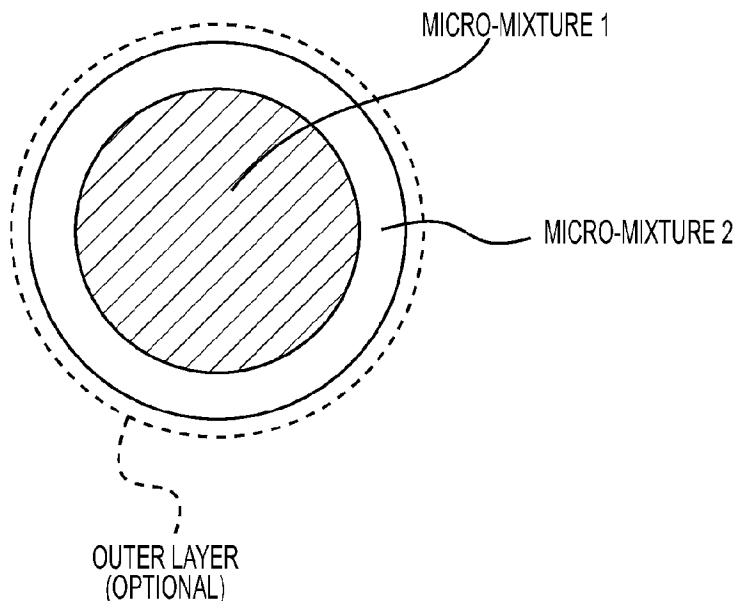




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(54) Title: ELECTRICALLY INSULATING MATERIAL FOR THERMAL SPRAYED COATINGS



(57) **Abrégé/Abstract:**

Compositions and method for preparing thermally sprayed coatings are disclosed. The inventive compositions include at least one component that is electrically-insulating and/or non-subliming at thermal spray temperatures; and at least one component that has a high coefficient of thermal expansion. The invention also provides a compositions and methods for preparing a coating comprising a spinel, from materials that do not comprise a spinel; and also provides non-spinel materials used to prepare coatings comprising spinel. The invention includes coatings made from the materials and methods; and articles comprising the coatings.

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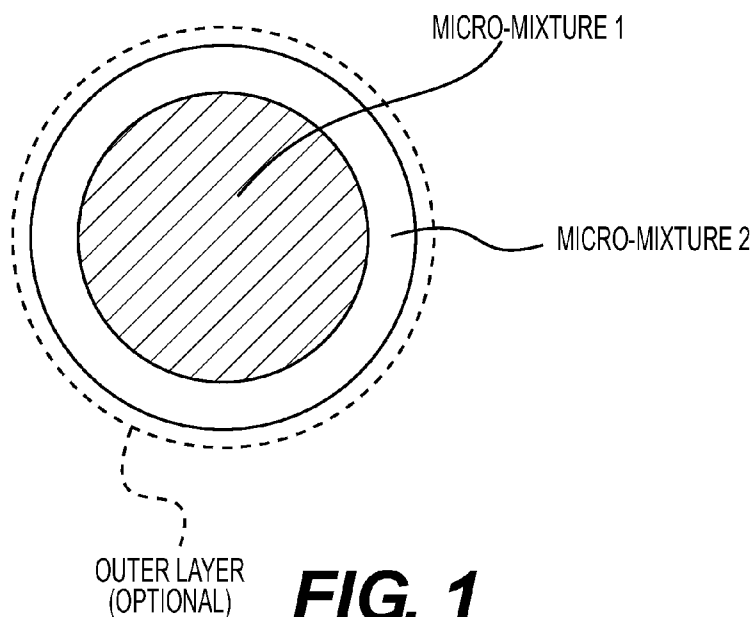
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(54) Title: ELECTRICALLY INSULATING MATERIAL FOR THERMAL SPRAYED COATINGS

**FIG. 1**

(57) Abstract: Compositions and method for preparing thermally sprayed coatings are disclosed. The inventive compositions include at least one component that is electrically-insulating and/or non-subliming at thermal spray temperatures; and at least one component that has a high coefficient of thermal expansion. The invention also provides a compositions and methods for preparing a coating comprising a spinel, from materials that do not comprise a spinel; and also provides non-spinel materials used to prepare coatings comprising spinel. The invention includes coatings made from the materials and methods; and articles comprising the coatings.

ELECTRICALLY INSULATING MATERIAL FOR THERMAL SPRAYED COATINGS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. provisional application 61/766,960, filed February 20, 2013.

BACKGROUND OF THE INVENTION

[0002] Many engineering applications require an insulating layer to be coated on a metallic body to provide certain functionality, for example, protection against chemical, mechanical, thermal or electrical influences. Most insulating materials in use today are ceramics. However, often due to the difference in the coefficients of thermal expansion between the ceramic coating and the underlying metallic body, high mechanical stresses are generated in the ceramic coating under thermal loads. These stresses readily lead to cracking and/or delamination of the coating. Therefore, a insulating material which has a coefficient of thermal expansion similar to that of the metallic material to be coated is desirable.

[0003] Metals generally have a coefficient of thermal expansion which is greater than 10 $\mu\text{m}/\text{m}/\text{K}$, therefore only a few oxides may be used for coating purposes. Stabilized zirconium oxide, for example, with coefficient of thermal expansion in the region of 11 $\mu\text{m}/\text{m}/\text{K}$ is used in turbo-machinery components as a thermal barrier coating and in electrical devices such as solid oxide fuel cells as an ionic conductor (electrolyte) at high temperature. However, the resistance of zirconium oxide to attack from metallic or oxide melts is lower than that of a number of other materials [Ref US patent 6,723,442; 6,764,771]. Zirconium oxide also loses its electrical insulating properties at high temperature where ionic conduction predominates.

[0004] For application of the coating by thermal spray process, the insulating material additionally needs to have suitable properties to withstand the process conditions and form coatings with desired functionality. For example, MgO has a high melting point, sufficient resistance to melts, high electrical insulation and a coefficient of thermal expansion of 13.5 $\mu\text{m}/\text{m}/\text{K}$. This implies that MgO is also a suitable coating material for metals. However, MgO is not a suitable material for use in a thermal spraying process, since MgO decomposes at high temperatures which occur in such processes, and the decomposition products are volatile.

[0005] Ceramics which are produced from a mixture of MgO and Al₂O₃ have good properties for use in combination with various metals. Sintered ceramics produced from MgO and Al₂O₃ are commercially available. They have the advantages of being highly resistant to chemical, thermal and mechanical attacks and of having a coefficient of thermal expansion which lies in the region of 11 µm/m/K. However, ceramics of this type have only limited suitability as coating material, since in practice they are not suitable for coating by way of a thermal spraying method. In these ceramics too, the MgO of the ceramic evaporates at the high temperatures which occur during thermal spraying.

[0006] US patent 6,723,442 describes a material based on the combination of MgAl₂O₄ spinel and MgO, a method of its production, a coating (or layer) produced from the material applied on a metallic body and the use of such coated metallic body as a component in a high temperature fuel cell. The material is described as comprising grains of MgO which are embedded in a matrix of the spinel MgAl₂O₄.

[0007] US patent 6,764,771 describes a (metallic) turbine blade coated with a thermal barrier coating which is based on an admixture of a spinel material selected from a group of CoMg₂O₄, CoFe₂O₄, CoCr₂O₄, CoTi₂O₄, CoAl₂O₄, NiMg₂O₄, NiTi₂O₄, TiMg₂O₄, TiFe₂O₄, TiCr₂O₄, and TiAl₂O₄, and oxide material selected from a group of MgO, HfO₂, CoO, NiO, and Cr₂O₃ and/or combinations thereof.

[0008] US patent application publication US2011/0033779 (Feb. 10, 2011) describes a several material compositions and combinations for use as insulation in solid oxide fuel cell (SOFC) systems.

[0009] There remains a need for materials and methods to deposit thermal spray coatings comprising, e.g., magnesium oxide and a spinel, preferably MgAl₂O₄.

SUMMARY OF THE INVENTION

[00010] It has surprisingly been found that it is possible to prepare a material to be used to provide temperature resistant, electrically insulating coatings with a coefficient of thermal

expansion tunable to match that of the coated metallic material using thermal spray process. It has also been surprisingly found that it is possible to prepare a coating on a substrate, the coating comprising a spinel, from starting materials that do not comprise a spinel.

[00011] In a preferred embodiment, the non-spinel starting materials are thermally deposited onto a substrate. In a preferred embodiment, the starting material is injected into a hot zone where it is heated and/or melted and is then propelled toward a surface for deposition thereon. The heating may be accomplished by any suitable method and equipment, e.g., with use of high temperature (such as a flame, fuel burning, or an electric arc). Without being bound by theory, it is believed that the non-spinel compounds react on the way to the surface, thereby forming a spinel in transit to the surface. It is also possible that the spinel does not form until the ejected material deposits on the surface.

[00012] The present invention provides a material comprising a core portion comprising a first mixture, and an encasing portion comprising a second mixture, the first mixture being rich in a high-CTE material (component B1) and poor in a non-sublimating electrical insulator (component A1); the second mixture being rich in a non-sublimating electrical insulator (component A2) and poor in a high-CTE material (component B2); and wherein at least one of components A1 and B1 has average particle size up to about 100 microns; and at least one of components A2 and B2 has average particle size up to about 20 microns; wherein the encasing portion at least partially encases the core portion.

[00013] The present invention also provides a thermal spray coating prepared by thermally spraying the material onto a substrate.

[00014] The present invention also provides a method of manufacturing a thermal spray coating comprising: obtaining the material; obtaining a substrate; and forming a coating on the substrate by applying the material to the substrate by a thermal spray process.

[00015] Components A1 and A2 are preferably independently chosen from one or both of a) one or more oxide of trivalent or tetravalent metals, or b) one or more salt with binding properties. Preferably, components A1 and A2 are independently chosen from one or more of oxide of Al, In, Ga, Y, Sc, Mg, Si, Ti, Ge, Zr, Hf, Sn, Nb, Mn, or a rare earth metal. Preferably, components A1 and/or A2 comprise Al_2O_3 .

[00016] Components B1 and B2 preferably have coefficients of thermal expansion at least about $10 \mu\text{m/m/K}$. Components B1 and B2 are preferably independently chosen from one or more of a simple oxide, a double oxide, a triple oxide, an alkali metal halide, an alkaline metal

halide, or a metal. Preferably, components B1 and/or B2 comprise, consist essentially of, or consist of, MgO.

[00017] Preferably, the material comprises a plurality of cores. Preferably, the cores comprise particles that are at least one of monolithic or an agglomerate of smaller particles. Preferably, the material comprises a plurality of agglomerated encased cores. Preferably, the core or plurality of cores further comprise an outer layer that is non-electrically conducting and non-sublimating. Preferably, the outer layer comprises one or both of a) one or more oxides of trivalent or tetravalent metals, or b) one or more salt with binding properties.

[00018] Preferably, the material comprises essentially no spinel. Preferably, the material further comprises a binder. Preferably, the material further comprises a dispersant.

[00019] Preferably, a thermal spray coating comprises one or more spinel. Preferably, the substrate of the thermal spray coating comprises iron, steel, aluminum, copper, Fe-Cr alloy, Cr-rich steel, cobalt, Co-alloy, nickel, Ni-alloy, bronze, or titanium.

[00020] Preferably, the thermal spray coating comprises a spinel. Preferably, the material does not comprise spinel, and the thermal spray coating comprises a spinel. Preferably, the material comprises Al₂O₃, and the thermal spray coating does not comprise Al₂O₃.

[00020a] In one aspect, the present invention provides a material comprising a core portion comprising a first mixture, and an encasing portion comprising a second mixture, the first mixture comprising at least 50 mol% but less than 100 mol% from one or more of a simple oxide, a double oxide, a triple oxide, an alkali metal halide, an alkaline metal halide, or a metal (component B1) and less than 50 mol% but more than 0 mol% of a non-sublimating electrical insulator independently chosen from one or both of a) one or more oxide of trivalent or tetravalent metals, or b) one or more salt with binding properties (component A1); the second mixture comprising at least 50 mol% but less than 100 mol% of a non-sublimating electrical insulator independently chosen from one or both of a) one or more oxide of trivalent or tetravalent metals, or b) one or more salt with binding properties (component A2) and less than 50 mol% but more than 0 mol% from one or more of a simple oxide, a double oxide, a triple oxide, an alkali metal halide, an alkaline metal halide, or a metal (component B2); wherein at least one of component A1 and component B1 has average particle size up to about 100 microns; and at least one of component A2 and component B2 has average particle size up to about 20 microns; wherein the encasing portion at least partially encases the core portion; and

wherein component B1 and component B2 have a coefficient of thermal expansion of at least $10 \mu\text{m/m/K}$ and the material is free from a spinel and forms a spinel under thermal spray conditions.

[00020b] In another aspect, the present invention provides a method of manufacturing a thermal spray coating comprising: providing a material as described herein; providing a substrate; and forming a coating on the substrate by applying the material to the substrate by a thermal spray process.

BRIEF DESCRIPTION OF THE DRAWINGS

[00021] Figure 1 is a schematic drawing illustrating a powder particle structure according to the current invention.

[00022] Figure 2 is a schematic drawing illustrating a powder particle structure according to the current invention.

[00023] Figure 3 is a schematic drawing illustrating a powder particle structure according to the current invention.

[00024] Figure 4 is a schematic drawing illustrating a powder particle structure according to the current invention.

[00025] Figure 5 is a schematic drawing illustrating a powder particle structure according to the current invention.

[00026] Figure 6 is a schematic drawing illustrating a powder particle structure according to the current invention.

[00027] Figure 7 is a schematic drawing illustrating a powder particle structure according to the current invention.

[00028] Figure 8 is a schematic drawing illustrating a powder particle structure according to the current invention.

[00029] Figure 9 is a schematic drawing illustrating a powder particle structure according to the current invention.

[00030] Figure 10 shows the morphology and cross-section of a powder according to the present invention; SEM powder images (at 500X) for the MgO- Al₂O₃ “clad” powder (a) Morphology, (b) Cross section.

[00031] Figure 11 shows the morphology and cross-section of a powder according to the present invention; SEM powder images (at 500X) for the MgO- Al₂O₃ “clad” powder (a) Morphology, (b) Cross section.

[00032] Figure 12 shows the morphology and cross-section of a powder according to the present invention; SEM powder images (at 500X) for the MgO- Al₂O₃ “clad” powder (a) Morphology, (b) Cross section.

[00033] Figure 13 shows the morphology and cross-section of a powder according to the present invention; SEM powder images (at 500X) for the MgO- Al₂O₃ “clad” powder (a) Morphology, (b) Cross section.

[00034] Figure 14 shows the morphology and cross-section of a powder according to the present invention; SEM powder images (at 500X) for the MgO- Al₂O₃ “clad” powder (a) Morphology, (b) Cross section.

[00035] Figure 15 shows the morphology and cross-section of a powder according to the present invention; SEM powder images (at 500X) for the MgO- Al₂O₃ “clad” powder (a) Morphology, (b) Cross section

[00036] Figure 16 shows the morphology and cross-section of a powder according to the present invention; SEM powder images (at 200X) for the MgO-Al₂O₃ “clad” powder (a) Morphology, (b) Cross section.

[00037] Figure 17 shows XRD patterns of an MgO/Aluminum nitride powder, and a coating made therefrom on a steel substrate.

[00038] Figure 18 is an XRD pattern for a material prepared according to Example 1.

[00039] Figure 19 is an XRD of a coating prepared by thermally spraying material prepared according to Example 1.

[00040] Figure 20 is an XRD pattern for a material prepared according to Example 2.

[00041] Figure 21 is an XRD of a coating prepared by thermally spraying material prepared according to Example 2.

[00042] Figure 22 shows SEM powder images (at 500X) for an MgO-Al₂O₃ powder: (a) Morphology, (b) Cross section.

[00043] Figure 23 shows SEM powder images (at 500X) for an MgO-Al₂O₃ powder: (a) Morphology, (b) Cross section.

BRIEF DESCRIPTION OF THE INVENTION

[00044] The present invention describes a material to be used to provide temperature resistant, electrically insulating coatings with a coefficient of thermal expansion tunable to match that of the coated metallic material using thermal spray process. The invention is based on a unique structure of the agglomerates which enables thermal spraying of some well known suitable materials which until now could not be processed by thermal spraying. The core of the material may be a metal or a ceramic, and these materials have a coefficient of thermal expansion >10 $\mu\text{m}/\text{m}/\text{K}$. Additionally, the core-coating or outer layer preferably electrically insulates the core material, and is suitable for thermal spray applications.

[00045] Preferably, there is no, or essentially no, spinel involved in this construct. This is in contrast to US Patent 6,723,442, which teaches spinel in the starting material. It is not necessary to start with a spinel material, or to use a starting material comprising a spinel. Rather, it is believed that a spinel forms with the heating and/or reheating of the material, in the flow of material toward the surface to be coated, or on the surface itself.

[00046] The starting material preferably comprises a powder comprising particles of two or more different compositions, the compositions comprising components A and/or B.

[00047] Component A is a component that is electrically insulating, and does not (or does not appreciably) sublime or evaporate at material deposition temperature (an insulating non-sublimating component). If a Component A reacts with a Component B (described below), the reaction product is preferably electrically insulating. The reaction product preferably comprises a spinel. Component A preferably comprises any compound or material (other than a spinel) that is capable of reacting with a Component B under thermal spray conditions to form a spinel on a surface. Suitable Components A include oxides of trivalent or tetravalent metals, or a salt. Preferred oxides include one or more of Al_2O_3 , In_2O_3 , Ga_2O_3 , Y_2O_3 , Sc_2O_3 , SiO_2 , TiO_2 , GeO_2 , ZrO_2 , HfO_2 , SnO_2 , NbO_2 , MnO_2 , or rare earth oxide (REO). Suitable salts for Component A include one or more of nitrates, sulfates, carbonates, acetates, phosphates, chlorides, and borates. Combinations of two or more Component A materials are also suitable. An especially preferred Component A comprises, consists essentially of, or consists of, Al_2O_3 .

[00048] The salt, when used, can preferably serve one or both of the following functions, preferably both. The salt preferably acts as a binder for larger particles. The salt preferably reacts with, or is capable of reacting with, Component B. The reaction product preferably includes a spinel. When Component A comprises, consists essentially of, or consists of, a salt, some preferred salts for Component A include:

- nitrates as well as water containing nitrates and/or nitrites;
- sulphates as well as water containing sulphates and/or sulphides;
- carbonates as well a water containing carbonates;
- acetates as well as water containing acetates;
- phosphates as well as water containing phosphates and/or phosphides;
- chlorides as well as water containing chlorides and/or chlorites;
- borates as well as water containing borates.

[00049] Component B is a component other than Component A, that has a high coefficient of thermal expansion (CTE). Preferably, a Component B has a CTE close to, or greater than, the CTE of the substrate to which the coating is applied. In a preferred embodiment, the CTE of Component B is greater than or about $10 \mu\text{m/m/K}$. Component B preferably includes any

compound or material (other than a spinel) that is capable of reacting with Component A under thermal spray conditions to form a spinel on a surface. Preferably, the higher CTE of component B can be used to tune the CTE of the coating to match that of the substrate.

[00050] The substrate can be any material on which a thermal spray coating can be applied. Preferably, the substrate is or comprises a metal, preferably iron, steel, aluminum, copper, Fe-Cr alloys, Cr rich steels, cobalt, Co-alloys (e.g., cobalt-based superalloys), nickel, Ni-alloys (e.g., nickel-based superalloys), bronze, or titanium. The substrate can comprise any part on which a thermal spray coating can be applied. Preferably, the substrate can be a gas or jet turbine, a SOFC component, an electrical part in high temperature machinery, an engine component, a casting mold, a plasma etching chamber component, etc.

[00051] Component B preferably comprises a simple oxide (e.g. MgO) or a double oxide (e.g. Li_2TiO_3) or a multiple oxide (e.g. $\text{PbxZr}(1-x)\text{TiO}_3$). An especially preferred Component B comprises, consists essentially of, or consists of, magnesium oxide (MgO). Another preferred Component B is an oxide with formula $\text{Z}(1-2)\text{MO}_{3-4}$ where Z = an alkali metal (Li, Na, K, Rb, Cs), Ba, or Mg; M = a group IV element (Ti, Hf, Zr, Si, Ge, Sn, Pb) and O = oxygen. See also US patent 3,833,387.

[00052] In another embodiment, component B comprises an alkali metal halide or an alkaline metal halide. A preferred halide is fluoride. See also US patent 5,043,305.

[00053] In another embodiment, component B comprises a metal or alloy having a high CTE. Some preferred examples include a group IV metal, a group VIII metal, a Group IB metal, a Group IIB metal, or any electrically conducting alloy of any of these, or comprising at least one of these.

[00054] When micro-mixtures 1 and 2 each comprise component A, component A in micro-mixture 1 can be the same as, or different from, component A in micro-mixture 2. Preferably, component A is the same in micro-mixtures 1 and 2. Similarly, when micro-mixtures 1 and 2 each comprise component B, component B in micro-mixture 1 can be the same as, or different from, component B in micro-mixture 2. Preferably, component B is the same in micro-mixtures 1 and 2.

[00055] As schematically shown in Figure 1, one preferred embodiment comprises particles having a core rich (e.g., >50 mol%) in component B and poor (e.g., <50 mol%) in component A (micro-mixture 1). The core has a core-coating thereon that is rich (e.g., >50 mol%) in component A and poor (e.g., <50 mol%) in component B (micro-mixture 2). The particle may additionally comprise an optional outer layer. Either or both of micro-mixtures 1 or 2 can additionally comprise other components, such as non-spinel oxides. These particles may also additionally comprise an optional outer layer (e.g., component C). A mixture rich in Component A (or B) includes a composition of 100% A (or B). In a preferred embodiment, component A comprises Al_2O_3 , component B comprises MgO , and component C comprises one or more of Co-oxide, Mn-oxide, ZnO , NiO , TiO_2 , or Cr_2O_3 .

[00056] As used herein, “rich” in a particular component means that the composition comprises a plurality, preferably a majority, mol percent of the mixture. Preferably, “rich” means at least 50 mol%, more preferably at least 60 mol%, 70 mol%, or 80 mol%, and includes 100%, or essentially 100%, of the component. Similarly, as used herein, “poor” in a particular component means that the composition comprises a minority mol percent of the mixture. Preferably, “poor” means less than 50 mol%, more preferably up to 40 mol%, 30 mol%, or 20 mol%, and includes none, or essentially none, of the component.

[00057] When component B comprises an electrically conductive material, it is preferred that any outer layer be electrically insulating. One preferred way to accomplish this comprises applying an outer layer to the core-shell particle, e.g., as shown in Figure 1. The outer layer could comprise any suitable electrically insulating material component C. In a preferred embodiment, component C comprises, essentially consists of, or consists of, a non-sublimating electrical insulator, such as a component A material.

[00058] Another preferred way to accomplish this comprises using a micro-mixture 2 that is electrically insulating. Micro-mixture 2 can comprise electrically conductive material (e.g., a component B material), so long as micro-mixture 2 is not electrically conductive.

[00059] In a preferred embodiment (e.g., per Figure 1), micro-mixture 1 comprises a component B-rich (>50 mol%) mix of A and B with particle sizes of either component < 20 microns (preferably < 5 microns). In a preferred embodiment, micro-mixture 2 comprises a component A-rich (>50 mol%) mix of A and B, with particle sizes of either component < 20 microns (preferably < 5 microns).

[00060] In another preferred embodiment (e.g., per Figure 2), micro-mixture 1 comprises a component B-rich (>50 ml%) mix of A, B, and C, with particle sizes of either component < 20 microns (preferably < 5 microns). In a preferred embodiment, micro-mixture 2 comprises a component A-rich (>50 mol%) mix of A, B, and C, with particle sizes of either component <20 microns (preferably < 5 microns). When a micro-mixture comprises components A, B and C, component A preferably comprises Al_2O_3 , and component C preferably comprises a non-sublimating electrical insulator other than Al_2O_3 . Several other structures and preferred embodiments are schematically shown in Figures 3-9.

[00061] Any amounts of Components A and B may be used to obtain a suitable coating on the surface, and may be adjusted by one of ordinary skill in the art using this disclosure as a guide. Preferably, the amounts of Components A and B used are suitable to form a coating comprising spinel and MgO. By regulating the relative amounts of Components A and B in the starting material, it is possible to regulate the proportion of MgO and spinel that are formed on the surface. Because the spinel and MgO generally have different coefficients of thermal expansion (CTEs), it is possible to control the CTE of the coating, preferably obtain a target CTE, by adjusting the proportions of A and B, e.g., in the core and/or in the core-coating layer.

[00062] The order of micro-mixtures 1 and 2 can be reversed as desired or required. That is, the core may comprise micro-mixture 2, and the core-coating may comprise micro-mixture 1. In a preferred embodiment, higher Al_2O_3 composition in the core-coating (e.g., Al_2O_3 -rich core coating) may help to prevent evaporation losses of MgO during heating or spraying.

[00063] In another embodiment, by suitably choosing the ratios of Components A and B, the structure (spinel + MgO) may naturally be produced in the deposited coatings which will have the desired properties in terms of electrical insulation, coefficient of thermal expansion, or both.

[00064] Materials according to the present invention may also comprise other ingredients, such as binders or dispersants.

[00065] Any suitable amount of binder may be used to obtain desired binding of the material. A binder is optional, such that there is no particular lower limit on the amount of

binder. Some salts (e.g., of Component A) have binding properties, which can reduce or eliminate any need for a binder. When used, the binder is typically used in an amount less than or about 15 parts by weight, more preferably less than or about 10 parts by weight, more preferably less than or about 6 parts by weight, more preferably 3 parts by weight, more preferably less than about 2 parts by weight, relative to 100 parts by weight of components A, B, and (if present) C. Some preferred embodiments have about 10, 6, 3, or 1 part by weight binder, or no binder. Some preferred binders include polyvinyl alcohol (PVA), povidone (PVP), carboxymethyl cellulose (CMC), paraffin wax, and combinations thereof.

[00066] A dispersant may optionally be used, e.g., in order to improve and/or facilitate preparation of the material. A dispersant is optional, such that there is no particular lower limit on the amount of dispersant. When used, dispersant is typically used in an amount less than about 2 parts by weight, more preferably less than about 1 parts by weight, relative to weight of components A, B, and (if present) C. Some preferred embodiments have about 0.5 part by weight dispersant. Any suitable dispersant can be used, and can be determined by one of ordinary skill in the art. Non-limiting preferred dispersants comprise an anionic polyelectrolyte, such as DISPEX® AA 4144 (manufactured by BASF), or NOPCOSPERSE® (available from San Nopco Limited, Japan).

[00067] In an embodiment an optional outermost layer (Figure 1) can be extended to one or more of a very large number of other suitable elements and/or compounds. This layer when reacting with the inner layers can produce other desired compositions. For example, if the outer layer has CoO and the micro-mixture 2 layer has for example, pure Al_2O_3 , they can produce CoAl_2O_4 .

[00068] This same idea is applied in Figure 1 (without the optional outer layer) which has only a core and a shell (core-coat) but each can have 3 possible components (A, B and C) where C can be extended to a very large number of other suitable elements and/or compounds.

[00069] The shapes of the core and the coated particle (e.g., as schematically shown in Figures 1 and 2), are not limited, and can be of any shape or configuration. Additionally, as shown for example in Figure 3, there can be multiple cores, and the core can be irregularly shaped.

[00070] Any thickness of the core-coat (e.g., micro-mixture 2) can be used. In a preferred embodiment, the thickness of the core-coat 2 is generally at least 0.1 microns, more preferably at least 1 or 2 microns. In a preferred embodiment, the thickness of the core-coat is up to 15 microns, more preferably 12 or 8 microns. A preferred range is 0.1–15 microns.

[00071] The particles may be of any size. The particles (e.g., as shown in Figures 1-9) may be monolithic or agglomerated. The particles are preferably of a size to permit use in thermal spray equipment to apply a coating on a surface. Without limiting the invention, as a general matter, average particle size will be less than 100 microns, more preferably less than 50 microns, more preferably less than 20 microns. As a general matter, the average particle sizes will be at least 0.5 microns, more preferably at least 1 micron, more preferably at least 4 microns.

[00072] In a preferred embodiment, for the micro-mixture 2, the particulate coating comprises an oxide, and does not comprise a salt.

[00073] In another preferred embodiment, the core is, or comprises, a metal, and the particle comprises an electrically insulating material coating, e.g., core-coat and/or outer layer.

[00074] Another preferred embodiment is shown in Figure 9, wherein multiple cores having, for example, size less than 10 microns are clad with component A. A preferred Component A for this cladding is, or comprises, a salt.

[00075] It can be seen in Figures 3 and 4 that there can be multiple coated cores that are agglomerated. In Figure 3, component B is completely encased in Component A. In Figure 4, Component B is partially encased in Component A, and to a small extent is not encased. The coating on the core can be as low as a hundred nanometers, and as high as about 10 microns.

[00076] It is possible to treat the cores in various manners prior to applying core-coating. As shown in Figures 6-9, the cores and/or particles can be regular or irregular in shape. For example, multiple cores may be fused and crushed and then agglomerated, to obtain various configurations. When cores are agglomerated, Component A can act as a coating or glue.

Some STMs showing morphologies and cross sections of materials according to the present invention are shown in Figures 10-16.

[00077] Materials of the present invention can be applied in any manner, preferably by thermal spray coating. Thermal spraying (often also referred to as flame spraying) is a group of processes wherein a finely divided feedstock material is heated and propelled as individual particles or droplets onto a surface to be coated (substrate). The thermal spray torch (or gun) generates the necessary heat by using combustible gases or an electric arc. As the materials are heated, they are changed to a plastic or molten state and are confined and accelerated by a compressed gas stream toward the substrate. The particles strike the substrate, flatten, and form thin platelets (splats) that conform and adhere to the irregularities of the prepared substrate and to each other. As the sprayed particles impinge upon the surface, they cool and build up, splat by splat, into a laminar structure forming the thermal spray coating.

Examples

[00078] Example 1

[00079] A powder is made according to the present invention, comprising 80 parts by weight MgO; 20 parts by weight Al_2O_3 ; 1 part by weight binder (PVA), and 0.5 parts by weight DISPEX® AA4144 dispersant.

[00080] All of the Al_2O_3 and 10% of the total MgO are wet milled to < 3 μm to create a fine sized intimate mixture. The remaining MgO (somewhat coarser in size) is added to DI water along with PVA, the dispersant and the mixture created above. The viscosity of the final slurry is maintained at 6.7 s (Zahn cup #4). The resulting slurry is then spray dried to achieve the desired particle size. The resulting powder has a core-shell structure, and a mean particle size of 16–17 μm . An XRD of the material is shown in Figure 18. SEM images showing morphology and cross-section are shown in Figure 22.

[00081] Example 2

[00082] A powder is made according to the present invention, comprising 80 parts by weight MgO; 20 parts by weight Al_2O_3 ; 1 part by weight binder (PVA), and 0.5 parts by weight dispersant DISPEX AA 4144®.

[00083] All of the Al_2O_3 and MgO is wet milled to $< 3 \mu\text{m}$ to create a fine-sized intimate mixture. DI water along with PVA, and DISPEX AA 4144® is added to mixture to adjust its properties. The viscosity of the final slurry is maintained at 7.5 s (Zahn cup #4). The resulting slurry is then spray dried to achieve the desired particle size. The resulting powder has mean particle size of 16–17 μm , and is an intimate mixture that is believed to have a structure similar to that of Figure 10. An XRD of the material is shown in Figure 20. SEM images showing morphology and cross-section are shown in Figure 23.

[00084] Example 3 - MgO -Spinel Coatings

[00085] Materials from Examples 1 and 2 are used to make coatings. For comparative purposes, a coating is also made from a spinel-containing comparative material comprising MgO as a major phase, and MgAl_2O_4 as a minor phase, the comparative material made according to U.S. Patent 6,723,442.

[00086] The powders are thermally sprayed onto 1"x3" aluminum substrates using a METCO® 9MB torch, G nozzle, and standard electrode and powder port clamps, using a single #2 or #6 powder port. Carrier gas flow is 3.7 or 2.7 nlpm, and the powder feed rate is 22.5 g/min. The surface speed is 150 ft/min, rotational speed is 48 rpm, the part diameter is 12 in., the step size is 0.19 in., and the traverse rate is 4 mm/s. The material is ejected onto an aluminum substrate with a 2.5 inch spray distance. Other parameters are as shown in Table 1.

Table 1

Example		L1	L2	L3	L4	L5	L6	L7	L8	L9	comp.
Material		Ex. 1	Ex. 2	Ex. 2	Ex. 1	Ex. 1	Ex. 1	Ex. 1	Ex. 2	Ex. 2	comp.
Parameter											
	units										
powder port	#	6	6	6	2	2	6	6	6	6	6
gun current	A	700	700	700	500	700	700	700	700	700	700
jambox voltage	V	63.0	60.7	58.5		62.3	60.7	58.4	60.6	62.7	63.5
gun power	kW	44.0	42.3	40.8		43.1	42.3	44.3	42.3	43.7	44.3
nitrogen flow	nlpm	38	30	24	30	30	30	24	30	38	38
carrier gas	nlpm	3.7	3.7	3.7	3.7	3.7	3.7	2.7	3.7	3.7	2.7
notes		1	2	2	1	1	1	1	2	2	

1) One preheat cycle at 4 mm/s; Multicoat/PT1220.

2) One preheat cycle at 4 mm/s; 2 min DE (3 cycles); Multicoat/PT1220.

[00087] The thermally sprayed layers of L1, L2, L3, and the comparative example are then analyzed by x-ray diffraction. The results are shown in Table 2. The XRDs of L1 and L2 are shown in Figures 19 and 21, respectively.

Table 2

Powder	Coating Phase Analysis
Coatings L1-L3	MgO (periclase) – Major phase MgAl ₂ O ₄ (spinel) – Minor Al ₂ O ₃ – not detected
Comparative Example	MgO (periclase) – Major phase MgAl ₂ O ₄ (spinel) – Minor Al ₂ O ₃ – not detected

[00088] Even though the powders of Examples 1 and 2 comprise no spinel, the coatings prepared therefrom surprisingly comprise effective amounts of spinel. Moreover, even though the powders of Examples 1 and 2 comprise significant amounts of Al₂O₃, Al₂O₃ is surprisingly not detected in the coatings.

[00089] Example 4

[00090] A salt-based powder is made by agglomeration using a conventional spray drying system. The slurry contains MgO powder with a mean diameter of 2 to 5 μ m and a water soluble alumina nitrite salt (Al(NO₃)₃·9H₂O). The weight ratio is 80% MgO and 20% salt. Water is used as a carrier during the agglomerating process. It is believed that the salt functions as a binder which glues the agglomerates during the spray drying process. It is believed that the microstructure of an individual agglomerate is similar to Figure 8 or 9.

[00091] The powder is thermally sprayed using a conventional HVOF torch (DIAMONDJET® 2600) with hydrogen as combustion gas. Plain steel substrate is used. The trajectory of the torch is a meander pattern.

[00092] Figure 17 shows an XRD diagram of MgO and aluminum nitride powder (lower line), and the coating made therefrom by thermal spraying (upper line). As can be seen, the XRD of the powder shows it comprises MgO. It is believed that the aluminum salt cannot be detected because the spray-dry manufacturing process renders the aluminum salt amorphous. The coating, however, shows reflections of pure MgO and Al₂O₃ (corundum). The major peaks are iron as the substrate is only covered with a thin (5 to 10 μ m) coating. This

demonstrates that it is possible to deposit MgO glued by a second phase (corundum or spinel) by thermal spraying.

[00093] The particulars shown herein are by way of example and for purposes of illustrative discussion of the embodiments of the present invention only and are presented in the cause of providing what is believed to be the most useful and readily understood description of the principles and conceptual aspects of the present invention. In this regard, no attempt is made to show structural details of the present invention in more detail than is necessary for the fundamental understanding of the present invention, the description taken with the drawings making apparent to those skilled in the art how the several forms of the present invention may be embodied in practice.

[00094] It is noted that the foregoing examples have been provided merely for the purpose of explanation and are in no way to be construed as limiting of the present invention. While the present invention has been described with reference to exemplary embodiments, it is understood that the words which have been used herein are words of description and illustration, rather than words of limitation. Changes may be made, within the purview of the present disclosure, without departing from the scope and spirit of the present invention in its aspects. Although the present invention has been described herein with reference to particular means, materials and embodiments, the present invention is not intended to be limited to the particulars disclosed herein; rather, the present invention extends to all functionally equivalent structures, methods and uses, such as are within the scope of the present disclosure.

CLAIMS:

1. A material comprising a core portion comprising a first mixture, and an encasing portion comprising a second mixture,

the first mixture comprising at least 50 mol% but less than 100 mol% from one or more of a simple oxide, a double oxide, a triple oxide, an alkali metal halide, an alkaline metal halide, or a metal (component B1) and less than 50 mol% but more than 0 mol% of a non-sublimating electrical insulator independently chosen from one or both of a) one or more oxide of trivalent or tetravalent metals, or b) one or more salt with binding properties (component A1);

the second mixture comprising at least 50 mol% but less than 100 mol% of a non-sublimating electrical insulator independently chosen from one or both of a) one or more oxide of trivalent or tetravalent metals, or b) one or more salt with binding properties (component A2) and less than 50 mol% but more than 0 mol% from one or more of a simple oxide, a double oxide, a triple oxide, an alkali metal halide, an alkaline metal halide, or a metal (component B2);

wherein at least one of component A1 and component B1 has average particle size up to about 100 microns; and

at least one of component A2 and component B2 has average particle size up to about 20 microns;

wherein the encasing portion at least partially encases the core portion; and

wherein component B1 and component B2 have a coefficient of thermal expansion of at least 10 $\mu\text{m}/\text{m}/\text{K}$ and the material is free from a spinel and forms a spinel under thermal spray conditions.

2. The material of claim 1, wherein component A1 and component A2 are independently chosen from one or more of oxides of Al, In, Ga, Y, Sc, Mg, Si, Ti, Ge, Zr, Hf, Sn, Nb, Mn, or of a rare earth metal.

3. The material of any one of claims 1 to 2, wherein component A1 and component A2 comprise Al_2O_3 .
4. The material of any one of claims 1 to 3, wherein component B1 and component B2 comprise MgO .
5. The material of any one of claims 1 to 4, comprising a plurality of cores.
6. The material of claim 5, wherein the cores comprise particles that are at least one of monolithic or an agglomerate of smaller particles.
7. The material of any one of claims 1 to 6, comprising a plurality of agglomerated encased cores.
8. The material of any one of claims 5 to 7, wherein the core or plurality of cores further comprises an outer layer that is non-electrically conducting and non-sublimating.
9. The material of claim 8, wherein the outer layer comprises one or both of a) one or more oxides of trivalent or tetravalent metals, or b) one or more salt with binding properties.
10. The material of any one of claims 1 to 9, further comprising a binder.
11. The material of any one of claims 1 to 10, further comprising a dispersant.
12. A method of manufacturing a thermal spray coating comprising:

providing a material according to any one of claims 1 to 11;

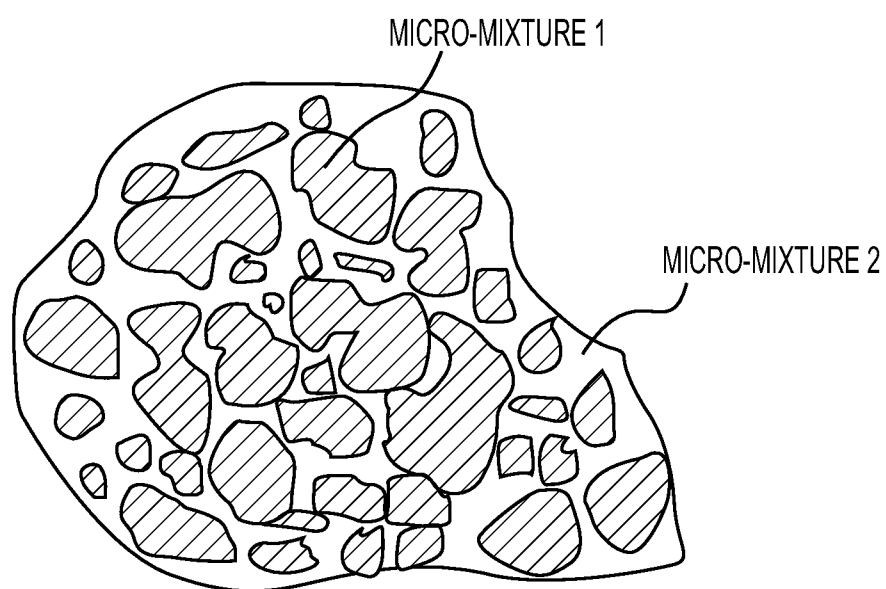
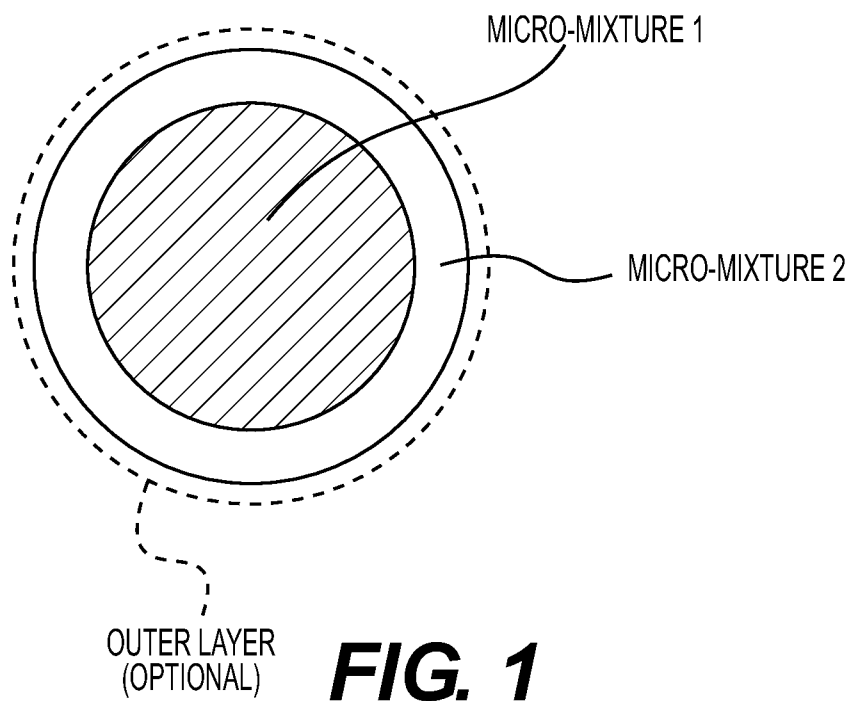
providing a substrate; and

forming a coating on the substrate by applying the material to the substrate by a thermal spray process.

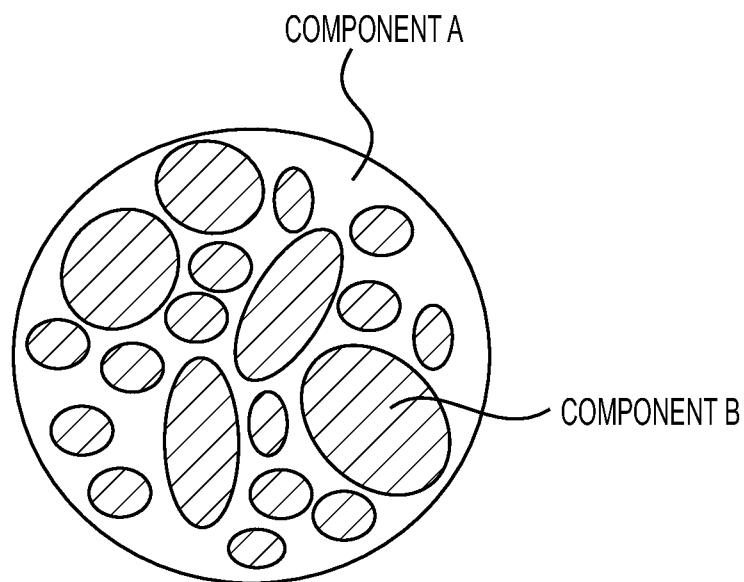
13. The method of claim 12, wherein the material comprises Al_2O_3 , and the thermal spray coating does not comprise Al_2O_3 .

14. The method of any one of claims 12 to 13, wherein the substrate comprises at least one of iron, steel, aluminum, copper, Fe-Cr alloy, Cr-rich steel, cobalt, Co-alloy, nickel, Ni-alloy, bronze, or titanium.

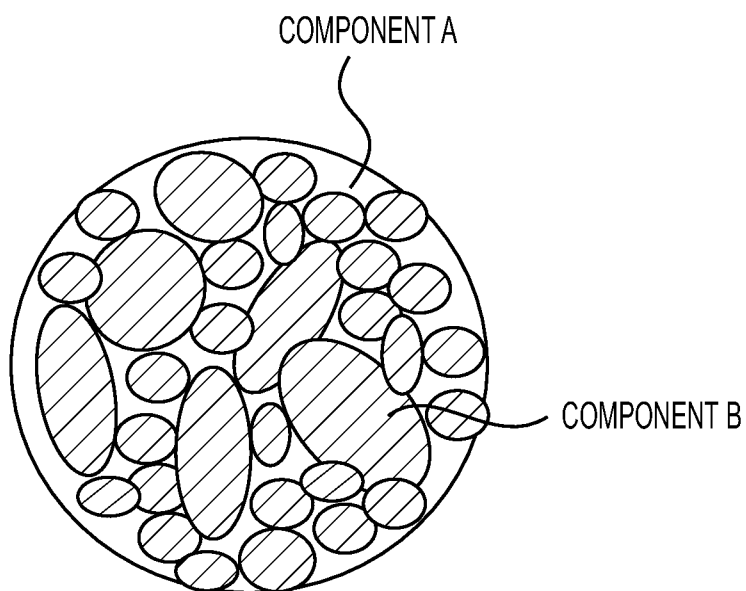
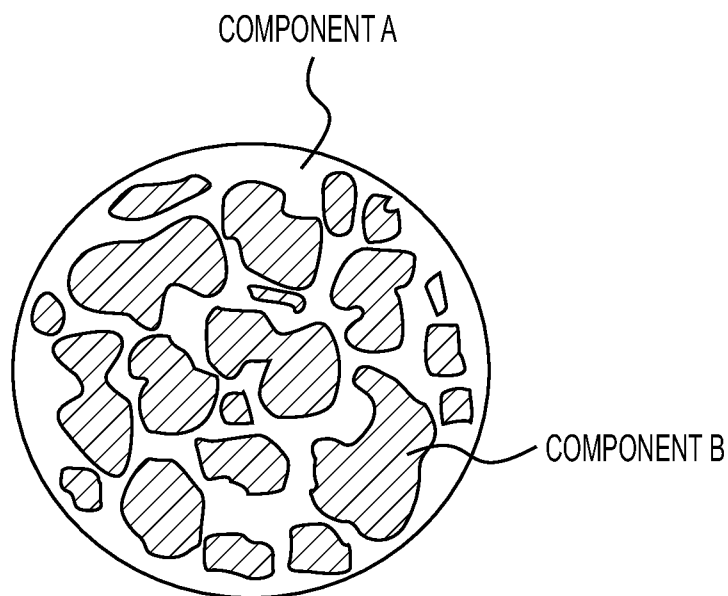
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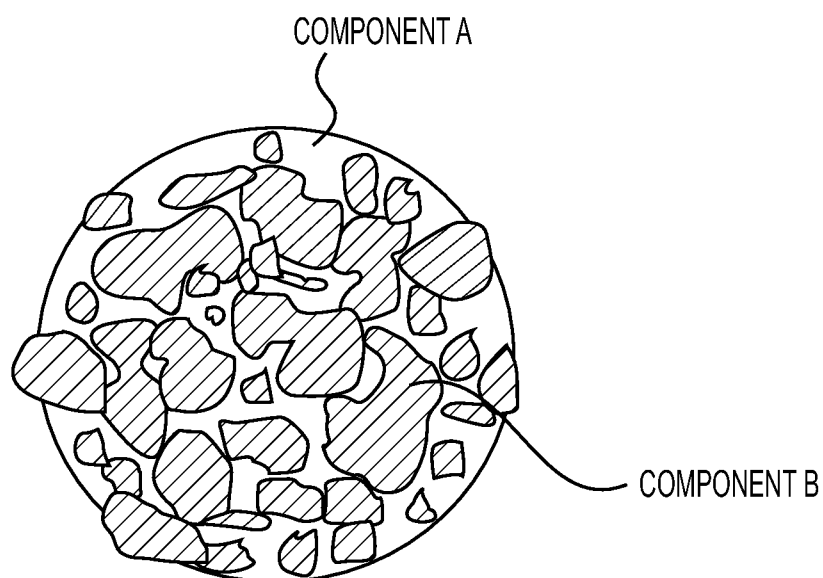
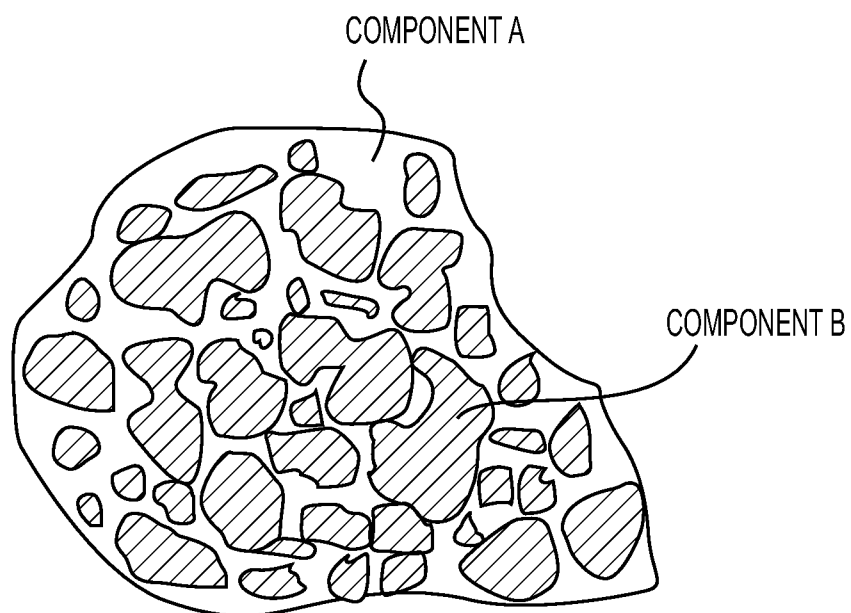
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**FIG. 3**

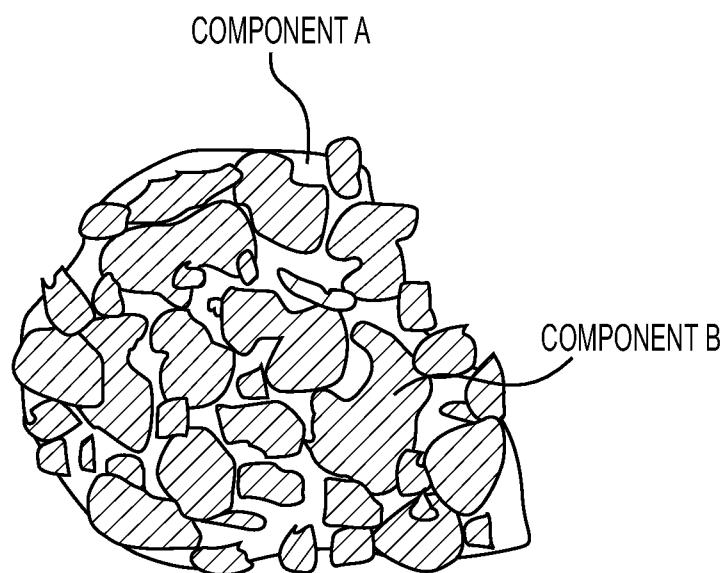
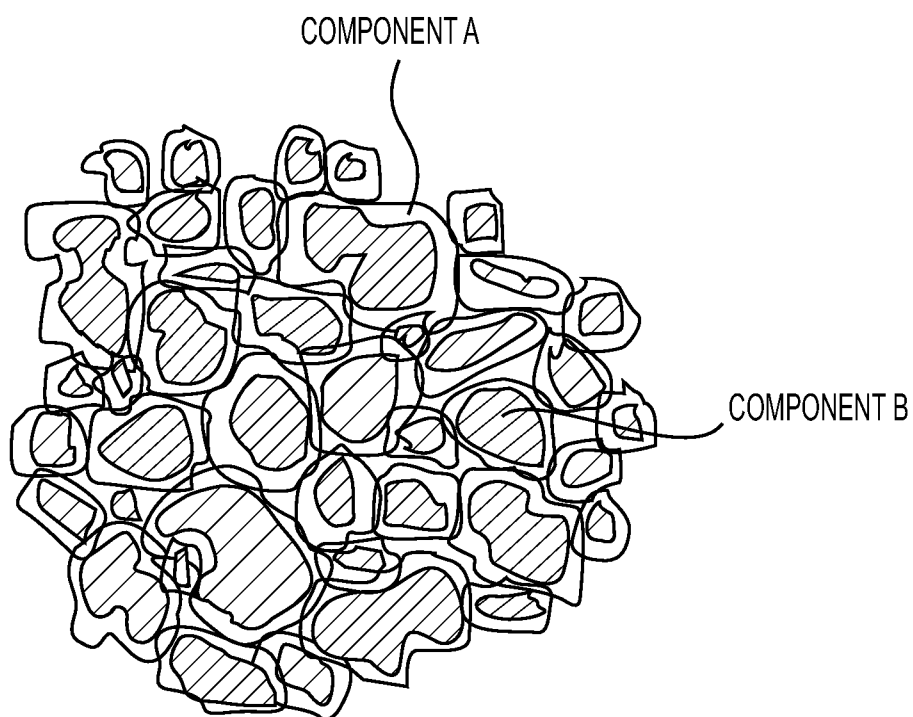
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**FIG. 4****FIG. 5**

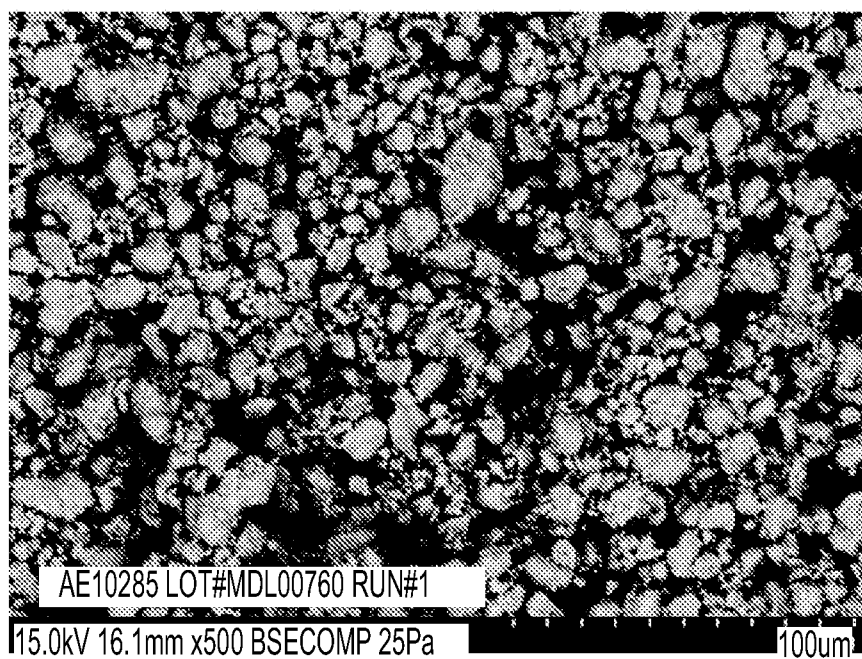
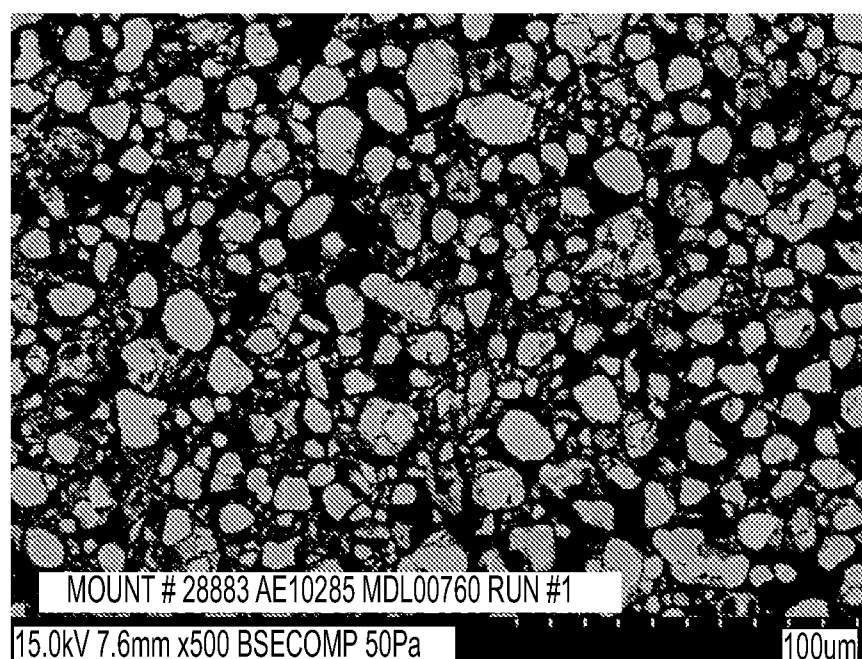
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**FIG. 6****FIG. 7**

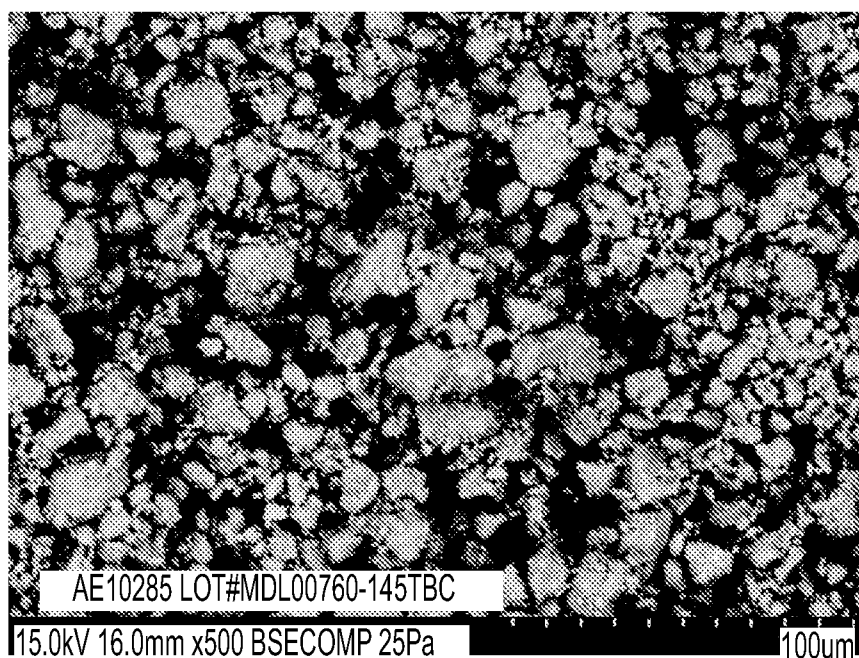
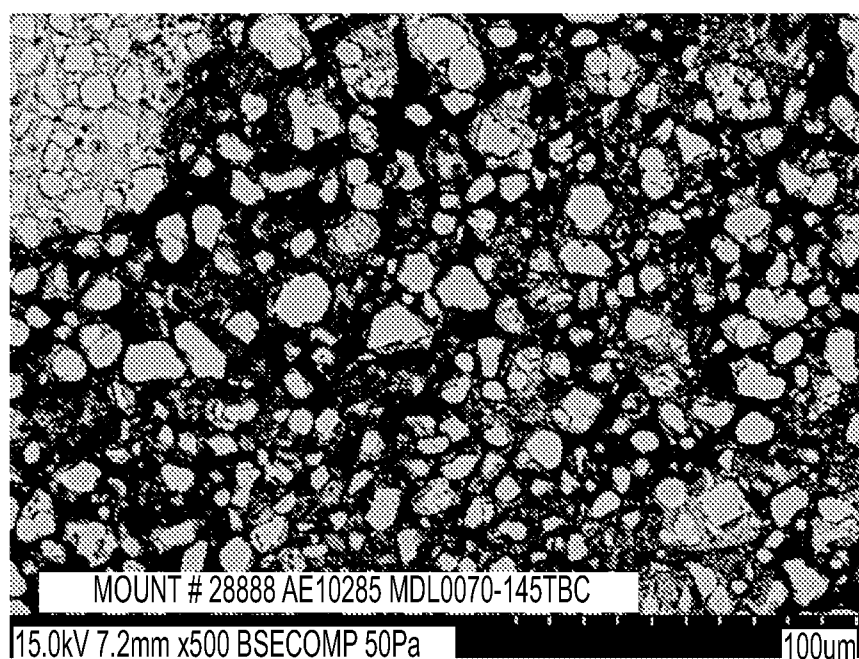
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**FIG. 8****FIG. 9**

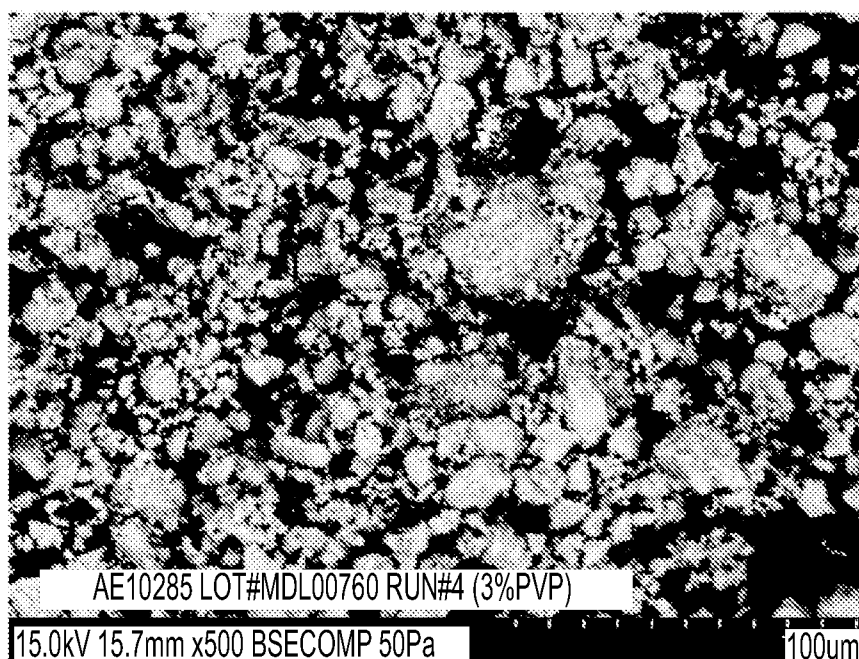
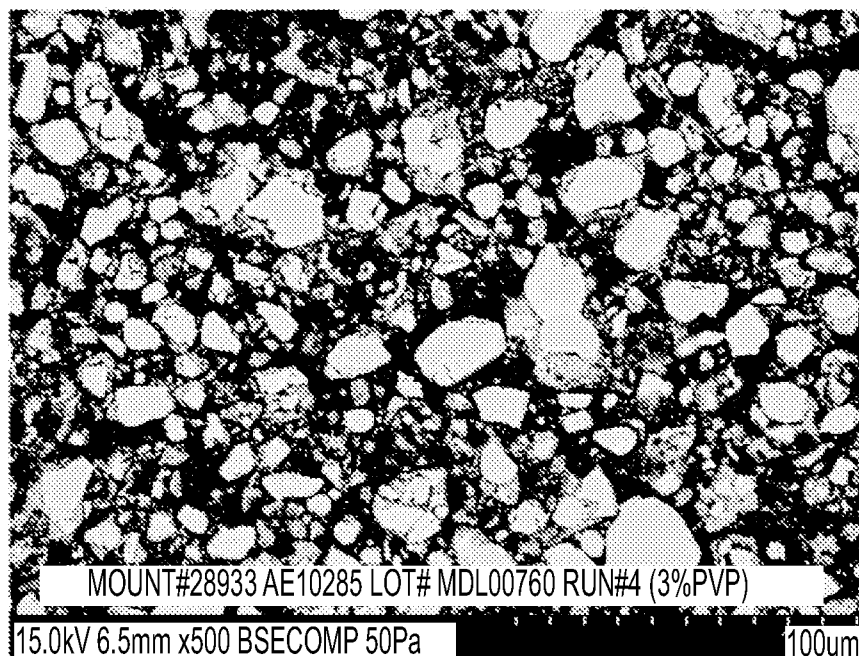
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**FIG. 10A****FIG. 10B**

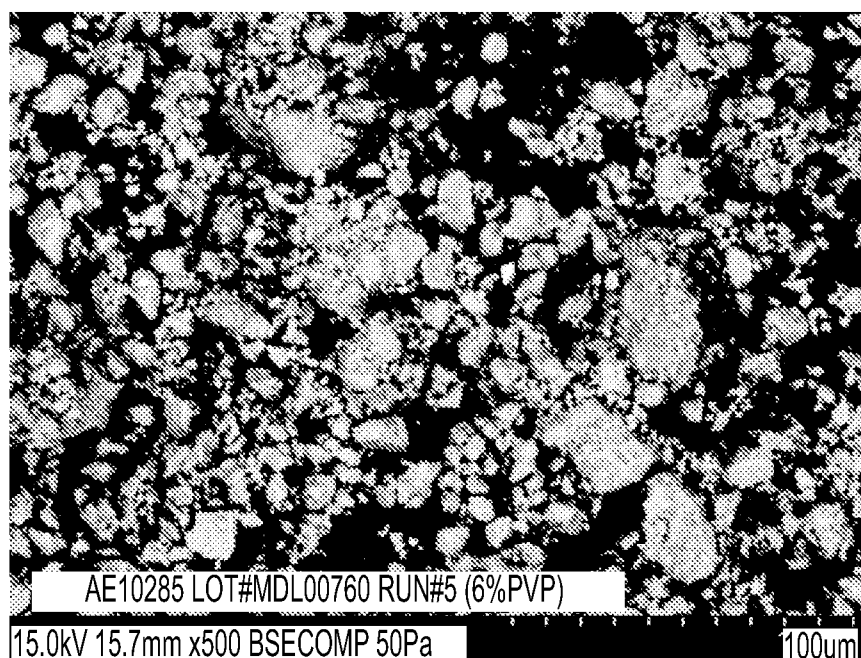
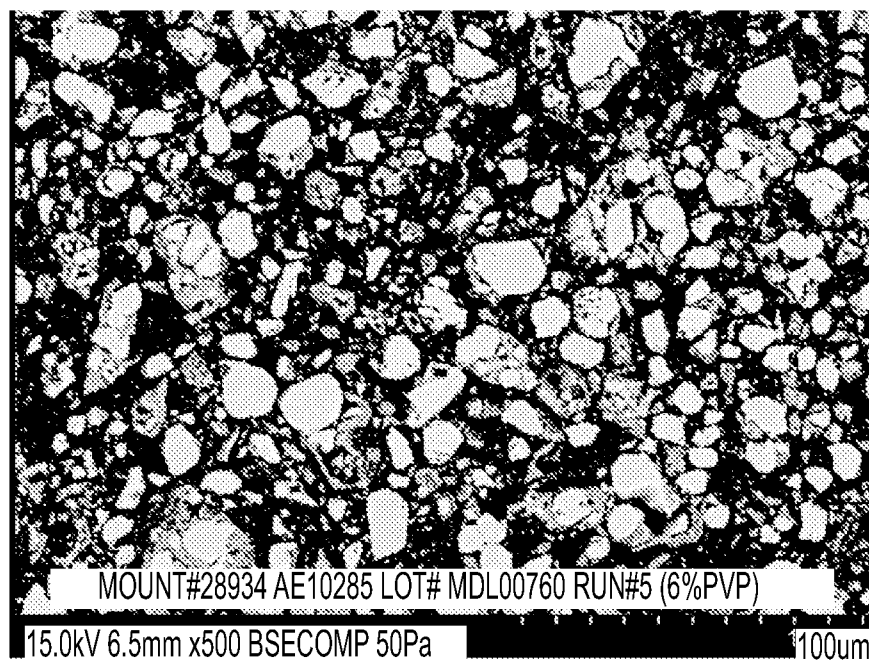
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**FIG. 11A****FIG. 11B**

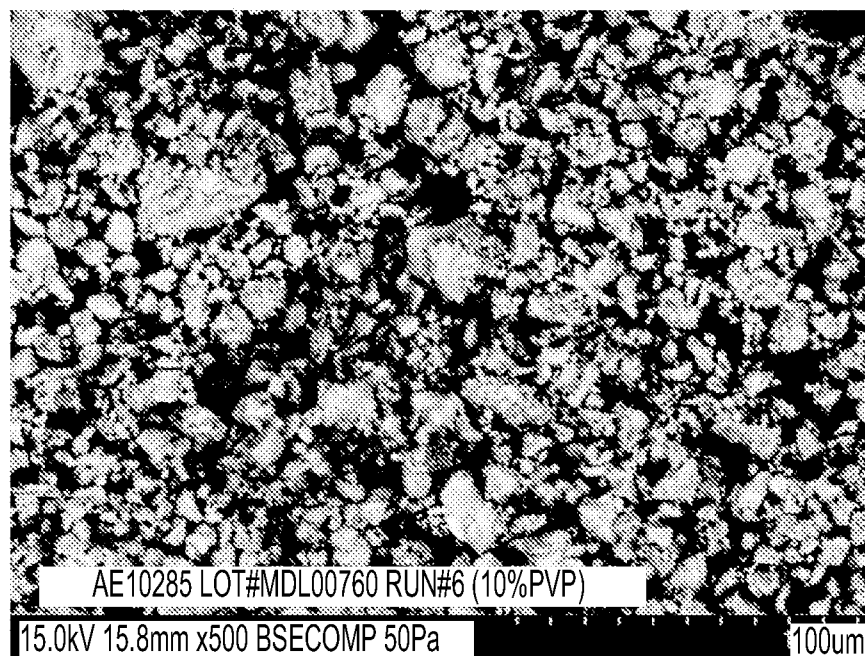
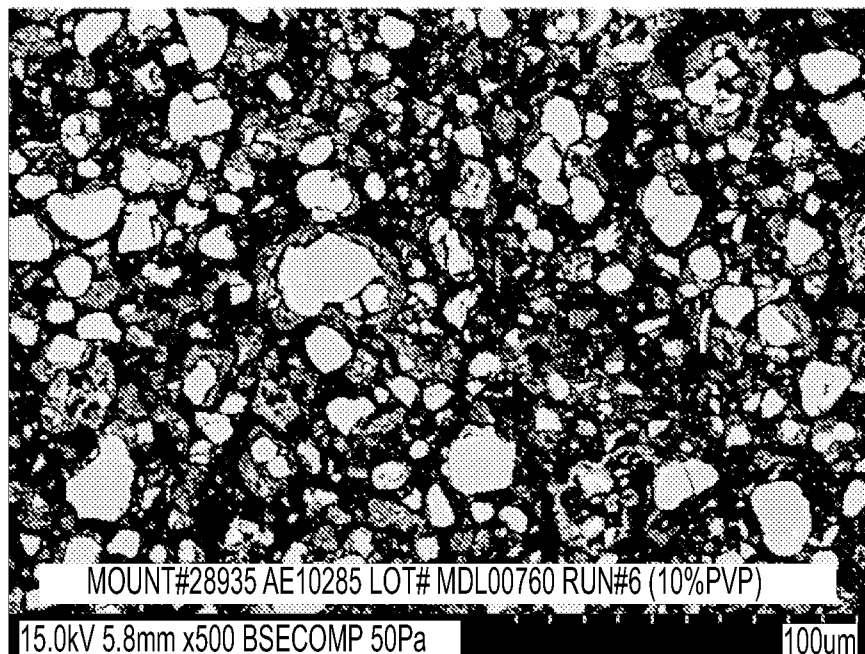
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**FIG. 12A****FIG. 12B**

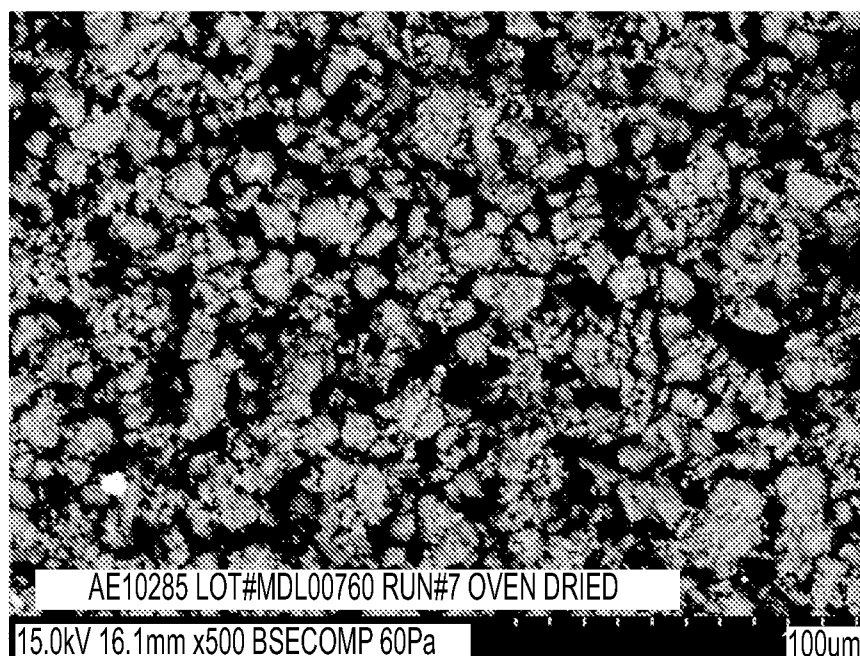
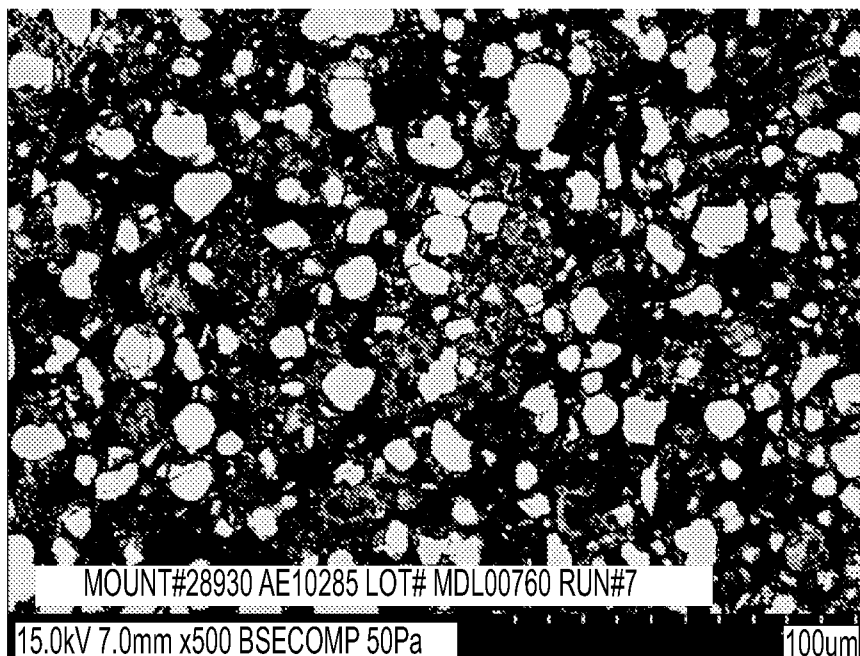
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**FIG. 13A****FIG. 13B**

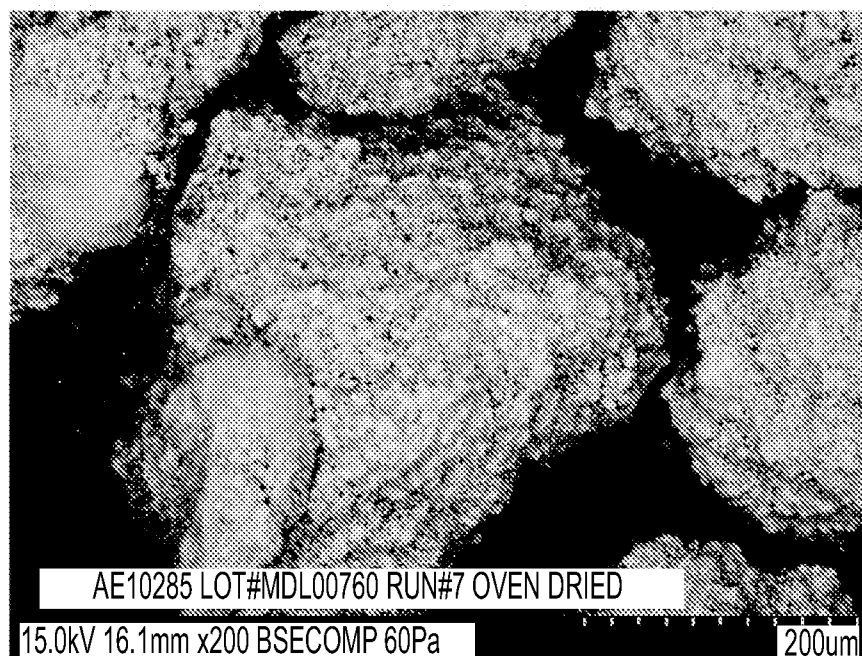
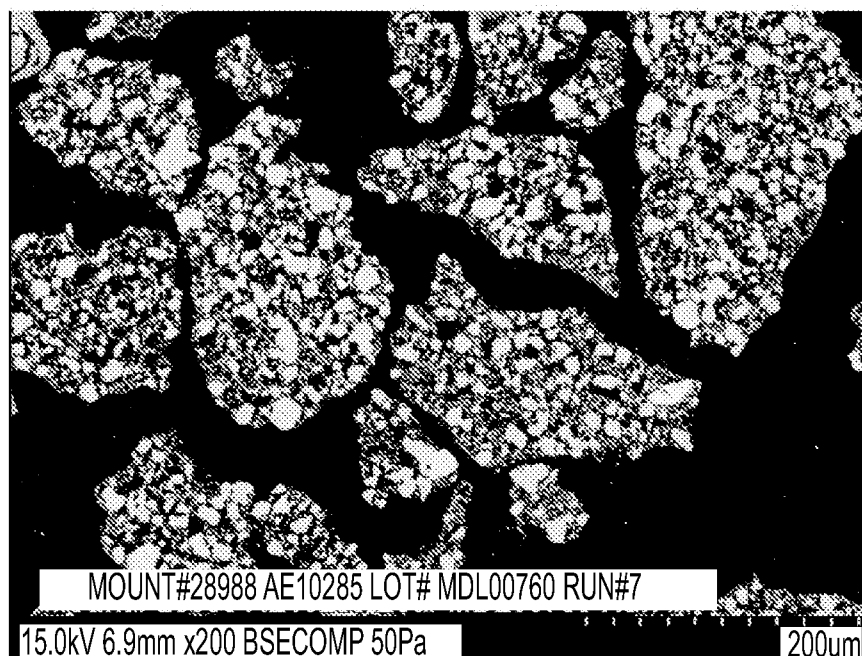
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**FIG. 14A****FIG. 14B**

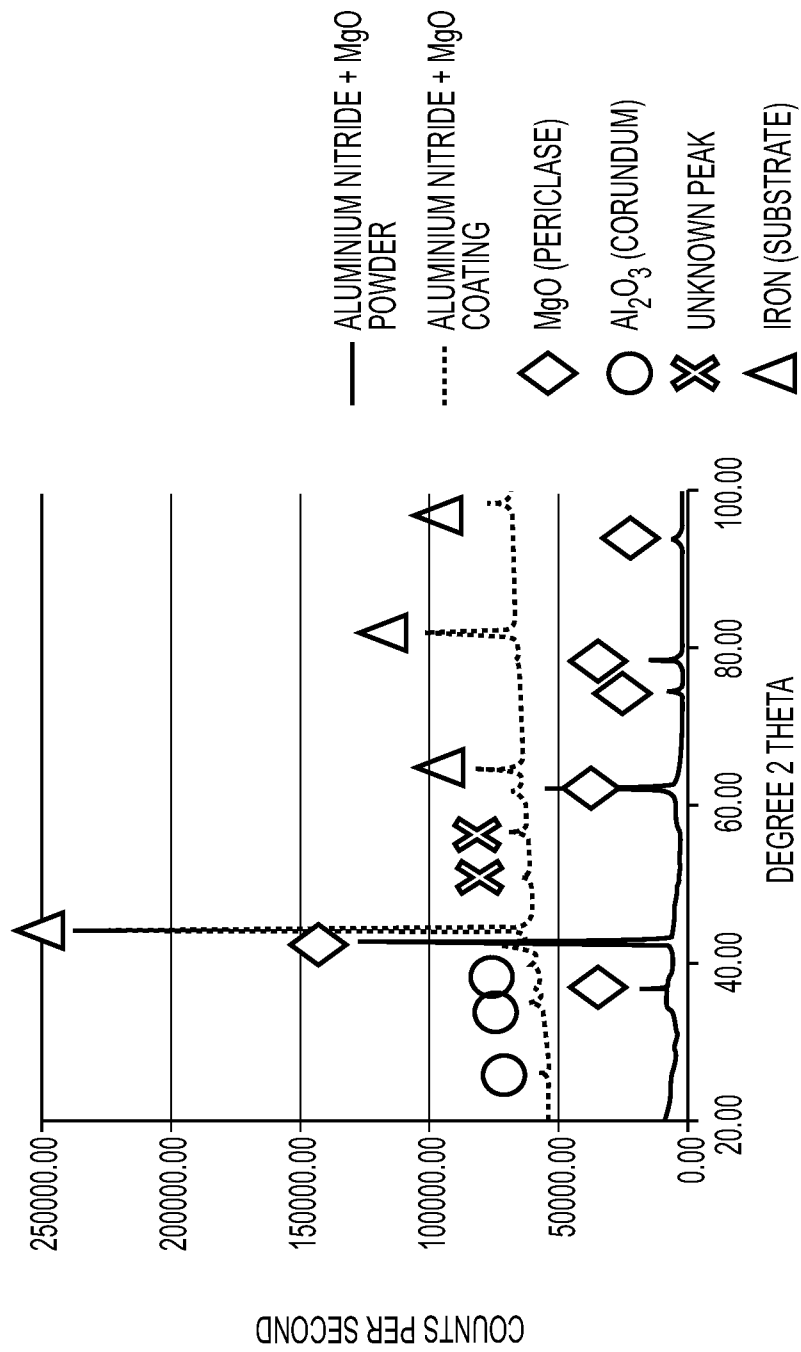
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**FIG. 15A****FIG. 15B**

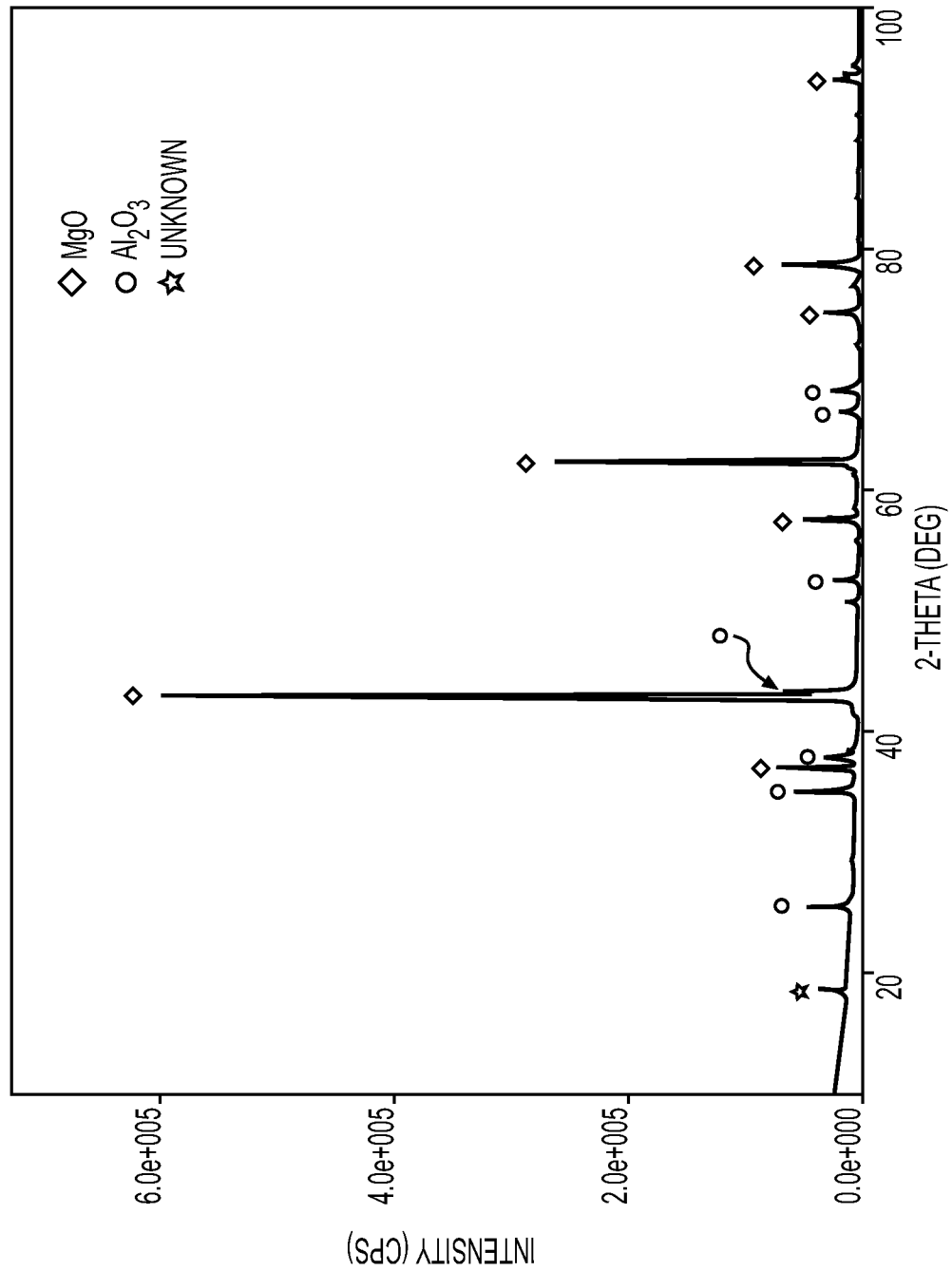
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**FIG. 16A****FIG. 16B**

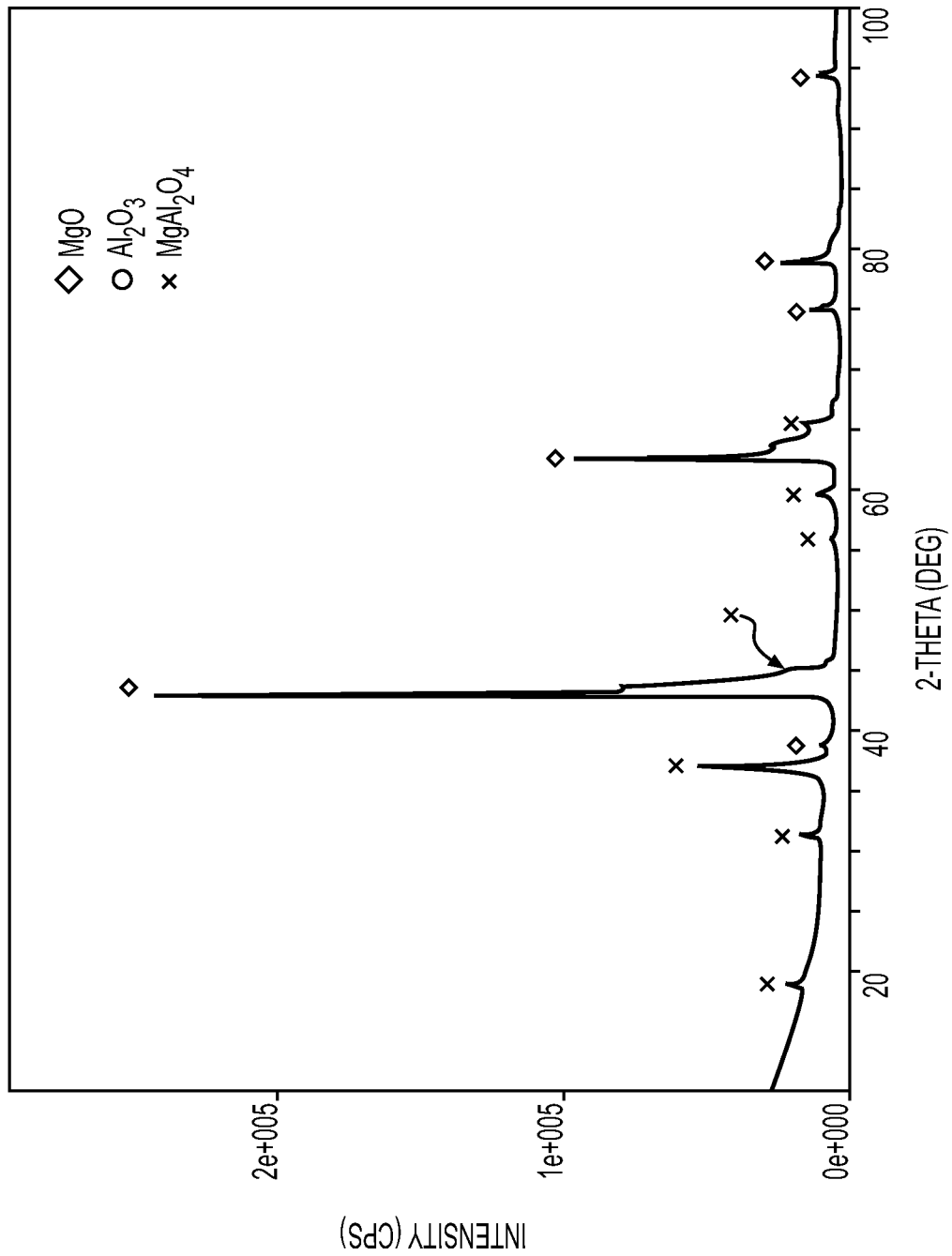
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**FIG. 17**

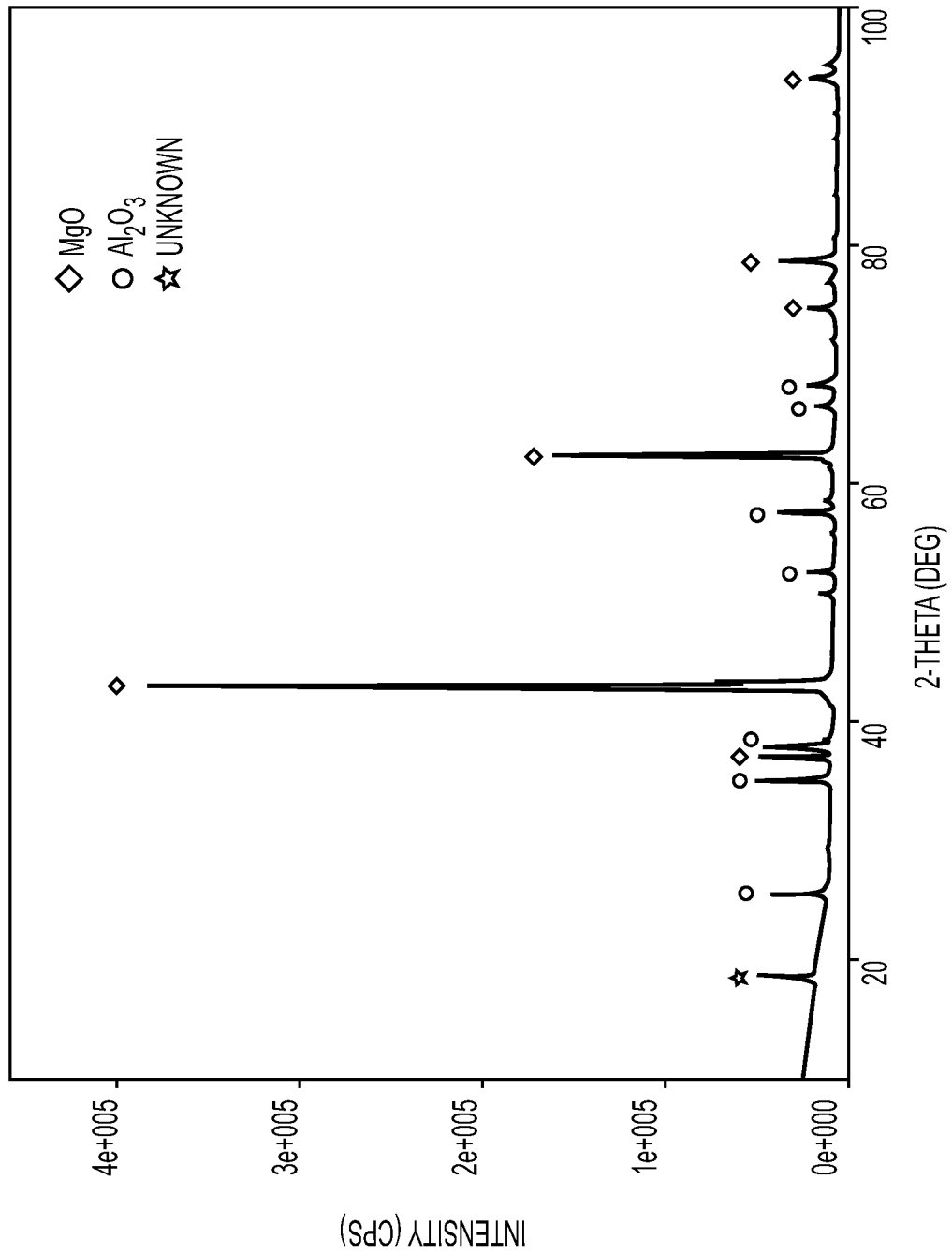
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**FIG. 18**

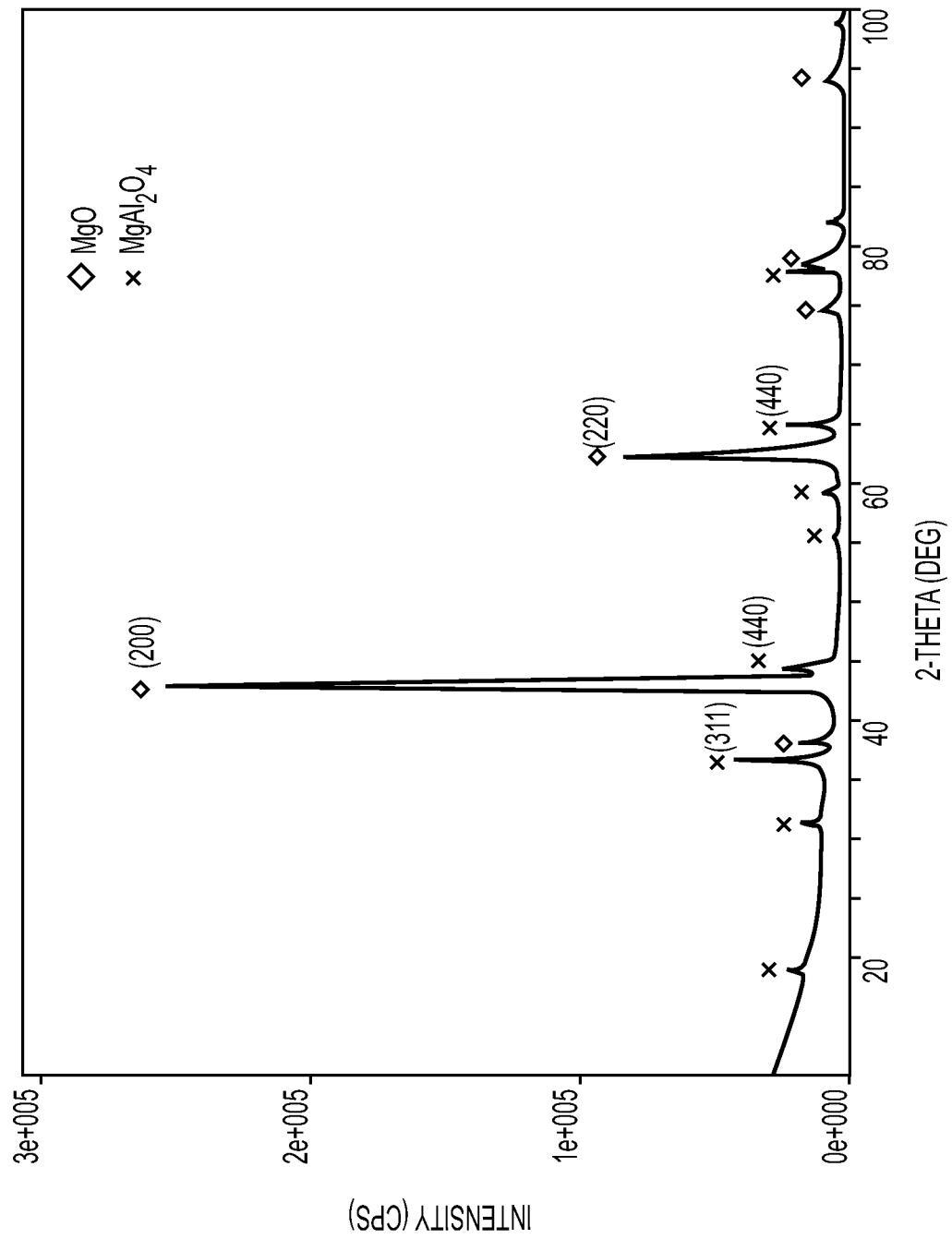
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**FIG. 19**

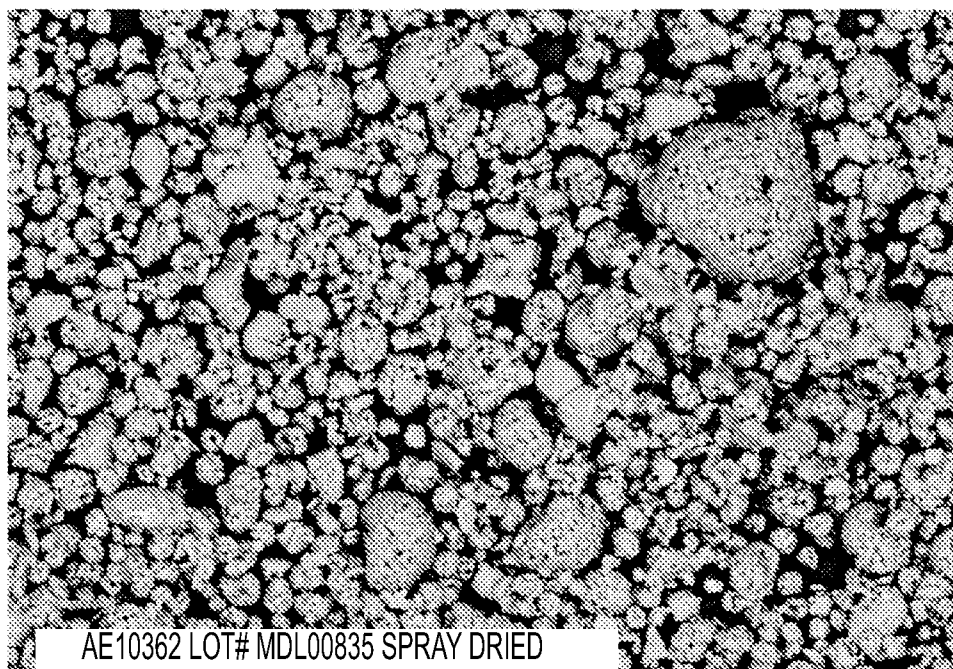
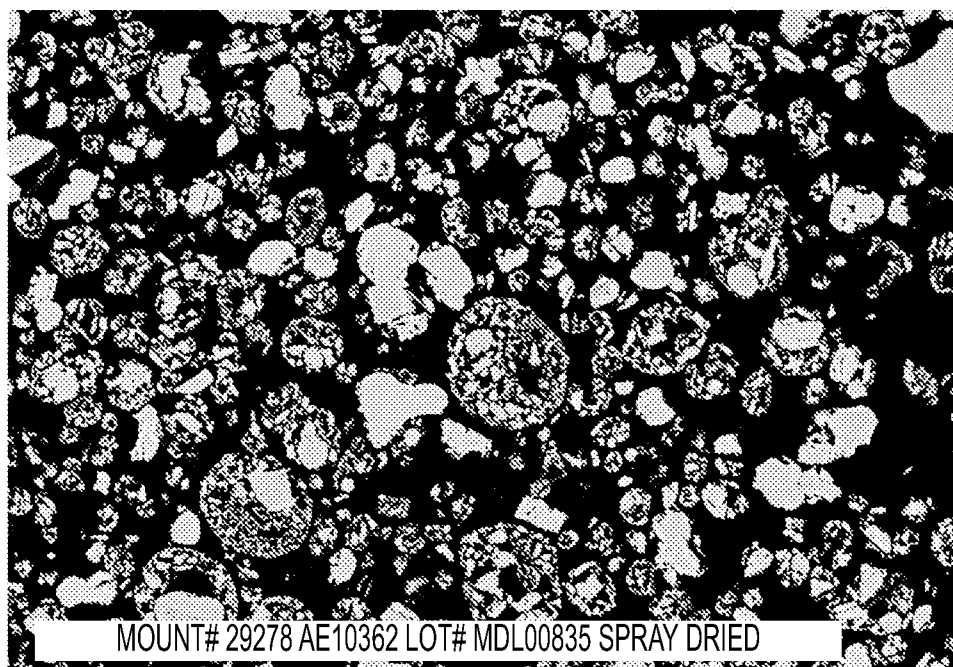
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**FIG. 20**

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**FIG. 21**

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***FIG. 22A******FIG. 22B***

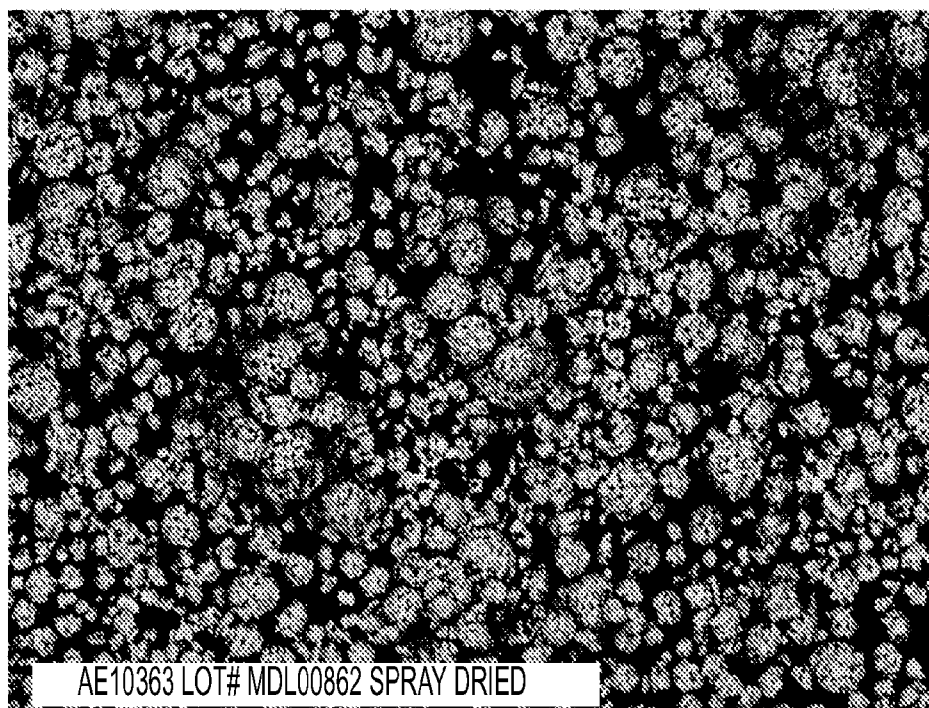


FIG. 23A

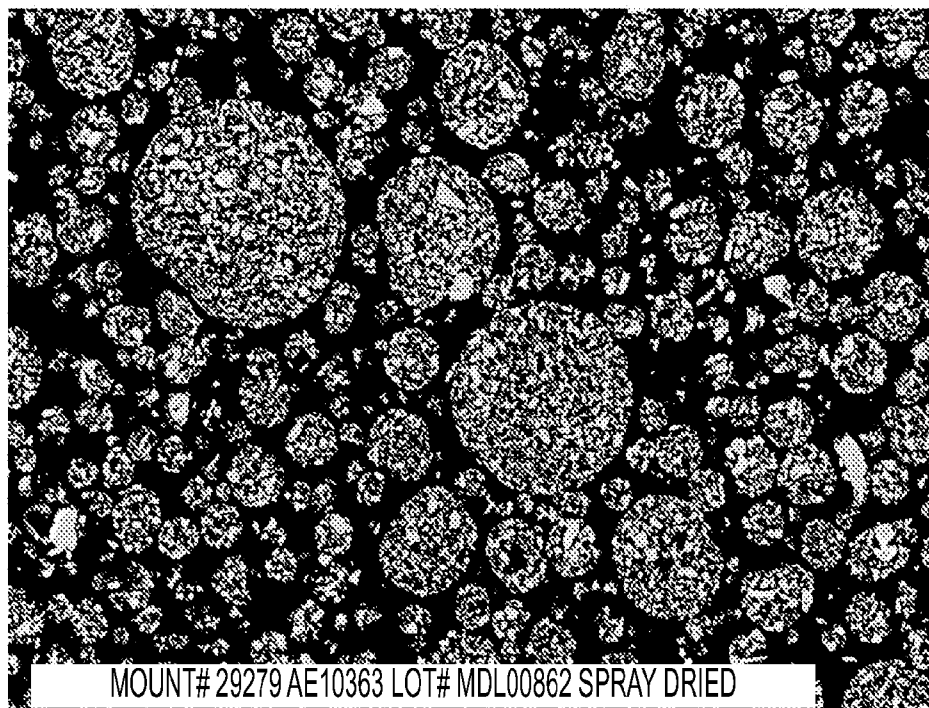


FIG. 23B

