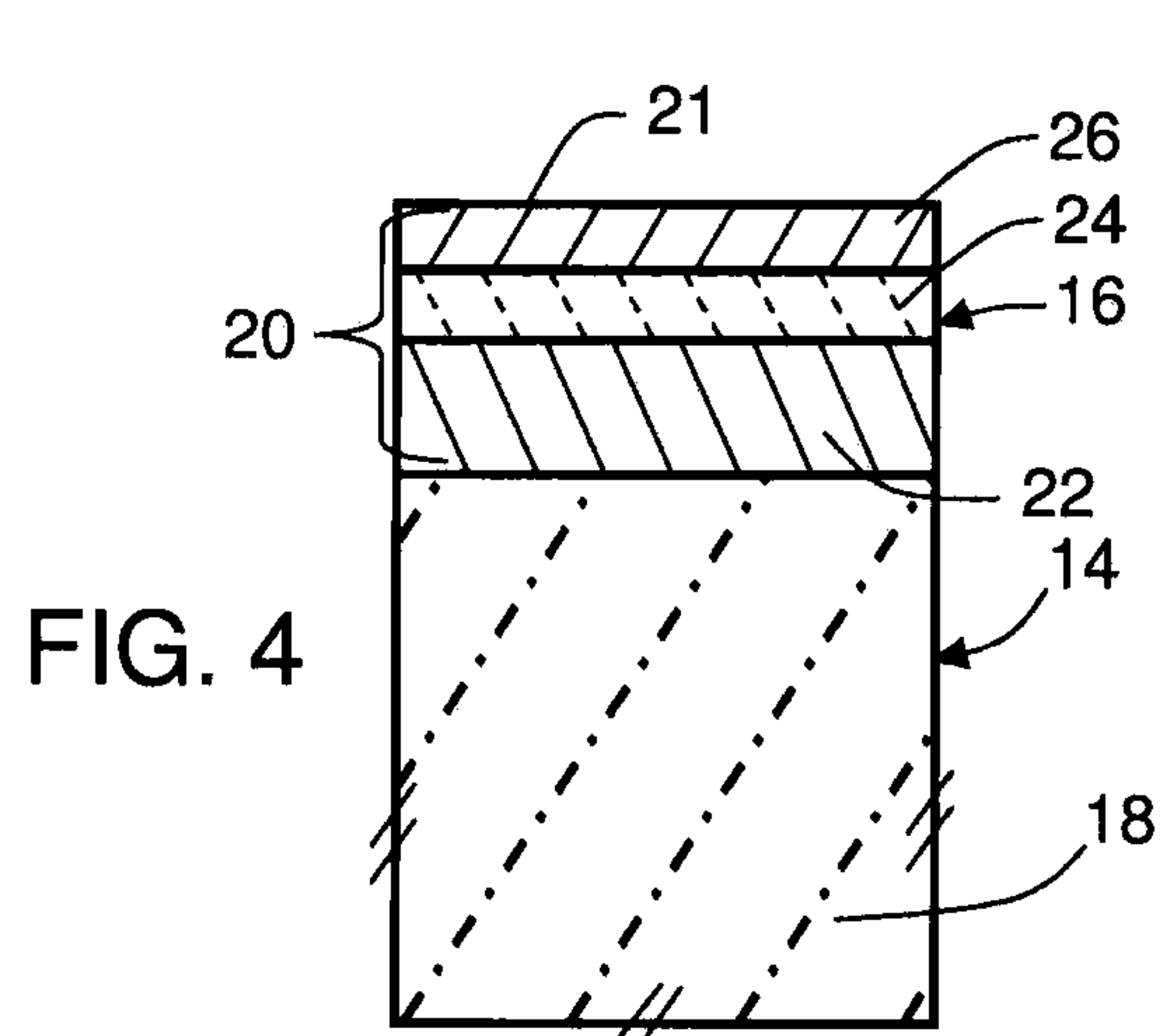


FIG. 4

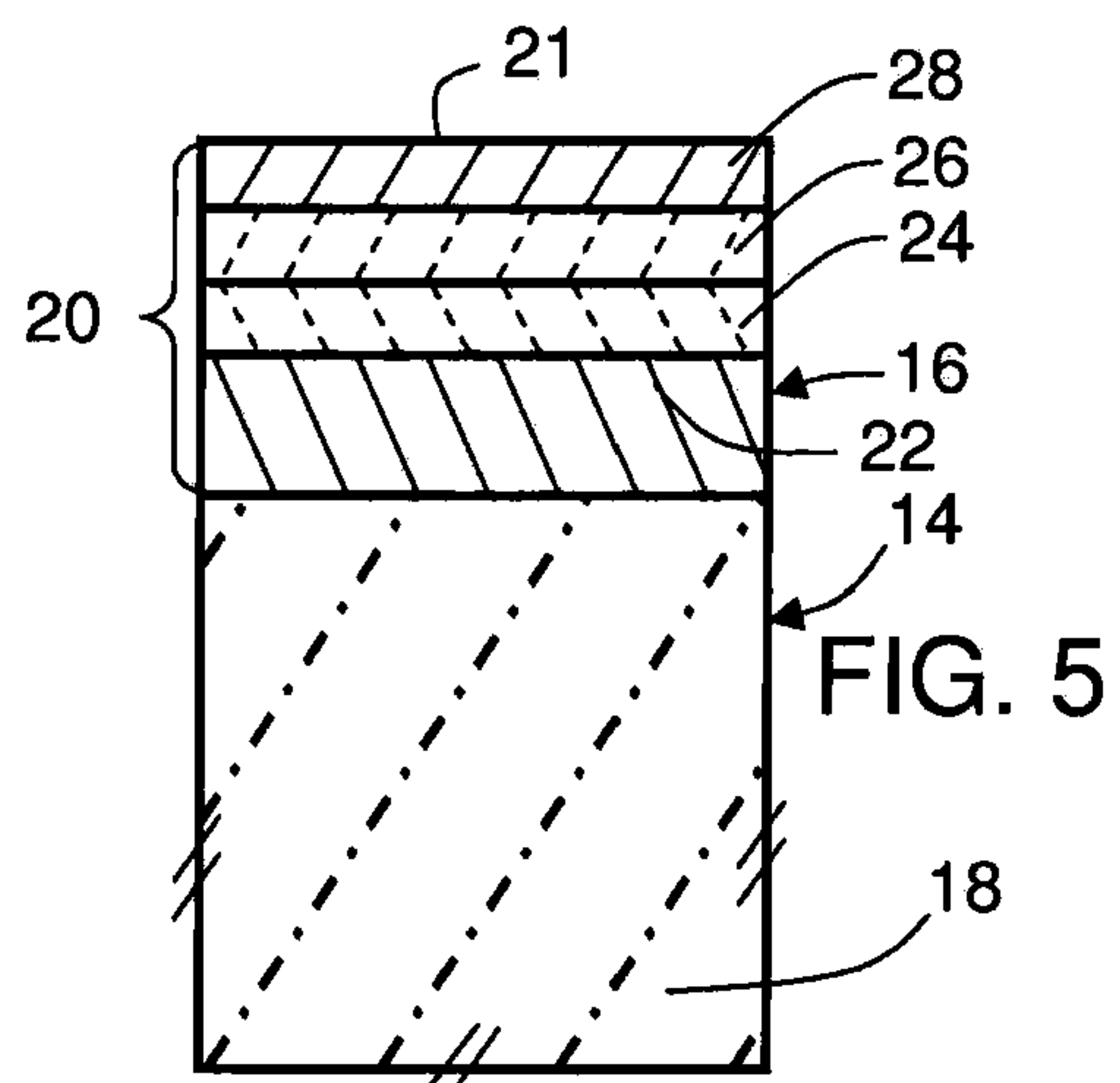
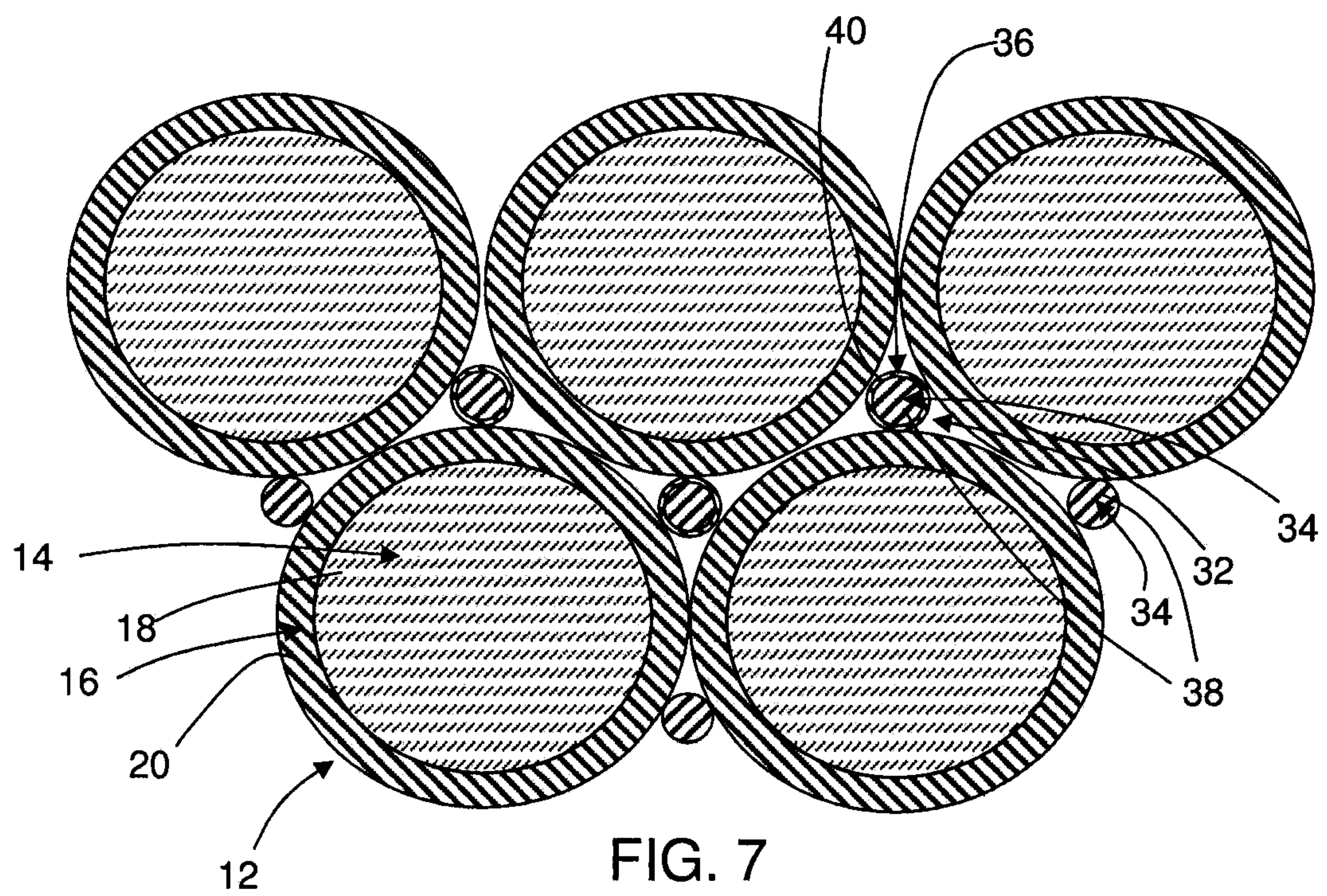
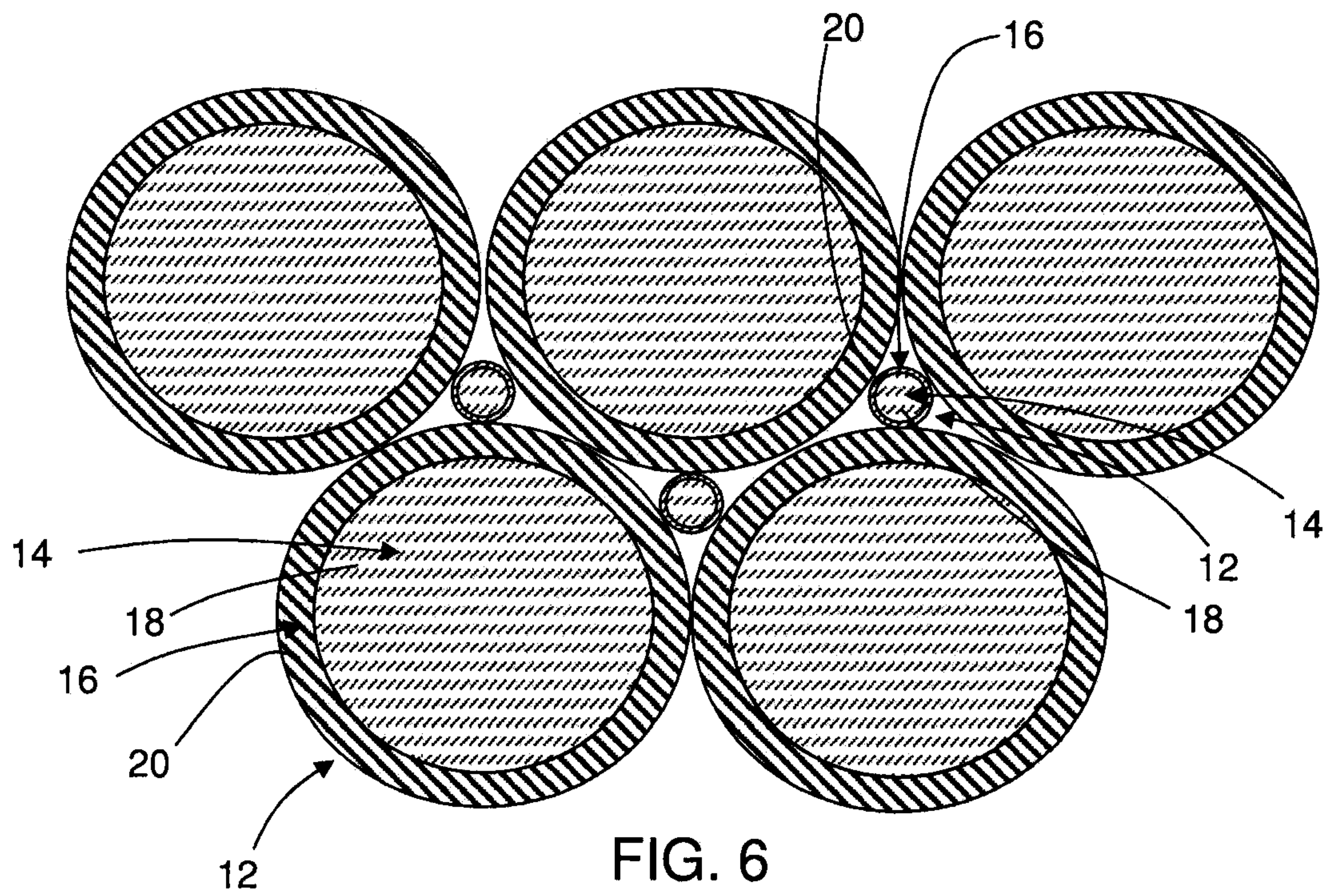


FIG. 5



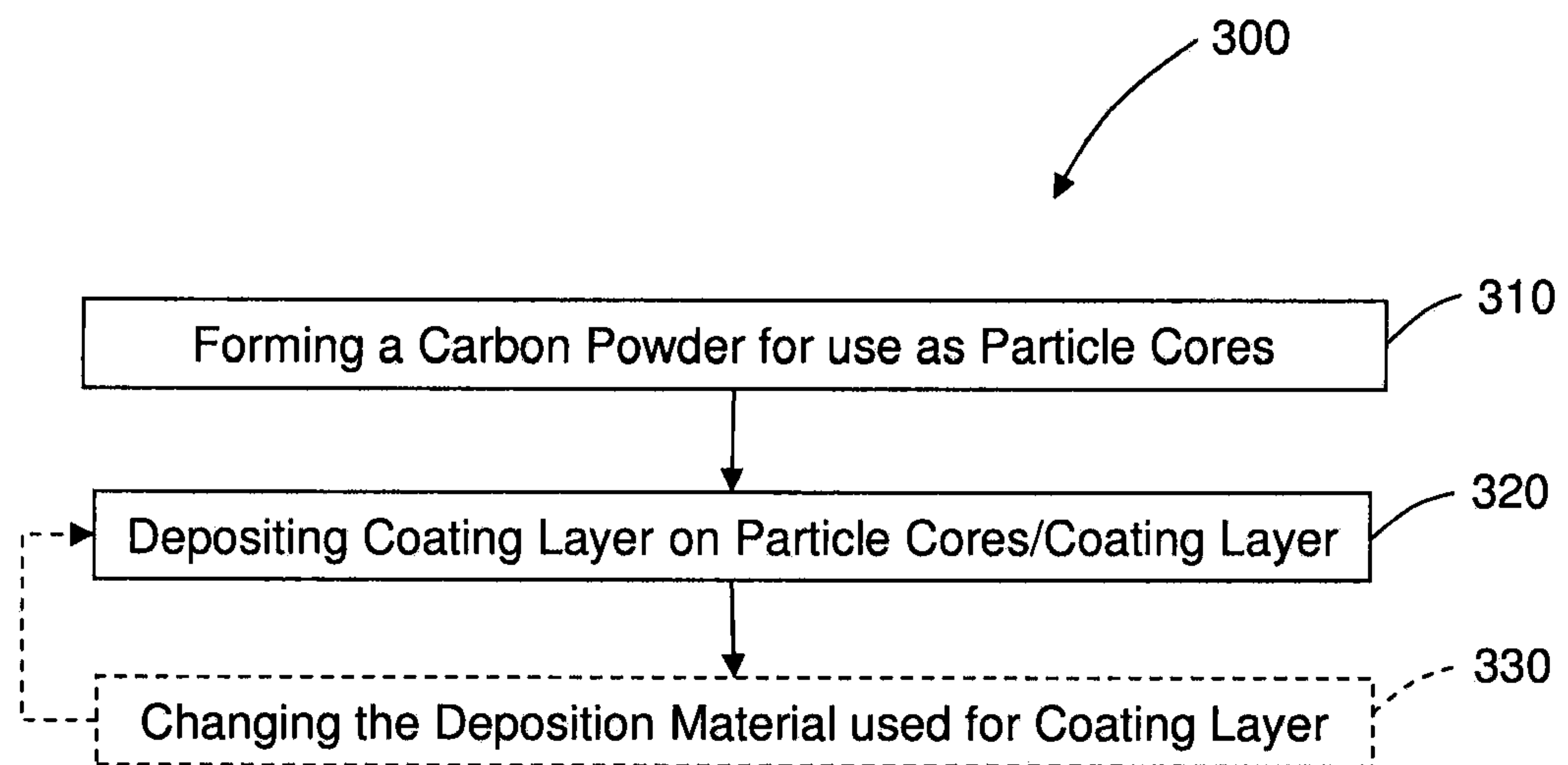


FIG. 8

4/7

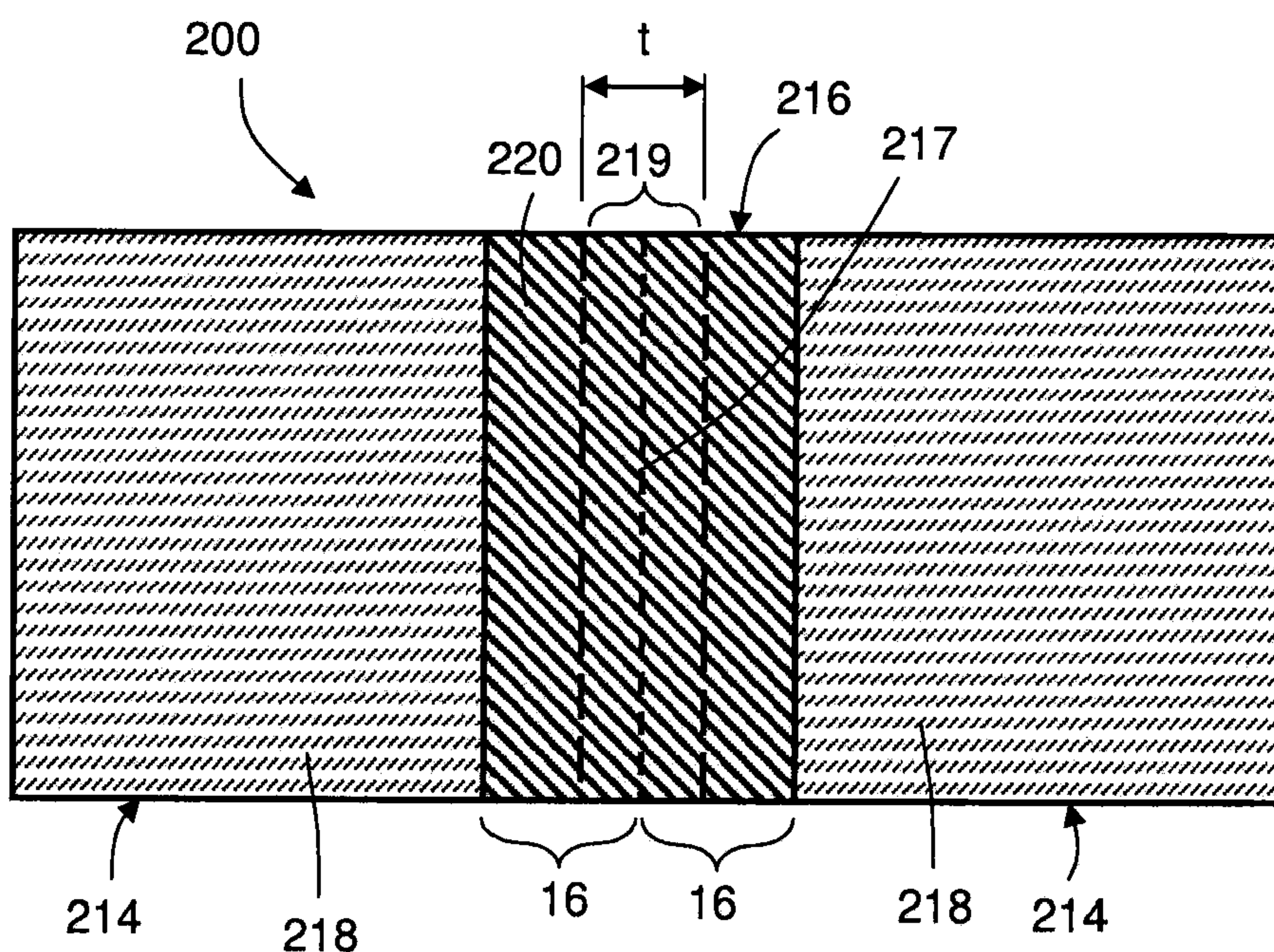


FIG. 9

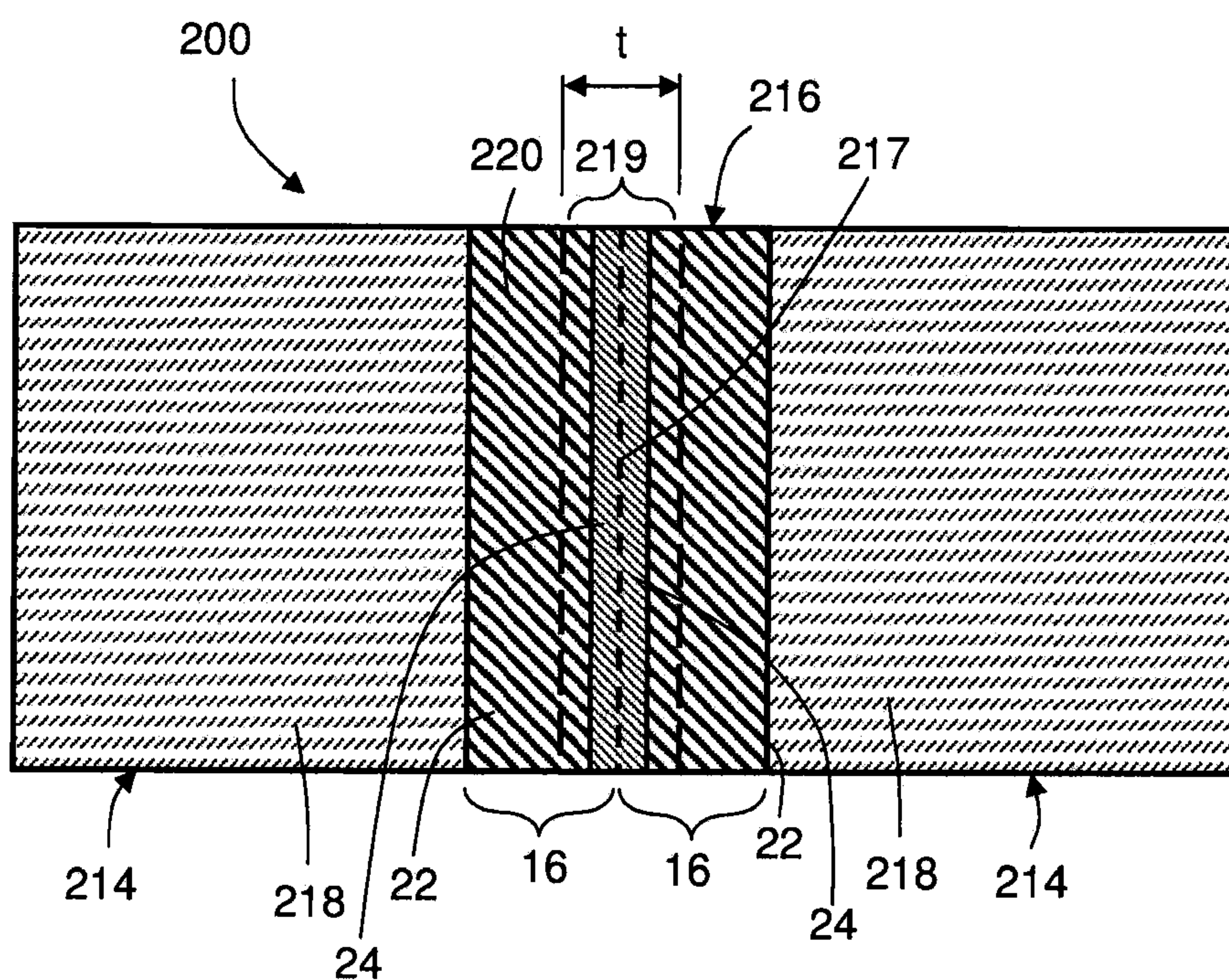


FIG. 12

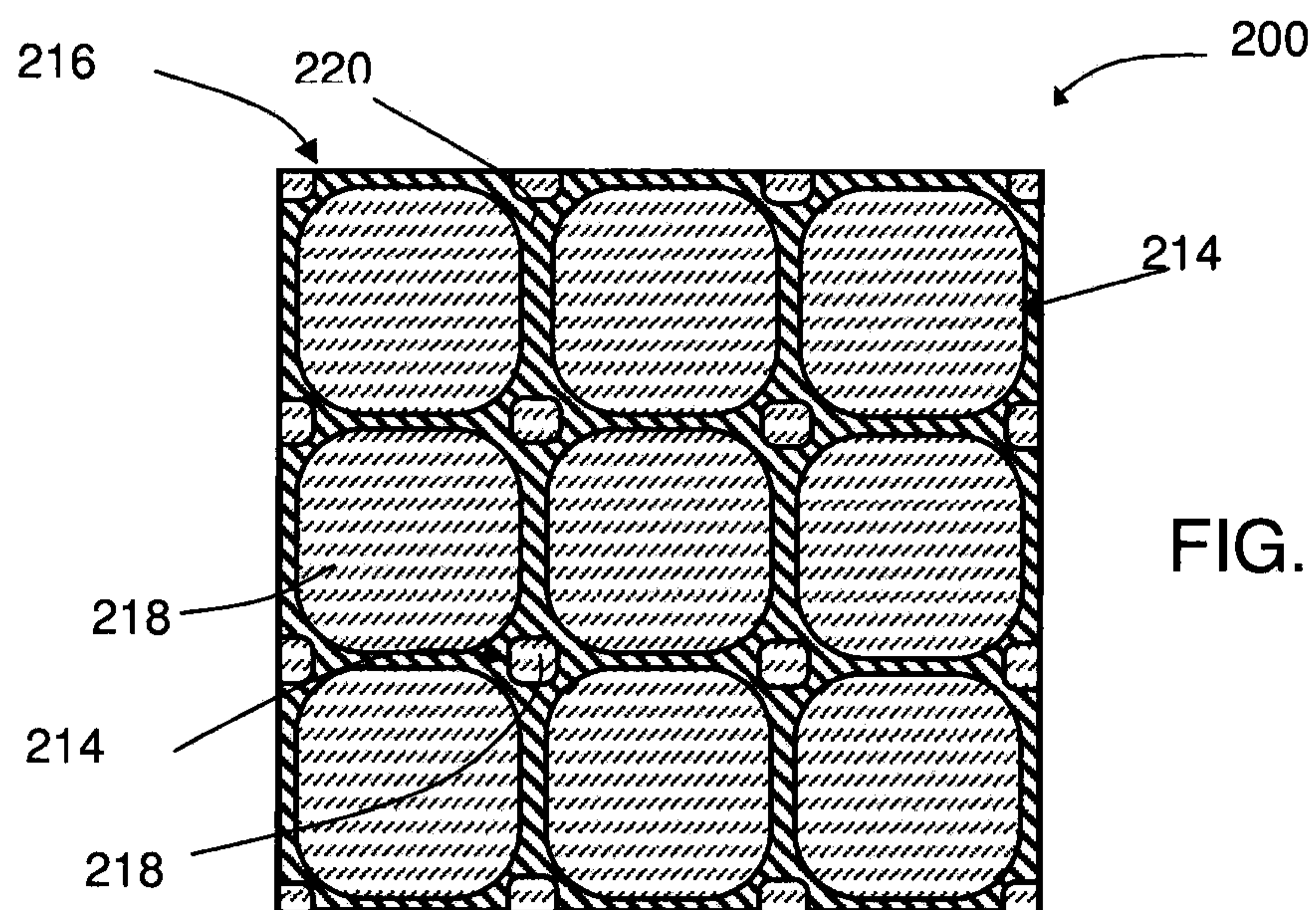


FIG. 10

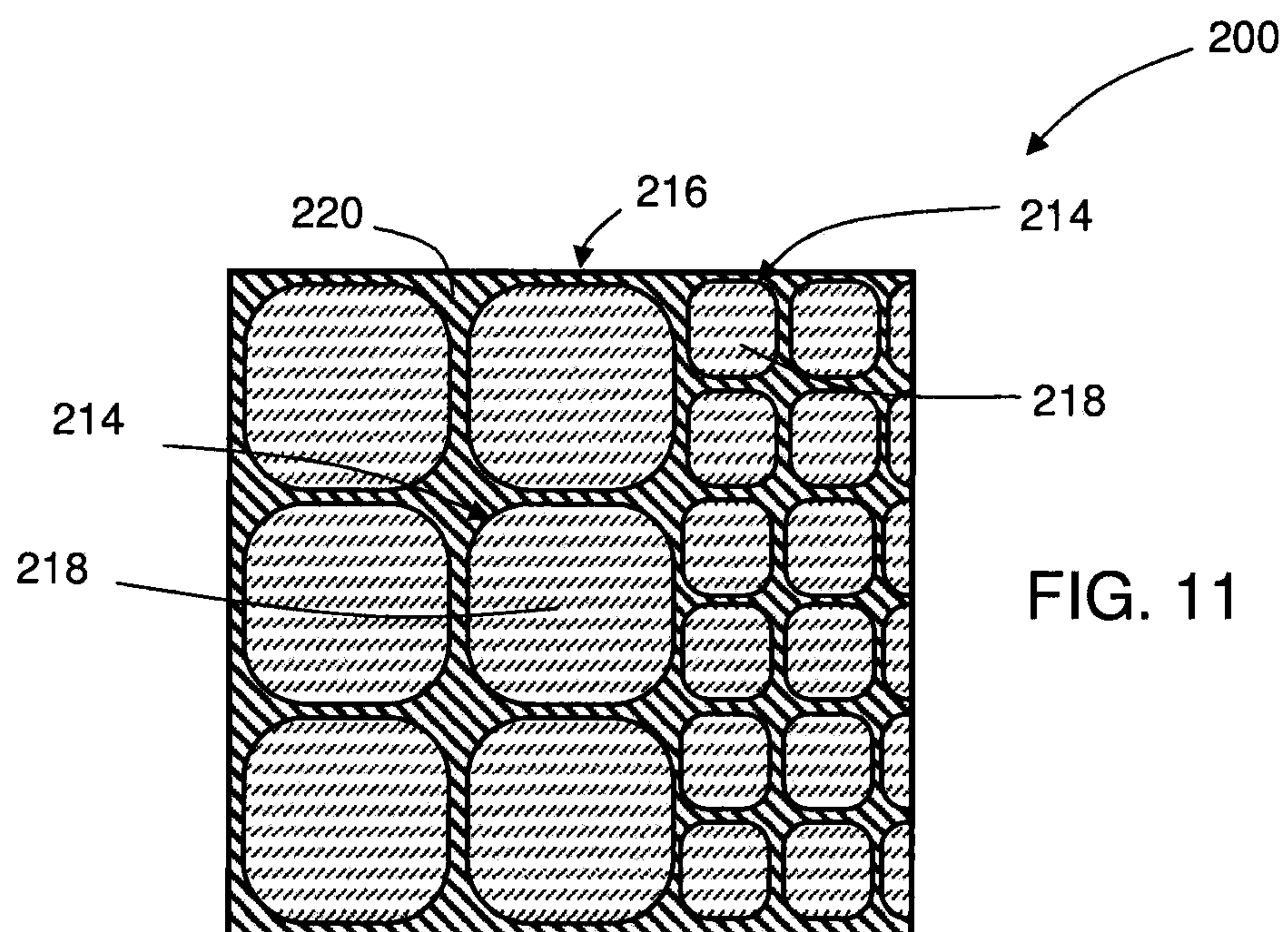


FIG. 11

6/7

