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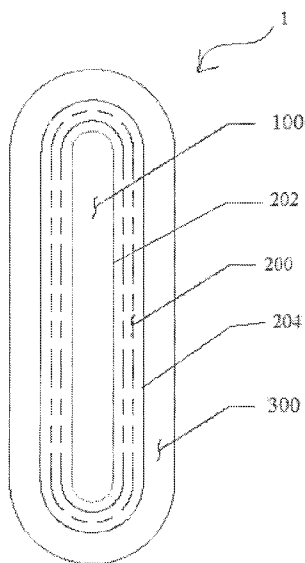


FIG. 1a

(57) **Abstract:** Embodiments of the present disclosure generally relate to electrodes useful for the electrolytic production of metal. In some embodiments, an electrode includes: a core; an outer shell; and an intermediate layer disposed between the core and the outer shell, wherein the intermediate layer covers at least a portion of the core, wherein the intermediate layer comprises an inner boundary and an outer boundary, wherein the intermediate layer electrically contacts the core at the inner boundary and electrically contacts the outer shell at the outer boundary, wherein the intermediate layer at the inner boundary has a first coefficient of thermal expansion that is substantially similar to a coefficient of thermal expansion of the core, and wherein the intermediate layer at the outer boundary has a second coefficient of thermal expansion that is substantially similar to a coefficient of thermal expansion of the outer shell.

WO 2017/223348 A1

MULTILAYER ELECTRODE

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims benefit of U.S. provisional application No. 62/353,246, filed June 22, 2016, which is herein incorporated by reference in its entirety.

FIELD

[0002] Embodiments of the present disclosure generally relate to electrodes useful for the electrolytic production of metal.

BACKGROUND

[0003] Hall-Heroult electrolytic cells are utilized to produce aluminum metal in the commercial production of aluminums form alumina that is dissolved in molten electrolyte and reduced by a DC electric current using electrodes.

SUMMARY

[0004] In some embodiments, an electrode includes: a core; an outer shell; and an intermediate layer disposed between the core and the outer shell, wherein the intermediate layer covers at least a portion of the core, wherein the intermediate layer comprises an inner boundary and an outer boundary, wherein the intermediate layer electrically contacts the core at the inner boundary and electrically contacts the outer shell at the outer boundary, wherein the intermediate layer at the inner boundary has a first coefficient of thermal expansion that is substantially similar to a coefficient of thermal expansion of the core, and wherein the intermediate layer at the outer boundary has a second coefficient of thermal expansion that is substantially similar to a coefficient of thermal expansion of the outer shell.

- [0005] In some embodiments, the core comprises one or more electrically conductive materials.
- [0006] In some embodiments, the core comprises at least one metal or metal alloy.
- [0007] In some embodiments, the at least one metal comprises at least one of: copper, nickel, iron, manganese, aluminum, cobalt, titanium, zinc or combinations thereof.
- [0008] In some embodiments, the at least one metal of the core is in the form of at least one of: a solid material, a metal foam, a metal powder, a metal wire, or combinations thereof.
- [0009] In some embodiments, the core comprises a cermet material having a continuous metal phase.
- [00010] In some embodiments, the cermet material comprises a structure of alternating metal fibers and ceramic fibers.
- [00011] In some embodiments, the cermet material comprises an interwoven microstructure.
- [00012] In some embodiments, the outer shell comprises one or more ceramic materials.
- [00013] In some embodiments, the ceramic material of the outer shell comprises at least one of oxides of iron, oxides of titanium, oxides of aluminum, oxides of chromium, oxides of zinc, oxides of vanadium, oxides of nickel, oxides of copper, oxides of ruthenium, oxides of tin, oxides of cobalt, nickel ferrites, copper ferrites, zinc ferrites, magnetite and combinations thereof.
- [00014] In some embodiments, the intermediate layer comprises one or more cermet materials and wherein the one or more cermet materials comprise a metallic phase and a ceramic phase.

[00015] In some embodiments, the metallic phase of the cermet material is continuous and the ceramic phase of the cermet material is discontinuous.

[00016] In some embodiments, the cermet material comprises 20 to 90 wt. % metal phase and the balance ceramic phase.

[00017] In some embodiments, the cermet material of the intermediate layer has a first ceramic concentration proximal the inner boundary of the intermediate layer and a second ceramic concentration proximal the outer boundary of the intermediate layer, and wherein the second ceramic concentration is greater than the first ceramic concentration.

[00018] In some embodiments, the coefficient of thermal expansion of the core is greater than the coefficient of thermal expansion of the outer shell.

[00019] In some embodiments, the core has a first electrical conductivity and the outer shell has a second electrical conductivity, and wherein the intermediate layer has a third electrical conductivity between the first electrical conductivity and second electrical conductivity.

[00020] In some embodiments, the intermediate layer comprises one or more sub-layers.

[00021] In some embodiments, a method of forming a multi-layer electrode, includes: coating a core material with a first cermet material via at least one of spray coating, dip coating, and slip casting to form a first coated core, wherein the first cermet material has a first coefficient of thermal expansion at an inner boundary electrically contacting the core, that is substantially similar to a coefficient of thermal expansion of the core material; coating the coated core with a second cermet material via at least one of spray coating, dip coating, and slip casting, to form a second coated core; and coating the second coated core with a ceramic material via at least one of spray coating, dip coating, and slip casting, wherein the second cermet material has a

second coefficient of thermal expansion at an outer boundary electrically contacting the ceramic material, that is substantially similar to a coefficient of thermal expansion of the ceramic material.

[00022] In some embodiments, coating the core with the cermet material further comprises: pressing a cermet powder on the core; and sintering the cermet powder.

[00023] In some embodiments, coating the core with the cermet material further comprises: forming a slurry comprising sub-micron size oxide powders and polymer binders; spray drying the slurry to form aggregated oxide granules; mixing the aggregated oxide granules with metal powder to produce a cermet powder blend; spray drying the slurry to form cermet granules; isostatically pressing the cermet granules onto the core to form a green intermediate layer; sintering the electrode to a temperature of 1000 to 1350 degrees Celsius in an inert gas atmosphere.

BRIEF DESCRIPTION OF THE DRAWINGS

[00024] Embodiments of the present invention, briefly summarized above and discussed in greater detail below, can be understood by reference to the illustrative embodiments of the invention depicted in the appended drawings. It is to be noted, however, that the appended drawings illustrate only typical embodiments of this invention and are therefore not to be considered limiting of its scope, for the invention may admit to other equally effective embodiments.

[00025] Figures 1A-1B depict a cross section of one embodiment of an electrode in accordance with some embodiments of the present invention.

[00026] Figures 2A-2E depict plan views of different embodiments of an electrode in accordance with some embodiments of the present invention.

[00027] Figures 3A-3B are micrographs of electrodes in accordance with some embodiments of the present invention.

[00028] Figures 4A-4B depict a core of an electrode in accordance with some embodiments of the present invention.

[00029] Figures 5A-5B depict the cermet material of the intermediate layer of an electrode in accordance with some embodiments of the present invention.

[00030] Figures 6A-6B depict a core of an electrode in accordance with some embodiments of the present invention.

[00031] To facilitate understanding, identical reference numerals have been used, where possible, to designate identical elements that are common to the figures. The figures are not drawn to scale and may be simplified for clarity. It is contemplated that elements and features of one embodiment may be beneficially incorporated in other embodiments without further recitation.

DESCRIPTION

[00032] The present invention will be further explained with reference to the attached drawings, wherein like structures are referred to by like numerals throughout the several views. The drawings shown are not necessarily to scale, with emphasis instead generally being placed upon illustrating the principles of the present invention. Further, some features may be exaggerated to show details of particular components.

[00033] The figures constitute a part of this specification and include illustrative embodiments of the present invention and illustrate various objects and features thereof. Further, the figures are not necessarily to scale, some features may be exaggerated to show details of particular components. In addition, any measurements, specifications and the like shown in the

figures are intended to be illustrative, and not restrictive. Therefore, specific structural and functional details disclosed herein are not to be interpreted as limiting, but merely as a representative basis for teaching one skilled in the art to variously employ the present invention.

[00034] Among those benefits and improvements that have been disclosed, other objects and advantages of this invention will become apparent from the following description taken in conjunction with the accompanying figures. Detailed embodiments of the present invention are disclosed herein; however, it is to be understood that the disclosed embodiments are merely illustrative of the invention that may be embodied in various forms. In addition, each of the examples given in connection with the various embodiments of the invention which are intended to be illustrative, and not restrictive.

[00035] Throughout the specification and claims, the following terms take the meanings explicitly associated herein, unless the context clearly dictates otherwise. The phrases "in one embodiment" and "in some embodiments" as used herein do not necessarily refer to the same embodiment(s), though it may. Furthermore, the phrases "in another embodiment" and "in some other embodiments" as used herein do not necessarily refer to a different embodiment, although it may. Thus, as described below, various embodiments of the invention may be readily combined, without departing from the scope or spirit of the invention.

[00036] In addition, as used herein, the term "or" is an inclusive "or" operator, and is equivalent to the term "and/or," unless the context clearly dictates otherwise. The term "based on" is not exclusive and allows for being based on additional factors not described, unless the context clearly dictates otherwise. In addition, throughout the specification, the meaning of "a," "an," and "the" include plural references. The meaning of "in" includes "in" and "on."

[00037] As used herein, “cermet material” is a composite material comprising a ceramic phase and a metallic phase. In some embodiments, the ceramic phase is a continuous phase and the metal phase is a discontinuous phase in the cermet material. In some embodiments, the metal phase is a continuous phase and the ceramic phase is a discontinuous phase in the cermet material.

[00038] As used herein, a “discontinuous phase” is a phase of a cermet material that is present in the cermet material as dispersed particles surrounded by the continuous phase of the cermet material.

[00039] As used herein, a “continuous phase” is a phase of a cermet material that surrounds the dispersed particles of the discontinuous phase.

[00040] As used herein, a “metallic phase” is a phase of a cermet material that comprises at least one alloy and/or elemental metal. In some embodiments, the metallic phase may comprise at least one of copper, nickel, iron, cobalt, titanium, aluminum, zinc, and/or alloys thereof.

[00041] As used herein, a “ceramic phase” is a phase of a cermet material that comprises at least one metal oxide. In some embodiments, the ceramic phase may comprise at least one ceramic material such as: a copper oxide, a nickel oxide, an iron oxide, a cobalt oxide, a titanium oxide, an aluminum oxide, a zinc oxide, and/or combinations thereof.

[00042] As used herein, a “ceramic concentration” is an amount of ceramic material per unit volume of cermet material.

[00043] As used herein, a “ceramic concentration gradient” is a difference in ceramic concentration along a direction within a cermet material.

[00044] Figures 1A and 1B depict an electrode 1 in accordance with some embodiments of the present disclosure. In some embodiments, the electrode 1 is suitable for use in an aluminum electrolysis cell. In some embodiments the electrode 1 is suitable for use as an anode in an aluminum electrolysis cell. In some embodiments, the electrode comprises a core 100, an outer shell 300; and an intermediate layer 200 disposed between the core 100 and the outer shell 300.

[00045] In some embodiments, the core 100 comprises one or more electrically conductive materials. In some embodiments, the core 100 comprises at least one metal. In some embodiments, the metal of the core 100 may comprise at least one of: copper, nickel, iron, manganese, aluminum, cobalt, titanium, aluminum, zinc and combinations thereof. In some embodiments, the core 100 comprises at least one metal alloy, including but not limited to: corrosion protected steel, carbon steel, nickel-chromium alloy (e.g. Inconel®), or nickel-chromium-molybdenum alloy (e.g. Hastelloy®). In some embodiments, the core 100 comprises at least one of: a solid material, a metal foam, a metal powder, a metal wire; and cermet having a continuous metal phase and a discontinuous ceramic phase. In some embodiments, the core 100 comprises a continuous metal phase and a continuous ceramic phase.

[00046] In some embodiments, as illustrated in Figure 4A, the core 100 comprises cermet having a layered metal 400/ceramic 402 structure. In some embodiments, the core 100 comprises a cermet having an alternating metal 400/ceramic 402 structure as illustrated in Figure 4B. In some embodiments, as illustrated in Figures 6A and 6B, the core 100 may comprise a cermet having an interwoven metal 400/ceramic 402 microstructure.

[00047] In some embodiments, the core 100 is cylindrical and has a diameter of 1/8 inch to 6 inches. In some embodiments, the core is cylindrical and has a diameter of 1/4 inch to 5

inches. In some embodiments, the core is cylindrical and has a diameter of 1/2 inch to 4 inches. In some embodiments, the core is cylindrical and has a diameter of 1 inch to 3 inches. In some embodiments, the core is cylindrical and has a diameter of about 2 inches.

[00048] In some embodiments, the core is non-cylindrically shaped and has a thickness of 1/8 inch to 4 inches and width of 1/2 inch to 12 inches. In some embodiments, the core is non-cylindrical shaped and has a thickness of 1/4 inch to 3 inches. In some embodiments, the core is non-cylindrical shaped and has a thickness of 1/2 inch to 2 inches. In some embodiments, the core is non-cylindrical shaped and has a thickness of about 1 inch. In some embodiments, the core is non-cylindrical shaped and has a width of 1 inch to 11 inches. In some embodiments, the core is non-cylindrical shaped and has a width of 2 inches to 10 inches. In some embodiments, the core is non-cylindrical shaped and has a width of 3 inches to 9 inches. In some embodiments, the core is non-cylindrical shaped and has a width of 4 inches to 8 inches. In some embodiments, the core is non-cylindrical shaped and has a width of 5 inches to 7 inches. In some embodiments, the core is non-cylindrical shaped and has a width of about 6 inches.

[00049] In some embodiments, the core has a height of 2 to 48 inches. In some embodiments, the core has a height of 4 to 46 inches. In some embodiments, the core has a height of 6 to 44 inches. In some embodiments, the core has a height of 8 to 42 inches. In some embodiments, the core has a height of 10 to 40 inches. In some embodiments, the core has a height of 12 to 36 inches. In some embodiments, the core has a height of 14 to 32 inches. In some embodiments, the core has a height of 16 to 28 inches. In some embodiments, the core has a height of 18 to 24 inches.

[00050] In some embodiments, the outer shell 300 comprises one or more ceramic materials. In some embodiments, the ceramic materials of the outer shell 300 comprise at least

one of oxides of iron, oxides of titanium, oxides of aluminum, oxides of chromium, oxides of zinc, oxides of vanadium, oxides of nickel, oxides of copper, oxides of ruthenium, oxides of tin, oxides of cobalt, nickel ferrites, copper ferrites, zinc ferrites, magnetite and combinations thereof.

[00051] In some embodiments, the outer shell 300 has a thickness of 1/4 inch to 3 inches. In some embodiments, the outer shell 300 has a thickness of 1/2 inch to 2 inches. In some embodiments, the outer shell 300 has a thickness of about 1 inch.

[00052] In some embodiments, the coefficient of thermal expansion of the core 100 is greater than the coefficient of thermal expansion of the outer shell 300. For example, Table 1 depicts non-limiting examples of materials suitable for use as the core, along with electrical conductivity and CTE values of the of the core material. Table 2 depicts non-limiting examples of materials suitable for use as the outer shell along with electrical conductivity and CTE values of the outer shell material. Thermal stresses arising from thermal expansion mismatch between the core 100 and the outer shell 300 can lead to cracking of the outer shell 300 during use of the electrode 1 in an aluminum electrolysis cell. Cracking of the outer shell can lead to corrosion of the core 100 from exposure to electrolytic bath chemicals in the aluminum electrolysis cell.

Table 1

	Name	EC(RT, S/cm)	EC(960C, S/cm)	CTE(RT-1000C, um/m C)
Examples of metallic core	Cu	516800	100500	21-24
	Steel	53560	8631	14.2
	In600	9648	8525	16.4
	Cu/Ni Foam	11246	2147	deformable
	Packed Cu/Ni Shots	104	1636	deformable

Table 2

	S#	Cu (-325)	EC(RT, S/CM)	EC(960C, S/cm)	CTE(RT-1000C, μM/M C)
Anode shell	Iron oxide		197	191	13.8
	Ni Ferrite		0.03	5.1	14.2

[00053] In some embodiments, the intermediate layer 200 may have coefficient of thermal expansion (CTE) that is between the coefficients of thermal expansion of the core 100 and the outer shell 300. Thus, in some embodiments, the intermediate layer 200 may serve to at least partially compensate for this difference in thermal expansion. Therefore, in some embodiments, the intermediate layer 200 may serve to prevent the outer shell 300 from cracking during use of the electrode 1 in an aluminum electrolysis cell. Furthermore, the intermediate layer 200 may add corrosion protection to the core 100.

[00054] In some embodiments, as depicted in Figure 1A-1B, the intermediate layer 200 has an inner boundary 202 and an outer boundary 204. The inner boundary 202 of the intermediate layer 200 contacts the core 100. The outer boundary 204 of the intermediate layer contacts the outer shell 300. In some embodiments, the intermediate layer 200 at the inner boundary 202 has a coefficient of thermal expansion that is substantially similar to a coefficient of thermal expansion of the core 100 and the intermediate layer 200 at the outer boundary 202 has a coefficient of thermal expansion that is substantially similar to a coefficient of thermal expansion of the outer shell 300. In some embodiments, the intermediate layer 200 may have an electrical conductivity that is between the electrical conductivities of the core 100 and the outer shell 300.

[00055] In some embodiments, the intermediate layer covers at least a portion of the core 100. In some embodiments, the intermediate layer covers at least 5% of the core. In some embodiments, the intermediate layer covers at least 10% of the core. In some embodiments, the intermediate layer covers at least 15% of the core. In some embodiments, the intermediate layer

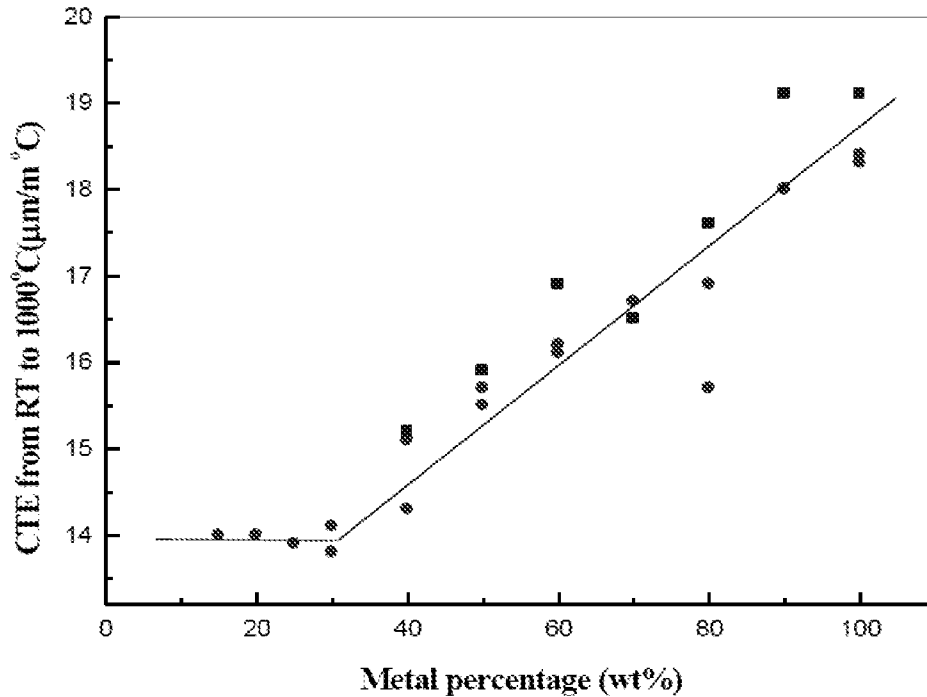
covers at least 20% of the core. In some embodiments, the intermediate layer covers at least 25% of the core. In some embodiments, the intermediate layer covers at least 30% of the core. In some embodiments, the intermediate layer covers at least 35% of the core. In some embodiments, the intermediate layer covers at least 40% of the core. In some embodiments, the intermediate layer covers at least 45% of the core. In some embodiments, the intermediate layer covers at least 50% of the core. In some embodiments, the intermediate layer covers at least 60% of the core. In some embodiments, the intermediate layer covers at least 70% of the core. In some embodiments, the intermediate layer covers at least 80% of the core. In some embodiments, the intermediate layer covers at least 90% of the core. In some embodiments, the intermediate layer covers at least 95% of the core.

[00056] In some embodiments, the intermediate layer 200 comprises one or more cermet materials. In some embodiments, the cermet material of the intermediate layer 200 comprises a metallic phase and a ceramic phase. In some embodiments, the cermet material of the intermediate layer is 20 to 90 wt% metal phase and the balance ceramic phase. In some embodiments, the cermet material of the intermediate layer is 40 to 90 wt% metal phase and the balance ceramic phase. In some embodiments, the cermet material of the intermediate layer is 60 to 90 wt% metal phase and the balance ceramic phase. In some embodiments, the cermet material of the intermediate layer is 80 to 90 wt% metal phase and the balance ceramic phase. In some embodiments, as shown in Figures 5A and 5B, the metallic phase 502 of the cermet material 500 is continuous and the ceramic phase 504 of the cermet material 500 is discontinuous. In some embodiments, the cermet material of the intermediate layer 200 has a first ceramic concentration proximal the inner boundary 202 of the intermediate layer 200 and a second ceramic concentration proximal the outer boundary 204 of the intermediate layer 200. In

some embodiments, the second ceramic concentration is higher than the first. In some embodiments, the cermet material of the intermediate layer 200 has a ceramic concentration gradient from the inner boundary to the outer boundary of the intermediate layer. In some embodiments, the ceramic concentration gradient increases from the inner boundary of the intermediate layer to the outer boundary of the intermediate layer.

[00057] Graph 1 shows the coefficient of thermal expansion (CTE) as a function of percent of metal phase in nickel ferrite cermet. The circular data points represent cermet of nickel ferrite and Cu and the square data point represent the cermet of nickel ferrite and Ni₃₀Cu. As shown in Graph 1, when the metallic phase (Cu or Ni₃₀Cu) is less than about 30 weight percentage, the CTEs of the cermet material is substantially constant. When the metallic phase (Cu or Ni₃₀Cu) is higher than 30 weight percentage, the CTEs of the cermet material increases proportionally with metallic phase percentage, indicating metallic phases becomes the continuous phase after reaching 30 wt.%.

Graph 1:



[00058] In some embodiments, the intermediate layer 200 may comprise one or more sub-layers of cermet material. In some embodiments, as depicted in Figure 1B, the intermediate layer 200 comprises, a first sub-layer 220 located proximal the inner boundary 202 of the intermediate layer 200, a third sub-layer 230 located proximal the outer boundary 204 of the intermediate layer 200, and a second sub-layer 210 located between the first sub-layer 220 and third sub-layer 230. In some embodiments, the first sub-layer 220 comprises a first cermet material, the second sub-layer 210 comprises a second cermet material, and the third sub-layer 230 comprises a third cermet material. In some embodiments, the first cermet material has a continuous metal phase and a discontinuous ceramic phase. In some embodiments, the third cermet material has a continuous ceramic phase and a discontinuous metal phase.

[00059] In some embodiments, the first cermet material comprises 70 to 90 wt. % metal phase. In some embodiments, the first cermet material comprises 72 to 88 wt. % metal phase. In some embodiments, the first cermet material comprises 75 to 85 wt. % metal phase. In some

embodiments, the first cermet material comprises 77 to 83 wt. % metal phase. In some embodiments, the first cermet material comprises about 80 wt. % metal phase.

[00060] In some embodiments, the first cermet material comprises 10 to 30 wt. % ceramic phase. In some embodiments, the first cermet material comprises 12 to 28 wt. % ceramic phase. In some embodiments, the first cermet material comprises 15 to 25 wt. % ceramic phase. In some embodiments, the first cermet material comprises 17 to 23 wt. % ceramic phase. In some embodiments, the first cermet material comprises about 20 wt. % ceramic phase.

[00061] In some embodiments, the second cermet material comprises 40 to 60 wt. % metal phase. In some embodiments, the second cermet material comprises 42 to 58 wt. % metal phase. In some embodiments, the second cermet material comprises 45 to 55 wt. % metal phase. In some embodiments, the second cermet material comprises 47 to 53 wt. % metal phase. In some embodiments, the second cermet material comprises about 50 wt. % metal phase.

[00062] In some embodiments, the second cermet material comprises 40 to 60 wt. % ceramic phase. In some embodiments, the second cermet material comprises 42 to 58 wt. % ceramic phase. In some embodiments, the second cermet material comprises 45 to 55 wt. % ceramic phase. In some embodiments, the second cermet material comprises 47 to 53 wt. % ceramic phase. In some embodiments, the second cermet material comprises about 50 wt. % ceramic phase.

[00063] In some embodiments, the third cermet material comprises 70 to 90 wt. % ceramic phase. In some embodiments, the third cermet material comprises 72 to 88 wt. % ceramic phase. In some embodiments, the third cermet material comprises 75 to 85 wt. % ceramic phase. In some embodiments, the third cermet material comprises 77 to 83 wt. %

ceramic phase. In some embodiments, the third cermet material comprises about 80 wt. % ceramic phase.

[00064] In some embodiments, the third cermet material comprises 10 to 30 wt. % metal phase. In some embodiments, the third cermet material comprises 12 to 28 wt. % metal phase. In some embodiments, the third cermet material comprises 15 to 25 wt. % metal phase. In some embodiments, the third cermet material comprises 17 to 23 wt. % metal phase. In some embodiments, the third cermet material comprises about 20 wt. % metal phase.

[00065] In some embodiments, the intermediate layer has a thickness of 1/16 to 1 inch. In some embodiments, the intermediate layer has a thickness of 1/8 to 1/2 inch. In some embodiments, the intermediate layer has a thickness of about 1/4 inch.

[00066] In some embodiments, the first sub-layer has a thickness of 1/8 inch to 4 inches. In some embodiments, the first sub-layer has a thickness of 1/4 inch to 3 inches. In some embodiments, the first sub-layer has a thickness of 1/2 inch to 2 inches. In some embodiments, the first sub-layer has a thickness of about 1 inch.

[00067] In some embodiments, the second sub-layer has a thickness of 1/4 inch to 2 inches. In some embodiments, the second sub-layer has a thickness of 1/2 inch to 1.5 inches. In some embodiments, the second sub-layer has a thickness of about 1 inch.

[00068] In some embodiments, the third sub-layer has a thickness of 1/4 to 1 inch. In some embodiments, the third sub-layer has a thickness of 3/8 to 7/8 inch. In some embodiments, the third sub-layer has a thickness of 1/2 to 3/4 inch. In some embodiments, the third sub-layer has a thickness of about 5/8 inch.

[00069] The electrode may be formed in a variety of shapes. Non-limiting examples of the shape of the electrode include cylindrical or non-cylindrical. For example, in some

embodiments as shown in Figure 2A, the electrode may have a rectangular shape when viewed from the top. In some embodiments, as shown in Figure 2B, the electrode may have a rounded rectangular shape when viewed from the top. In some embodiments, as shown in Figure 2C, the electrode may be pill shaped when viewed from the top. In some embodiments, as shown in Figure 2D, the electrode may be elliptical when viewed from the top. In some embodiments, as shown in Figure 2E, the electrode may have a circular shape when viewed from the top.

[00070] Figure 3A is a micrograph of one embodiment of an electrode in accordance with the present invention. As shown in Figure 3A, the electrode includes a core comprised of wires 110, an outer shell 310 comprised of ceramic material, and an intermediate layer 210 comprised of cermet material having a continuous metal phase and a discontinuous ceramic phase.

[00071] Figure 3B is a micrograph of another embodiment of an electrode in accordance with the present invention. As shown in Figure 3B, the electrode includes a core comprised of solid metal material 120, an outer shell 320 comprised of ceramic material, and an intermediate layer 220 comprised of cermet material. The embodiment of Figure 3B depicts an intermediate layer 220 having an increasing ceramic concentration gradient from the solid metal material 120 of the core to the outer shell 320 of ceramic material.

[00072] In some embodiments, a method of forming a multi-layer electrode, includes coating a core material with a first cermet material via at least one of spray coating, dip coating, and slip casting to form a first coated core, wherein the first cermet material has a first coefficient of thermal expansion at an inner boundary electrically contacting the core, that is substantially similar to a coefficient of thermal expansion of the core material; coating the coated core with a second cermet material via at least one of spray coating, dip coating, and slip casting, to form a second coated core; and coating the second coated core with a ceramic material via at

least one of spray coating, dip coating, and slip casting, wherein the second cermet material has a second coefficient of thermal expansion at an outer boundary electrically contacting the ceramic material, that is substantially similar to a coefficient of thermal expansion of the ceramic material.

[00073] In some embodiments, the coating with the cermet material (e.g. first cermet material or second cermet material) comprises pressing a cermet powder onto the underlying material (e.g. electrode core) and sintering the cermet powder.

[00074] In some embodiments, coating the core with cermet material comprises producing a cermet powder blend. In some embodiments, the step of producing a cermet powder blend includes mixing aggregated oxide granules with metal powder. In some embodiments, the aggregated oxide granules may be produced, for example, by forming a slurry of sub-micron size oxide powders and polymer binders or a slurry of sub-micron size oxide powders, polymer binders, and metal powders, and then spray drying the slurry to form aggregated oxide granules that flow and deform readily during forming. In some embodiments, the cermet powder blend may be mixed into a slurry and spray dried to form cermet granules. In some embodiments, the cermet granules may be pressed isostatically onto the core at an isostatic pressure to form a green intermediate layer. In some embodiments, the isostatic pressure is 5 to 35 kpsi (thousand pounds per square inch). In some embodiments, the green intermediate layer may be heated in an inert atmosphere. In some embodiments the inert atmosphere comprises Ar and/or N₂ with oxygen concentration below 100ppm. In some embodiments, the core with green intermediate layer is placed in a furnace and exposed to a first temperature of 400 to 600 degrees C to burn out the polymer binder. In some embodiments, the heating rate is from 10 to 180 degrees C/hr. In some

embodiments, the electrode with green intermediate layer is exposed to a second temperature of 1000 to 1350 degrees Celsius to sinter the cermet granules and form a cermet intermediate layer.

[00075] While a number of embodiments of the present invention have been described, it is understood that these embodiments are illustrative only, and not restrictive, and that many modifications may become apparent to those of ordinary skill in the art. Further still, the various steps may be carried out in any desired order (and any desired steps may be added and/or any desired steps may be eliminated).

Claims

1. An electrode, comprising:
 - a core;
 - an outer shell; and
 - an intermediate layer disposed between the core and the outer shell,wherein the intermediate layer covers at least a portion of the core,
 - wherein the intermediate layer comprises an inner boundary and an outer boundary,
 - wherein the intermediate layer electrically contacts the core at the inner boundary and electrically contacts the outer shell at the outer boundary,
 - wherein the intermediate layer at the inner boundary has a first coefficient of thermal expansion that is substantially similar to a coefficient of thermal expansion of the core, and
 - wherein the intermediate layer at the outer boundary has a second coefficient of thermal expansion that is substantially similar to a coefficient of thermal expansion of the outer shell.
2. The electrode of claim 1, wherein the core comprises one or more electrically conductive materials.
3. The electrode of claim 2, wherein the core comprises at least one metal or metal alloy.

4. The electrode of claim 3, wherein the at least one metal comprises at least one of: copper, nickel, iron, manganese, aluminum, cobalt, titanium, zinc or combinations thereof.
5. The electrode of claim 3, wherein the at least one metal of the core is in the form of at least one of: a solid material, a metal foam, a metal powder, a metal wire, or combinations thereof.
6. The electrode of claim 1, wherein the core comprises a cermet material having a continuous metal phase.
7. The electrode of claim 6, wherein the cermet material comprises a structure of alternating metal fibers and ceramic fibers.
8. The electrode of claim 6, wherein the cermet material comprises an interwoven microstructure.
9. The electrode of claim 1, wherein the outer shell comprises one or more ceramic materials.
10. The electrode of claim 9, wherein the ceramic material of the outer shell comprises at least one of oxides of iron, oxides of titanium, oxides of aluminum, oxides of chromium, oxides of zinc, oxides of vanadium, oxides of nickel, oxides of copper, oxides of

ruthenium, oxides of tin, oxides of cobalt, nickel ferrites, copper ferrites, zinc ferrites, magnetite and combinations thereof.

11. The electrode of claim 1, wherein the intermediate layer comprises one or more cermet materials and wherein the one or more cermet materials comprise a metallic phase and a ceramic phase.

12. The electrode of claim 11, wherein the metallic phase of the cermet material is continuous and the ceramic phase of the cermet material is discontinuous.

13. The electrode of claim 11, wherein the cermet material comprises 20 to 90 wt. % metal phase and the balance ceramic phase.

14. The electrode of claim 11, wherein the cermet material of the intermediate layer has a first ceramic concentration proximal the inner boundary of the intermediate layer and a second ceramic concentration proximal the outer boundary of the intermediate layer, and wherein the second ceramic concentration is greater than the first ceramic concentration.

15. The electrode of claim 1, wherein the coefficient of thermal expansion of the core is greater than the coefficient of thermal expansion of the outer shell.

16. The electrode of claim 1, wherein the core has a first electrical conductivity and the outer shell has a second electrical conductivity, and wherein the intermediate layer has a third

electrical conductivity between the first electrical conductivity and second electrical conductivity.

17. The electrode of claim 1, wherein the intermediate layer comprises one or more sub-layers.

18. A method of forming a multi-layer electrode, comprising:

coating a core material with a first cermet material via at least one of spray coating, dip coating, and slip casting to form a first coated core, wherein the first cermet material has a first coefficient of thermal expansion at an inner boundary electrically contacting the core, that is substantially similar to a coefficient of thermal expansion of the core material;

coating the coated core with a second cermet material via at least one of spray coating, dip coating, and slip casting, to form a second coated core; and

coating the second coated core with a ceramic material via at least one of spray coating, dip coating, and slip casting, wherein the second cermet material has a second coefficient of thermal expansion at an outer boundary electrically contacting the ceramic material, that is substantially similar to a coefficient of thermal expansion of the ceramic material.

19. The method of claim 19, wherein coating the core with the cermet material further comprises:

pressing a cermet powder on the core; and

sintering the cermet powder.

20. The method of claim 19, wherein coating the core with the cermet material further comprises:

forming a slurry comprising sub-micron size oxide powders and polymer binders;

spray drying the slurry to form aggregated oxide granules;

mixing the aggregated oxide granules with metal powder to produce a cermet powder blend;

spray drying the slurry to form cermet granules;

isostatically pressing the cermet granules onto the core to form a green intermediate layer;

sintering the electrode to a temperature of 1000 to 1350 degrees Celsius in an inert gas atmosphere.

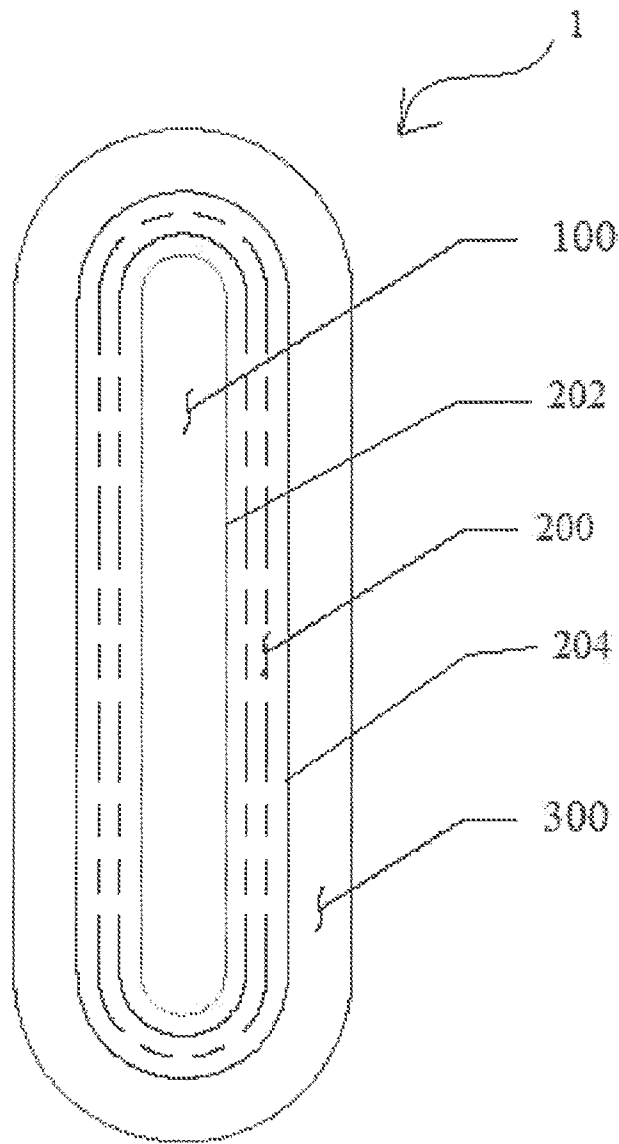


FIG. 1a

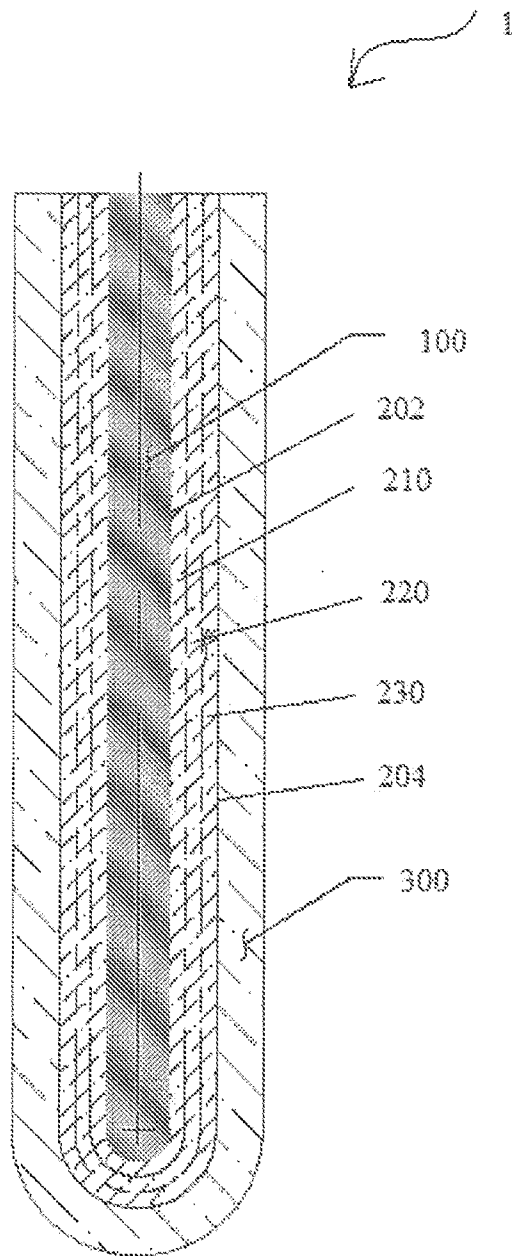


FIG. 1b

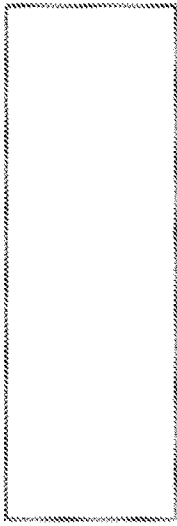


FIG. 2a

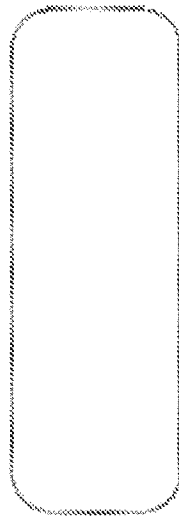


FIG. 2b

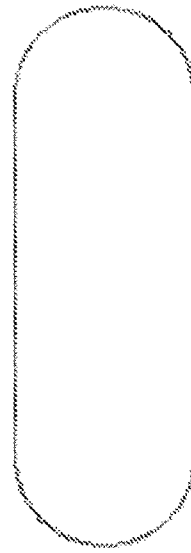


FIG. 2c



FIG. 2d

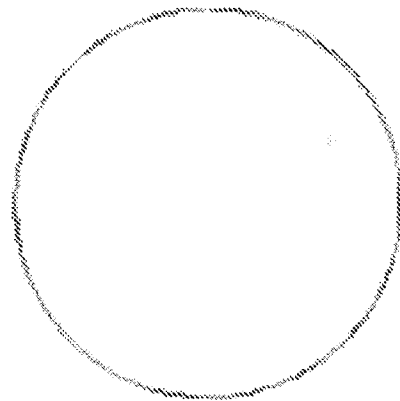


FIG. 2e

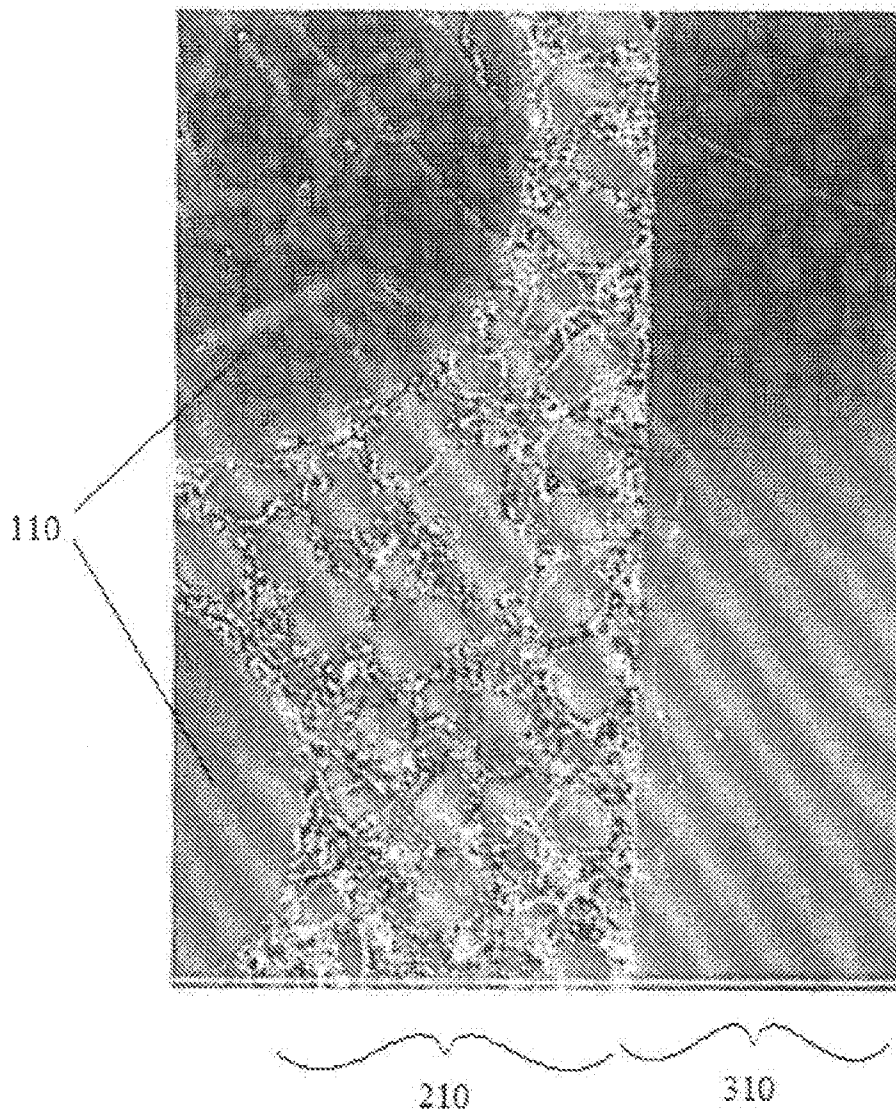


FIG. 3a

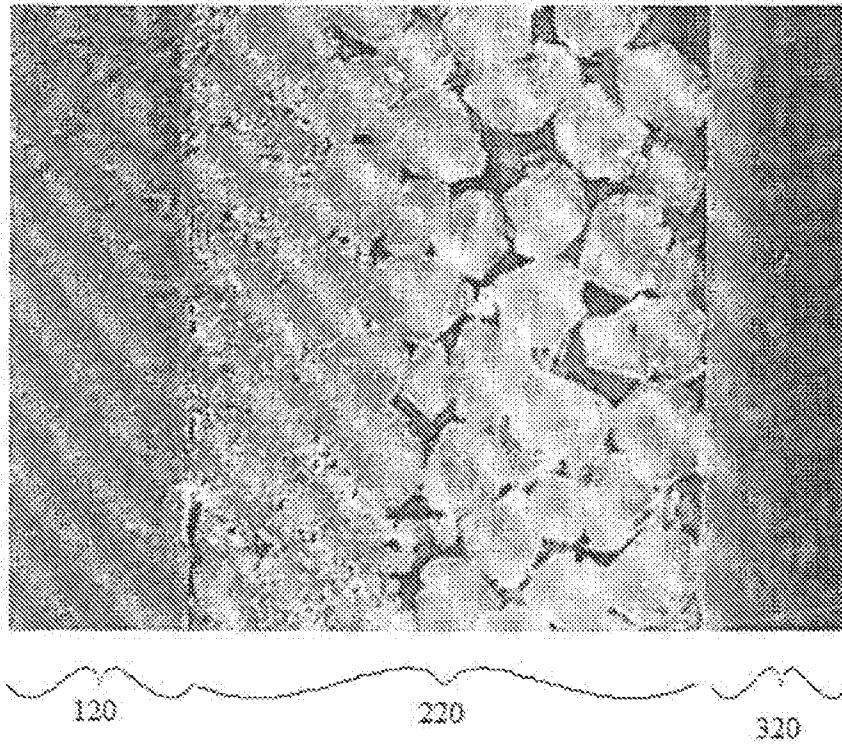


FIG. 3b

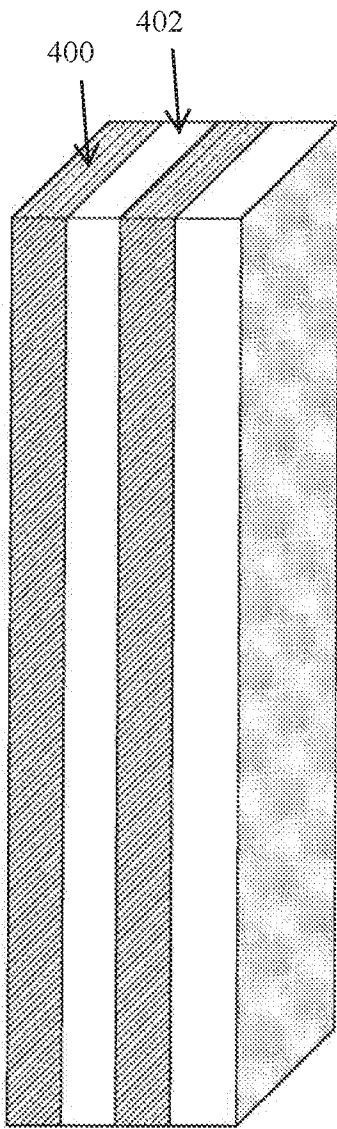


FIG 4a

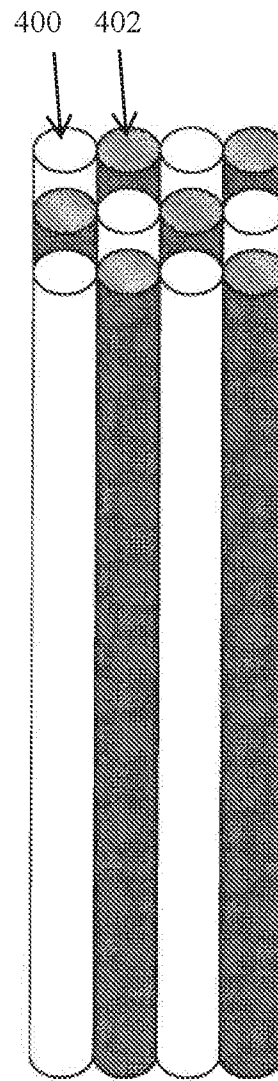


FIG. 4b

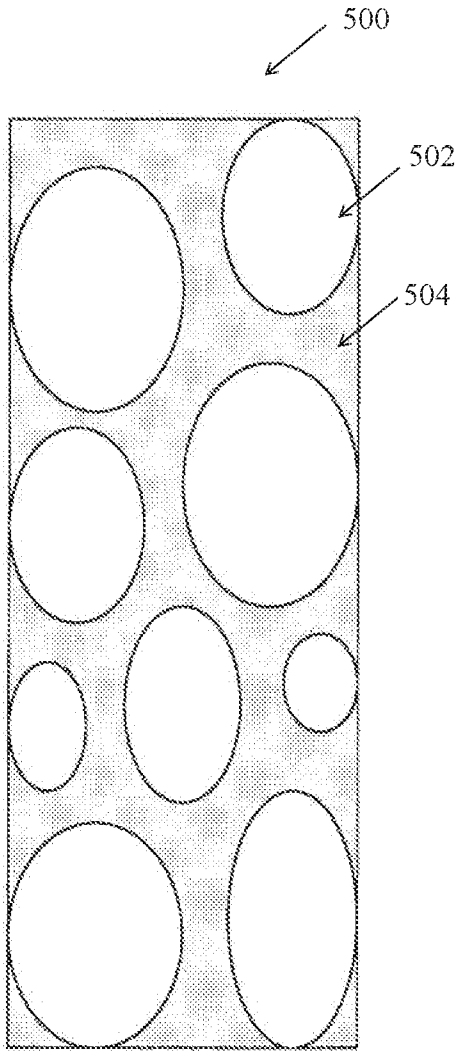


FIG. 5a

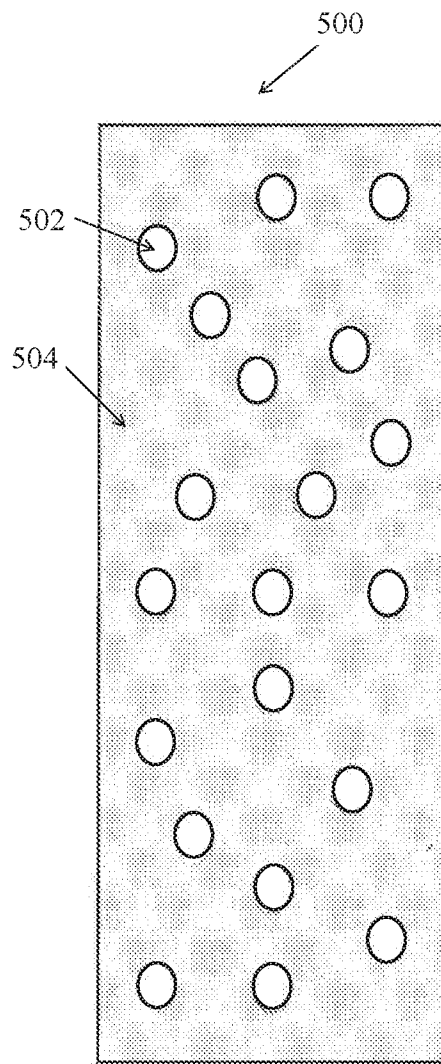


FIG. 5b

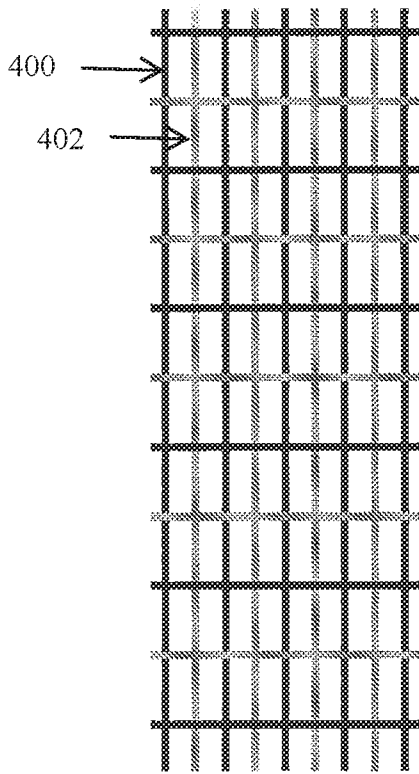


FIG. 6a

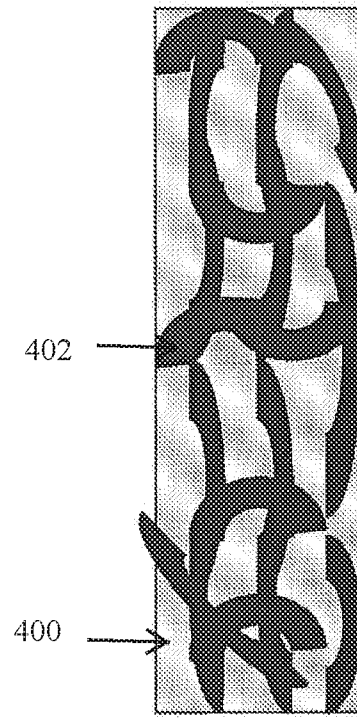


FIG. 6b

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 17/38814

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

- 1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

- 2. Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

- 3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

-----see supplemental box-----

- 1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
- 2. As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
- 3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

- 4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-17

- Remark on Protest**
- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
 - The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
 - No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 17/38814

A. CLASSIFICATION OF SUBJECT MATTER
 IPC(8) - H01L 51/52, H01L 51/44 (2017.01)
 CPC - H01L 51/5218, Y02E 10/549, H01L 2251/308

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History Document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

See Search History Document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6,077,415 A (Duruz et al.) 20 June 2000 (20.06.2000) Abstract, col 2 ln 45-70; col 3 ln 10-60; col 4 ln 20-40; and entire document	1-17
Y	US 4,624,766 A (Boxall et al.) 25 November 1986 (25.11.1986) Abstract, col 4 ln 30-35; col 7 ln 30-35; col 20 ln 10-30; col 25 ln 55-60 and entire document	1-17
A	US 2004/0108205 A1 (Larsen) 10 June 2004 (10.06.2004) Abstract, Figure 1; para [005]-[012]	1-17
E/A	US 2017/0275773 A1 (Alcoa USA) 28 September 2017 (28.09.2017) entire document	1-17

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

10 October 2017 (10.10.2017)

Date of mailing of the international search report

30 OCT 2017

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
 P.O. Box 1450, Alexandria, Virginia 22313-1450
 Facsimile No. 571-273-8300

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300
 PCT OSP: 571-272-7774

-----continued from Box III -----

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I: Claims 1-17 is directed towards an electrode.

Group II: Claims 18-20 is directed towards a method of forming a multi-layer electrode.

The inventions listed as Groups I-II do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Special Technical Features:

Group I requires an electrode, comprising: a core; an outer shell; and an intermediate layer disposed between the core and the outer shell, wherein the intermediate layer covers at least a portion of the core not required by Group II.

Group II requires a method of forming a multi-layer electrode, comprising: coating a core material with a first cermet material via at least one of spray coating, dip coating, and slip casting to form a first coated core, wherein the first cermet material has a first coefficient of thermal expansion at an inner boundary electrically contacting the core, that is substantially similar to a coefficient of thermal expansion of the core material; coating the coated core with a second cermet material via at least one of spray coating, dip coating, and slip casting, to form a second coated core; and coating the second coated core with a ceramic material via at least one of spray coating, dip coating, and slip casting, wherein the second cermet material has a second coefficient of thermal expansion at an outer boundary electrically contacting the ceramic material, that is substantially similar to a coefficient of thermal expansion of the ceramic material not required by groups I.

Shared Technical Features:

Groups I-II share the common feature of an electrode having a core; an outer shell; and an intermediate layer disposed between the core and the outer shell wherein the intermediate layer at the inner boundary has a first coefficient of thermal expansion that is substantially similar to a coefficient of thermal expansion of the core, and wherein the intermediate layer at the outer boundary has a second coefficient of thermal expansion that is substantially similar to a coefficient of thermal expansion of the outer shell. However, these shared technical features do not represent a contribution over prior art, because the shared technical feature is obvious over US 6,077,415 A to Duruz et al. (hereinafter Duruz) in view of US 4,624,766 A to Boxall et al. (hereinafter Boxall). Duruz discloses a electrode having a core, an outer shell and an intermediate layer disposed between the core and the outer shell (col 2 ln 45-70; The invention relates to a composite, high-temperature resistant, non-carbon, metal-based anode; the conductive layers consist of a at least one layer on the metal-based core structure; one or more intermediate protective layers on the outermost oxygen barrier layer and an electrochemically active layer on the outermost intermediate layer). Duruz does not disclose the thermal expansion coefficients. However, Boxall discloses a electrode used for aluminum production (col 4 ln 30-35; Such coated cathodes combine the advantages of conventional carbon linings, such as structural integrity and low cost, with desired properties attained by use of the Refractory Hard Materials) that discloses the matching of thermal coefficients (col 7 ln 30-35; once the coating composition has been carbonized to a rigid, hard solid, it is critical that the thermal expansion coefficient of the coating be essentially equal to the thermal expansion coefficient of the cathode substrate). As both Duruz and Boxall disclose the methods of making layered electrodes; it would have been obvious to a person having ordinary skill in the art to know that the layered electrode disclosed by Duruz can have a matched thermal expansion coefficients as disclosed by Boxall as it provides for a better electrode (Boxall; col 3 ln 60-70; Mechanisms of de-bonding are believed to involve high stresses generated by the thermal expansion mismatch) through routine experimentation.

As the shared technical features were known in the art at the time of the invention, they cannot be considered special technical features that would otherwise unify the groups. Therefore, Groups I-II lack unity under PCT Rule 13.