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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))*

[Continued on next page]

(54) **Title**: INTERMETALLIC METALLIC COMPOSITE, METHOD OF MANUFACTURE THEREOF AND ARTICLES COMPRISING THE SAME

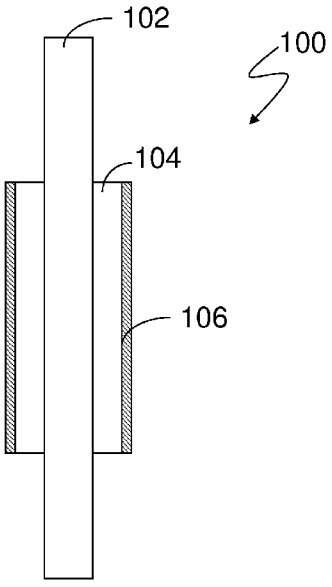


Figure 1

(57) **Abstract**: Disclosed herein is an article comprising a plurality of domains fused together; wherein the domains comprise a core comprising a first metal; and a first layer disposed upon the core; the first layer comprising a second metal; the first metal being chemically different the second metal. Disclosed herein too is a method comprising rolling a sheet in a roll mill; the sheet comprising a first metal and having disposed upon each opposing face of the sheet a first layer that comprises a second metal; the second metal being chemically different from the first metal; cutting the sheet into a plurality of sheets; stacking the plurality of sheets; and rolling the stacked sheets in the roll mill to form a blank.

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INTERMETALLIC METALLIC COMPOSITE, METHOD OF MANUFACTURE THEREOF AND ARTICLES COMPRISING THE SAME

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S. Application No. 13/189150, filed on July 22, 2011, which is incorporated herein by reference in its entirety.

BACKGROUND

1. Field of the Invention

[0001] This disclosure relates to intermetallic metallic composites, methods of manufacture thereof and articles comprising the same.

2. Description of the Related Art

[0002] In performing underground operations such as, for example oil and natural gas exploration, carbon dioxide sequestration, exploration and mining for minerals such as iron, uranium, and the like, exploration for water, and the like, it is often desirable to first drill a borehole that penetrates into the formation.

[0003] Once a borehole has been drilled, it is desirable for the borehole to be completed before minerals, hydrocarbons, and the like can be extracted from it. A completion involves the design, selection, and installation of equipment and materials in or around the borehole for conveying, pumping, or controlling the production or injection of fluids into the borehole. After the borehole has been completed, the extraction of minerals, oil and gas, or water can begin.

[0004] Sealing systems, such as packers, are commonly deployed in a borehole as completion equipment. Packers are often used to isolate portions of a borehole from one another. For example, packers are used to seal the annulus between a tubing string and a wall (in the case of uncased or open hole) or casing (in the case of cased hole) of the borehole, isolating the portion of the borehole uphole of the packer from the portion of the borehole downhole of the packer.

[0005] Sealing systems that isolate one portion of the borehole from another portion of the borehole generally employ an expandable component and a support member. The support member protects the expandable component until the expandable component is expanded in the borehole to effect the isolation. In order to expand the expandable component, it is desirable to first remove the support member. Removing the support

member at the wrong rate can result in improper isolation of one part of the borehole from another. It is therefore desirable to use a support member that can be removed in a controlled fashion when desired.

SUMMARY

[0006] Disclosed herein is an article comprising a plurality of domains fused together; wherein the domains comprise a core comprising a first metal; and a first layer disposed upon the core; the first layer comprising a second metal; the first metal being chemically different the second metal; the article being used as a supporting element in a sealable system for oil exploration.

[0007] Disclosed herein too is an article comprising a plurality of domains fused together; wherein the domains comprise an intermetallic fine grained alloy that comprises a first metal and a second metal; wherein the domains comprise a gradient in composition between the first metal and the second metal; and wherein the first metal is chemically different the second metal.

[0008] Disclosed herein too is a method comprising rolling a sheet in a roll mill; the sheet comprising a first metal and having disposed upon each opposing face of the sheet a first layer that comprises a second metal; the second metal being chemically different from the first metal; cutting the sheet into a plurality of sheets; stacking the plurality of sheets; and rolling the stacked sheets in the roll mill to form a blank.

[0009] Disclosed herein too is a method comprising disposing upon a tube string, a sealing system; the sealing system comprising a expandable component and a support member; wherein the support member comprises a plurality of domains fused together; wherein the domains comprise a core comprising a first metal; and a first layer disposed upon the core; the first layer comprising a second metal; the first metal being chemically different the second metal; introducing the tube string into a well; and dissolving the support member.

BRIEF DESCRIPTION OF THE FIGURES

[0010] For detailed understanding of the present disclosure, references should be made to the following detailed description of the preferred embodiment, taken in conjunction with the accompanying drawings, in which like elements have been given like numerals and wherein:

Figure 1 is a depiction of an exemplary prior art sealing system; and

Figure 2 is a depiction of an exemplary microstructure that is present in the article.

DETAILED DESCRIPTION

[0011] The invention now will be described more fully hereinafter with reference to the accompanying drawings, in which various embodiments are shown. This invention may, however, be embodied in many different forms, and should not be construed as limited to the embodiments set forth herein. Rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the invention to those skilled in the art. Like reference numerals refer to like elements throughout.

[0012] It will be understood that when an element is referred to as being "on" another element, it can be directly on the other element or intervening elements may be present therebetween. In contrast, when an element is referred to as being "directly on" another element, there are no intervening elements present. As used herein, the term "and/or" includes any and all combinations of one or more of the associated listed items.

[0013] It will be understood that, although the terms "first," "second," "third" etc. may be used herein to describe various elements, components, regions, domains, layers and/or sections, these elements, components, regions, domains, layers and/or sections should not be limited by these terms. These terms are only used to distinguish one element, component, region, domain, layer or section from another element, component, region, domain, layer or section. Thus, "a first element," "component," "region," "domain," "layer" or "section" discussed below could be termed a second element, component, region, domain, layer or section without departing from the teachings herein.

[0014] The terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting. As used herein, the singular forms "a," "an" and "the" are intended to include the plural forms as well, unless the context clearly indicates otherwise. It will be further understood that the terms "comprises" and/or "comprising," or "includes" and/or "including" when used in this specification, specify the presence of stated features, regions, integers, steps, operations, elements, and/or components, but do not preclude the presence or addition of one or more other features, regions, integers, steps, operations, elements, components, and/or groups thereof.

[0015] Unless otherwise defined, all terms (including technical and scientific terms) used herein have the same meaning as commonly understood by one of ordinary skill in the

art to which this disclosure belongs. It will be further understood that terms, such as those defined in commonly used dictionaries, should be interpreted as having a meaning that is consistent with their meaning in the context of the relevant art and the present disclosure, and will not be interpreted in an idealized or overly formal sense unless expressly so defined herein.

[0016] Exemplary embodiments are described herein with reference to cross sectional illustrations that are schematic illustrations of idealized embodiments. As such, variations from the shapes of the illustrations as a result, for example, of manufacturing techniques and/or tolerances, are to be expected. Thus, embodiments described herein should not be construed as limited to the particular shapes of regions as illustrated herein but are to include deviations in shapes that result, for example, from manufacturing. For example, a region illustrated or described as flat may, typically, have rough and/or nonlinear features. Moreover, sharp angles that are illustrated may be rounded. Thus, the regions illustrated in the figures are schematic in nature and their shapes are not intended to illustrate the precise shape of a region and are not intended to limit the scope of the present claims.

[0017] The transition term "comprising" is inclusive of the transition terms "consisting of" and "consisting essentially of".

[0018] All "inclusive" numerical ranges included herein are interchangeable and are inclusive of end points and all numerical values that lie between the endpoints.

[0019] As used herein a "borehole" may be any type of borehole in an earth formation such as a well, including, but not limited to, a producing well, a non-producing well, an experimental well, an exploratory well, a well for storage or sequestration, and the like. Boreholes may be vertical, horizontal, some angle between vertical and horizontal, diverted or non-diverted, and combinations thereof, for example a vertical borehole with a non-vertical component.

[0020] The term "support member" refers to a device that supports the expandable component and the tubing string. The "support member" may also function to protect, guard and/or shield the expandable component from damage prior to its removal.

[0021] The term "expandable" as used in the "expandable component", can encompass a variety of means by which the expansion can occur. The expansion can occur for example, through swelling, inflation via pressure, thermal expansion, and the like, or a combination thereof. Some expandable components may be actuated by hydraulic pressure transmitted either through the tubing bore, annulus, or a control line. Other expandable

components may be actuated via an electric line deployed from the surface of the borehole. Furthermore, some expandable components have been used that employ materials that respond to the surrounding borehole fluids and borehole to form a seal. [0022] Disclosed herein is an article for a sealing system that comprises a plurality of multilayered metallic domains that may comprise particles. In an exemplary embodiment, the article is a support member for a sealing system that is used in underground boreholes. Each domain comprises a metallic core that comprises a first metal. Disposed upon the metallic core is a first layer that comprises a second metal. The first layer may have disposed thereon an optional second layer that comprises a third metal. These multilayered metallic domains each function as a galvanic cell when exposed to borehole fluids. In one embodiment, these multilayered metallic domains are manufactured into a support member for a sealing system that can be dissolved in a controlled manner (when exposed to borehole fluids) to expose an expandable component to the surrounding borehole fluids. The surrounding borehole fluids cause it to swell to form a seal that isolates one portion of the borehole from another portion of the borehole.

[0023] Disclosed herein too is a method of manufacturing a support member that comprises the plurality of fused multilayered metallic domains that may comprise sheets or lamina. The method comprises manufacturing a sheet from the first metal and disposing upon the opposing surfaces of the sheet a layer of a second metal. An optional third layer of metal may then be disposed upon the opposing surfaces of the sheet. The sheet is then cut into several smaller sheets, which are stacked on one another to form a stack. The stack is subjected to roll milling until it is reduced to a thickness that is a fraction of the original thickness of the stacked sheets. The first multilayered sheet is once again cut into several sheets, which are stacked one on another and subjected to rolling to produce a second multilayered sheet. The process of forming sheets, cutting and stacking them, and then rolling them is repeated several times to produce a final sheet. The final sheet is then cut, stacked as before and forged into a desired shape (hereinafter termed the "article").

[0024] Figure 1 is a depiction of an exemplary sealing system 100. The sealing system 100 is disposed around a tubing string 102 and comprises an expandable component 104 and a support member 106. The support member 106 supports the expandable component 104 during the introduction of the tubing string 102 into the reservoir and prevents the expandable component 104 from degrading prior to the point at which it has to be utilized.

[0025] When the tubing string 102 has reached the point in the well at which it is to be used, the support member 106 is removed from the sealing system 100 and the expandable component 104 is subjected to expansion to isolate one portion of the wellbore from another portion of the wellbore.

[0026] In order to effect the desired use of the expandable component 104, the removal of the support member 106 has to be accomplished under controlled conditions. It is therefore desirable to have a support member 106 manufactured from a material that can be removed in a controlled fashion so that the swelling of the expandable component 104 can be brought about at the desired time to isolate one portion of the wellbore from another.

[0027] In an exemplary embodiment, the support member 106 is manufactured by stacking several multilayered metal sheets and repeatedly passing these sheets through a roll mill. In each "pass" through the roll mill, the thickness of the stack is reduced to about 15 to about 30% of the original thickness of the stack. A "pass" as defined herein is the process by which the original stack is reduced in thickness to about 15 to about 30% of the original thickness of the stack. A pass may involve multiple trips between the roll mills. In one embodiment, the thickness of the stack is reduced to about 20 to about 28% of the original thickness of the stack. In another embodiment, the thickness of the stack is reduced to about 22 to about 26% of the original thickness of the stack.

[0028] It is generally desirable to conduct a number of passes in the roll mill so as to reduce the thickness of the original sheet to about 1/8 to about 1/15 of its original thickness, specifically about 1/10 to about 1/13 of its original thickness. The number of passes conducted during the roll milling is about 2 to about 15, specifically about 3 to about 14 and more specifically about 5 to about 10.

[0029] The rolling process may be a cold rolling process or a hot rolling process. Cold rolling processes are generally conducted below the recrystallization temperature of the metal, while hot rolling processes are generally conducted at a temperature above the recrystalization temperature of the metal. The recrystallization temperature in consideration would be that for the metal or alloy having the highest recrystallization temperature of all of the metals in the article. In an exemplary embodiment, the rolling process is a hot rolling process. The rolling process is generally conducted at a temperature of about 150 to about 450 °C. In an exemplary embodiment, the rolling process is generally conducted at a temperature of about 400 to about 437°C.

[0030] The process of forming multilayered sheets that are repeatedly rolled, cut and stacked produces a structure that comprises fine grained structure, including intermingled domains of a first and a second metal and their combinations. The structure of the domains in the article is similar to that which would be obtained from the sintering of individual particles each of which comprise a core and a plurality of layers disposed upon this core to begin with. In other words, the product comprises multistructured domains that contact one another. The multilayered domains in the article contact one another and have interstices located between these domains. In one embodiment, these domains are fused to one another. The domains may have gradients in composition between the first metal and the second metal. It may also have gradients in composition between the second metal and the third metal as well as between the first metal and the third metal.

[0031] In one embodiment, the domains may alternatively also comprise a fine-grained alloy rich in small intermetallic compound domains between the first metal and the second metal, the first metal and the third metal and the second metal and the third metal, with no layers between these respective metals. The presence of a fine grained alloy results in a number of advantages. Fine grained alloys with concentration gradients produce effective galvanic cells. These structures produce an improvement in strength due to fine grain sizes and dense intergranular regions over other structures that contain layered domains.

[0032] Figure 2 is a depiction of an exemplary microstructure for articles manufactured by the method described herein. The Figure 2 depicts the microstructure of an exemplary article 200 comprising the domains 202 described herein. As may be seen in Figure 2, each domain comprises the core 204 that comprises the first metal, the first layer 206 that comprises the second metal, and the optional third layer 208 that comprises the third metal. As noted above, some domains may comprise a fine grained alloy that comprises an intermetallic compound.

[0033] The core may have an average domain size of about 44 to about 1400 micrometers. In an exemplary embodiment, the core may have an average domain size of about 63 to about 105 micrometers. The average domain size is a radius of gyration.

[0034] The core with the first layer disposed thereon may have an average domain size of about 45.1 to about 1445 micrometers. In an exemplary embodiment, the core with the first layer disposed thereon may have an average domain size of about 64.6 to about 108 micrometers.

[0035] The core with the first and the second layer disposed thereon may have an average domain size of about 45 to about 1600 micrometers. In an exemplary embodiment, the core with the first and the second layer disposed thereon may have an average domain size of about 65 to about 110 micrometers.

[0036] In one embodiment, in one method of manufacturing the support member, a sheet comprising a first metal is coated on its opposing faces with a layer of a second metal. The sheet may have an original thickness of about 0.05 to about 0.20 centimeters, specifically about 0.08 to about 0.18 centimeters, and more specifically about 0.1 to about 0.15 centimeters. Each layer of second metal may have a thickness of about 0.005 centimeters to about 0.02 centimeters, specifically about 0.003 to about 0.015 centimeters, and more specifically about 0.001 centimeters to about 0.013 centimeters. An optional third metal layer may be disposed on the opposing faces of the sheet to contact the second metal layer. The thickness of each third metal layer can be the same as the thickness of each second metal layer.

[0037] The first metal is generally present in an amount of about 60 to about 95 weight percent (wt%) based on the total weight of the article. An exemplary amount of the first metal is about 90 to about 92 wt% based on the total weight of the article.

[0038] The second metal is generally present in an amount of about 5 to about 40 wt%, based on the total weight of the article. An exemplary amount of the second metal is about 8 to about 10 wt% based on the total weight of the article.

[0039] The third metal is generally present in an amount of about 0.0001 to about 3 weight percent (wt%) based on the total weight of the article. An exemplary amount of the third metal is about 0.01 to about 0.1 wt% based on the total weight of the article.

[0040] In one embodiment, the layer of second metal may be disposed upon the sheet by techniques involving vapor deposition. Examples of suitable techniques for disposing the second layer include chemical or physical vapor deposition.

[0041] Chemical vapor deposition includes atmospheric chemical vapor deposition, low pressure chemical vapor deposition, ultrahigh vacuum chemical vapor deposition, aerosol assisted vapor deposition, direct liquid injection chemical vapor deposition, microwave plasma assisted chemical vapor deposition, plasma enhanced chemical vapor deposition, atomic layer chemical vapor deposition, hot wire (hot filament) chemical vapor deposition, metal organic chemical vapor deposition, combustion chemical vapor deposition, vapor phase epitaxy, rapid thermal chemical vapor deposition, hybrid physical chemical vapor deposition,

or a combination comprising at least one of the foregoing processes. If combinations of the foregoing chemical vapor deposition processes are used, they may be employed simultaneously or sequentially.

[0042] Physical vapor deposition includes cathodic arc deposition, electron beam physical vapor deposition, evaporative deposition, pulsed laser deposition, sputter deposition or a combination comprising at least one of the foregoing processes. If combinations of the foregoing physical vapor deposition processes are used, they may be employed simultaneously or sequentially. Combinations of physical vapor deposition processes and chemical vapor deposition processes may also be used.

[0043] In another embodiment, the layer of second metal may be disposed upon the sheet by techniques involving electroless plating, electroplating, dip-coating or cold spraying. Combinations of such methods can also be used to apply the second layer to the sheet.

[0044] The first metal and the second metal are selected such that they are capable of forming a galvanic cell that can undergo corrosion in the presence of borehole fluids. In other words, if the first metal forms the anode of the galvanic cell, the second metal forms the cathode and vice versa. The first metal is different in composition from the second metal. The third metal is generally selected to control the rate of corrosion of the galvanic cell.

[0045] The first metal and the second metal may comprise transition metals, alkali metals, alkaline earth metals, or combinations thereof so long as the first metal is not the same as the second metal. The first metal may comprise aluminum, magnesium zinc, copper, iron, nickel, cobalt, or the like, or a combination comprising at least one of the foregoing metals. The second metal may comprise aluminum, magnesium zinc, copper, iron, nickel, cobalt, or the like, or a combination comprising at least one of the foregoing metals so long as it is chemically different from the first metal. In one embodiment, the second metal is electrolytically different from the first metal

[0046] The third metal may comprise nickel, aluminum, magnesium zinc, copper, iron, cobalt, or the like, or a combination comprising at least one of the foregoing metals so long as it is chemically different from the first metal. In one embodiment, the third metal is chemically different from the first metal and from the second metal. In another embodiment, the third metal is electrolytically different from the first metal and from the second metal.

[0047] In one exemplary embodiment, the first metal comprises aluminum, while the second metal comprises magnesium. The third metal may comprise nickel.

[0048] In another exemplary embodiment, the first metal comprises magnesium, while the second metal comprises aluminum. The third metal may comprise nickel.

[0049] In one embodiment, the sheet obtained after being subjected to a reduction in thickness may be stacked and forged in a roll mill into a blank. The blank may then be extruded into a desired shape to form the desired article. In an exemplary embodiment, the sheet obtained after being subjected to a 2 to 5-pass reduction in thickness may be stacked and forged in a roll mill into a blank. The blank is then be extruded into a final desired shape.

[0050] In another embodiment, the sheet obtained after being subjected to a reduction in thickness may be stacked and forged in a roll mill or in a press into round stock.

[0051] The process is advantageous in that it can be conducted rapidly when compared with a comparative sintering process involving powders. It also is desirable because it does not involve the formation and pressing of metal powders, which can sometimes be difficult. The process described herein can be advantageously used for manufacturing sheet stock for rolled tube, stamped flat items, billet materials for balls, and the like.

[0052] Support members manufactured by this method are advantageous because their dissolution by borehole fluids can be controlled. This permits the swelling of the expandable component to be controlled as well.

[0053] The article described herein can be used as a support member for a sealing system for underground wells from which oil and natural gas are extracted. In one method of using the support member, it is disposed upon an expandable component in a sealing system to support the expandable component until it is desired to have the expandable component expand and form a seal. When the tube string with the sealing system is moved underground during oil exploration, the borehole fluids interact with the support member setting up plurality of galvanic cells within the support member. The galvanic cells become operative causing the eventual corrosion of the support member and the exposure of the expandable component to the borehole fluids. The expandable component expands to causing sealing of one portion of the borehole from another portion of the well.

[0054] While the invention has been described in detail in connection with a number of embodiments, the invention is not limited to such disclosed embodiments. Rather, the invention can be modified to incorporate any number of variations, alterations, substitutions or equivalent arrangements not heretofore described, but which are commensurate with the scope of the invention. Additionally, while various embodiments of the invention have been

described, it is to be understood that aspects of the invention may include only some of the described embodiments. Accordingly, the invention is not to be seen as limited by the foregoing description, but is only limited by the scope of the appended claims.

CLAIMS

What is claimed is:

1. An article comprising:

a plurality of domains fused together; wherein the domains comprise:

a core comprising a first metal; and

a first layer disposed upon the core; the first layer comprising a second metal; the first metal being chemically different the second metal.

2. The article of Claim 1, wherein the article is used as a supporting element in a sealable system for oil exploration.

3. The article of Claim 1, wherein the article is used as an actuating ball for a borehole system.

4. The article of Claim 1, further comprising a second layer that is disposed upon the first layer, wherein the second layer comprises a third metal that is different from the first metal and the second metal.

5. The article of Claim 1, wherein the first metal is aluminum, magnesium, zinc, copper, iron, nickel, cobalt, or a combination comprising at least one of the foregoing metals.

6. The article of Claim 1, wherein the first metal is aluminum.

7. The article of Claim 1, wherein the first metal is magnesium.

8. The article of Claim 1, wherein the second metal is aluminum, magnesium, zinc, copper, iron, nickel, cobalt, or a combination comprising at least one of the foregoing metals.

9. The article of Claim 1, wherein the second metal is aluminum.

10. The article of Claim 1, wherein the second metal is magnesium.

11. The article of Claim 4, wherein the third metal is nickel.

12. The article of Claim 1, wherein the article is manufactured by rolling a sheet comprising the first metal and coated on each of its opposing faces with a first layer comprising the second metal.

13. An article comprising:

a plurality of domains fused together; wherein the domains comprise:

an intermetallic fine grained alloy that comprises a first metal and a second metal; wherein the domains comprise a gradient in composition between the first metal and the second metal; and wherein the first metal is chemically different the second metal.

14. The article of Claim 13, wherein the article is used as a supporting element in a sealable system for oil exploration.

15. The article of Claim 13, wherein the article is used as an actuating ball for a borehole system.

16. The article of Claim 13, wherein the fine grained alloy further comprises a third metal.

17. The article of Claim 13, wherein the first metal is aluminum.

18. The article of Claim 13, wherein the first metal is magnesium.

19. The article of Claim 13, wherein the second metal is aluminum.

20. The article of Claim 13, wherein the second metal is magnesium.

21. The article of Claim 16, wherein the third metal is nickel.

22. A method comprising:

rolling a sheet in a roll mill; the sheet comprising a first metal, and having disposed upon each opposing face of the sheet a first layer that comprises a second metal; the second metal being chemically different from the first metal;

cutting the sheet into a plurality of sheets;

stacking the plurality of sheets; and

rolling the stacked sheets in the roll mill to form a blank.

23. The method of Claim 22, wherein the rolling in the roll mill is hot rolling.

24. The method of Claim 23, wherein the sheet further comprises a second layer of a third metal; the second layer being disposed upon the opposing faces of the sheet; wherein the third metal is chemically different from the first metal and the second metal.

25. The method of Claim 22, further comprising extruding the blank.

26. The method of Claim 22, further comprising winding the blank into a spool.

27. A method comprising:

disposing upon a tube string, a sealing system; the sealing system comprising:

a expandable component and a support member;

wherein the support member comprises:

a plurality of domains contacting one another; wherein the domains comprise:

a core comprising a first metal; and

a first layer disposed upon the core; the first layer comprising a second metal; the first metal being chemically different the second metal;

introducing the tube string into a well; and

dissolving the support member.

28. The method of Claim 27, further comprising swelling the expandable component.

29. The method of Claim 27, wherein a rate of dissolution of the support member is controlled.

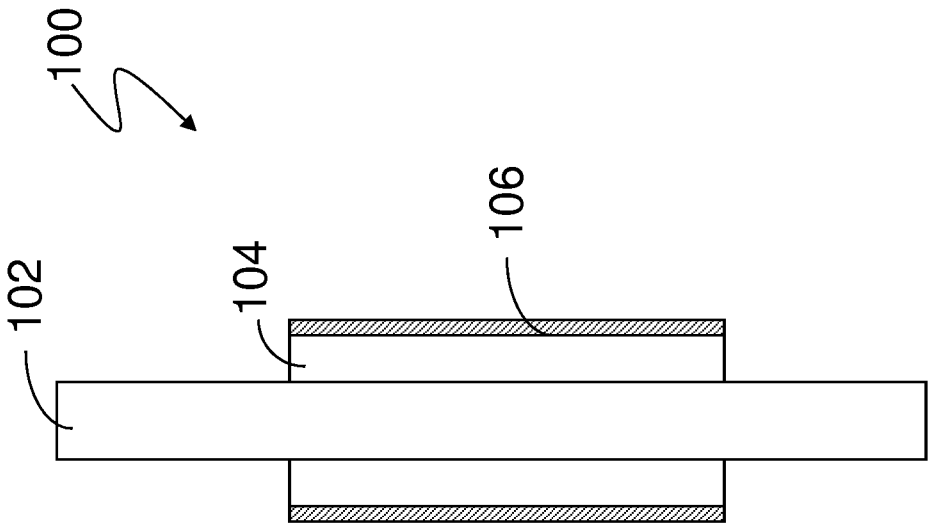


Figure 1

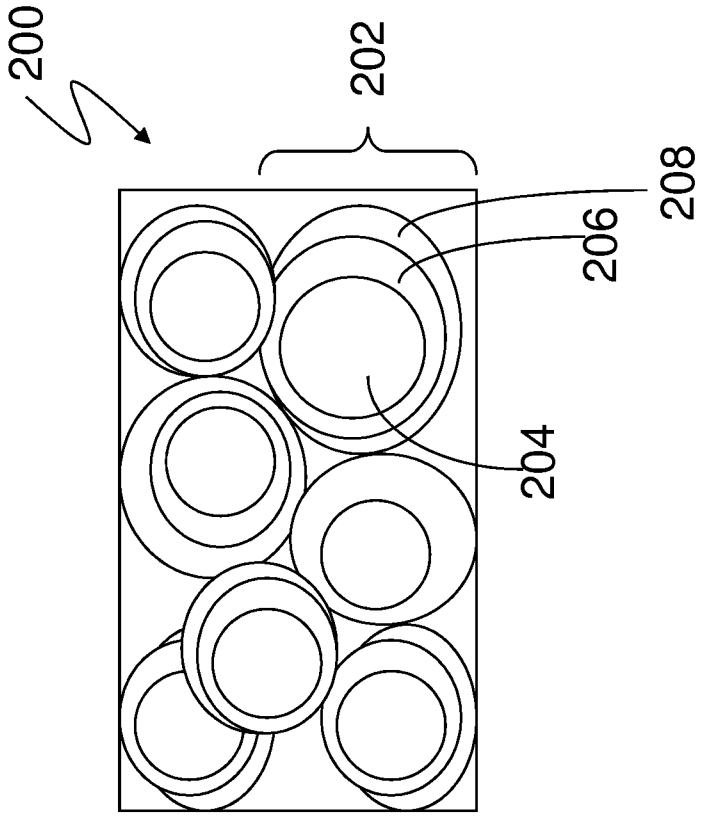


Figure 2