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(54) BONDED THERMITE COMPOSITION

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(60) Provisional application No. 62/813,852, filed on Mar. 5, 2019.

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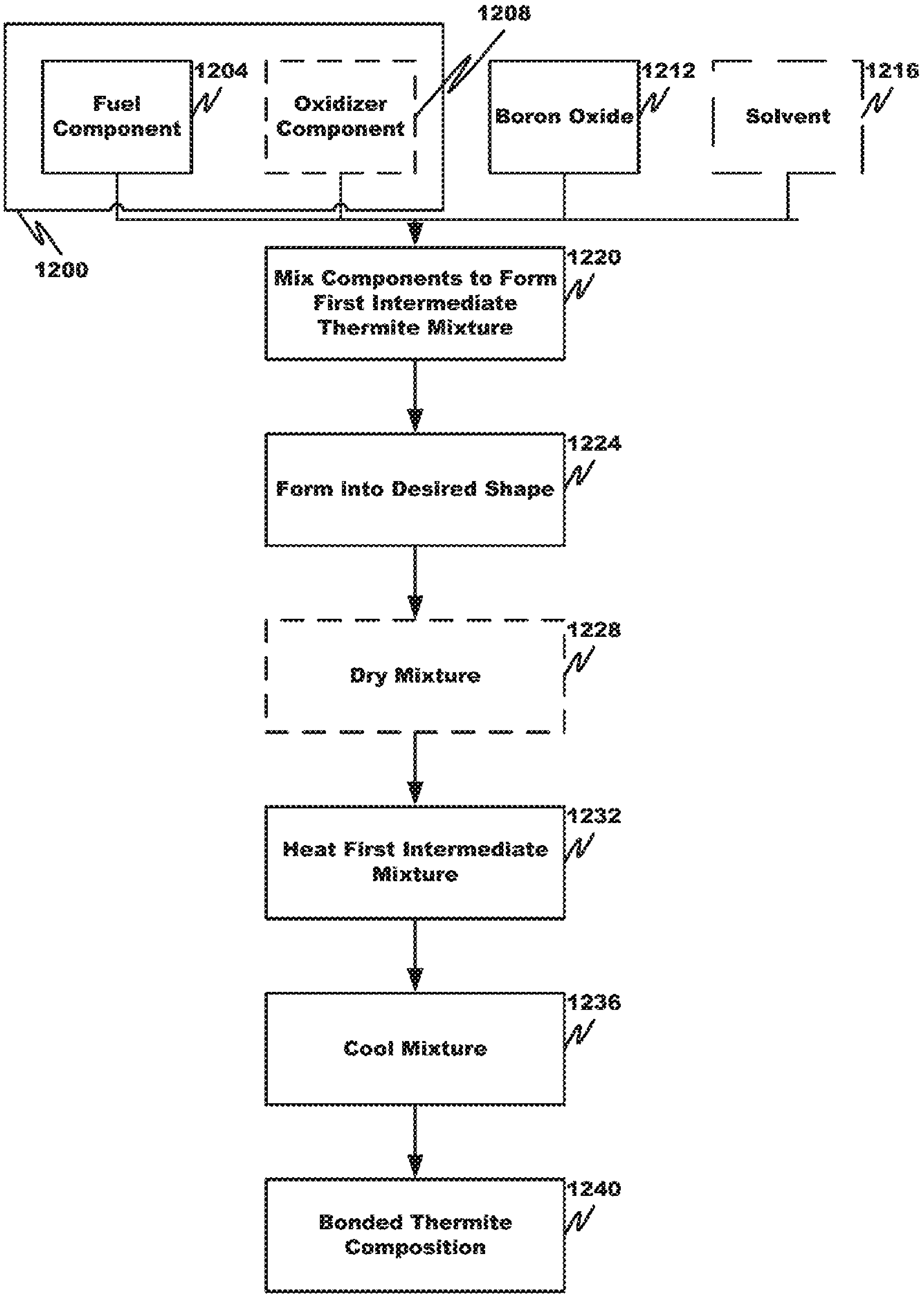
(57) ABSTRACT

Thermite mixtures shaped or cast into a desired solid form and having sufficient structural integrity to withstand rough handling and challenging operating conditions, and methods of making such solid forms, are provided. When reacted, the thermite mixtures advantageously produce little or no off-gas. The solid thermite forms may further include other materials that confer advantageous physical or chemical properties before, during, or after reaction of the thermite mixture.



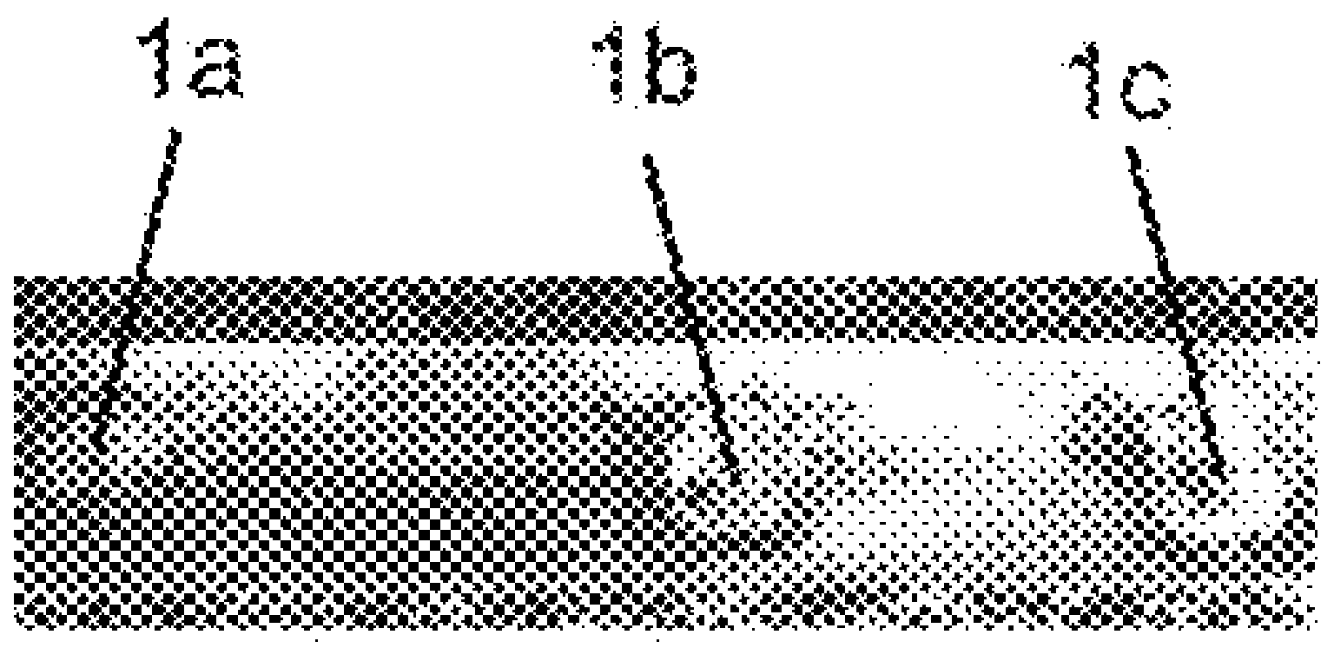


FIG. 1

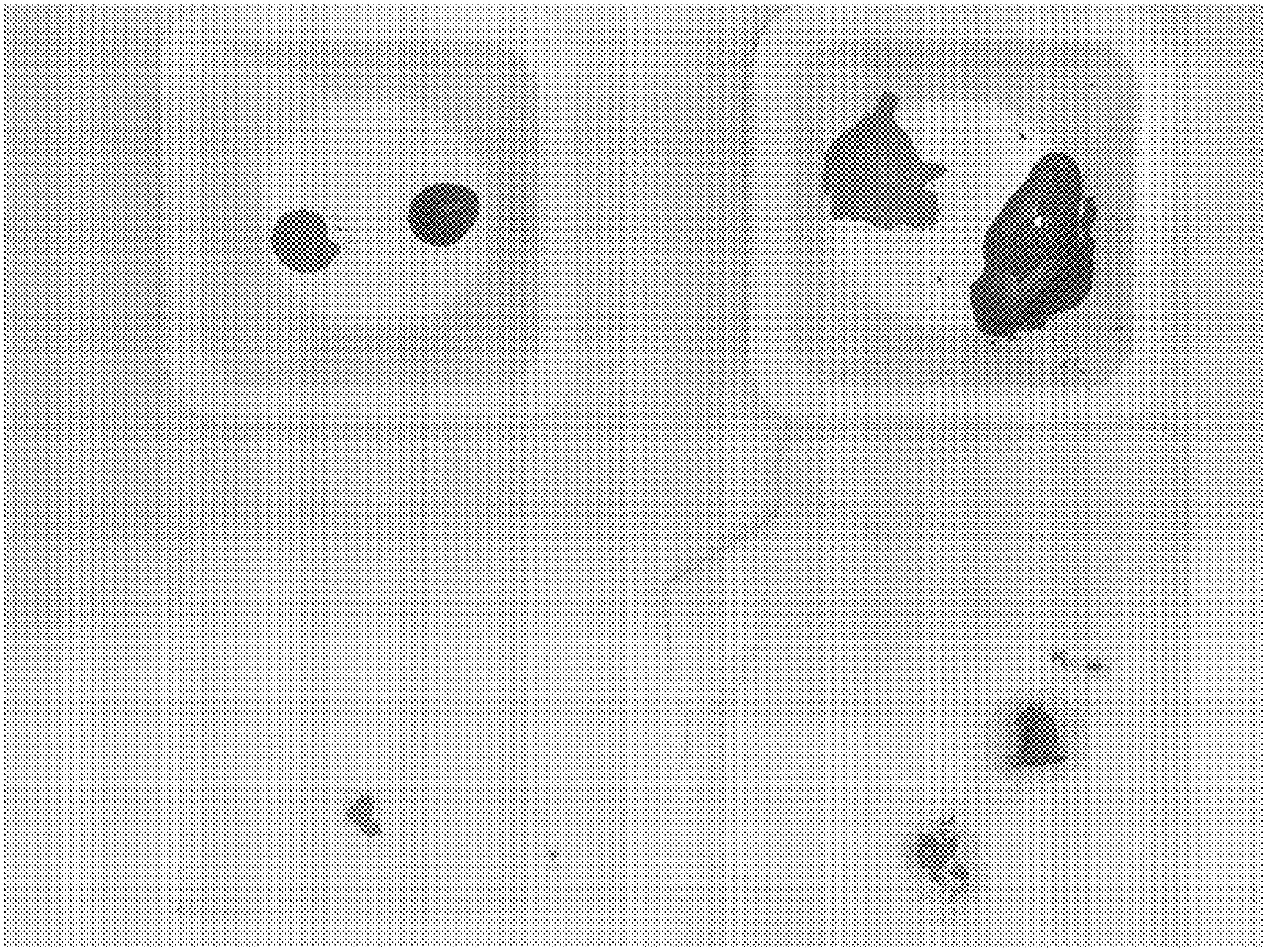


FIG. 2

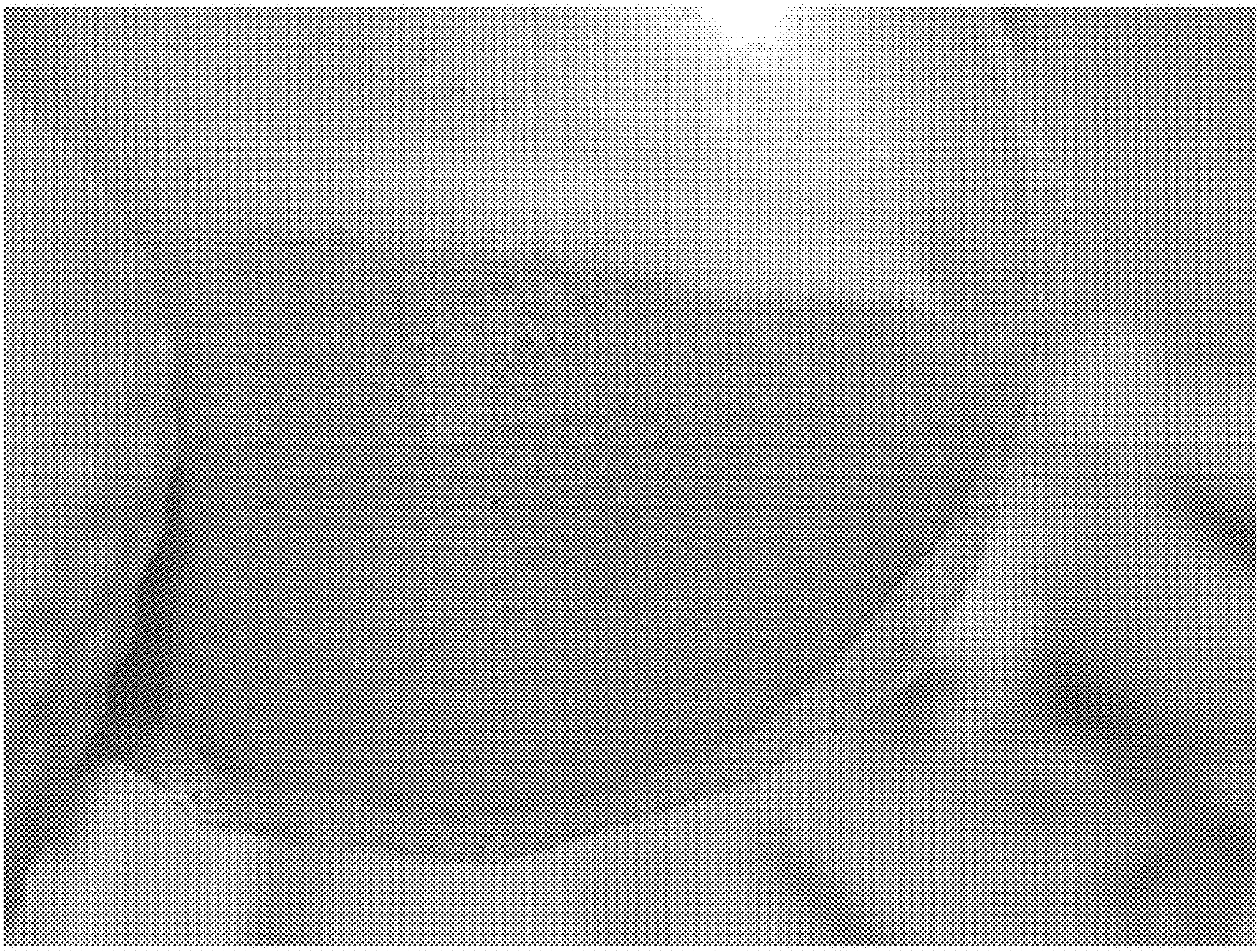


FIG. 3A

FIG. 3B

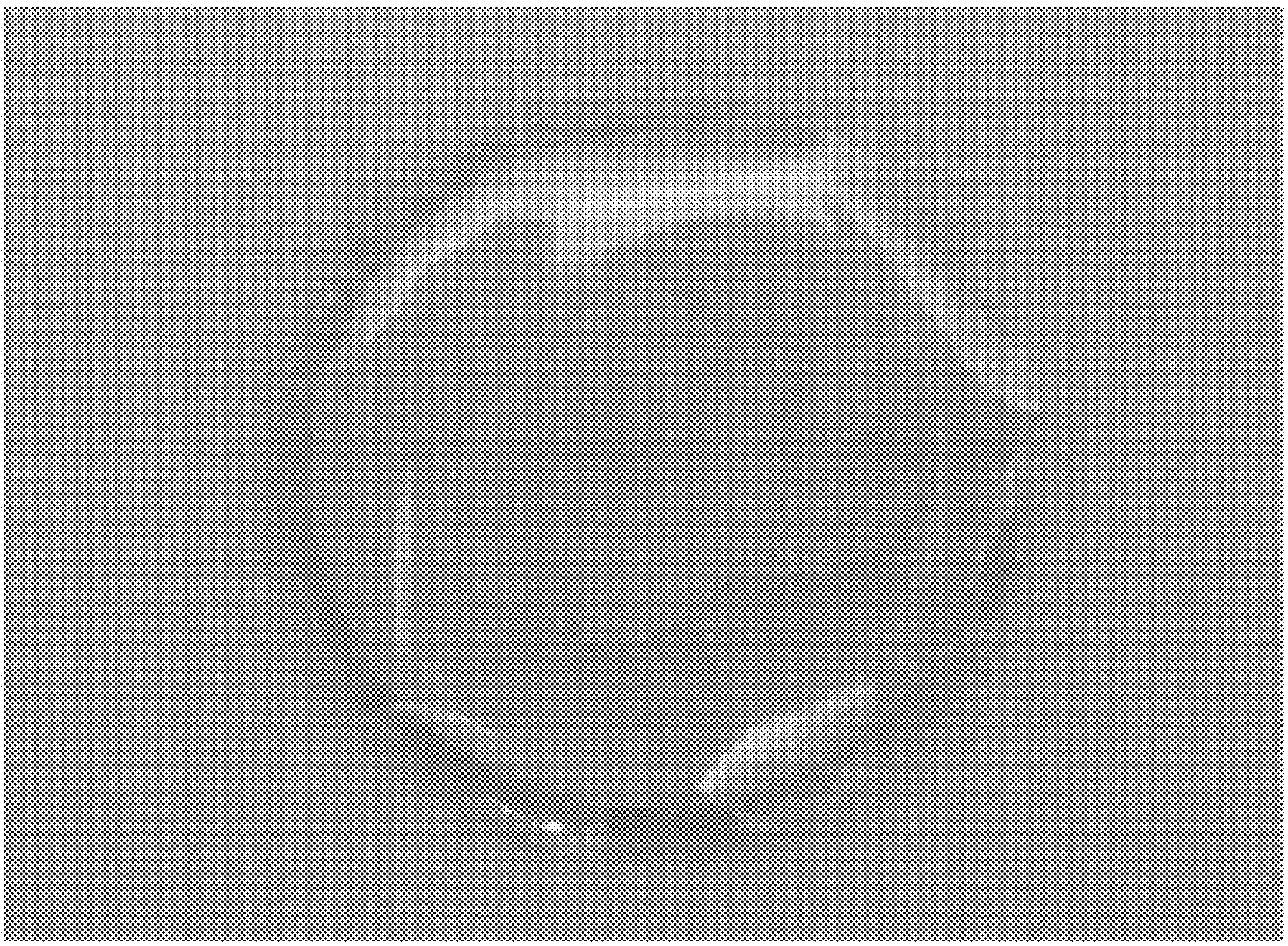


FIG. 4

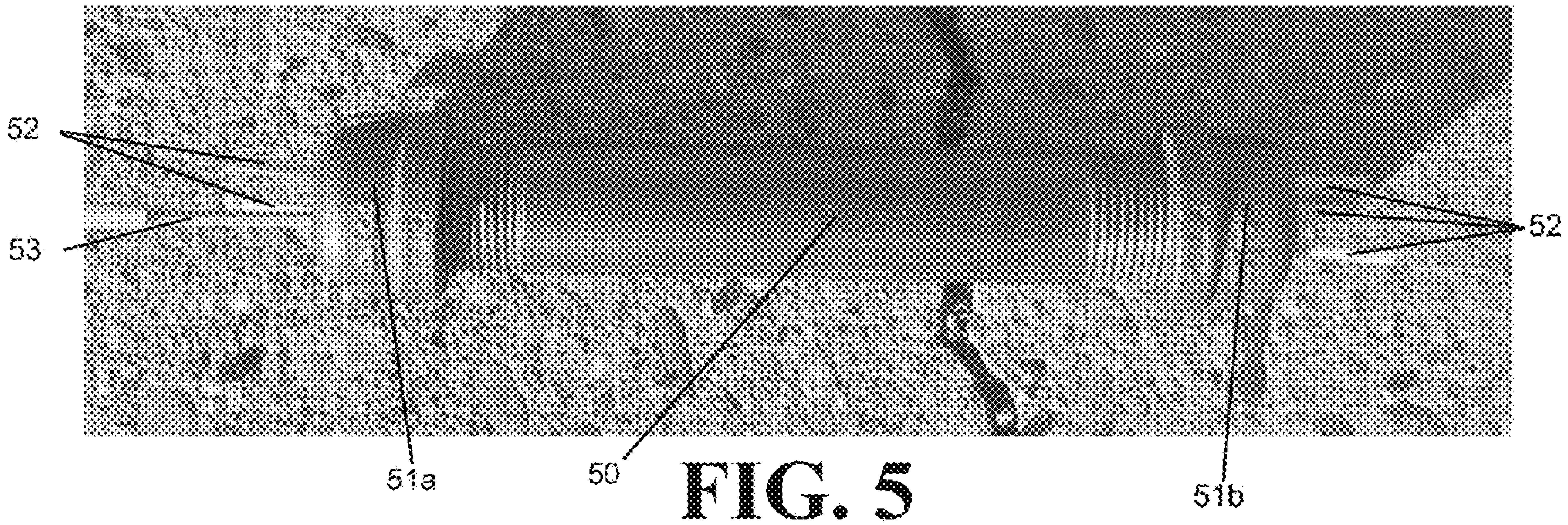


FIG. 5

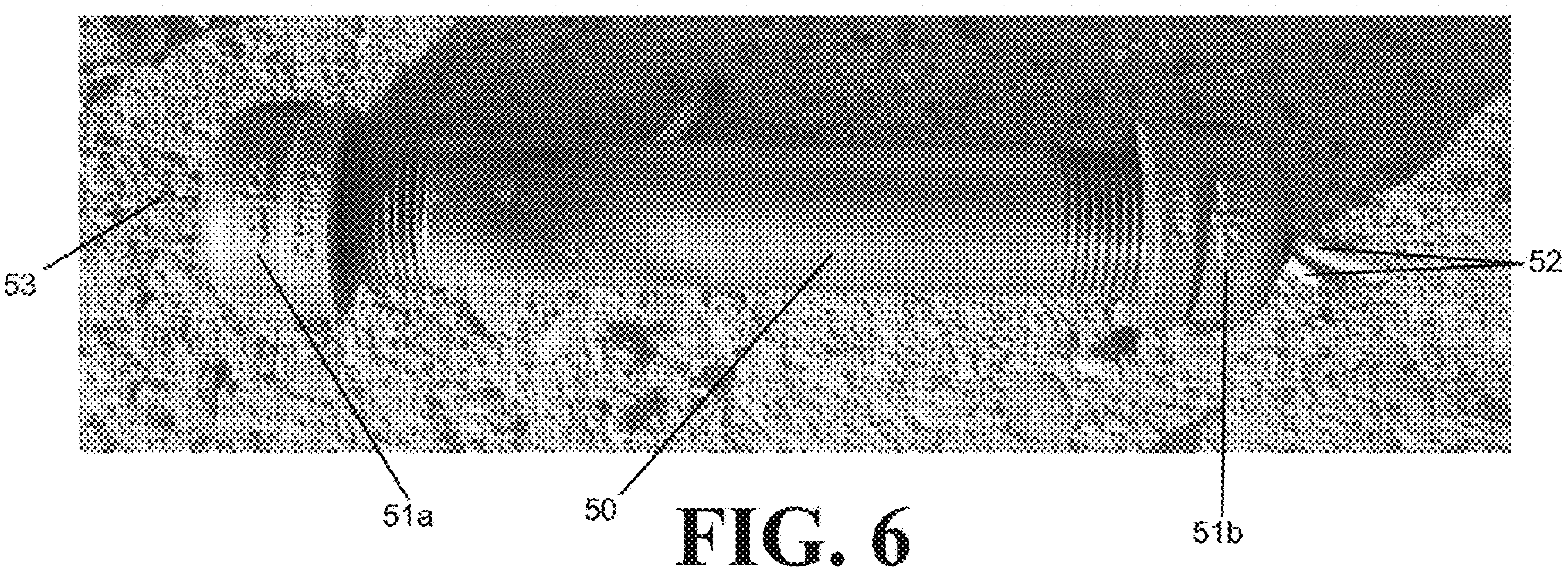


FIG. 6

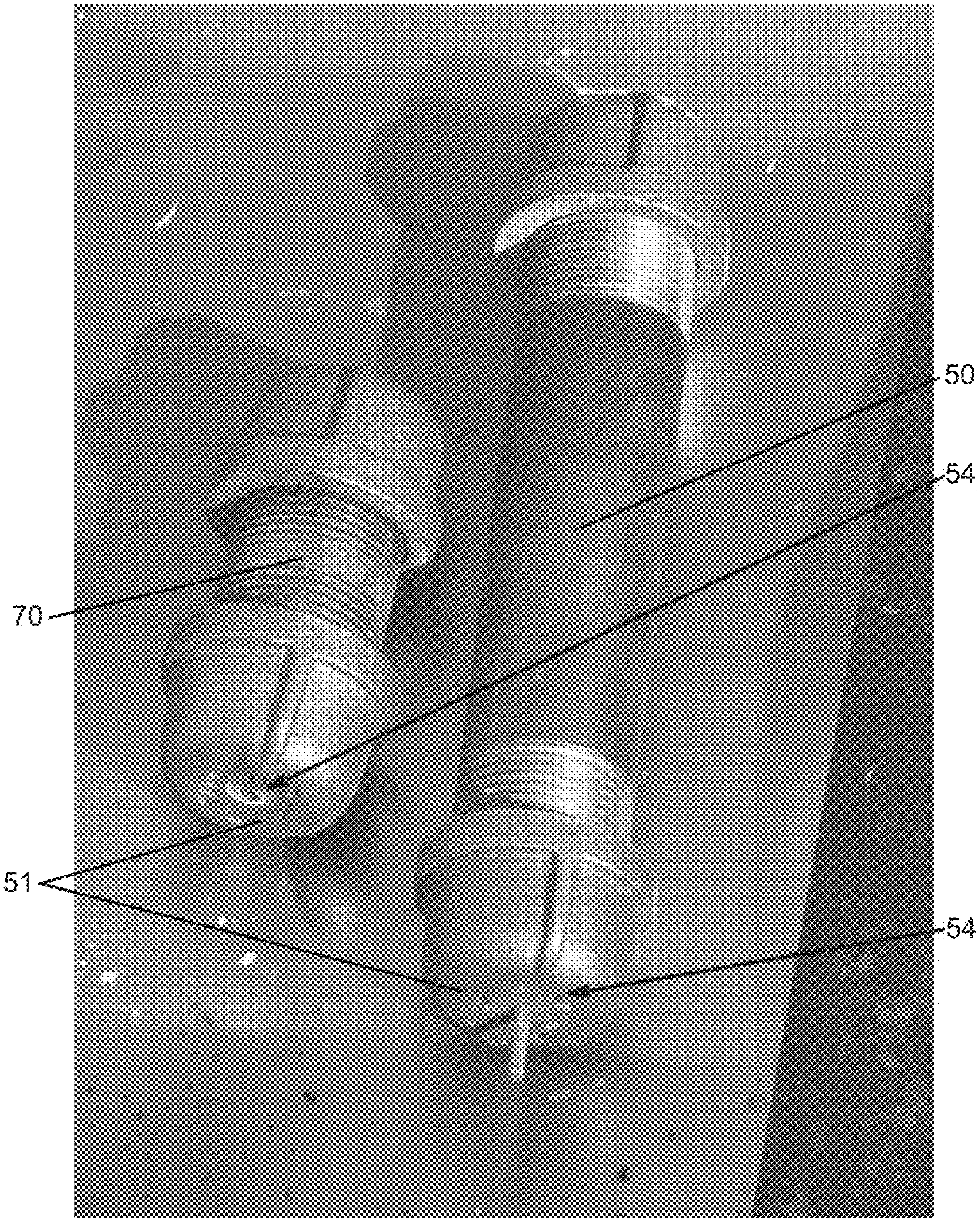


FIG. 7

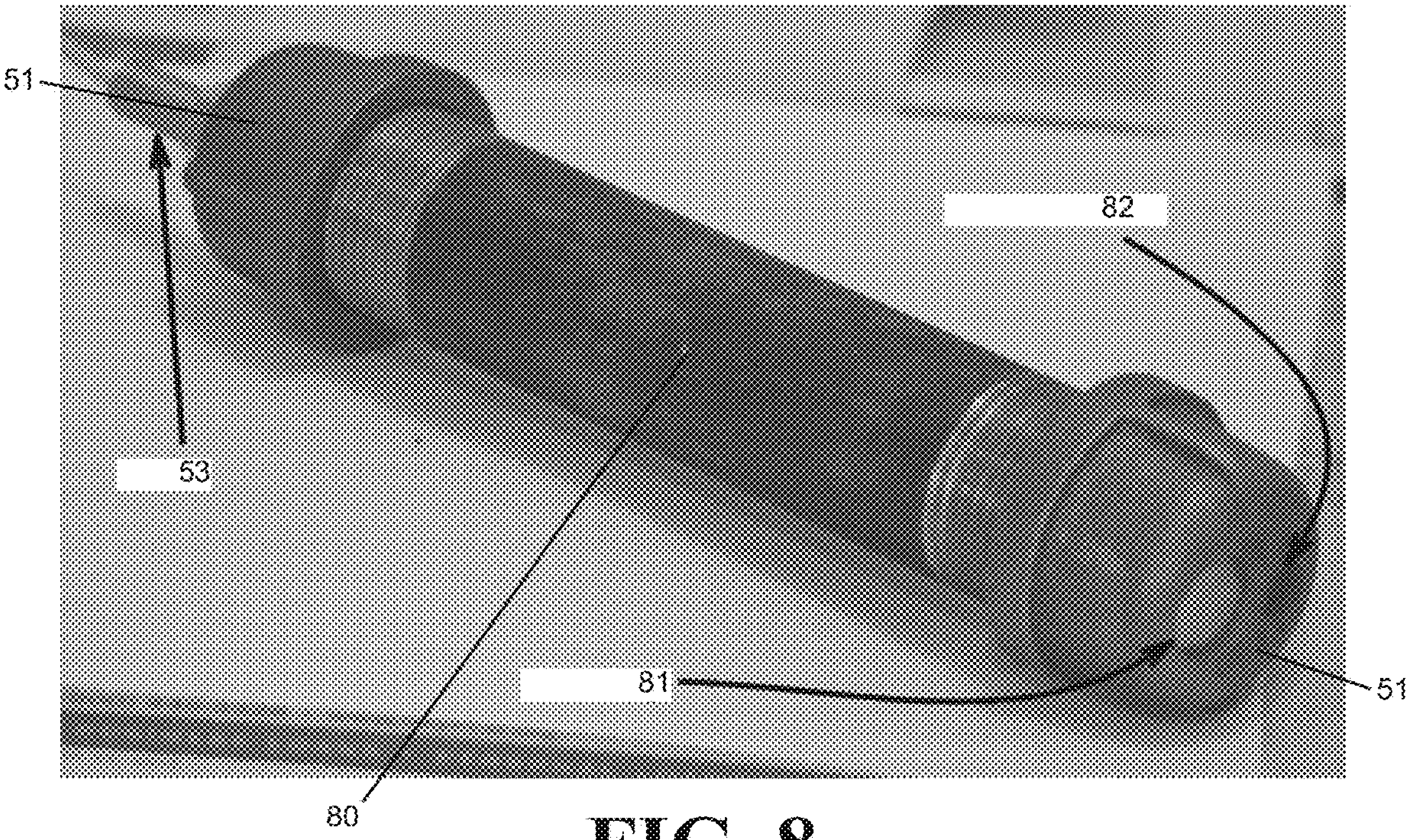


FIG. 8

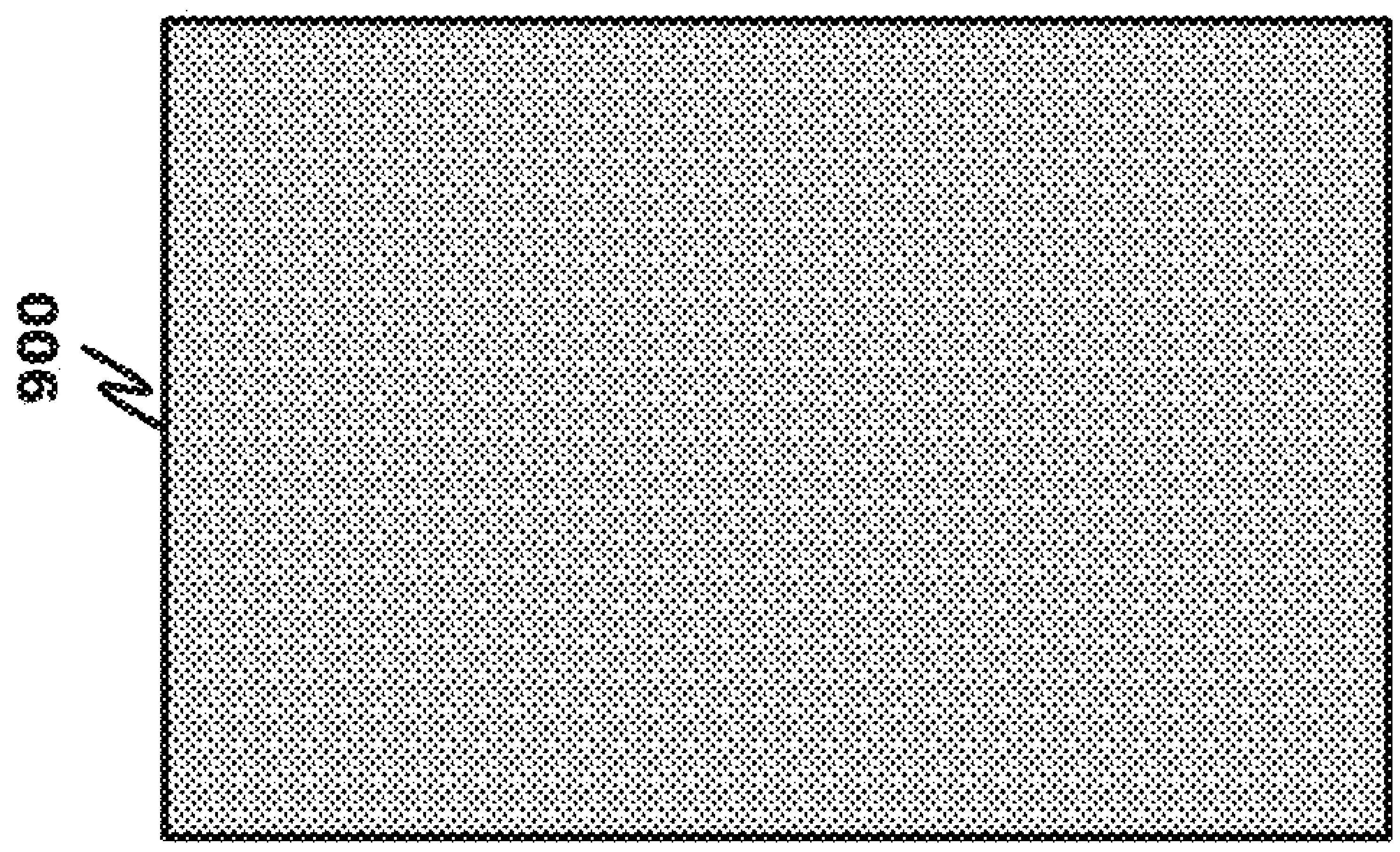


Fig. 9

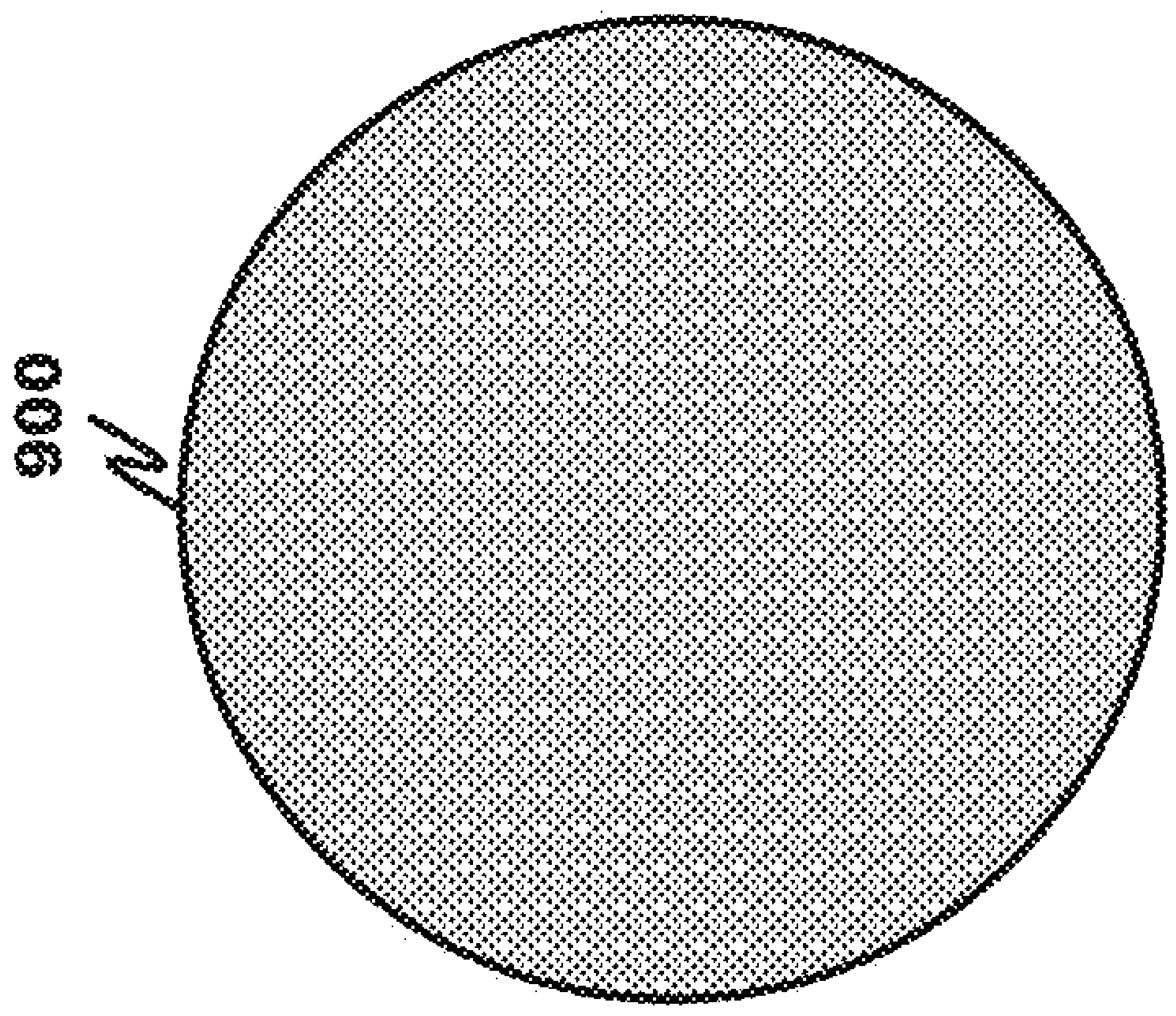


Fig. 10

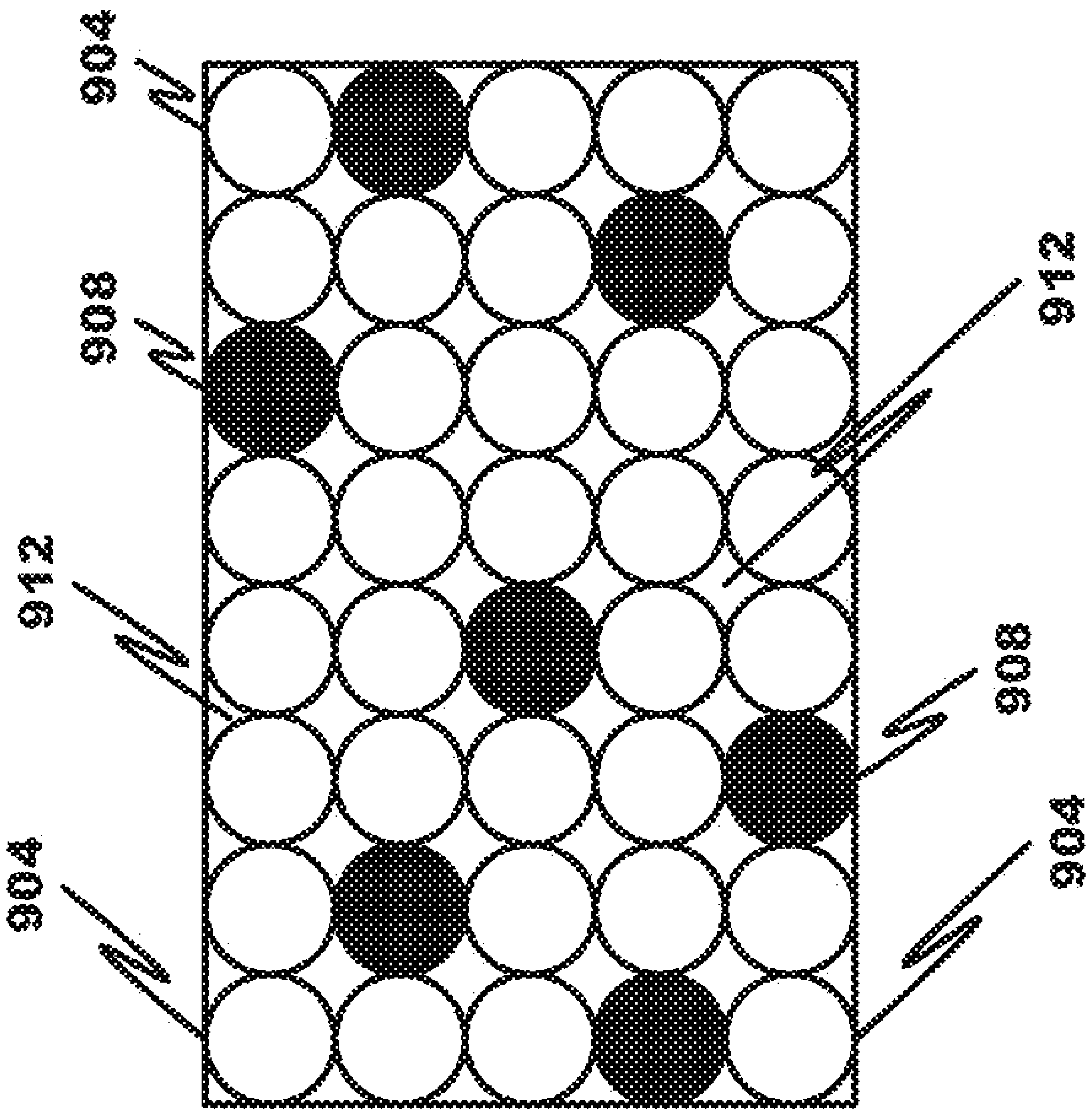


Fig. 11

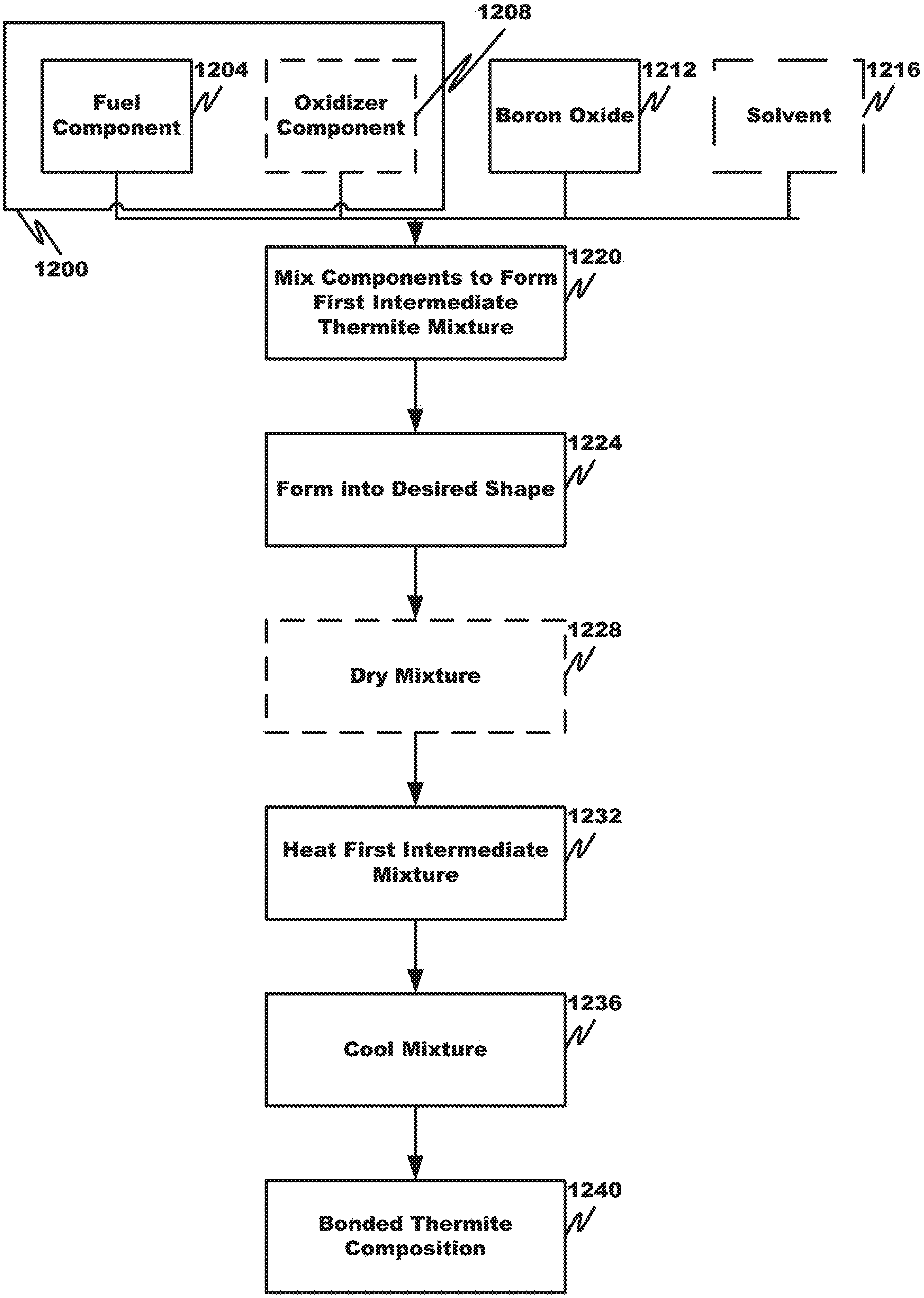

1208
Fuel Component
1204
Oxidizer Component
Boron Oxide
1212
Solvent
1216
1200
Mix Components to Form First Intermediate Thermite Mixture
1220
Form into Desired Shape
1224
Dry Mixture
1228
Heat First Intermediate Mixture
1232
Cool Mixture
1236
Bonded Thermite Composition
1240

Fig. 12

BONDED THERMITE COMPOSITION

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application is a divisional of U.S. patent application 16/810,409, filed 5 Mar. 2020, which claims the benefit of priority under 35 U.S.C. § 119(e) to U.S. Provisional Patent Application 62/813,852, filed 5 Mar. 2019. The entireties of both of these applications are incorporated herein by reference.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

[0002] This invention was made with government support under Contract 80NSSC18C0032 awarded by the National Aeronautics and Space Administration. The government has certain rights in the invention.

FIELD

[0003] The present disclosure relates generally to solid masses comprising thermite mixtures, and particularly to methods for creating such solid masses and controlling chemical and physical behavior, characteristics, and properties thereof.

BACKGROUND

[0004] The thermite reaction, i.e. the exothermic reduction-oxidation reaction between a metal powder fuel and a metal oxide when ignited by heat, has been known for well over a century; see, e.g., U.S. Pat. No. 906,009, entitled "Manufacture of thermic mixtures," issued 8 Dec. 1908 to Goldschmidt ("Goldschmidt"), the entirety of which is incorporated herein by reference. The thermite reaction is generally non-explosive but can create intense heat and high temperatures, and thus finds a wide variety of useful applications, including but not limited to welding (e.g. to join railway tracks), metal refining, disabling munitions, incendiary weapons, and pyrotechnic initiators (e.g. for fireworks).

[0005] Many improvements and purpose-specific adaptations have been made to the basic thermite reaction. Particularly, many previous attempts have been made to shape, cast, mold, or **30** press thermite mixtures into a preselected physical form, thereby enabling easier storage and transportation, providing for a desired spatial pattern or improved spatial distribution of ignition, etc. However, these previous attempts have generally suffered from a number of drawbacks.

[0006] U.S. Pat. No. 3,254,996, entitled "Method of preparing a sintered incendiary bomblet," issued 7 Jun. 1966 to MacDonald ("MacDonald I"), the entirety of which is incorporated herein by reference, discloses methods for preparing a solid form of thermite by solid-phase sintering.

[0007] However, the methods of MacDonald I require both very high pressure (50 tons per square inch) and sintering under a reducing atmosphere of hydrogen gas. Both of these requirements greatly increase the complexity and difficulty of processing the thermite mixture into the desired physical form, which can be prohibitive in many applications and for many skilled artisans.

[0008] U.S. Pat. No. 3,325,316, entitled "Pyrotechnic compositions of metal matrix with oxide dispersed therein," issued 13 Jun. 1967 to MacDonald ("MacDonald II"), the entirety of which is incorporated herein by reference, discloses methods for melting the metal (in MacDonald II's case, aluminum or magnesium) of the thermite mixture and subsequently mixing a solid metal oxide into the molten metal to form the thermite mixture, then allowing the mixture to cool to produce a solid form. Solid forms of thermite made by the methods of MacDonald II are not only difficult and potentially dangerous to manufacture due to the very high temperatures needed to melt the metal and the equipment and expertise needed to mix the metal oxide into the molten metal, but are difficult to ignite; MacDonald II discloses that a very large quantity of energy (e.g. dropping the solid thermite forms from an airplane or applying an oxyacetylene torch) is needed to ignite the thermite mixture.

[0009] U.S. Pat. No. 3,344,210, entitled "Method of making solid thermite pellets," issued 26 Sep. 1967 to Silvia ("Silvia"), the entirety of which is incorporated herein by reference, discloses the use of Bullseye pistol powder, or a similar "sensitizing agent," as a binder to bind a thermite mixture into a solid form. By design, however, pistol powder and similar "sensitizing agents" are propellants—they necessarily generate a significant quantity of gas upon ignition. The formation of a gas makes the compositions of Silvia unsuitable for many applications, e.g. where careful control of the composition of the atmosphere surrounding the thermite composition is required or where the excess pressure of offgas formation cannot be accommodated.

[0010] U.S. Pat. No. 4,019,932, entitled "Incendiary composition," issued 26 Apr. 1977 to Schroeder ("Schroeder"), the entirety of which is incorporated herein by reference, discloses the use of silicone as a binder to bind a thermite mixture into a solid form. However, Schroeder discloses only that its methods are suitable for use with thermite mixtures in which the metal fuel is magnesium; the present inventor has found that the use of silicone as a binder according to the methods of Schroeder produces unsatisfactory results in thermite mixtures in which the metal fuel is aluminum. This represents a significant drawback of Schroeder, as the increased reactivity of magnesium (relative to aluminum) limits its suitability for many applications. Moreover, as with the sensitizing agents of Silvia, silicone binders may produce offgases, and in particular combustion byproduct gases such as carbon dioxide, when the thermite mixture is ignited.

[0011] There is thus a need in the art for methods of making thermite compositions capable of being shaped, cast, molded, or pressed into a preselected physical form that do not require the extreme heat or pressure, or other challenging operating conditions, of prior art methods. It is further advantageous to provide solid thermite compositions that can be ignited relatively easily and that produce little or no unwanted combustion byproduct gas or other offgas during reaction.

SUMMARY

[0012] Embodiments and configurations of the present disclosure can address these and other needs.

[0013] In aspects of the present disclosure, a bonded thermite composition comprises a thermite mixture, comprising a metal in a metallic form and a metal oxide; and a glassy binding phase, comprising boron oxide other than the metal oxide.

[0014] In embodiments, the metal may be selected from the group consisting of aluminum, magnesium, silicon, manganese, an alloy of magnesium and aluminum, and combinations thereof.

[0015] In embodiments, the metal oxide may be selected from the group consisting of vanadium (V) oxide, iron (III) oxide, iron (II,III) oxide, copper (II) oxide, copper (I) oxide, tin (IV) oxide, titanium dioxide, manganese dioxide, manganese (III) oxide, chromium (III) oxide, cobalt (II) oxide, silicon dioxide, nickel (II) oxide, silver oxide, molybdenum trioxide, lead (II,IV) oxide, bismuth (III) oxide, and combinations thereof.

[0016] In embodiments, the boron oxide may comprise boron trioxide.

[0017] In embodiments, the bonded thermite composition may be substantially free of water and organic materials.

[0018] In embodiments, the bonded thermite composition may further comprise at least one fiber of an inorganic material. The inorganic material may, but need not, be selected from the group consisting of aluminum, silicon dioxide, and combinations thereof.

[0019] In embodiments, the thermite mixture may comprise from about 80% to about 120% of the stoichiometric amount of metal required for complete reaction with the metal oxide.

[0020] In embodiments, the bonded thermite composition may comprise from about 50 wt % to about 99 wt % of the thermite mixture and from about 1 wt % to about 50 wt % of the glassy binding phase.

[0021] In embodiments, the bonded thermite composition may have an equibiaxial strength of at least about 0.5 MPa.

[0022] In aspects of the present disclosure, a method for making a bonded thermite composition comprises heat-treating a mixture of a thermite and a boron oxide precursor to form molten boron oxide, wherein the thermite comprises a metal in a metallic form and a metal oxide; and cooling the mixture to solidify the molten boron oxide and form a glassy binding phase comprising boron oxide.

[0023] In embodiments, the boron oxide may comprise diboron trioxide and the boron oxide precursor may be selected from the group consisting of diboron trioxide, boric acid, and combinations thereof.

[0024] In embodiments, during the heat-treating step, the liquid boron trioxide may facilitate liquid-phase sintering of at least one of the metal and the metal oxide.

[0025] In embodiments, the method may further comprise adding a solvent to the mixture. The solvent may, but need not, be water. The method may, but need not, further comprise casting the mixture into a mold.

[0026] In embodiments, the thermite mixture may comprise from about 80% to about 120% of the stoichiometric amount of metal required for complete reaction with the metal oxide.

[0027] In embodiments, the bonded thermite composition may comprise from about 50 wt % to about 99 wt % of the thermite mixture and from about 1 wt % to about 50 wt % of the glassy binding phase.

[0028] In embodiments, the metal may be selected from the group consisting of metallic aluminum, magnesium, silicon, manganese, an alloy of magnesium and aluminum, and

[0029] In embodiments, the metal oxide may be selected from the group consisting of vanadium(V) oxide, iron(III) oxide, iron(II,III) oxide, copper(II) oxide, copper(I) oxide, tin(IV) oxide, titanium dioxide, manganese dioxide, manganese(III) oxide, chromium(III) oxide, cobalt(II) oxide, silicon dioxide, nickel(II) oxide, silver oxide, molybdenum trioxide, and combinations thereof.

[0030] In embodiments, the mixture may further comprise at least one fiber of an inorganic material. The inorganic material may, but need not, be selected from the group consisting of aluminum, silicon dioxide, and combinations thereof.

[0031] In embodiments, the bonded thermite composition may be substantially free of water and organic materials.

[0032] In embodiments, the bonded thermite composition may have an equibiaxial strength of at least about 0.5 MPa.

[0033] In embodiments, the heat-treating step may be carried out under an oxidizing or inert atmosphere.

[0034] In aspects of the present disclosure, a method for limiting production of an offgas from a thermite reaction comprises (a) providing a bonded thermite composition, comprising (i) a thermite mixture, comprising a metal in a metallic form and a metal oxide; and (ii) a glassy binding phase, comprising boron trioxide; and (b) igniting the thermite mixture.

[0035] In embodiments, the offgas may be selected from the group consisting of carbon monoxide, carbon dioxide, water, and combinations thereof and the bonded thermite composition may be substantially free of water and organic materials.

[0036] In embodiments, the metal may be selected from the group consisting of metallic aluminum, magnesium, silicon, or manganese, an alloy of magnesium and aluminum, and combinations thereof, and the thermite mixture may comprise from about 80% to about 120% of the stoichiometric amount of metal required for complete reaction with the metal oxide.

[0037] In embodiments, the bonded thermite composition may comprise from about 50 wt % to about 99 wt % of the thermite mixture and from about 1 wt % to about 50 wt % of the glassy binding phase.

[0038] In embodiments, the metal oxide may be selected from the group consisting of vanadium (V) oxide, iron (III) oxide, iron (II,III) oxide, copper (II) oxide, copper (I) oxide, tin (IV) oxide, titanium dioxide, manganese dioxide, manganese (III) oxide, chromium (III) oxide, cobalt (II) oxide, silicon dioxide, nickel (II) oxide, silver oxide, molybdenum trioxide, lead (II,IV) oxide, and bismuth (III) oxide and combinations thereof.

[0039] In embodiments, the bonded thermite composition may further comprise at least one fiber of an inorganic material. In embodiments, the bonded thermite composition may have an equibiaxial strength of at least about 0.5 MPa.

[0040] In embodiments, substantially no offgas may be produced in the igniting step.

[0041] In aspects of the present disclosure, a bonded composition comprises a metal in a metallic form; and a glassy binding phase, comprising boron oxide.

[0042] In embodiments, the metal in a metallic form may be part of a thermite mixture, and the thermite mixture may further comprise a metal oxide other than boron oxide. The metal oxide may, but need not, be selected from the group consisting of vanadium (V) oxide, iron (III) oxide, iron (II,III) oxide, copper (II) oxide, copper (I) oxide, tin (IV) oxide, titanium dioxide, manganese dioxide, manganese (III) oxide, chromium (III) oxide, cobalt (II) oxide, silicon dioxide, nickel (II) oxide, silver oxide, molybdenum trioxide, lead (II,IV) oxide, and bismuth (III) oxide, and combinations thereof. The bonded composition may, but need not, be substantially free of water and organic materials. The thermite mixture may, but need not, comprise from about 80% to about 120% of the stoichiometric amount of metal required for complete reaction with the metal oxide. The bonded composition may, but need not, comprise from about 50 wt % to about 99 wt % of the thermite mixture and from about 1 wt % to about 50 wt % of the glassy binding phase. The bonded composition may, but need not, further comprise at least one fiber of an inorganic material, which may, but need not, be selected from the group consisting of aluminum, silicon dioxide, and combinations thereof.

[0043] In embodiments, the metal may be selected from the group consisting of aluminum, magnesium, silicon, manganese, an alloy of magnesium and aluminum, and combinations thereof.

[0044] In embodiments, the boron oxide may comprise boron trioxide.

[0045] In embodiments, the bonded composition may have an equibiaxial strength of at least about 0.5 MPa.

[0046] One advantage of the compositions and methods of the present disclosure is that thermite mixtures may be shaped, cast, or molded into a physically durable form with sufficient strength to withstand rough handling and comparable physical conditions. Thermite mixture compositions made according to the methods of the prior art generally lack sufficient structural integrity to hold a desired shape, particularly if handled roughly or otherwise subjected to significant physical forces. By contrast, thermite mixture compositions of the present disclosure have a high degree of structural integrity and can be shaped, cast, or molded into a desired physical shape that can remain cohesive and withstand challenging operating conditions. Even more particularly, the shaped, cast, or molded thermite article holds its shape after shaping, casting, or molding, with minimal shrinkage, expansion, or warping.

[0047] Another advantage of the compositions and methods of the present disclosure is that thermite mixtures may be shaped, cast, or molded by known casting techniques. By way of non-limiting example, casting techniques by which the thermite compositions of the present disclosure may suitably be shaped, cast, or molded include, but are not necessarily limited to, slip or solid casting, extrusion, tape casting, pressing, injection molding, plastic forming, and additive manufacturing.

[0048] Another advantage of the compositions and methods of the present disclosure is that a substantially continuous spatial distribution of the thermite mixture throughout the entire volume of the solid form can be maintained, thus ensuring reliable propagation of ignition throughout the entire volume. This feature can be particularly advantageous in applications in which the spatial distribution of and/or propagation of ignition throughout the entirety of the thermite mixture is important and/or difficult to achieve, such as under zero gravity or microgravity conditions (e.g. in space) or when the thermite mass is likely or certain to be subjected to high acceleration forces (e.g. during launch of a spacecraft). This feature also allows those of ordinary skill in the art to design the solid thermite form in such a way as to provide for a desired spatial pattern of propagation of ignition throughout the solid form.

[0049] Another advantage of the compositions and methods of the present disclosure is that unlike other binder materials, such as propellants (e.g. gunpowder) and silicone, the boron trioxide of the binding phase of the present disclosure generates little or no combustion byproduct gas or other offgas during ignition of the thermite mixture. Particularly, unlike organic binders, boron trioxide does not react with oxygen in the surrounding atmosphere to produce carbon monoxide, carbon dioxide, water, or other undesired gaseous byproducts. The present disclosure thus allows for use of solid thermite forms in applications in which other binders are not suitable, e.g. where careful control of the composition of the atmosphere surrounding the thermite composition is required or where the excess pressure of offgas formation cannot be accommodated.

[0050] Another advantage of the compositions and methods of the present disclosure is that additives may be provided as part of the solid thermite composition that can enhance the utility of the thermite composition and/or provide other advantages and benefits. By way of non-limiting example, the structural integrity and/or other mechanical characteristics of the solid thermite form may be improved by adding fibers of inorganic material to the solid thermite composition, which may in turn offer additional advantages, such as modifying the viscosity of the reaction products remaining after ignition of the thermite mixture.

[0051] Another advantage of the compositions and methods of the present disclosure is that the binding phase does not appreciably affect the thermal output of the thermite mixture. Because boron trioxide is present in relatively small amounts relative to the thermite mixture and does not decompose to form reaction byproducts or otherwise consume energy, the full energy of the thermite reaction is available to do useful work. Indeed, even the relatively small amount of energy that goes toward melting the boron trioxide during ignition of the thermite is eventually returned to the reaction system as the reaction products cool and solidify.

[0052] These and other advantages will be apparent from the disclosure of the aspects, embodiments, and configurations contained herein.

[0053] As used herein, “at least one,” “one or more,” and “and/or” are open-ended expressions that are both conjunctive and disjunctive in operation. For example, each of the expressions “at least one of A, B and C,” “at least one of A, B, or C,” “one or more of A, B, and C,” “one or more of A, B, or C,” “A, B, and/or C,” and “A, B, or C” means A alone, B alone, C alone, A and B together, A and C together, B and C together, or A, B and C together. When each one of A, B, and C in the above expressions refers to an element, such as X, Y, and Z, or class of elements, such as X_1-X_n, Y_1-Y_m, and Z_1-Z_o, the phrase is intended to refer to a single element selected from X, Y, and Z, a combination of elements selected from the same class (e.g., X_1 and X_2) as well as a combination of elements selected from two or more classes (e.g., Y_1 and Z_o).

[0054] It is to be noted that the term “a” or “an” entity refers to one or more of that entity. As such, the terms “a” (or “an”), “one or more” and “at least one” can be used interchangeably herein. It is also to be noted that the terms “comprising,” “including,” and “having” can be used interchangeably.

[0055] The term “boron oxide” refers to any one or more of the oxides of boron, specifically boron trioxide (B_2O_3), boron monoxide (B_2O), and boron suboxide (B_6O).

[0056] The term "boron oxide precursor" refers to a boron oxide or any compound that decomposes upon heating to form boron oxide.

[0057] The term "boron trioxide precursor" refers to diboron trioxide or any compound that decomposes upon heating to form diboron trioxide. Examples of diboron trioxide precursors as that term is used herein include, but are not necessarily limited to, diboron trioxide (B_2O_3), boric acid (H_3BO_3 or $B(OH)_3$), metaboric acid (HBO_2), tetraboric acid ($H_2B_4O_7$), and other boron oxide precursors or materials including boron oxide or a precursor in its physical form (such as a frit).

[0058] The term "frit" refers to a ceramic composition that has been fused, quenched, and granulated. Frits, as that term is used herein, may (but need not) comprise materials, such as sand and fluxes, adapted to be melted in a crucible to make glass.

[0059] The term "glassy" refers to any solid phase of material having a structure that is at least partially, and often mostly or completely, amorphous. By way of non-limiting example, a "glassy" boron oxide phase means a solid phase of boron oxide in which the boron oxide has a structure that is partially, mostly, or completely amorphous.

[0060] The term "means" as used herein shall be given its broadest possible interpretation in accordance with 35 U.S.C., Section 112(f) and/or Section 112, Paragraph 6. Accordingly, a claim incorporating the term "means" shall cover all structures, materials, or acts set forth herein, and all of the equivalents thereof. Further, the structures, materials or acts and the equivalents thereof shall include all those described in the summary of the disclosure, brief description of the drawings, detailed description, abstract, and claims themselves.

[0061] The term "thermite" refers to a mixture of a fuel (such as a metal powder comprising one or more of aluminum, magnesium, titanium, zinc, silicon, and/or boron) and an oxidizer (such as a metal oxide comprising one or more of vanadium (V) oxide, iron (III) oxide, iron (**11**,**111**) oxide, copper (II) oxide, copper (I) oxide, tin (IV) oxide, titanium dioxide, manganese dioxide, manganese (III) oxide, chromium (III) oxide, cobalt (II) oxide, silicon dioxide, nickel (II) oxide, silver oxide, molybdenum trioxide, lead (II,IV) oxide, and bismuth (III) oxide. When ignited by heat, thermite undergoes an exothermic reduction-oxidation (redox) reaction.

[0062] Unless otherwise noted, all component or composition levels are in reference to the active portion of that component or composition and are exclusive of impurities, for example, residual solvents or by-products, which may be present in commercially available sources of such components or compositions.

[0063] All percentages and ratios are calculated by total composition weight, unless indicated otherwise.

[0064] It should be understood that every maximum numerical limitation given throughout this disclosure is deemed to include each and every lower numerical limitation as an alternative, as if such lower numerical limitations were expressly written herein. Every minimum numerical limitation given throughout this disclosure is deemed to include each and every higher numerical limitation as an alternative, as if such higher numerical limitations were expressly written herein. Every numerical range given throughout this disclosure is deemed to include each and every narrower numerical range that falls within such broader numerical range, as if such narrower numerical ranges were all expressly written herein. By way of example, the phrase from about 2 to about 4 includes the whole number and/or integer ranges from about 2 to about 3, from about 3 to about 4 and each possible range based on real (e.g., irrational and/or rational) numbers, such as from about 2.1 to about 4.9, from about 2.1 to about 3.4, and so on.

[0065] The preceding is a simplified summary of the disclosure to provide an understanding of some aspects of the disclosure. This summary is neither an extensive nor exhaustive overview of the disclosure and its various aspects, embodiments, and configurations. It is intended neither to identify key or critical elements of the disclosure nor to delineate the scope of the disclosure but to present selected concepts of the disclosure in a simplified form as an introduction to the more detailed description presented below. As will be appreciated, other aspects, embodiments, and configurations of the disclosure are possible utilizing, alone or in combination, one or more of the features set forth above or described in detail below.

BRIEF DESCRIPTION OF THE DRAWINGS

[0066] The accompanying drawings are incorporated into and form a part of the specification to illustrate several examples of the present disclosure. These drawings, together with the description, explain the principles of the disclosure. The drawings simply illustrate preferred and alternative examples of how the disclosure can be made and used and are not to be construed as limiting the disclosure to only the illustrated and described examples. Further features and advantages will become apparent from the following, more detailed, description of the various aspects, embodiments, and configurations of the disclosure, as illustrated by the drawings referenced below.

[0067] FIG. **1** is a photograph illustrating the reaction products left after ignition of three bonded thermite composition samples utilizing various binders.

[0068] FIG. **2** is a photograph illustrating a side-by-side comparison of a thermite slurry including commercially available boric acid as a precursor and a thermite slurry including a boron trioxide-containing frit as a precursor material.

[0069] FIGS. **3**A and **3**B are photographs illustrating an obverse aspect and a reverse aspect, respectively, of a sintered thermite composition free of any binder after equibiaxial strength testing.

[0070] FIG. **4** is a photograph illustrating an obverse aspect of a sintered thermite composition containing boron trioxide as a binder after equibiaxial strength testing.

[0071] FIG. **5** is a photograph illustrating a semi-closed crucible before firing of a pressed thermite composition free of any binder.

[0072] FIG. **6** is a photograph illustrating the semi-closed crucible of FIG. **5** after firing of the pressed thermite composition.

[0073] FIG. **7** is a photograph illustrating two crucibles, respectively having a single vent and multiple vents, for measuring offgas production from thermite reactions.

[0074] FIG. **8** is a photograph illustrating a closed crucible with a pressure gauge port for measuring offgas production from thermite reactions;

[0075] FIG. **9** is a side view of a bonded thermite composition in accordance with an embodiment of the present disclosure;

[0076] FIG. **10** is a top view of the bonded thermite composition of FIG. **9**;

[0077] FIG. **11** is an exploded view of the bonded thermite composition of FIG. **9** showing the fuel and oxidizer particulates and boron oxide binder; and

[0078] FIG. **12** is a flow chart showing a method of manufacturing the bonded thermite composition.

DETAILED DESCRIPTION

The Bonded Thermite Composition

[0079] The present disclosure provides for thermite mixtures, i.e. mixtures of a metal and a metal oxide, that are physically stabilized by cementing together particles of the metal and/or the metal oxide with diboron trioxide (B_2O_3), also known as boron trioxide, which can act not only as a binder but also as an oxidizer of the thermite fuel component (s). A boron trioxide precursor can be provided and, together with the thermite mixture, is heat-treated to form molten boron trioxide; in embodiments in which the boron trioxide precursor is not boron trioxide itself, the heat-treating first causes chemical decomposition of the boron trioxide precursor to form solid boron trioxide, which melts upon further heating to form a substantially continuous boron trioxide phase and substantially discontinuous phase of other components in the thermite composition. In some embodiments, the molten boron trioxide may facilitate liquid-phase sintering of the metal and/or the metal oxide to further strengthen the composition. Optionally, further additives may be provided as part of the composition to provide additional advantageous or beneficial features; by way of non-limiting example, one or more fibers of inorganic material may be added to the composition to provide additional physical strength to the cemented thermite composition. The solid bonded thermite composition is thus formed by cooling the mixture of the fuel component(s) and optionally other oxidizer component(s) of thermite and boron trioxide (and, optionally, one or more additives), whereupon the molten boron trioxide solidifies to form a glassy binding phase that cements the thermite mixture.

[0080] Thermite mixtures can comprise two components—a metal powder fuel component and a metal oxide oxidizer component—and in the practice of the present disclosure, any thermite formulation as known and described in the art may be combined with the boron trioxide. By way of first non-limiting example, the metal powder fuel may be selected from the group consisting of aluminum, magnesium, silicon, manganese, an alloy of magnesium and aluminum, and combinations thereof. By way of second non-limiting example, the metal oxide may be selected from the group consisting of vanadium (V) oxide, iron (III) oxide, iron (II,III) oxide, copper (II) oxide, copper (I) oxide, tin (IV) oxide, titanium dioxide, manganese dioxide, manganese (III) oxide, chromium (III) oxide, cobalt (II) oxide, silicon dioxide, nickel (II) oxide, silver oxide, molybdenum trioxide, lead (II,IV) oxide, bismuth (III) oxide, and combinations thereof. Those of ordinary skill in the art will understand how to select an appropriate thermite mixture, i.e. an appropriate metal powder fuel and an appropriate metal oxide, for a desired application; for example, it may in some embodiments be necessary or desirable for the metal powder fuel to include at least some aluminum due to aluminum's lower reactivity and sensitivity as compared to, e.g., magnesium. It is to be expressly understood that the scope of the present disclosure encompasses the use of any and all thermite mixtures in the methods and compositions described herein.

[0081] FIGS. **9-11** depict an exemplary bonded thermite composition **900** in accordance with the present disclosure. The composition **900** has been formed into a dimensionally stable cylindrical shape. While a cylindrical shape has been depicted, it is be understood that the composition may be formed into any desired shape depending on the application. FIG. **11** depicts an exploded view of the composition **900** showing the fuel component particles **904** and oxidizer component particles **908** bound together by the continuous or semi-continuous boron oxide binder **912**. While the various particles are shown as being spherical particles of uniform size, it is to be understood that the particles can be varying sizes, such as a size distribution defined by a Gaussian or normal distribution, and shapes and packing densities depending on the application.

[0082] The bonded thermite composition can vary depending on the application. In some embodiments, the fuel component of the thermite composition comprises, on a molar basis, one or more elemental metals or metalloids or alloys thereof as the primary component and boron trioxide and optionally one or more other oxidizers as a minority component. In one formulation, the thermite mixture comprises typically between about 60% and about 140%, more typically between about 65% and about 135%, more typically between about 70% and about 130%, more typically between about 75% and about 125%, more typically between about 80% and about 120%, more typically between about 85% and about 115%, more typically between about 90% and about 110%, more typically between about 95% and about 105%, and more typically about 100% of the stoichiometric amount of metal required for complete reaction with the metal oxide.

[0083] In some formulations, the boron trioxide or boron trioxide precursor is combined in relatively small quantities with the other thermite components. By way of non-limiting example, the boron trioxide precursor may be present in an amount sufficient to yield a glassy boron trioxide binding phase that makes up between about 1 wt % and about 50 wt % of the finished thermite composition. At these relatively low addition rates, the boron trioxide precursor and/or boron trioxide binding phase can provide the advantages and benefits described herein without negatively affecting the reactivity or other chemical properties of the thermite mixture.

[0084] In some formulations, the metal fuel component comprises at least some metallic or elemental aluminum. On a molar basis, the metal fuel component comprises typically at least about 12.5%, more typically at least about 25%, and even more typically at least about 37.5% but typically no more than about 87.5%, more typically no more than about 75% and even more typically no more than about 62.5% metallic or elemental aluminum, with the balance being one or more other metals, such as metallic or elemental magnesium, silicon, or manganese, an alloy of magnesium and aluminum, and combinations thereof In some formulations, the metal fuel component may be substantially free of metallic or elemental aluminum. In some formulations, substantially all of the metal fuel component may be metallic or elemental aluminum. In some formulations, the fuel component is substantially free of magnesium due to its higher reactivity (e.g., contains no more than about **2.5** wt.% magnesium).

[0085] In some formulations, the oxidizer component may consist essentially of one or more metal oxides other than boron oxide. Stated differently, the oxidizer component, on a molar basis, may be at least about 75%, at least about 80%, at least about 85%, at least about 90%, at least about 95%, or at least about 97.5% metal oxide(s) other than boron oxide. Non-limiting examples of metal oxides other than boron oxide suitable for use in these embodiments include vanadium (V) oxide, iron (III) oxide, iron (II,III) oxide, copper (II) oxide, copper (I) oxide, tin (IV) oxide, titanium dioxide, manganese dioxide, manganese (III) oxide, chromium (III) oxide, cobalt (II) oxide, silicon dioxide, nickel (II) oxide, silver oxide, molybdenum trioxide, lead (II,IV) oxide, bismuth (III) oxide, and combinations thereof.

[0086] In some formulations, the oxidizer component may comprise a combination of boron oxide and one or more metal oxides other than boron oxide. Stated differently, the oxidizer component, on a molar basis, may have a boron oxide:metal oxide(s) other than boron oxide ratio of at least about 30:70, at least about 35:65, at least about 40:60, or at least about 45:55, or alternatively no more than about 70:30, no more than about 65:35, no more than about 60:40, or no more than about 55:45, or alternatively about 50:50. Non-limiting examples of metal oxides other than boron oxide suitable for use in these embodiments include vanadium (V) oxide, iron (III) oxide, iron (II,III) oxide, copper (II) oxide, copper (I) oxide, tin (IV) oxide, titanium dioxide, manganese dioxide, manganese (III) oxide, chromium (III) oxide, cobalt (II) oxide, silicon dioxide, nickel (II) oxide, silver oxide, molybdenum trioxide, lead (II,IV) oxide, bismuth (III) oxide, and

[0087] In some formulations, the oxidizer component may be substantially free of metal oxides other than boron oxide. Stated differently, the oxidizer component, on a molar basis, may be at least about 75%, at least about 80%, at least about 85%, at least about 90%, at least about 95%, or at least about 97.5% boron oxide.

[0088] In embodiments, cemented thermite compositions according to the present disclosure may optionally include one or more additives that confer additional advantageous properties to the cemented thermite composition. Such additives may improve chemical and/or physical properties of the cemented thermite composition prior to reaction of the thermite mixture (e.g. by improving the pre-reaction structural integrity, physical strength, mechanical properties, etc. of the cemented thermite composition), during reaction of the thermite mixture (e.g. by modifying the reaction rate of the thermite mixture), and/or after reaction of the thermite mixture (e.g. by altering the viscosity of the thermite reaction products). By way of first non-limiting example, cemented thermite compositions according to the present disclosure may include at least one fiber of a metal to provide additional physical strength and structural integrity of the cemented thermite composition; in some embodiments, the metal of the fiber may, but need not, be a metal (e.g. aluminum) amenable to thermite reactions, and may thus participate in and be partially consumed during reaction of the thermite mixture to replace and/or augment the metal of the thermite mixture. By way of second non-limiting example, cemented thermite compositions according to the present disclosure may include at least one fiber of an inorganic material to provide additional physical strength and structural integrity of the cemented thermite composition and/or modify the viscosity of thermite reaction products; inorganic materials suitable for this purpose include, but are not necessarily limited to, silicon dioxide. Other species may be added to the mixture to further control its properties before, during, or after reaction, such as modifying reaction rate or the viscosity of the products.

[0089] The thermite composition of the present disclosure can be at least substantially free of water, organic material (e.g., silicon and polysiloxane and polytetrafluoroethylene), and other offgas-generating or offgassing components to reduce offgas generation. Typically, the thermite composition comprises no more than about 1 wt %, more typically no more than about 0.75 wt %, even more typically no more than about 0.5 wt %, and even more typically no more than about 0.25 wt % water and no more than about 1 wt %, more typically no more than about 0.75 wt %, even more typically no more than about 0.5 wt %, and even more typically no more than about 0.25 wt % organic (or carbon-containing) material.

[0090] In embodiments, the thermite composition, when combusted, generates little or substantially no offgas. Typically, the thermite composition, when combusted, produces no more than about 10 mmol of offgas per gram of thermite composition, no more than about 9 mmol of offgas per gram of thermite composition, no more than about 8 mmol of offgas per gram of thermite composition, no more than about 7 mmol of offgas per gram of thermite composition, no more than about 6 mmol of offgas per gram of thermite composition, no more than about 5 mmol of offgas per gram of thermite composition, no more than about 4 mmol of offgas per gram of thermite composition, no more than about 3 mmol of offgas per gram of thermite composition, no more than about 2 mmol of offgas per gram of thermite composition, or no more than about 1 mmol of offgas per gram of thermite composition.

[0091] In embodiments, the thermite composition is self-supporting and dimensionally stable and able to withstand rough handling and comparable physical conditions. Typically, the thermite composition has an equibiaxial strength testing following ASTM method C1499-09 or ring on ring testing strength of at least about 0.5 MPa, more typically of at least about 0.75 MPa, more typically of at least about 1 MPa, even more typically of at least about 1.25 MPa , even more typically of at least about 1.5 MPa, even more typically of at least about 1.75 MPa, and even more typically of at least about 2 MPa.

The Method of Manufacturing the Thermite Composition

[0092] With reference to FIG. **12**, an embodiment of manufacturing the bonded thermite composition is depicted. In step **1220**, a boron trioxide precursor **1212** is contacted and mixed with a thermite mixture **1200** comprising one or more metal fuel component(s) **1204** (typically including some metallic aluminum) and optionally one or more other metal oxide oxidizer component(s) **1208** to form a first intermediate thermite mixture. The boron oxide precursor **1212** may be provided in a pure or nearly pure form, e.g. as commercial boric acid, boron trioxide, etc., or the thermite mixture may be mixed with another material or article that includes the boron trioxide precursor in addition to other components. Particularly, the boron trioxide precursor can be provided in the form of a frit. An optional solvent **1216**, such as water, may be added to facilitate mixing of the various components.

[0093] The thermite mixture and boron trioxide precursor are thoroughly mixed (step **1220**) and then shaped, cast, molded, or pressed into a desired form, e.g. a desired shape of the finished cemented thermite composition (step **1224**). In some embodiments, the thermite mixture and boron trioxide precursor may be mixed dry, i.e. without any solvents or other liquid additives, while in other embodiments the liquid solvent **1216** may be added to facilitate thorough mixing and easier shaping; suitable solvents include, but are not necessarily limited to, water, and the quantity of solvent may be no more than about 50 wt %, no more than about 45 wt %, no more than about 40 wt %, no more than about 35 wt %, no more than about 30 wt %, no more than about 25 wt %, no more than about 20 wt %, no more than about 15 wt %, no more than about 10 wt %, or no more than about 5 wt % of the total composition. The thermite composition may be shaped, cast, molded, or pressed into the desired shape by any suitable known method, including but not limited to slip casting, extrusion, tape casting, pressing, injection molding, plastic forming, and additive manufacturing.

[0094] Once the thermite composition has been shaped, cast, molded, or pressed into the desired form, it is optionally dried (e.g. to remove at least a portion of the solvent, if provided) (step **1228**) and is then heated (step **1232**). Most commonly, the thermite composition is heated in a furnace, kiln, or similar device, but it is to be expressly understood that any heating means or mechanism may be used to heat the thermite composition within the scope of the present disclosure. Likewise, while the heating of the thermite composition is most commonly carried out under air, the scope of the present disclosure also includes embodiments in which the thermite composition is heated under a controlled atmosphere other than air, as known and described in the art. In embodiments, the atmosphere under which the thermite composition is heated may be an oxidizing atmosphere (e.g. air), an inert atmosphere (e.g. argon), or a reducing atmosphere (e.g. hydrogen). In many embodiments, it may be desirable to provide an oxidizing atmosphere, as under these atmospheres any organic materials present in the thermite composition may be burned off during heating, but it is to be expressly understood that the heating may suitably be carried out under reducing atmospheres as well. More particularly, it may be desirable to provide a relatively dry atmosphere for heating the thermite composition, such as an atmosphere in which the partial pressure of water is less than about 75% of the saturation pressure, less than about 50% of the saturation pressure, less than about 25% of the saturation pressure, less than about 20% of the saturation pressure, less than about 15% of the saturation pressure, less than about 10% of the saturation pressure, less than about 5% of the saturation pressure, less than about 4% of the saturation pressure, less than about 3% of the saturation pressure, less than about 2% of the saturation pressure, or less than about 1% of the saturation pressure.

[0095] In some embodiments in which the boron trioxide precursor is provided as part of a material or article containing other components, the heating of the material or article can cause melting of one or more of the other components, e.g. a carrier species, thereby allowing the boron trioxide to dissociate from the material or article and disperse throughout the thermite mixture. The carrier species and/or other components of the material or article may, but need not always, be removed from the thermite composition subsequent to heating.

[0096] In embodiments in which the boron trioxide precursor is not boron trioxide itself, the heating of the thermite composition causes the boron trioxide precursor to decompose to boron trioxide. Generally, such decomposition occurs at a lower temperature than the melting point of boron trioxide; by way of non-limiting example, boric acid decomposes to boron trioxide at a temperature of between about 300 ° C. and about 330 ° C.

[0097] Regardless of which boron trioxide precursor is used, the thermite composition is generally heated to a temperature sufficient to cause at least a substantial fraction of the boron trioxide to melt, i.e. typically between about 450 ° C. and about 510 ° C., to ensure that the molten boron trioxide phase is distributed substantially uniformly throughout the thermite mixture. In some embodiments, however, the thermite composition may be heated to a somewhat lower temperature that results in incomplete melting, or merely softening, of the boron trioxide; in these embodiments, a pressure or force may be applied to the boron trioxide phase to cause physical deformation of the softened or partially melted boron trioxide, thereby achieving a more uniform spatial distribution of the boron trioxide phase throughout the thermite mixture.

[0098] In embodiments, the thermite composition may be heated under a fluid pressure that is less than, about equal to, or greater than atmospheric pressure. By way of first non-limiting example, the thermite composition may be heated under a fluid pressure of no more than about 75 kPa, no more than about 50 kPa, or no more than about 25 kPa. By way of second non-limiting example, the thermite composition may be heated under a fluid pressure of at least about 125 kPa, at least about 150 kPa, or at least about 175 kPa. It may in some embodiments be desirable to provide a 30 sub- or superatmospheric pressure to achieve a desired chemical or physical characteristic of the thermite composition; by way of non-limiting example, a pressure below or above atmospheric pressure may favor the evaporation or other removal of water, organic materials, impurities, or other undesired components from the thermite composition.

[0099] In embodiments, the thermite composition may be heated under an applied mechanical pressure, e.g. a sintering pressure. Typically, the mechanical pressure may be applied by an industrial press having a force rating of at least about 10 tons, at least about 20 tons, at least about 30 tons, at least about 40 tons, at least about 50 tons, at least about 60 tons, at least about 70 tons, at least about 80 tons, at least about 90 tons, or at least about 100 tons, or alternatively no more than about 100 tons, no more than about 90 tons, no more than about 80 tons, no more than about 70 tons, no more than about 60 tons, no more than about 50 tons, no more than about 40 tons, no more than about 30 tons, no more than about 20 tons, or no more than about 10 tons.

[0100] Finally, the thermite composition is cooled (step **1236**) to allow the boron trioxide to solidify into a glassy binding phase to form the bonded thermite composition **1240**. The glassy boron trioxide binding phase physically binds, or cements, the thermite mixture into the desired solid form and ensures a desired spatial distribution of the thermite mixture throughout a cohesive solid mass. The boron oxide and other oxidizers are typically combined with the metal fuel components before heating for optimal results and for ease of manufacturing. In particular, melting of the metal fuel before contact with the oxidizer(s) can complicate manufacturing.

[0101] The metal fuel component **1204** (such as aluminum) may be added in the form of fibers to physically strengthen the thermite prior to reaction; such metal fibers may replace all or part of the metal fuel needed in the base thermite mixture.

Experimental

[0102] The following examples are provided to illustrate certain aspects, embodiments, and configurations of the disclosure and are not to be construed as limitations on the disclosure, as set forth in the appended claims. All parts and percentages are by weight unless otherwise specified.

EXAMPLE 1:

Comparison of Binding Materials

[0103] This Example demonstrates the effect of various binding materials on the performance of cemented thermite compositions.

[0104] Samples of bonded thermite compositions were prepared, using aluminum as the metal powder fuel of the thermite mixture and plaster of Paris as the binder. In addition, two samples of solid-form thermite composition were prepared according to the methods disclosed in Schroeder (i.e. using silicone as the binder), except that, where Schroeder discloses the use of thermite mixtures in which the metal fuel is magnesium, aluminum was used as the metal fuel, as in the other samples prepared and tested according to this Example. This modification to the disclosure of Schroeder was made to assess the suitability of silicone binders to make solid-form thermite compositions in which the metal fuel is a metal other than magnesium; Schroeder does not disclose any such embodiments, but magnesium is too reactive and/or sensitive for use as the metal fuel in many applications, and thus a binder that is effective to bind a wide variety of thermite mixtures is desirable.

[0105] After preparation of the three thermite compositions samples, the samples were placed in a metal bed on level ground and heat was applied to attempt to ignite each sample. The products remaining after attempted ignition were then visually inspected.

[0106] Referring now to FIG. **1**, the remnants of the three thermite composition samples after attempted ignition are illustrated. As illustrated in FIG. **1**, the sample **1***a* including plaster of Paris was successfully ignited and exhibited substantially complete reaction; the reaction products are visually similar to an iron-containing slag, as is typical of thermite mixtures allowed to completely react. However, the two samples **1***b*, **1***c* comprising the silicone binder of Schroeder failed to ignite despite multiple attempts; as illustrated in FIG. **1**, these samples are substantially unreacted, and the only visible change to the samples after attempted ignition is a scorched white surface as a result of exposure of superficial layers of the sample to the heat source.

[0107] Without wishing to be bound by any particular theory, the present inventor hypothesizes that silicone binders as disclosed by Schroeder negatively affect the reactivity and/or sensitivity of metal fuels in thermite mixtures, and thus that such binders are unsuitable, or less suitable, for use in solid-form thermite compositions in which the metal fuel is less reactive and/or sensitive than magnesium. Additionally, even if solid-form thermite compositions comprising a less reactive and/or sensitive metal fuel (e.g. aluminum) and a silicone binder could be successfully ignited, silicone, being an organic material, would have the potential to react with oxygen present in the thermite's oxidizer component to yield additional offgases such as carbon dioxide. Such offgas production makes the compositions of Schroeder unsuitable or undesirable for many applications.

EXAMPLE 2:

Comparison of Boron Trioxide Precursors

[0108] This Example demonstrates the effect of the use of certain types of frit, as opposed to a substantially pure form, as the source of boron trioxide precursor in cemented thermite compositions.

[0109] Two samples of a thermite slurry composition were prepared according to the methods disclosed herein, using aluminum as the metal powder fuel of the thermite mixture and vanadium(V) oxide as the metal oxide (i.e. oxidizer) of the thermite mixture. In the first thermite slurry sample, the boron trioxide precursor was provided in the form of an off-the-shelf ceramic frit comprising boron trioxide in addition to other components. In the second thermite slurry sample, the boron trioxide precursor was provided in the form of commercially available boric acid. The thermite mixtures and boron trioxide precursors of both samples were mixed with an amount of water sufficient to homogenize the samples and provide an appropriate texture, consistency, viscosity, etc. of the slurry. Thus, the two slurry samples contained identical metal fuel, metal oxide/oxidizer, and solvent; the only difference between the two slurries was the source and composition of the boron trioxide precursor.

[0110] After preparation of the two thermite slurry samples, the samples were placed in weigh boats and wiped once with a paper towel to remove at least a portion of water-soluble slurry components. The remaining slurries and water-soluble wipe products were then visually inspected.

[0111] Referring now to FIG. **2**, the remnants of the two thermite slurry samples are illustrated. As illustrated in FIG. **2**, the slurry samples have markedly different physical appearances. The slurry sample comprising commercially available boric acid as the boron trioxide precursor (on the left in both weigh boats, with the wipe specimen on the lefthand paper towel) is characterized by a yellow-ochre color and little or no removal of water-soluble compounds by wiping with a paper towel. This result is broadly consistent with many other thermite slurries prepared according to the methods disclosed herein. The slurry sample comprising an off-the-shelf frit as the boron trioxide precursor material (on the right in both weigh boats, with the wipe specimen on the righthand paper towel), by contrast, is characterized by a dark green color and significant residue removed by wiping with a paper towel, i.e. a significant quantity of water-soluble compounds.

[0112] Without wishing to be bound by any particular theory, the present inventor hypothesizes that the results illustrated in FIG. **2** are the result of an undesirable change in the chemistry of the thermite slurry caused by chemically reactive species present in the frit material. Particularly, it is believed that a chemically reactive species in the frit material induced a reduction reaction in the vanadium(V) oxide and caused a change in the oxidation state of the vanadium from vanadium(V) (V^{+5}) to vanadium(III) (V^{+3}), and thus a decomposition from vanadium(V) oxide (vanadium pentoxide, V_2O_5) to vanadium(III) oxide (vanadium trioxide, V_2O_3) and other vanadium(III) species. The observed results are consistent with the hypothesized change in oxidation state—while vanadium(V) oxide is a brown/yellow solid (consistent with the color of the slurry in which commercially available boric acid was used), vanadium(III) is known to form a metal aquo complex in aqueous solution ($[V(H_2O)_6]^{+3}$) characterized by a green color. By reducing the oxidation state of the vanadium, the frit used in the dark green slurry illustrated in FIG. **2** has degraded the oxidative capability of the vanadium oxidizer and thus significantly decreased, or even destroyed, the reactivity of the thermite mixture.

[0113] It is to be expressly understood that the result illustrated in FIG. **2** should not be interpreted as a teaching that frits in general are unsuitable for use as boron trioxide precursors in the practice of the present disclosure. Indeed, in many embodiments, frits may represent an inexpensive, readily available, or otherwise desirable boron trioxide precursor, and may have the same performance as a substantially pure form of the boron trioxide precursor (or may even incorporate additional substances, such as aluminum or silicon dioxide, that can improve certain properties of the cemented thermite composition); likewise, the frit incorporated into the dark green slurry illustrated in FIG. **2** may have been usable to no ill effect in conjunction with a different thermite oxidizer component. Instead, the result of this Example illustrates merely that those of ordinary skill in the art should take care to ensure that frits used as boron trioxide precursors do not contain species that may induce undesirable chemical reactions in the thermite mixture, particularly reduction reactions in the oxidizer of the thermite mixture.

EXAMPLE 3:

Strength Improvement Resulting from Incorporation of Boron Trioxide

[0114] This Example demonstrates the improvement in mechanical properties, and specifically in physical strength, achieved by inclusion of a boron trioxide binding phase in bonded thermite compositions.

[0115] Two sample thermite compositions were prepared according to the methods disclosed herein. The first of these two samples (hereinafter "Sample B") did not include a boron trioxide binding phase, while the second of the samples (hereinafter "Sample G") incorporated 5 wt % boron trioxide into the pre-kilning slurry; the two samples were otherwise identical. The samples were cast in molds having a nominal diameter of 40 mm and then sintered in a kiln according to identical kilning profiles. Each of the resulting cemented thermite compositions took the form of a disk of material having a yellow color.

[0116] Both thermite compositions were then subjected to equibiaxial strength testing according to ASTM method C1499-09, colloquially known as "ring on ring" testing. Sample B was found to have an equibiaxial strength of 0.220 MPa, while Sample G was found to have an equibiaxial strength of 1.38 MPa, approximately 6.3 times as strong as Sample B. The two samples were then visually inspected to determine the nature of the fracture and of the material of each sample.

[0117] Referring now to FIG. **3**A, the obverse aspect of Sample B is illustrated. As illustrated in FIG. **3**A, the obverse aspect of Sample B includes two faintly visible fracture lines (indicated by arrows). A first approximately horizontal fracture line sweeps across a bottom portion of the thermite composition disk, while a second approximately vertical fracture line runs approximately along a vertical diameter of the disk, nearly at a right angle relative to the horizontal fracture line.

[0118] The fracture pattern illustrated in FIG. **3**A is consistent with a low-strength sample; the orientation and small number of the fracture lines is recognizable as a low-energy/low-strength failure pattern.

[0119] Referring now to FIG. **3**B, the reverse aspect of Sample B is illustrated. As illustrated in FIG. **3**B, the reverse aspect of Sample B includes a single faintly visible fracture line (indicated by arrows). The fracture line present on the reverse aspect of Sample B is recognizable as a continuation of the approximately vertical fracture line illustrated in FIG. **3**A. The orientation and small number of fracture lines on the reverse aspect is likewise consistent with a low-energy/low-strength failure and thus a low-strength sample of material.

[0120] Referring now to FIG. **4**, the obverse aspect of Sample G is illustrated. As illustrated in FIG. **4**, the obverse aspect of Sample G includes several plainly visible fracture lines, oriented in several non-orthogonal directions across the obverse face of Sample G. This fracture pattern is consistent with a medium-strength/medium-energy failure, and thus with a medium-strength sample of material.

[0121] A comparison of FIGS. **3**A, **3**B, and **4** illustrates that, as assessed by both quantitative measurement of equibiaxial strength and qualitative characterization of fracture pattern, thermite compositions enhanced with a boron trioxide binding phase have significantly greater physical strength than a sintered thermite composition without a boron trioxide binding phase. The cemented thermite compositions of the present disclosure are thus capable of withstanding significantly more challenging operating conditions, including but not limited to rough handling and/or significant acceleration forces, than the thermite compositions of the prior art.

EXAMPLE 4:

Pressure Testing into Evince Low Offgas Production from Cemented Thermite

[0122] This Example demonstrates the advantageously low offgas production rate during reaction achieved by inclusion of a boron trioxide binding phase in cemented thermite compositions.

[0123] In many embodiments, it is advantageous or necessary for thermite reactions to be carried out in an entirely closed crucible, i.e. a reaction vessel having little or no ability to vent gases to relieve pressure within the reaction chamber. This is particularly true of embodiments in which the thermite reaction is adapted to be carried out in an aeronautical or astronautical environment, e.g. aboard an aircraft or spacecraft; fluid pressures and gas environment compositions in such applications must generally be tightly controlled, and the ability to vent offgases of thermite combustion in these applications is frequently limited or nonexistent. It is thus crucial to provide thermite compositions that can be reacted with little or no production of offgases, particularly combustion byproduct gases such as carbon dioxide.

[0124] Referring now to FIG. **5**, a semi-closed crucible **50** for thermite reaction is illustrated. The semi-closed crucible **50** of FIG. **5** was manufactured by fitting a 6" length of steel pipe with steel endcaps **51***a,b*. A 0.125" diameter hole was drilled into each end cap **51**, and the crucible was loaded with a pressed (but not cemented, i.e. with no binding phase present) thermite composition comprising iron oxide as the oxidizer; the use of a pressed but not cemented thermite composition ensured that no water was present in the thermite composition, as the presence of water can contribute to the production of offgases. Five of the six vent holes were plugged with dowels **52** that could be ejected in case of substantial pressure buildup within the reaction chamber; the sixth vent hole was used to insert an igniter **53** (in the form of a sparkler wand) into the reaction chamber.

[0125] Referring now to FIG. **6**, the semi-closed crucible **50** of FIG. **5** is illustrated after reaction of the thermite composition contained within the reaction chamber. As illustrated in FIG. **6**, three of the five dowel plugs **52** have been fully ejected from the endcaps **51** of the crucible, and a fourth has been partially expelled, but one has remained fully in place, and the igniter **53** has likewise remained in place within the vent hole. The fact that not all of the dowel plugs **52** and igniter **53** have been ejected from the vent holes of the crucible **50** indicates that pressure buildup inside the crucible **50**, i.e. generation of offgases during the thermite reaction, has not been extreme.

[0126] Referring now to FIG. **7**, a mostly closed crucible **70** and the semi-closed crucible **50** illustrated in FIGS. **5** and **6** are illustrated. The mostly closed crucible **70** was manufactured by a method similar to that used to manufacture the semi-closed crucible **50**, except that the length of the reaction chamber was shortened to **2**" and the number of vent holes **54** was reduced to one per endcap **51**.

[0127] Referring now to FIG. **8**, a fully closed crucible **80** is illustrated. The fully closed crucible **80** was manufactured by a method similar to that used to manufacture the semi-closed crucible **50** illustrated in FIGS. **5-7**, except that in place of the three vent holes **54** in each end cap **51** of the semi-closed crucible **50**, only three holes total were bored into endcaps **51***a,b* of the fully closed crucible **80**, each of which was fitted with a device—as illustrated in FIG. **8**, an igniter **53** in the single hole of endcap **51***a* and a burst cap **81** and a pressure gauge **82** in the two holes of endcap **51***b*—to ensure airtightness of the reaction chamber. This configuration ensured that all offgases generated by the thermite reaction would remain within the reaction chamber and that only in an extreme case (i.e. sufficient excess pressure to cause the burst cap to rupture) would the crucible **80** become less than fully closed.

[0128] Into all three crucibles illustrated in FIGS. **5-8**, a cemented thermite composition, comprising vanadium(V) oxide as the oxidizer and a boron trioxide binding phase, was placed into the reaction chamber and ignited. The thermite reaction proceeded to completion in each crucible, with no apparent physical manifestation of excessive pressure within any crucible. Pressure within the fully closed crucible **80** illustrated in FIG. **8** was measured by the pressure gauge **82** as **40** psi several seconds after firing, indicating little pressure rise and therefore minimal formation of offgases due to thermite reaction.

[0129] In certain applications, e.g. thermal gas generators used aboard aircraft and/or spacecraft, a number of stringent operating parameters must be achieved. By way of first non-limiting example, the thermite reaction must reliably go to completion, without leaving unreacted thermite or other reactants in the reaction chamber. By way of second non-limiting example, the thermite reaction must be safely contained, i.e. without allowing hot or toxic reactants or reaction products to escape the reaction chamber. By way of third non-limiting example, the thermite reaction cannot create thrust or a motive force that may cause a reaction vessel or surrounding items to move; in particular, the production of significant quantities of offgas must be avoided, as in these applications the release of offgas from a thermite reaction (causing either a catastrophic uncontained failure due to rupture of a sealed crucible, or unwanted thrust forcing an aircraft or spacecraft off-course in the case of a semi-contained failure) would be disastrous.

[0130] The embodiments of use of a cemented thermite composition described in Example **4** avoid this danger and achieve the safety advantages needed for these and other sensitive operating conditions. Particularly, the data indicate that total pressure inside the reaction chamber of the crucible generally peaks in a range of between about 100 psi and about 200 psi. The testing data of Example 4 also indicate that this increase in pressure is due at least in part, and probably substantially, to the heating of residual gas within the crucible rather than the formation of new offgases; this can be inferred from the fact that pressure within the crucible decreases toward the pre-reaction pressure as the gases within the reaction chamber cool. Pressures in the range of 100 to 200 psi are well within the containment abilities of standard crucibles, and thus the present disclosure represents an improvement over prior thermite reaction methods that result in offgas production that drive the total pressure above **200** psi; such pressures are much more difficult to safely contain and would require a much heavier (and for many aeronautical and astronautical applications, prohibitively heavy) crucible.

[0131] A number of variations and modifications of the disclosure can be used. It would be possible to provide for some features of the disclosure without providing others.

[0132] The present disclosure, in various aspects, embodiments, and configurations, includes components, methods, processes, systems and/or apparatus substantially as depicted and described herein, including various aspects, embodiments, configurations, sub-combinations, and subsets thereof. Those of skill in the art will understand how to make and use the various aspects, aspects, embodiments, and configurations, after understanding the present disclosure. The present disclosure, in various aspects, embodiments, and configurations, includes providing devices and processes in the absence of items not depicted and/or described herein or in various aspects, embodiments, and configurations hereof, including in the absence of such items as may have been used in previous devices or processes, e.g., for improving performance, achieving ease and/or reducing cost of implementation.

[0133] The foregoing discussion of the disclosure has been presented for purposes of illustration and description. The foregoing is not intended to limit the disclosure to the form or forms disclosed herein. In the foregoing Detailed Description for example, various features of the disclosure are grouped together in one or more, aspects, embodiments, and configurations for the purpose of streamlining the disclosure. The features of the aspects, embodiments, and configurations of the disclosure may be combined in alternate aspects, embodiments, and configurations other than those discussed above. This method of disclosure is not to be interpreted as reflecting an intention that the claimed disclosure requires more features than are expressly recited in each claim. Rather, as the following claims reflect, inventive aspects lie in less than all features of a single foregoing disclosed aspect, embodiment, or configuration. Thus, the following claims are hereby incorporated into this Detailed Description, with each claim standing on its own as a separate preferred embodiment of the disclosure.

[0134] Moreover, though the description of the disclosure has included description of one or more aspects, embodiments, or configurations and certain variations and modifications, other variations, combinations, and modifications are within the scope of the disclosure, e.g., as may be within the skill and knowledge of those in the art, after understanding the present disclosure. It is intended to obtain rights which include alternative aspects, embodiments, and configurations to the extent permitted, including alternate, interchangeable and/or equivalent structures, functions, ranges or steps to those claimed, whether or not such alternate, interchangeable and/or equivalent structures, functions, ranges or steps are disclosed herein, and without intending to publicly dedicate any patentable subject matter.

1. A method for making a bonded thermite composition, comprising:

heat-treating a mixture of a thermite and a boron oxide precursor to form molten boron oxide, wherein the thermite comprises a fuel component and an oxidizer component; and

cooling the mixture to solidify the molten boron oxide and form a glassy binding phase comprising boron oxide.

2. The method of claim **1**, wherein the boron oxide comprises diboron trioxide and wherein the boron oxide precursor is selected from the group consisting of diboron trioxide, boric acid, and combinations thereof.

3. The method of claim **1**, wherein, during the heat-treating step, the liquid boron trioxide facilitates liquid-phase sintering of at least one of the fuel component and the oxidizer component.

4. The method of claim **1**, further comprising adding a solvent to the mixture.

5. The method of claim **4**, wherein the solvent is water.

6. The method of claim **4**, further comprising casting the mixture into a mold.

7. The method of claim **1**, wherein the thermite mixture comprises from about 80% to about 120% of the stoichiometric amount of the fuel component required for complete reaction with the oxidizer component.

8. The method of claim **1**, wherein the bonded thermite composition comprises from about 50 wt % to about 99 wt % of the thermite mixture and from about 1 wt % to about 50 wt % of the glassy binding phase.

9. The method of claim **1**, wherein the fuel component is selected from the group consisting of metallic aluminum, magnesium, silicon, manganese, an alloy of magnesium and aluminum, and combinations thereof.

10. The method of claim **1**, wherein the oxidizer component is selected from the group consisting of vanadium(V) oxide, iron(III) oxide, iron(II,III) oxide, copper(II) oxide, copper(I) oxide, tin(IV) oxide, titanium dioxide, diboron trioxide, manganese dioxide, manganese(III) oxide, chromium(III) oxide, cobalt(II) oxide, silicon dioxide, nickel(II) oxide, silver oxide, molybdenum trioxide, and combinations thereof.

11. The method of claim **1**, wherein the mixture further comprises at least one fiber of an inorganic material.

12. The method of claim **11**, wherein the inorganic material is selected from the group consisting of aluminum, silicon dioxide, and combinations thereof.

13. The method of claim **1**, wherein the bonded thermite composition is substantially free of water and organic materials.

14. The method of claim **1**, wherein the heat-treating step is carried out under an oxidizing or inert atmosphere.

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