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(54) CONTROLLED ELECTROLYTIC METALLIC MATERIALS FOR WELLBORE SEALING AND STRENGTHENING

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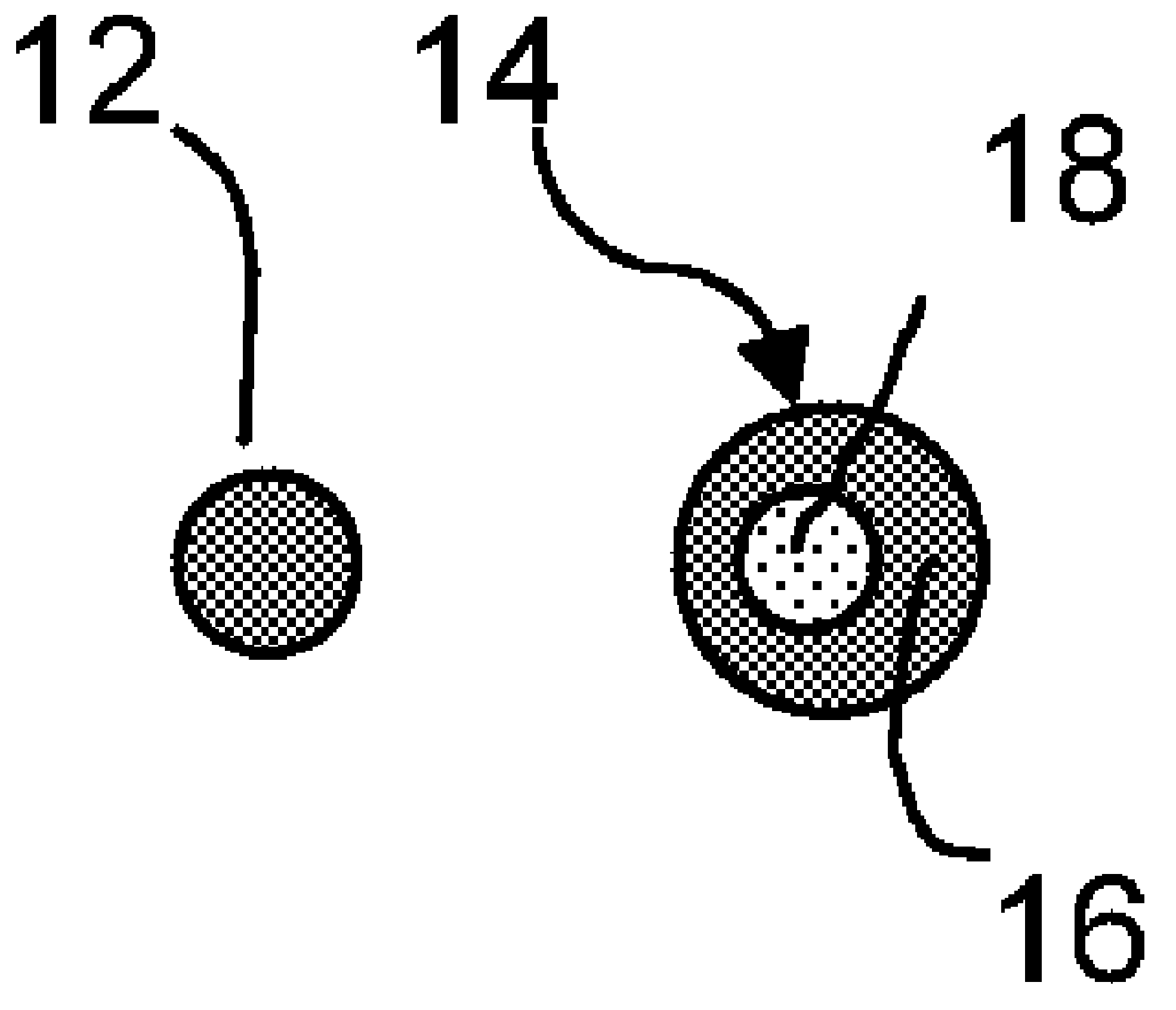
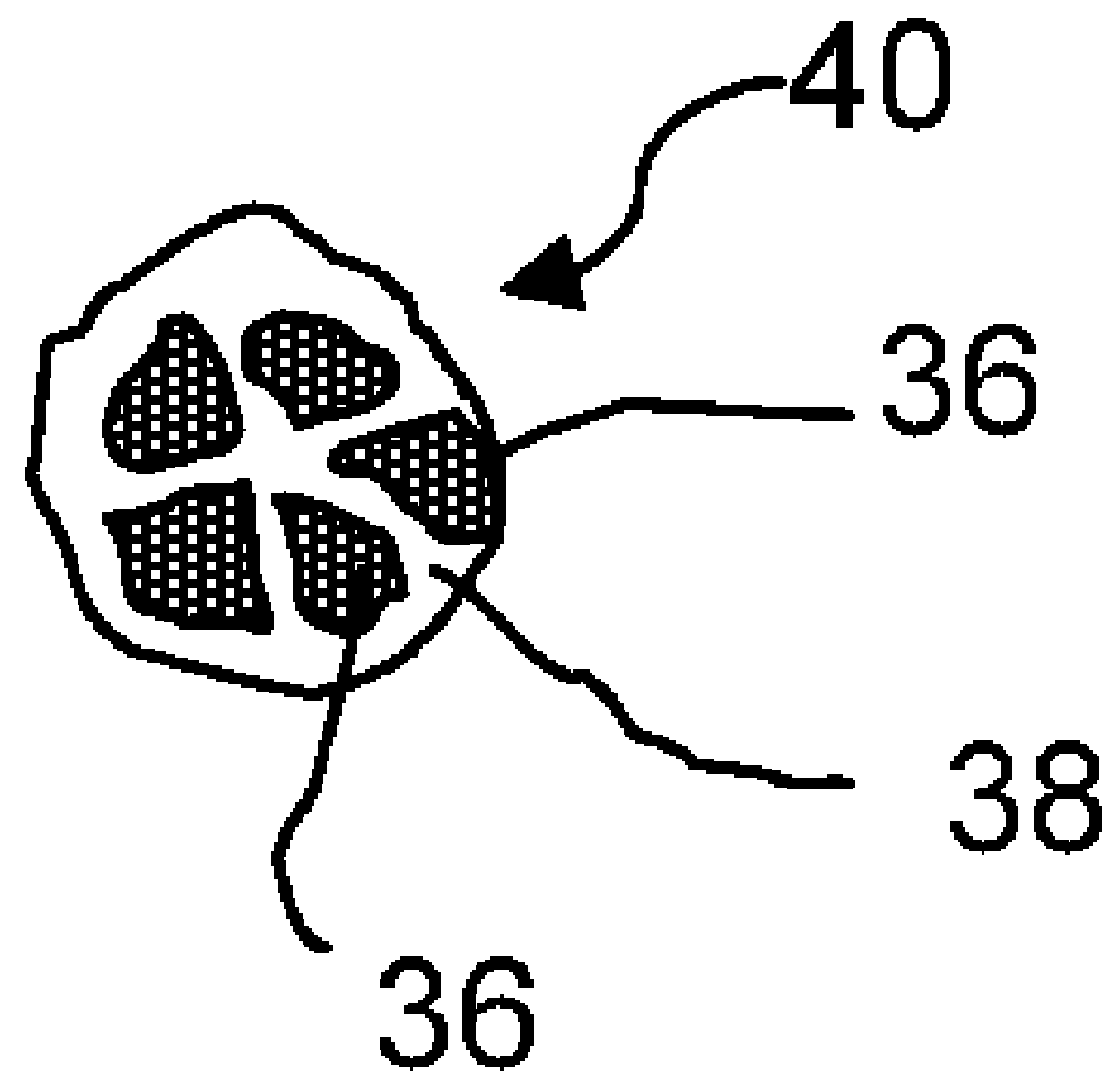
(57) **ABSTRACT**

Contacting the wellbore with a fluid composition and forming a metallic powder barrier at or near the tip of a fracture extending from the wellbore into a subterranean formation may strengthen a wellbore. The fluid composition may include a base fluid and a metallic powder having a plurality of metallic powder particles. The base fluid may include a drilling fluid, a completion fluid, a servicing fluid, a fracturing fluid, and mixtures thereof. The metallic powder particles may have a particle core and a metallic coating layer. The particle core may include a core material selected, such as magnesium, zinc, aluminum, manganese, vanadium, chromium, molybdenum, iron, cobalt, silicon, nitride, tungsten, and a combination thereof. The metallic coating layer may be disposed on the particle core thereby forming a metallic powder particle. The metallic powder particles may be configured for solid-state sintering to one another to form the metallic particle compacts.





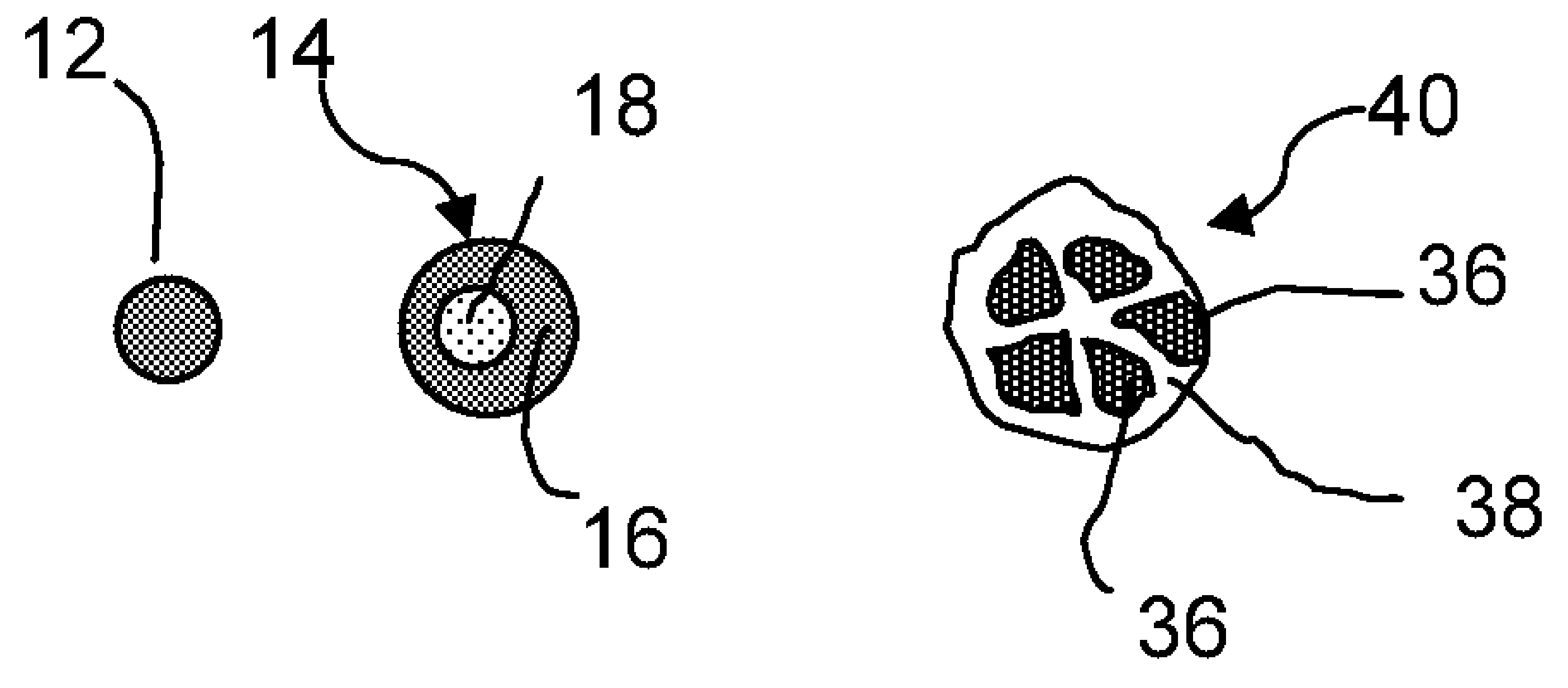


FIG. 1

CONTROLLED ELECTROLYTIC METALLIC MATERIALS FOR WELLBORE SEALING AND STRENGTHENING

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of Provisional Patent Application No. 61/695,474 filed Aug. 31, 2012, which is incorporated by reference herein in its entirety.

TECHNICAL FIELD

[0002] The present invention relates to sealing and strengthening a wellbore by contacting the wellbore with a fluid composition and forming a metallic powder barrier at or near the tip of a fracture extending from the wellbore into a subterranean formation.

BACKGROUND

[0003] Drilling fluids used in the drilling of subterranean oil and gas wells along with other drilling fluid applications and drilling procedures are known. In rotary drilling there are a variety of functions and characteristics that are expected of drilling fluids, also known as drilling muds, or simply "muds". The functions of a drilling fluid include, but are not necessarily limited to, cooling and lubricating the bit, lubricating the drill pipe, carrying the cuttings and other materials from the hole to the surface, and exerting a hydrostatic pressure against the borehole wall to prevent the flow of fluids from the surrounding formation into the borehole.

[0004] Drilling fluids are typically classified according to their base fluid. In water-based muds, solid particles are suspended in water or brine. Oil can be emulsified in the water, which is the continuous phase. Brine-based drilling fluids, of course are a water-based mud (WBM) in which the aqueous component is brine. Oil-based muds (OBM) are the opposite or inverse. Solid particles are suspended in oil, and water or brine is emulsified in the oil and therefore the oil is the continuous phase. Oil-based muds can be either all-oil based or water-in-oil macroemulsions, which are also called invert emulsions. In oil-based mud, the oil may consist of any oil that may include, but is not limited to, diesel, mineral oil, esters, or alpha-olefins. OBMs as defined herein also include synthetic-based fluids or muds (SBMs). SBMs often include, but are not necessarily limited to, olefin oligomers of ethylene, esters made from vegetable fatty acids and alcohols, ethers and polyethers made from alcohols and polyalcohols, paraffinic, or aromatic, hydrocarbons alkyl benzenes, terpenes and other natural products and mixtures of these types. OBMs and SBMs are also sometimes collectively referred to as "non-aqueous fluids" (NAFs).

[0005] Damage to a reservoir is particularly harmful if it occurs while drilling through the pay zone or the zone believed to hold recoverable oil or gas. In order to minimize such damage, a drill-in fluid may be pumped through the drill pipe while drilling through the pay zone.

[0006] Another type of fluid used in oil and gas wells is a completion fluid. A completion fluid is pumped down a well after drilling operations are completed and during the completion phase. Drilling mud typically is removed or displaced from the well using a completion fluid, which may be a clear brine. Then, the equipment required to produce fluids to the surface is installed in the well. A completion fluid must have sufficient density to maintain a differential pressure with the wellbore, which controls the well.

[0007] When drilling through a rock formation, mud may be lost into the formation through fractures (small or large fissures) of the formation. In other instances, fractures may be induced while drilling, such as in the case of drilling with a high overbalanced pressure through depleted sands. With both types of fractures, i.e. naturally-occurring or induced, severe fluid loss may occur, especially when drilling with an oil-based drilling mud. Examples of fluids that may be lost include, but are not limited to water or oil from drilling and completion fluids, typically used for downhole purposes, and the like. Another example is water invasion into shale formations, which may weaken the wellbore causing stability problems, such as a hole collapse.

[0008] Solid particles from the aforementioned types of fluids may physically plug or bridge across flowpaths at or near the fracture tip of the porous formation. Chemical reactions between the drilling fluid and the formation rock and fluids may precipitate solids or semisolids to plug pore spaces. It will also be understood that the drilling fluid, e.g. oil-based mud, is deposited and concentrated at the borehole face and partially inside the formation. However, the solid particles plugging or bridging across the formation may only be desirable for a temporary amount of time because the plugging can also cause a reduction of hydrocarbon production. Many operators are interested in improving formation clean up and removing the formed plugging material after drilling into reservoirs.

[0009] It would be advantageous to design a fluid composition having potentially degradable particles where the degradable particles may seal the wellbore or form a plug at or near the fracture tip for purposes of strengthening the wellbore and allow for the degradation of the plug if so desired.

SUMMARY

[0010] There is provided, in one form, a method for sealing and/or strengthening a wellbore. A fluid composition may contact the wellbore where the fluid composition includes a fluid and a metallic powder having a plurality of metallic powder particles. The metallic powder may form a metallic powder barrier at or near the tip of a fracture extending from the wellbore into a subterranean formation. The fluid may be a drilling fluid, a completion fluid, a servicing fluid, a fracturing fluid, and mixtures thereof. Each metallic powder particle may include a particle core, and a metallic coating layer disposed on the particle core. The particle core may have or include a core material with a melting temperature (T_p), and the core material may be or include magnesium, zinc, aluminum, manganese, vanadium, chromium, molybdenum, iron, cobalt, silicon, nitride, tungsten, and a combination thereof. The metallic coating layer disposed on the particle core may include a metallic coating material having a melting temperature (T_c).

[0011] In an alternative non-limiting embodiment, the metallic powder particles described above may be configured for solid-state sintering to one another at a predetermined sintering temperature (T_S) where T_S is less than T_P and T_C to form a metallic particle compact. The metallic powder particles and/or the metallic particle compacts may degrade after a predetermined condition including, but not necessarily limited to, a temperature change, the presence of an acid, an amount of time, or a combination thereof. A metallic powder barrier that includes the metallic powder particles may form at or near the tip of the fracture that may reduce additional growth of the fracture as compared to a wellbore contacted with a fluid composition absent the metallic powder.

[0012] The metallic powder barrier formed from the metallic powder appears to control the fracture size and strengthen the wellbore.

BRIEF DESCRIPTION OF THE DRAWING

[0013] FIG. **1** is a non-limiting, schematic illustration of three types of metallic powder particles with degradable portions thereof.

[0014] It will be appreciated that the various structures and parts thereof schematically shown in FIG. **1** are not necessarily to scale or proportion since many proportions and features have been exaggerated for clarity and illustration.

DETAILED DESCRIPTION

[0015] A method has been discovered for strengthening and sealing a wellbore that involves the use of at least partially degradable metallic powder particles blended with a base fluid, such as but not necessarily limited to a drilling fluid, a completion fluid, a servicing fluid, a fracturing fluid, and mixtures thereof to form a fluid composition. Once a fracture is induced within a subterranean reservoir, various fluids may be lost into the formation, also termed 'lost circulation' of fluid.

[0016] To prevent loss of water or other fluids into the formation, the metallic powder particles may be carried into these fractures and act as proppants and thereby strengthen the wellbore by forming a stress cage around the wellbore. The concentration of the metallic powder within the fluid composition may range from about 0.05 wt % independently to about 10 wt %, alternatively from about 0.05 wt % independently to about 3 wt %. When the term "independently" is used herein with respect to a parameter range, it is to be understood that all lower thresholds may be used together with all upper thresholds to form suitable and acceptable alternative ranges. The fluid composition may be pumped into the wellbore to form a metallic powder barrier at or near the tip of a fracture extending from the wellbore into a subterranean formation.

[0017] 'Metallic powder barrier' is defined herein to be a material intended to form a blockage or block passage of a fluid into or out of the wellbore and/or formation, such as but not limited to, a plug, a sealant, a bridging material, and combinations thereof. Such a barrier may be useful on small scale to block pore space of a formation, or on a larger scale to form a plug and create multiple zones within a wellbore. The metallic powder barrier formed may reduce additional growth of the fracture as compared to contacting the wellbore with a fluid composition absent the metallic powder. The metallic powder barrier may also reduce the amount of fluid lost in the formation. In one non-limiting embodiment, the metallic powder barrier may form a seal on the wellbore to prevent solid and fluid going from or into the formation and/or prevent pressure transmission.

[0018] The degradable metallic powder particles and/or metallic particle compacts may be designed to be pumpable along with the base fluid. With time, these metallic powder particles and/or metallic particle compacts will either degrade partially or completely in downhole formation water, fracturing fluid (i.e. mixture of water and/or brine), other fluids, or other conditions. Some of these metallic powder particles and/or metallic particle compacts may degrade in hydrocarbons if the hydrocarbons contain H_2S, CO_2, and other acid gases that cause degradation of the materials. Oxides, nitrides, carbides, intermetallics or ceramic coatings that are partially or fully resistant of these dissolvable metallic powder particles and/or metallic particle compacts may be dissolved with a second fluid, such as an acid or brine-based fluids. This allows for a metallic powder barrier to form at or near the fracture tip for a period of time that the metallic powder barrier is needed, and then the degradable metallic powder particles and/or metallic particle compacts within the metallic powder barrier may be degraded according to predetermined conditions or once the metallic powder barrier is no longer needed. By "at or near" is meant within a few inches, e.g. about 2 inches independently to about 4 inches from the tip of the fracture, or alternatively, less than 1 inch from the tip of the fracture.

[0019] In a non-limiting embodiment, the metallic powder particles may be oil-wet from the oil-based muds. A surfactant may contact the metallic powder particles and/or formed metallic powder barrier to change at least a portion of the metallic powder particles from oil-wet to water-wet; alternatively, a mesophase fluid may be injected into the wellbore to change the metallic powder particles from oil-wet to water-wet. More specifically, the surfactant (in the absence of a mesophase fluid) or the mesophase fluid may reverse the wettability, remove and/or minimize the metallic powder barrier formed from the metallic powder particles at or near the fracture tip. Mesophase fluids are defined herein as selected from the group of a miniemulsion, a nanoemulsion, macroemulsion or a microemulsion in equilibrium with excess oil or water or both (Winsor III), a single-phase microemulsion (Winsor IV) as defined by U.S. Pat. No. 8,235,120, which is incorporated herein by reference.

[0020] In an alternative non-limiting embodiment, the metallic powder particles may be water-wet from the water-based muds. A surfactant may contact the metallic powder particles and/or formed metallic powder barrier to change at least a portion of the metallic powder particles from water-wet to oil-wet; alternatively, a mesophase fluid may be injected into the wellbore to change the metallic powder particles from water-wet to oil-wet. More specifically, the surfactant (in the absence of a mesophase fluid) or the mesophase fluid may reverse the wettability, remove and/or minimize the metallic powder barrier formed from the metallic powder particles at or near the fracture tip.

[0021] In this instance, the metallic powder particles may be oil-wet (or non-polar), so the mesophase fluid may be water-continuous. Mesophase fluids also include collections of components that make these emulsions. These mesophase fluids may be formed either prior to introduction into a wellbore or formed in situ. That is, it is not necessary to completely form the mesophase fluid (e.g. microemulsion) on the surface and pump it downhole. The in situ mesophase fluid (e.g. microemulsion, nanoemulsion, etc.) may be formed when at least one surfactant and a polar phase (usually, but not limited to water or brine) contacts the non-polar metallic powder particles and solubilizes the non-polar material thereon. Such mesophase fluids may also be introduced as pills to carry out the same function.

[0022] The mesophase fluid may include at least one surfactant, an oil-based fluid, an aqueous-based fluid, and an optional co-surfactant. The surfactant may be or include, but is not limited to an extended chain surfactant, a non-extended chain surfactant, a co-surfactant, and combinations thereof. The surfactant may be or include, but is not limited to nonionic, anionic, cationic, amphoteric surfactants, extended chain surfactants, and combinations thereof. Suitable nonionic surfactants include, but are not necessarily limited to, alkyl polyglycosides, sorbitan esters, polyglycol esters, methyl glucoside esters, alcohol ethoxylates or alkylphenol ethoxylates. Suitable anionic surfactants include, but are not necessarily limited to, alkali metal alkyl sulfates, alkyl or alkylaryl sulfonates, linear or branched alkyl ether sulfates and sulfonates, alcohol polypropoxylated and/or polyethoxylated sulfates, alkyl or alkylaryl disulfonates, alkyl disulfates, alkyl sulphosuccinates, alkyl ether sulfates, linear and branched ether sulfates, and mixtures thereof. Suitable cationic surfactants include, but are not necessarily limited to, arginine methyl esters, alkanolamines and alkylenediamides.

[0023] The optional co-surfactant may be a surface-active substance, such as but not limited to, mono or poly-alcohols, low molecular weight organic acids or amines, polyethylene glycol, low ethoxylation solvents and mixtures thereof.

[0024] Once the metallic powder particles are water-wet, the second fluid may be an almost neutral fluid (‘almost neutral’ is defined herein to mean a pH ranging from about 6.5 to about 7.5, e.g. water) and injected into the wellbore to dissolve the metallic powder particles. Although an acidic solution (e.g. a fluid having a pH less than about 6.5) may dissolve the metallic powder particles quicker than an almost neutral fluid, the acidic solution may corrode the well equipment downhole. For example, the metallic powder barrier formed from the powder particles may be used to aid in completion of a well; use of an acidic solution would corrode and/or dissolve the completion equipment for the finished well. Thus, depending on the use of the metallic powder particles and the metallic powder barrier formed therefrom, one skilled in the art must assess whether to use a second fluid that is acidic or almost neutral.

[0025] The degradable portions of the metallic powder particles and/or metallic particle compacts may be lightweight, high-strength and have selectably and controllably degradable materials. Fully-dense, sintered metallic particle compacts may be formed from coated metallic powder particles having lightweight particle cores. A coating may be formed on the particle core having at least one layer, alternatively from about 1 layer independently to about 10 layers depending on the thickness of each layer. The powder particle core may be or include an electrochemically-active (e.g. having relatively higher standard oxidation potentials), lightweight, and/or high-strength material.

[0026] The powder particles may degrade over a period of time ranging from about 0.5 hours independently to about 4 weeks, alternatively from about 10 minutes independently to about 2 weeks, or from about 5 minutes independently to about 24 hours.

[0027] These metallic powder particles and/or metallic particle compacts provide a unique and advantageous combination of mechanical strength properties, such as compression and shear strength, low density and selectable and controllable corrosion properties, particularly rapid and controlled dissolution in various wellbore fluids, and combinations thereof. For example, the particle core and coating layers of these metallic powder particles may be selected to provide sintered metallic particle compacts suitable for use as high strength engineered materials having a compressive strength and shear strength comparable to various other engineered materials, including carbon, stainless and alloy steels, but which also have a low density comparable to various polymers, elastomers, low-density porous ceramics and composite materials.

[0028] The selectable and controllable degradation or disposal characteristics described may also allow the dimensional stability and strength of materials to be maintained until the metallic powder particles and/or metallic particle compacts are no longer needed. In one non-limiting example, it may be beneficial to degrade the metallic powder particles at or near the fracture tip prior to producing the well to allow for the well to be produced at full capacity. Once the metallic powder barrier having the metallic particles is no longer needed, a condition may be changed to promote the degrading of the metallic particles, such as but not limited to a predetermined environmental condition, such as a wellbore condition, including but not necessarily limited to wellbore fluid temperature, pressure or pH value, salt or brine composition, etc. The degrading of the metallic powder particles may occur by a method, such as but not limited to dissolving the metallic powder particles, degrading the metallic powder particles, corroding the metallic powder particles, melting the metallic powder particles, and combinations thereof.

[0029] As yet another example, these metallic powder particles and/or metallic particle compacts may be configured to provide a selectable and controllable degradation, disintegration or disposal in response to a change in an environmental condition. An example of an environmental condition may include, but is not necessarily limited to, a transition from a very low dissolution rate to a very rapid dissolution rate in response to a change in a property or condition of a wellbore proximate an article formed from the metallic particle compact, including a property change in a wellbore fluid that is in contact with the metallic powder particles and/or metallic particle compacts. Such property changes may be or include, but are not necessarily limited to a temperature change, the presence of an acid, an amount of time, and combinations thereof.

[0030] In one non-limiting embodiment, these degradable powder particles may be called controlled electrolytic metallics (CEM) particles. Methods for using these metallic powder particles and/or metallic particle compacts are described further below, as well as in U.S. patent application Ser. No. 12/633,686 entitled COATED METALLIC POWDER AND METHOD OF MAKING THE SAME, filed Dec. 8, 2009, which is herein incorporated by reference in its entirety.

[0031] Magnesium or other reactive materials could be used in the powders to make the degradable metal portions, for instance, aluminum, zinc, manganese, molybdenum, tungsten, copper, iron, calcium, cobalt, tantalum, rhenium, nickel, silicon, rare earth elements, and alloys thereof and combinations thereof. As used herein, rare earth elements include Sc, Y; lanthanide series elements, including La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Te, Dy, Ho, Er, Tm, or Lu; or actinide series elements, including Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Bk, Cf, Es, Fm, Md, or No; or a combination of rare earth elements.

[0032] These metals may be used as pure metals or in any combination with one another, including various alloy combinations, such as amalgams and/or other physical combinations of these materials, including binary, tertiary, or quaternary alloys of these materials. Nanoscale metallic and/or non-metallic coatings could be applied to these electrochemically active metallic powder particles and/or metallic particle compacts to further strengthen the material and to provide a means to accelerate or decelerate the degrading rate.

[0033] Degradable enhancement additives include, but are not necessarily limited to, magnesium, aluminum, nickel, iron, cobalt, copper, tungsten, rare earth elements, and alloys thereof and combinations thereof. It will be observed that some elements are common to both lists, that is, those metals which can form degradable metals and degradable metal compacts and those which can enhance such metals and/or compacts. The function of the metals, alloys or combinations depends upon what metal or alloy is selected as the major particle core first.

[0034] The relative degradable rate depends on the value of the standard potential of the additive or coating relative to that of the particle core. For instance, to make a relatively more slowly degrading particle core, the coating composition needs to have a lower standard potential than that of the particle core. An aluminum particle core with a magnesium coating is a suitable example. Or, to make this particle core dissolve faster, the standard potential of the particle core needs to be lower than that of the coating. A non-limiting example of the latter situation would be a magnesium particle core with a nickel coating.

[0035] These electrochemically active metals or metals with nanoscale coatings may be degraded by a number of common wellbore fluids, including any number of ionic fluids or highly polar fluids. Non-limiting examples of such fluids include, but are not limited to, sodium chloride (NaCl), potassium chloride (KCl), hydrochloric acid (HCl), calcium chloride ($CaCl_2$), sodium bromide (NaBr), calcium bromide ($CaBr_2$), zinc bromide ($ZnBr_2$), sodium formate, potassium formate, or cesium formate.

[0036] Alternatively, relatively non-degradable metallic powder particles (e.g. a ceramic portion) may be designed to where only the coating of each particle degrades in a downhole environment, while the rest of the metallic powder particle remains in place as part of the barrier at or near the tip of the fracture. For instance, these non-degradable metallic powder particles include high strength intermetallic particles or ceramic particles of oxides, nitrides, carbides, or specifically MgO in a non-limiting example. The metallic powder particles could be solid or hollow. The degradable coatings include, but are not limited to, the reactive metals with corrosion enhancement coatings mentioned above.

[0037] It will be appreciated that in the embodiment where there is a degradable coating over all or a majority of a degradable particle core, there may be applications where the coating should be relatively more easily degraded than the particle core, and other applications where the particle core is relatively more easily degraded than the coating. Indeed, multiple coatings over a particle core may be used to provide further control over the degradation of the metallic powder particles and/or metallic particle compacts. Combinations of different fluids and metallic powder particles and/or metallic particle compacts with different layers or portions that degrade at different rates will provide many ways to design and control the formed metallic powder barrier at or near the fracture tip depending on the desired wellbore strengthening properties, the length of time desired for a formed barrier, etc.

[0038] The dissolvable metallic powder particles and/or metallic particle compacts may be spherical, elongated, rod-like or another geometric shape. In another non-limiting embodiment, they may be flake or granular in shape to reduce fluid losses to the formation. One non-limiting example of the flake shape is SOLUFLAKE™ from Baker Hughes.

[0039] The dissolvable metallic powder cores and/or metallic particle compacts formed from the metallic powder particles may be either uncoated or coated. Uncoated particle cores may be reactive metals such as magnesium, aluminum, zinc, manganese or their alloys, or metals with degradable enhancement additives included in the particle core. Coated particles may have a particle core and at least one metallic coating layer. The particle core of a coated powder particle may be of metals such as magnesium, zinc, aluminum, manganese, vanadium, chromium, molybdenum, iron, cobalt, silicon, nitride, tungsten, and combinations thereof.

[0040] The metallic coating material may be or include, but is not limited to, Al, Zn, Mn, Mg, Mo, W, Cu, Fe, Si, Ca, Co, Ta, Re, Ni, an oxide thereof, a carbide thereof, a nitride thereof, and a combination of any of the aforementioned materials. The metallic coating material may be a different chemical composition than the chemical composition of the particle core. The metallic coating layer could be such that it accelerates or decelerates the degradation of the metallic powder particle. These metallic powder particles could be such that they degrade either partially or completely over a period of time. The degradation rate may be controlled by the composition of the base fluid, such as but not limited to a drilling fluid, a completion fluid, a servicing fluid, a fracturing fluid, and mixtures thereof.

[0041] In a non-limiting embodiment, the core material may be Mg—Zn, Mg—Al, Mg—Mn, Mg—Zn—Y and combinations thereof. When the core material is an Mg—Al—X alloy, the X may be or include Zn, Mn, Si, Ca, Y, and combinations thereof. Additionally, the Mg—Al—X alloy may be up to about 85 wt % of Mg, up to about 15 wt % Al, and up to about 5 wt % X.

[0042] In an alternative procedure, it is conceived that these degradable metallic powder particles and/or metallic particle compacts may be designed so that a stimulation or second fluid triggers the degradation of the powder particle compacts and/or powder particles. After the metallic powder barrier has formed at or near the fracture, a subsequent dosing of a second fluid, different from the base fluid initially used to deliver the degradable metallic powder particles and/or metallic particle compacts into the wellbore, will trigger the dissolution of the degradable particle phase or degradable particle compact phase. The additional stimulation fluid treatments may include an acid or brine or seawater, heated water or steam, or even fresh water—something that provides chemical and/or physical stimuli for triggering the dissolvable material to actually dissolve or degrade. The acid may be a mineral acid (where examples include, but are not necessarily limited to HCl, H_2SO_4, H_2PO_4, HF, and the like), and/or an organic acid (where examples include, but are not necessarily limited to acetic acid, formic acid, fumaric acid, succinic acid, glutaric acid, adipic acid, citric acid, and the like). In another embodiment, the acid or brine may be the internal phase of an emulsion stimulation of a cleanup fluid.

[0043] The size of the metallic powder particle may range from about 25 nm independently to about 5000 μm, alternatively from about 100 nm independently to about 750 μm. For a coated powder particle, i.e. one having a powder particle core and a powder particle coating, the particle core may have a diameter ranging from about 1 nm independently to about 300 μm, alternatively from about 50 nm to about 500 μm. The metallic coating layer disposed on the particle core may have a melting temperature (Tc). The thickness of the metallic coating layer may range from about 25 nm independently to about 2500 nm, or from about 100 nm independently to about 500 nm. The metallic powder particles may be configured for solid-state sintering to one another at a predetermined sintering temperature (Ts) where Ts is less than Tp and Tc to form a metallic particle compact. The size of the metallic particle compact ranges from about 500 μm independently to about 20 cm.

[0044] The invention will now be illustrated with respect to certain examples, which are not intended to limit the invention in any way but simply to further illustrate it in certain specific embodiments.

[0045] Shown in FIG. **1** is one version of a metallic powder particle **12** that is completely degradable, and an alternate embodiment of a metallic powder particle **14** that has a portion **16** that is degradable at a first rate, and a portion **18** that is degradable at a second rate. In the particular, alternative embodiment of metallic powder particle **14** shown in FIG. **1**, metallic powder particle **14** may have a generally central particle core **18** that is relatively more slowly degradable compared to portion **16**, which is relatively more rapidly degradable and is a relatively uniform coating over the generally central particle core **18**. It should be understood that the rates of degradation between portion **16** and portion **18** may be reversed. In another non-limiting embodiment, portion **18** is essentially not degradable in the process. However, it will be appreciated that metallic powder particle **14** may have other configurations, for example degradable portion **16** may not be uniformly applied over generally central particle core **18**.

[0046] These coatings may be formed by any acceptable method known in the art and suitable methods include, but are not necessarily limited to, chemical vapor deposition (CVD) including fluidized bed chemical vapor deposition (FBCVD), as well as physical vapor deposition, laser-induced deposition and the like, as well as sintering and/or compaction. In another non-limiting version, the particle may be formed of two approximately equal, or even unequal, hemispheres, one of which is a relatively insoluble portion **18** and the other of which is a relative dissolvable portion.

[0047] Also shown in FIG. **1** is a different embodiment of a metallic particle compact **40**, which may have powder particle cores **36** and a thin metallic coating layer **38** thereon. Such metallic particle compacts **40** do not necessarily have a metallic coating layer **38** over the entire metallic particle compact **40**. In a non-limiting instance, note that powder particle core **36** on the right side of metallic particle compact **40** is not covered by coating **38**. Metallic particle compacts **40** may be reduced in size or degraded uniformly. In an alternative non-limiting embodiment of a metallic particle compact, at least two of the metallic powder particles **12**, **14**, **40**, and combinations thereof, may be sintered together to form a metallic particle compact.

[0048] In a different non-limiting embodiment, the particles of FIG. **1** may be engineered to have increased strength, at least up until the powder particles begin to degrade. In a non-limiting example, the portion **16** may be ceramic (e.g. an inorganic, nonmetallic material) and the portion **18** may be metal.

[0049] It will be further understood that although metallic powder particles **12** and **14** are shown as spheres, they may be other shapes including, but not necessarily limited to, irregular rod-like, acicular, dendritic, flake, nodular, irregular, and/or porous. In another non-limiting version, the metallic powder particle may be hollow or porous. For example, the metallic powder particle may only have a coating but not a powder particle core.

[0050] In another non-restrictive embodiment, the degradable portions of metallic powder particles **12** and **14** are made from a degradable metal sintered and/or compacted from a metallic composite powder comprising a plurality of metallic powder particles. These smaller powder particles are not to be confused with metallic powder particles **12** and **14**. Each metallic powder particle may comprise a particle core, where the particle core comprises a core material comprising Mg, Al, Zn or Mn, or a combination thereof, having a melting temperature (T_P). The powder particle may additionally comprise a metallic coating layer disposed on the powder particle core and comprising a metallic coating material having a melting temperature (T_C), wherein the powder particles are configured for solid-state sintering to one another at a predetermined sintering temperature (T_S), and T_S is less than T_P and T_C. Alternatively, T_S is slightly higher that T_P and T_C for localized micro-liquid state sintering, By "slightly higher" is meant about 10 to about 50° C. higher than the lowest melting point of all the phases involved in the material for localized micro-liquid sintering.

[0051] There are at least three different temperatures involved: T_P for the particle core, T_C for the coating, and a third one T_{PC} for the binary phase of P and C. T_{PC} is normally the lowest temperature among the three. In a non-limiting example, for a Mg particle with an Aluminum coating, according to a Mg—Al phase diagram, T_P=650° C., T_C=660° C. and T_{PC}=437 to <650° C. depending on wt % ratio of the Mg—Al system. Therefore, for completed solid-state sintering, the predetermined process temperature needs to be less than T_{PC}. For micro-liquid phase sintering at the core-coating interface, the temperature may be 10-50 degree C. higher than T_{PC} but less than T_P and T_C. A temperature higher than T_P or T_C may be too much, causing macro melting and destroying the coating structure.

[0052] The proportion of base fluid may be greater than that of completely degradable metallic powder particle **12**. In one non-limiting embodiment, the proportion of degradable particles within the total fluid composition may range from about 0.05 wt % independently to about 10 wt %, alternatively from about 0.05 wt % independently to about 3 wt %.

[0053] The completely dissolvable metallic powder particle **12** need not be the same or approximately the same size as the metallic powder particle **14**. In one non-limiting embodiment, average particle size of the metallic powder particle **12** may range from about 100 nm independently to about 100 microns, alternatively from about 100 nm independently to about 1 micron.

[0054] After placement of the metallic powder barrier, at least a portion of the degradable metallic powder particle **12** may be degraded and removed therefrom, which thereby reduces the size of the barrier. This may be beneficial when it is desirable to have a barrier of varying sizes over a period of time, or alternatively it may be beneficial to degrade the metallic powder particles once the barrier is no longer needed. The second fluid may degrade the metallic powder particles of the barrier. "Second fluid" is defined herein to mean any fluid added into the wellbore after the fluid formulation has been pumped into the wellbore, which may include but is not necessarily limited to a fluid that is the same base fluid as the first fluid but has been altered for purposes of degrading the particles.

[0055] The second fluid may contain corrosive material, such as select types and amounts of acids and salts, to control the rate of degradation of the particles. In another embodiment, the fluid formulation that introduced the metallic powder particles into the fracture may be removed or displaced, and subsequently a second fluid may be introduced to degrade the metallic powder particles **12**. This second fluid may suitably be, but is not necessarily limited to, fresh water, brines, acids, hydrocarbons, emulsions, and combinations thereof so long as it is designed to dissolve all or at least a portion of the dissolvable metallic powder particles **12**. While all of the metallic powder particles **12** may be removed, as a practical matter, in an alternate embodiment, it may not be possible to contact and degrade all of the dissolvable metallic powder particles **12** with the subsequent fluid and thus remove or degrade all of them. In one non-limiting embodiment, at least 90% to about 100% of the barrier may be removed, alternatively at least 50%, and in another non-limiting embodiment at least 10%.

[0056] A third fluid may also be used for further degrading of the metallic powder particles. "Third fluid" is defined herein as any fluid used after the second fluid that may degrade the metallic powder particles in a different manner than that of the second fluid.

[0057] In the foregoing specification, the invention has been described with reference to specific embodiments thereof, and has been demonstrated as effective in providing methods and compositions for strengthening a wellbore. However, it will be evident that various modifications and changes can be made thereto without departing from the broader spirit or scope of the invention as set forth in the appended claims. Accordingly, the specification is to be regarded in an illustrative rather than a restrictive sense. For example, specific combinations of or types of base fluids, metallic particle compacts, metallic particles, particle cores, metallic coating layers, second fluids, third fluids, and other components falling within the claimed parameters, but not specifically identified or tried in a particular composition or method, are expected to be within the scope of this invention. Further, it is expected that the components and proportions of the base fluid and metallic powder particles and procedures for strengthening the wellbore or forming a metallic powder barrier at or near the fracture tip may change somewhat from one application to another and still accomplish the stated purposes and goals of the methods described herein. For example, the methods may use different pressures, pump rates, additional fluids, and/or different steps than those exemplified herein.

[0058] The words "comprising" and "comprises" as used throughout the claims is interpreted "including but not limited to".

[0059] The present invention may suitably comprise, consist or consist essentially of the elements disclosed and may be practiced in the absence of an element not disclosed. For instance, a method for strengthening a wellbore may consist of or consist essentially of contacting the wellbore with a fluid composition having a base fluid and a metallic powder having a plurality of metallic particles, and forming a metallic powder barrier at or near the tip of a fracture extending from the wellbore into a subterranean formation, where the method further consists of or consists essentially of degrading the metallic powder particles after a predetermined condition, and reducing additional growth of the fracture as compared to contacting the wellbore with a fluid composition absent the metallic powder.

What is claimed is:

1. A method for strengthening a wellbore comprising:
contacting the wellbore with a fluid composition, wherein the fluid composition comprises:
a base fluid selected from the group consisting of a drilling fluid, a completion fluid, a servicing fluid, a fracturing fluid, and mixtures thereof; and
metallic powder comprising a plurality of metallic powder particles, each powder particle comprising:
a particle core comprising a core material having a melting temperature (T_p), and wherein the core material is selected from the group consisting of magnesium, zinc, aluminum, manganese, vanadium, chromium, molybdenum, iron, cobalt, silicon, nitride, tungsten, and a combination thereof; and
a metallic coating layer disposed on the particle core, wherein the metallic coating layer comprises a metallic coating material having a melting temperature (T_c); and
forming a first metallic powder barrier at or near the tip of a fracture extending from the wellbore into a subterranean formation with the metallic powder.

2. The method of claim **1**, wherein the metallic powder particles are configured for solid-state sintering to one another at a predetermined sintering temperature (T_s) to form a metallic particle compact, and wherein T_s is less than T_p and T_c.

3. The method of claim **2**, wherein the size of the metallic particle compact ranges from about 500 μm to about 20 cm.

4. The method of claim **1**, wherein the fluid composition comprises a concentration of the metallic powder in an amount ranging from about 0.05 wt % to about 10 wt % of the total fluid composition.

5. The method of claim **1** further comprising reducing additional growth of the fracture as compared to the wellbore absent the metallic powder barrier.

6. The method of claim **1**, further comprising reducing an amount of the base fluid lost to the formation as compared to the amount of fluid lost to the formation in the absence of the metallic powder barrier.

7. The method of claim **1**, further comprising forming a second metallic powder barrier on the wellbore to prevent solid and fluid going from or into the formation.

8. The method of claim **1**, further comprising contacting the metallic powder barrier with a surfactant to reverse the wettability of at least a portion of the metallic powder particles therein.

9. The method of claim **6**, wherein the surfactant is part of a mesophase fluid selected from the group consisting of a miniemulsion, a nanoemulsion, a macroemulsion, and combinations thereof.

10. The method of claim **1** further comprising degrading at least a portion of the metallic powder barrier after a predetermined condition selected from the group consisting of a temperature change, the presence of an acid, an amount of time, and combinations thereof.

11. The method of claim **8**, wherein the degrading the metallic powder particles occurs by a method selected from the group consisting of dissolving the metallic powder particles, disintegrating the metallic powder particles, corroding the metallic powder particles, melting the metallic powder particles, and combinations thereof.

12. The method of claim **1**, wherein the core material is selected from the group consisting of an Mg—Zn alloy, an Mg—Al alloy, an Mg—Mn alloy, an Mg—Zn—Y alloy, and combinations thereof.

13. The method of claim **1**, wherein the size of the powder particle ranges from about 25 nm to about 5000 μm.

14. The method of claim **1**, wherein the particle core has a diameter ranging from about 1 μm to about 300 μm.

15. The method of claim **1**, wherein the core material comprises an Mg—Al—X alloy; and wherein X is selected from the group consisting of Zn, Mn, Si, Ca, Y, and combinations thereof.

16. The method of claim **13**, wherein the Mg—Al—X alloy comprises up to about 85 wt % of Mg, up to about 15 wt % Al, and up to about 5 wt % X.

17. The method of claim **1**, wherein the metallic coating material is selected from the group consisting of Al, Zn, Mn, Mg, Mo, W, Cu, Fe, Si, Ca, Co, Ta, Re, Ni, an oxide thereof, a carbide thereof, a nitride thereof, and a combination of any of the aforementioned materials; and wherein the metallic coating material has a different chemical composition than the chemical composition of the particle core.

18. A method for strengthening a wellbore comprising:

contacting the wellbore with a fluid composition, wherein the fluid composition comprises:

a base fluid selected from the group consisting of a drilling fluid, a completion fluid, a servicing fluid, a fracturing fluid, and mixtures thereof; and

a metallic powder comprising a plurality of metallic powder particles, each powder particle comprising:

a particle core comprising a core material having a melting temperature (T_p), and wherein the core material is selected from the group consisting of magnesium, zinc, aluminum, manganese, vanadium, chromium, molybdenum, iron, cobalt, silicon, nitride, tungsten, and a combination thereof; and

a metallic coating layer disposed on the particle core, wherein the metallic coating layer comprises a metallic coating material having a melting temperature (T_c); and

wherein the metallic powder particles are configured for solid-state sintering to one another at a predetermined sintering temperature (T_S), and T_S is less than T_P and T_C to form a metallic particle compact; and

forming a metallic powder barrier with the metallic powder at or near the tip of a fracture extending from the wellbore into a subterranean formation to reduce additional growth additional growth of the fracture as compared to the fracture in the absence of the metallic powder barrier; and

degrading at least a portion of the metallic powder barrier after a predetermined condition selected from the group consisting of a temperature change, the presence of an acid, an amount of time, and combinations thereof.

19. A method for strengthening a wellbore comprising:

contacting the wellbore with a fluid composition, wherein the fluid composition comprises:

a base fluid selected from the group consisting of a drilling fluid, a completion fluid, a servicing fluid, a fracturing fluid, and mixtures thereof; and

a metallic powder comprising a plurality of metallic powder particles ranging in size from about 25 nm to about 5000 nm, each powder particle comprising:

a particle core comprising a core material having a melting temperature (T_p), and wherein the core material is selected from the group consisting of magnesium, zinc, aluminum, manganese, vanadium, chromium, molybdenum, iron, cobalt, silicon, nitride, tungsten, and a combination thereof; and

a metallic coating layer disposed on the particle core, wherein the metallic coating layer comprises a metallic coating material having a melting temperature (T_c); and

forming a metallic powder barrier at or near the tip of a fracture extending from the wellbore into a subterranean formation with the metallic powder;

contacting the metallic powder barrier with a surfactant to reverse the wettability of at least a portion of the metallic powder particles therein.

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