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(54) Title: PLATING OR COATING METHOD FOR PRODUCING METAL-CERAMIC COATING ON A SUBSTRATE

(57) Abstract: A plating or coating method for producing a metal-ceramic composite coating on a substrate is provided. The method comprises adding a sol of a ceramic phase to a plating solution or electrolyte and controlling the pH, degree of mixing, and/ or temperature of the plating solution or electrolyte. An item or surface comprising a substrate and a metal-ceramic composite coating on the substrate, the metal-ceramic composite coating comprising a ceramic phase of dispersed amorphous ceramic particles having an average diameter of from 1 to 100 nm is also provided.



**“PLATING OR COATING METHOD FOR PRODUCING METAL-CERAMIC
COATING ON A SUBSTRATE”**

FIELD OF INVENTION

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The invention relates to an improved plating or coating method for producing a metal-ceramic composite coating on a substrate.

BACKGROUND

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In electroplating, sometimes referred to as electrodeposition, a conductive item to be metal plated, which forms a cathode, and an anode, are immersed in an electrolyte containing one or more dissolved metal salts. A battery or rectifier supplies direct current. In one method, the anode is of the plating metal and metal of the anode is oxidised and dissolved into the electrolyte. At the
15 cathode, the dissolved metal ions are reduced and plated onto the cathode/item. In another method, the anode is not consumable and ions of the plating metal are provided in the electrolyte and must be periodically replenished.

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Electroless plating or deposition is a non-galvanic plating or coating method in which a reducing agent, typically sodium hypophosphite, in aqueous solution reduces metal ions of the plating metal in solution from the anode, which deposit onto the cathode/item. Electroless nickel plating may be used to deposit a coating of nickel, for example Ni-P or Ni-B, onto a substrate which may be a metal or plastic substrate.

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Plating or coating of an item or surface is typically carried out to provide a desired property to a surface or item that otherwise lacks that property, or to improve a property, such as abrasion or wear resistance, corrosion resistance, or a particular appearance, for example.

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It is an object of the present invention to provide an improved method of plating or coating, or to at least provide the public with a useful choice.

SUMMARY OF INVENTION

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In broad terms in one aspect the invention comprises a plating or coating method for producing a metal-ceramic composite coating on a substrate, the method comprising adding a sol of a ceramic

phase to a plating solution or electrolyte and controlling the pH, degree of mixing, and/or temperature of the plating solution or electrolyte.

5 In another aspect the invention comprises an item or surface plated or coated by a plating or coating method of the invention as described or defined herein.

10 In another aspect, the invention comprises an item or surface comprising a substrate and a metal-ceramic composite coating on the substrate, the metal-ceramic composite coating comprising a ceramic phase of dispersed amorphous ceramic particles having an average diameter of from 1 to 100 nm.

The following embodiments apply to any of the aspects above.

15 In one embodiment, the pH, degree of mixing, or temperature of the plating solution or electrolyte is controlled. In one embodiment, the pH and degree of mixing; the pH and temperature; or the degree of mixing and temperature of the plating solution or electrolyte is controlled. In one embodiment, the pH, degree of mixing, and temperature of the plating solution or electrolyte is controlled.

20 In one embodiment, the pH, degree of mixing, and/or temperature is controlled such that nanoparticles of the ceramic phase form directly onto or at the substrate.

25 In one embodiment, the pH, degree of mixing, and/or temperature is controlled such that the metal-ceramic coating forms on the substrate with a predominantly crystalline structure. In one embodiment, the metal-ceramic coating, other than the ceramic phase, is substantially crystalline.

30 In one embodiment, the pH, degree of mixing, and/or temperature is controlled to substantially avoid formation of nanoparticles or microparticles of the ceramic phase, and/or agglomeration of particles of the ceramic phase, in the plating solution or electrolyte.

35 In one embodiment, the pH, degree of mixing, and/or temperature is controlled to reduce (compared to a corresponding plating or coating method wherein the pH, degree of mixing, and/or temperature is not controlled) or prevent the precipitation of visible particles and/or agglomerates of the ceramic phase in the plating solution or electrolyte.

In one embodiment, the pH, degree of mixing, and/or temperature is controlled to reduce (compared to a corresponding plating or coating method wherein the pH, degree of mixing, and/or temperature is not controlled) or prevent the formation of particles and/or agglomerates of particles of the ceramic phase having an average diameter more than 100, more than 50, more than 30, more than 25, more than 20, or more than 15 nm in the plating solution or electrolyte.

In one embodiment, the pH, degree of mixing, and/or temperature is controlled such that the average diameter of particles of the ceramic phase in the plating solution or electrolyte is less than about 2 nm or less than about 1 nm.

In one embodiment, the pH, degree of mixing, and/or temperature is controlled to provide particles of the ceramic phase in the plating solution or electrolyte that remain in suspension in the plating solution or electrolyte without mixing and/or at a temperature lower than the temperature at which the sol is added to the plating solution or electrolyte.

In one embodiment, the pH, degree of mixing, and/or temperature is controlled such that amorphous particles of the ceramic phase having an average diameter from about 1 to about 100, from about 3 to about 100, from about 1 to about 50, from about 3 to about 50, from about 1 to about 30, from about 3 to about 30, from about 1 to about 25, from about 3 to about 25, from about 1 to about 20, from about 3 to about 20, from about 1 to about 12, or from about 3 to about 12 nm are incorporated into the metal-ceramic composite coating.

In one embodiment, the pH, degree of mixing, and/or temperature is controlled such that the amorphous particles of the ceramic phase are dispersed throughout the metal-ceramic composite coating. In one embodiment, the pH, degree of mixing, and/or temperature is controlled such that the amorphous particles of the ceramic phase are substantially uniformly dispersed throughout the metal-ceramic coating.

In one embodiment, the pH of the plating solution or electrolyte is controlled prior to, during, or after addition of the sol to the plating solution or electrolyte. In one embodiment, the pH is controlled during addition of the sol. In one embodiment, the pH is controlled during plating or coating.

In one embodiment, the pH of the plating solution or electrolyte is monitored. In one embodiment, the pH is monitored during addition of the sol and, optionally, during plating or coating. In one

embodiment, the pH is monitored by colorimetric or electrometric methods. In one embodiment, the pH is monitored using a pH meter.

In one embodiment, the pH of the plating solution or electrolyte is maintained within a predetermined pH range during addition of the sol and, optionally, during plating or coating. In one embodiment, the predetermined pH range is less than about 1, less than about 0.9, less than about 0.8, less than about 0.7, less than about 0.6, less than about 0.5, less than about 0.4, less than about 0.3, or less than about 0.2 pH units. In one embodiment, the predetermined pH range is suitable for plating or coating the substrate with the metal-ceramic composite coating.

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In one embodiment, the pH is maintained within a predetermined pH range during addition of the sol and, optionally, during plating or coating, wherein the predetermined pH range is suitable for plating or coating the substrate with the metal-ceramic composite coating and is effective to substantially avoid formation of nanoparticles or microparticles of the ceramic phase, and/or agglomeration of particles of the ceramic phase.

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In one embodiment, the pH of the plating solution or electrolyte is adjusted prior to, during, or after addition of the sol. In one embodiment, the pH of the plating solution or electrolyte is adjusted prior to or during addition of the sol. In one embodiment, the pH is adjusted during addition of the sol.

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In one embodiment, the pH of the plating solution is adjusted prior to or during addition of the sol such that the pH of the plating solution or electrolyte is maintained within the predetermined pH range during addition of the sol.

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In one embodiment, the pH is adjusted by adding acid or base. In one embodiment, the acid or base is an organic or inorganic acid or base.

In one embodiment, the pH of the plating solution or electrolyte is maintained at a pH of less than about 8, less than about 7, less than about 6, less than about 5, less than about 4, less than about 3, or less than about 2 during addition of the sol.

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In one embodiment, the pH is from about 2 to about 7, from about 2 to about 6, from about 2 to about 5, from about 2 to about 4, from about 3 to about 7, from about 3 to about 6, from about 3 to about 5, from about 4 to about 7, from about 4 to about 6, from about 5 to about 7, or from

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about 5 to about 6. In another embodiment, the pH is from about 7 to about 14, from 8 to 14, 9 to 14, 10 to 14, 11 to 14, 12 to 14, 8 to 13.5, 9 to 13.5, 10 to 13.5, 11 to 13.5, 11.5 to 13.5, 8 to 13, 9 to 13, 10 to 13, 11 to 13, 11.5 to 13, or from 12 to 13.

- 5 In one embodiment, the pH, degree of mixing, and/or temperature of the plating solution or electrolyte is controlled during plating or coating of the substrate. In one embodiment, the pH of the plating solution or electrolyte is controlled during plating or coating of the substrate.

10 In one embodiment, the method further comprises controlling the rate of sol addition to the plating solution or electrolyte.

In one embodiment, the method comprises adding a ceramic phase to the plating solution or electrolyte as a sol in an amount sufficiently low that nanoparticles of the ceramic phase form directly onto or at the substrate.

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In another embodiment, the method comprises adding a ceramic phase to the plating solution or electrolyte as a sol in an amount sufficiently low that the metal-ceramic coating forms on the substrate with a predominantly crystalline structure.

- 20 In another embodiment, the method comprises adding a ceramic phase to the plating solution as a sol in an amount sufficiently low as to substantially avoid formation of nanoparticles of the ceramic phase, and/or agglomeration of particles of the ceramic phase, in the plating solution or electrolyte.

25 In certain embodiments the sol is added while carrying out the plating or coating and at a rate of sol addition controlled to be sufficiently low that nanoparticles of the ceramic phase form directly onto or at the substrate and/or that the metal-ceramic coating forms on the substrate with a predominantly crystalline structure and/or to substantially avoid formation of nanoparticles of the ceramic phase, and/or agglomeration of particles of the ceramic phase, in the plating solution or electrolyte. In these embodiments in which the sol is added to the plating solution at a controlled

30 slow rate during plating, a sol having a sol concentration of 20 to 250 or more preferably 25 to 150 grams of the ceramic phase per litre of the sol may be added to the plating solution at a rate of 30 to 250 or more preferably 100 to 150 mls of sol per litre of the plating solution, and the sol may be added at a rate in the range 0.001 to 0.1 or more preferably 0.005 to 0.02 mls per second.

In other embodiments the sol is added prior to carrying out the plating or coating. The sol is added in a low amount such that nanoparticles of the ceramic phase form directly onto or at the substrate and/or that the metal-ceramic coating forms on the substrate with a predominantly crystalline structure and/or to substantially avoid formation of nanoparticles of the ceramic phase, and/or agglomeration of particles of the ceramic phase, in the plating solution or electrolyte. In these 5 embodiments in which the sol is added to the plating solution prior to plating, a sol having a sol concentration of 20 to 250 or more preferably 25 to 150 grams of the ceramic phase per litre of the sol may be added to the plating solution in a ratio of 0.5 to 100 or more preferably 1.25 to 25 mls of sol per litre of the plating solution.

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In other embodiments sol may be added both prior to and during the plating or coating.

In some embodiments, the sol is added to the plating solution or electrolyte at a rate of about 0.06 to about 250 mL/L of the plating solution or electrolyte per minute. In some embodiments, the sol 15 is added to the plating solution or electrolyte at a rate of about 1 to about 250 mL/L of the plating solution or electrolyte per minute.

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In one embodiment, the sol has a concentration such that the sol is substantially free of visible agglomerates of the ceramic phase. In one embodiment, the sol is substantially free of particles of 20 the ceramic phase having an average diameter of more than 2 nm.

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In one embodiment, the method comprises adding the sol at a rate of 0.5 to 250 mls of sol per litre of the plating solution.

25 In one embodiment, the sol is added at a rate of 30 to 250 mls of sol per litre of the plating solution.

In one embodiment, the sol is added at a rate of 100 to 150 mls per liter of the plating solution.

In one embodiment, the method comprises adding the sol in a ratio of 0.5 to 100 mls of sol per litre of the plating solution. In one embodiment, the method comprises adding the sol in a ratio of 1.25 30 to 25 mls of sol per litre of the plating solution.

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In certain embodiments, the sol is added at a rate from about 1.25 to about 50 mls of sol per litre of the plating solution.

In one embodiment, the sol is aqueous. In one embodiment, the aqueous sol comprises at least about 75, 80, 85, or 90% water.

5 In an alternate embodiment, the sol is organic. In one embodiment, the organic sol comprises an aprotic or protic organic solvent that is not reactive under the plating or coating conditions. In one embodiment, the organic solvent is an alcohol or ketone. In one embodiment, the organic solvent comprises ethanol. In one embodiment, the organic sol comprises at least about 60, 65, 70, 75, 80, or 85% organic solvent. In one embodiment, the method comprises, after addition of the sol to the plating solution or electrolyte, removing the organic solvent from the plating solution or electrolyte.
10 In some embodiments, the organic solvent is removed from the plating solution or electrolyte periodically during and/or after addition of the sol and/or plating or coating.

In one embodiment, the method comprises producing at least one additional coating on the substrate prior to or after producing the metal-ceramic composite coating.
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In one embodiment, the ceramic phase is a single or mixed oxide, carbide, or nitride, of a metal or metalloid, or a combination of any two or more thereof.

20 In one embodiment, the ceramic phase is a single or mixed oxide, carbide, nitride, silicate, boride of a metal or metalloid selected from periods 5 to 7 of groups 3 to 12, periods 2 to 6 of group 13, periods 3 to 6 of group 14, and periods 4 to 6 of group 15 of the periodic table, or a combination of any two or more thereof.

25 In certain embodiments the ceramic phase is a single or mixed oxide, carbide, nitride, silicate, boride of Ti, W, Si, Zr, Al, Y, Cr, Fe, Pb, Co, or a rare earth element.

30 In one embodiment, the ceramic phase comprises TiO_2 , AlO_2 , Al_2O_3 , ZrO_2 , SiC , SiO_2 , SiC , CeO_2 , or ZnO . In certain embodiments, the ceramic phase comprises TiO_2 , AlO_2 , Al_2O_3 , ZrO_2 , or SiC . In certain embodiments, the ceramic phase comprises, TiO_2 , AlO_2 , ZrO_2 , or SiC .

In one embodiment, the coating, other than the ceramic phase comprises a metal or metalloid selected from periods 5 and 6 of group 3, periods 5 to 7 of groups 4 to 12, periods 3 to 6 of group 13, and periods 4 to 6 of groups 14 and 15, or an alloy of any two or more thereof.

In one embodiment, the coating, other than the ceramic phase comprises a metal or metalloid selected from Zn, Cd, Cu, Ni, Cr, Sn, Au, Ag, Pb, Ru, Rh, Pd, Os, Ir, Fe, Co, In, As, Sb, Bi, Mn, Re, Al, Zr, Ti, Hf, V, Nb, Ta, W, and Mo, or an alloy of any two or more thereof.

- 5 In certain embodiments, the coating, other than the ceramic phase comprises Ni, Ni-P, Ni-W-P, Ni-Cu-P, Ni-B, Au-Ni, Ni-Zn, Ni-Co, Ni-W, Ni-Fe, Cr, Cu, Zn, Ag, Au, or Pd.

In certain embodiments, the coating, other than the ceramic phase comprises Ni, Ni-P, Ni-W-P, Ni-Cu-P, Ni-B, Au-Ni, Ni-Zn, Ni-Co, Cr, Cu, Ag, Au, or Pd.

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In certain embodiments the coating, other than the ceramic phase comprises Ni, Ni-P, Ni-W-P, Ni-Cu-P, Ni-B, Cu, Ag, Au, or Pd.

- 15 In certain embodiments, the coating, other than the ceramic phase comprises Au-Ni, Ni-Co, Ni-P, Ni-B, or Ni-Zn. In certain embodiments, the coating, other than the ceramic phase comprises Au-Ni, Ni-Co, or Ni-Zn. In certain embodiments, the coating, other than the ceramic phase comprises Ni-Co or Ni-Zn.

- 20 In certain embodiments, the ceramic phase comprises a single or mixed oxide, carbide, nitride, silicate, boride of Ti, W, Si, Zr, Al, Y, Cr, Fe, Pb, Co, or a rare earth element; and the coating, other than the ceramic phase comprises Ni, Ni-P, Ni-W-P, Ni-Cu-P, Ni-B, Au-Ni, Ni-Zn, Ni-Co, Ni-W, Ni-Fe, Cr, Cu, Zn, Ag, Au, or Pd.

- 25 In certain embodiments, the ceramic phase comprises TiO_2 , AlO_2 , Al_2O_3 , ZrO_2 , SiC, SiO_2 , SiC, CeO_2 , or ZnO; and the coating, other than the ceramic phase comprises Ni, Ni-P, Ni-W-P, Ni-Cu-P, Ni-B, Au-Ni, Ni-Zn, Ni-Co, Ni-W, Ni-Fe, Cr, Cu, Zn, Ag, Au, or Pd.

- 30 In certain embodiments, the ceramic phase comprises TiO_2 , Al_2O_3 , or ZrO_2 ; and the coating, other than the ceramic phase comprises Ni, Ni-P, Ni-W-P, Ni-Cu-P, Ni-B, Au-Ni, Ni-Zn, Ni-Co, Ni-W, Ni-Fe, Cr, Cu, Zn, Ag, Au, or Pd.

- 35 In certain embodiments, the ceramic phase comprises TiO_2 , Al_2O_3 , or ZrO_2 ; and the coating, other than the ceramic phase comprises Ni, Ni-P, Ni-W-P, Ni-Cu-P, Ni-B, Au-Ni, Ni-Zn, Ni-Co, Ni-W, Ni-Fe, Cr, Cu, Zn, Ag, Au, or Pd.

In certain embodiments, the ceramic phase comprises TiO_2 , Al_2O_3 , or ZrO_2 ; and the coating, other than the ceramic phase comprises Ni, Ni-P, Ni-B, Au-Ni, Ni-Zn, Ni-Co, Cu, Zn, Ag, or Au.

5 In certain embodiments, the metal-ceramic composite coating comprises Au-Ni- TiO_2 , Ni-Co- TiO_2 , Ni-Zn- Al_2O_3 , Ni-P- TiO_2 , Ni-B- TiO_2 , Cu- TiO_2 , Ni-P- ZrO_2 , Ni- TiO_2 , Au- TiO_2 , Ag- TiO_2 , Cu- ZrO_2 , or Cu- Al_2O_3 . In certain embodiments, the metal-ceramic composite coating comprises Au-Ni- TiO_2 , Ni-Co- TiO_2 , Ni-Zn- Al_2O_3 , Ni-P- TiO_2 , Ni-B- TiO_2 , Cu- TiO_2 , Ni-P- ZrO_2 , Ni- TiO_2 , Au- TiO_2 , Cu- ZrO_2 , or Cu- Al_2O_3 .

10 In certain embodiments, the metal-ceramic composite coating comprises Au-Ni- TiO_2 , Ni-Co- TiO_2 , Ni-Zn- Al_2O_3 , Ni-B- TiO_2 , Ni-P- ZrO_2 , or Ag- TiO_2 . In certain embodiments, the metal-ceramic composite coating comprises Au-Ni- TiO_2 , Ni-Co- TiO_2 , Ni-Zn- Al_2O_3 , Ni-B- TiO_2 , or Ni-P- ZrO_2 . In certain embodiments, the metal-ceramic composite coating comprises Au-Ni- TiO_2 , Ni-Co- TiO_2 , Ni-Zn- Al_2O_3 , or Ni-B- TiO_2 . In certain embodiments, the metal-ceramic composite coating comprises Au-Ni- TiO_2 , Ni-Co- TiO_2 , or Ni-Zn- Al_2O_3 . In certain embodiments, the metal-ceramic composite coating comprises Ni-Co- TiO_2 or Ni-Zn- Al_2O_3 . In certain embodiments, the metal-ceramic composite coating comprises Ag- TiO_2 .

20 In one embodiment, the method comprises producing at least one additional coating on the substrate prior to producing the metal-ceramic composite coating.

In certain embodiments, the method comprises producing at least one additional coating on the substrate prior to or after producing the metal-ceramic composite coating; and the metal-ceramic coating, other than the ceramic phase comprises Ni-P.

25 In certain embodiments, the additional coating comprises Ni, and the additional coating is produced prior to producing the metal-ceramic composite coating.

30 In certain embodiments, the additional coating comprises Ni-P, and the additional coating is produced prior to producing the metal-ceramic composite coating.

In certain embodiments, the metal-ceramic composite coating comprises Ni-P- ZrO_2 , the additional coating comprises Ni-P, and the additional coating is produced prior to producing the metal-ceramic composite coating.

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In certain embodiments, the metal-ceramic composite coating comprises Ni-P-ZrO₂; the additional coating comprises Ni-P; the additional coating is produced prior to producing the metal-ceramic composite coating; and the phosphorus content of the metal-ceramic coating is greater than the phosphorus content of the additional coating.

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The method of plating or coating comprises contacting a substrate with the plating solution or electrolyte. In certain embodiments, the substrate is a metal substrate or a non-metallic substrate.

In certain embodiments, the substrate is a metal substrate. In certain embodiments, the substrate
10 comprises steel, Mg, Al, Zn, Sn, Cu, Ti, Ni, Co, Mo, Pb or an alloy thereof.

In certain embodiments the substrate is a metal substrate such as a mild steel, alloy steel, Mg, Al, Zn, Sn, Cu, Ti, Ni, Co, Mo, Pb or an alloy. In certain embodiments, the substrate comprises mild steel, alloy steel, carbon steel, stainless steel, brass, or Mg, Cu, Al or an alloy thereof.

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In other embodiments the substrate is a non-metallic substrate such as a plastics or ceramic substrate.

The term 'sol' in this specification means a solution or colloidal suspension of the ceramic phase or
20 a precursor thereof. Without wishing to be bound by theory, it is believed that molecules of the ceramic phase such as molecules of TiO₂ or precursors thereof such as oxyhydroxides exist in the sol, and during the plating process react to form the metal – ceramic composite coating.

The plating process may be an electroless plating or coating process or alternatively be a galvanic
25 plating process. Where the plating process is a galvanic plating process the plating current may be in the range 10 mA/cm² to 300 mA/cm² preferably 20 mA/cm² to 100 mA/cm². In some embodiments, the plating current is in the range of 5 to 300, 5 to 250, 5 to 200, 5 to 150, 5 to 125, 5 to 100, 10 to 300, 10 to 250, 10 to 200, 10 to 150, 10 to 125, 10 to 100, 15 to 300, 15 to 250, 15 to 200, 15 to 150, 15 to 125, 15 to 100, 20 to 300, 20 to 250, 20 to 200, 20 to 150, 20 to 125, or 20 to
30 100 mA/cm².

In certain embodiments the plating current is continuous. In other embodiments, the plating current is pulsed.

In certain embodiments, the plating current is pulsed at a rate of from about 1 to 1000 Hz and a pulse width of from about 1 to 50%. In certain embodiment, the pulse rate is from about 10 to 1000, 20 to 1000, 30 to 1000, 50 to 1000, 75 to 1000, 100 to 1000, 10 to 800, 20 to 800, 30 to 800, 50 to 800, 75 to 800, 100 to 800, 10 to 700, 20 to 700, 30 to 700, 50 to 700, 75 to 700, 100 to 700, 10 to 600, 20 to 600, 30 to 600, 50 to 600, 75 to 600, 100 to 600, 10 to 500, 20 to 500, 30 to 500, 50 to 500, 75 to 500, 100 to 500, 10 to 400, 20 to 400, 30 to 400, 50 to 400, 75 to 400, 100 to 400, 10 to 250, 20 to 250, 30 to 250, 50 to 250, 75 to 250, or 100 to 250 Hz. In certain embodiments, the pulse width is from about 5 to 50, 10 to 50, or 20 to 50%.

10 In some embodiments, the temperature and/or degree of mixing is controlled prior to, during, or after addition of the sol. In some embodiments, the temperature and/or degree of mixing is controlled during addition of the sol. In some embodiments, the temperature and/or degree of mixing is controlled during plating or coating.

15 In certain embodiments, the temperature and/or degree of mixing is monitored during addition of the sol and, optionally, during plating or coating.

In certain embodiments, the temperature and/or degree of mixing is maintained within a predetermined range during addition of the sol and, optionally, during plating or coating. In certain 20 embodiments, the predetermined range is suitable for plating or coating the substrate with the metal-ceramic composite coating.

In certain embodiments, the temperature is maintained within $\pm 2, 1, 0.75, 0.5,$ or 0.25 °C of a predetermined temperature.

25 In certain embodiments, the temperature during addition of the sol and/or during plating or coating is from about room temperature to 90 °C.

In certain embodiments, the temperature is about room temperature. In an alternate embodiment, 30 the temperature is from about 35 to 45 °C, for example, 40 °C.

In one embodiment, the method is a galvanic plating or coating process and the temperature is from about room temperature to 90 °C, from about room temperature to 85 °C, from about 35 to 85 °C, from about room temperature to 45 °C, from about 35 to 45 °C, about room temperature, or about 35 40 °C.

In another embodiment, the temperature is from about 75 to 95 °C, for example from about 80 to 90 °C. In certain embodiments, the temperature is about 80 °C.

- 5 In one embodiment, the method is an electroless plating or coating process and the temperature during plating or coating is from about 75 to 95, from about 80 to 90, or about 80 °C.

In some embodiments, the degree of mixing is controlled such that the sol of the ceramic phase is substantially uniformly dispersed throughout the plating solution or electrolyte. In some
10 embodiments, the degree of mixing is controlled such that the sol of the ceramic phase is substantially uniformly dispersed throughout the plating solution or electrolyte and the formation of nanoparticles or microparticles of the ceramic phase, and/or agglomeration of particles of the ceramic phase is substantially avoided.

- 15 In some embodiments, the degree of mixing is controlled by controlling the degree of agitation of the plating solution or electrolyte. In some embodiments, the degree of mixing is controlled by mechanical agitation, gas agitation, vibratory agitation, or any combination of any two or more thereof. In some embodiments, the mechanical agitation comprises rotating a member (for example, a bar, blade, impeller, or paddle) in the plating solution or electrolyte or rocking a vessel
20 comprising the plating solution or electrolyte. In some embodiments, the gas agitation comprises bubbling air or another gas suitable for the plating solution through the plating solution or electrolyte. In some embodiments, the vibratory agitation comprises ultrasonic agitation.

In some embodiments, the degree of mixing is controlled by rotating a member in the plating
25 solution or electrolyte. In some embodiments, the rate of rotation is from about 50 rpm to 1500 rpm, for example 100 to 1200 rpm.

In certain embodiments, the rate of rotation is from about 50 to 150, from about 75 to 125, or about 100 rpm. In other embodiments, the rate of rotation is from 100 to 300, from about 150 to 250, or
30 about 200 rpm. In other embodiments, the rate of rotation is from about 400 to 1500, from about 500 to 1400, from about 550 to 1300, from about 600 to 1200, from about 700 to 1200, from about 800 to 1200, from about 1000 to 1200, or about 1200.

In certain embodiments, the rate of rotation is maintained within \pm 200, 150, 100, 75, 50, 25, 20, 15,
35 10, or 5 rpm of a predetermined rate.

In one embodiment, the metal-ceramic composite coating comprises Au-Ni-TiO₂;

the ceramic phase comprises TiO₂;

the pH of the plating solution or electrolyte during addition of the sol, and optionally
5 during plating or coating, is from about 3 to 5;

the temperature of the plating solution during addition of the sol, and optionally during
plating or coating, is from about 35 to 45 °C; and

the sol of the ceramic phase is added to the plating solution or electrolyte in an amount
from about 10 to about 15 mL/L of plating solution or electrolyte.

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In one embodiment, the metal-ceramic composite coating comprises Au-Ni-TiO₂;

the ceramic phase comprises TiO₂;

the pH of the plating solution or electrolyte during addition of the sol, and optionally
during plating or coating, is about 3.8;

15 the temperature of the plating solution or electrolyte during addition of the sol, and
optionally during plating or coating, is about 40 °C; and

the sol of the ceramic phase is added to the plating solution or electrolyte in an amount of
about 12.5 mL/L of plating solution or electrolyte.

20 In one embodiment, the metal-ceramic composite coating comprising Au-Ni-TiO₂ is produced
using a current density of about 80 mA/cm².

In one embodiment, the metal-ceramic composite coating comprises Ni-Co-TiO₂;

the ceramic phase comprises TiO₂;

25 the pH of the plating solution or electrolyte during addition of the sol, and optionally
during plating or coating, is from about 2 to 4;

the temperature of the plating solution during addition of the sol, and optionally during
plating or coating, is from about 50 to 60 °C; and

30 the sol of the ceramic phase is added to the plating solution or electrolyte in an amount
from about 10 to 15 mL/L of plating solution or electrolyte.

In one embodiment, the metal-ceramic composite coating comprises Ni-Co-TiO₂;

the ceramic phase comprises TiO₂;

35 the pH of the plating solution or electrolyte during addition of the sol, and optionally
during plating or coating, is about 3.5;

the temperature of the plating solution during addition of the sol, and optionally during plating or coating, is about 55 °C; and

the sol of the ceramic phase is added to the plating solution or electrolyte in an amount from about 12.5 mL/L of plating solution or electrolyte.

5 In one embodiment, the metal-ceramic composite coating comprising Ni-Co-TiO₂ is produced using current density of about 20 mA/cm².

In one embodiment, the metal-ceramic composite coating comprises Ni-Zn-Al₂O₃;

10 the ceramic phase comprises Al₂O₃;

the pH of the plating solution or electrolyte during addition of the sol, and optionally during plating or coating, is from about 1 to 3;

the temperature of the plating solution during addition of the sol, and optionally during plating or coating, is from about 35 to 45 °C; and

15 the sol of the ceramic phase is added to the plating solution or electrolyte in an amount from about 4 to about 8 mL/L of plating solution or electrolyte.

In one embodiment, the metal-ceramic composite coating comprises Ni-Zn-Al₂O₃;

the ceramic phase comprises Al₂O₃;

20 the pH of the plating solution or electrolyte during addition of the sol, and optionally during plating or coating, is about 2;

the temperature of the plating solution during addition of the sol, and optionally during plating or coating, is about 40 °C; and

25 the sol of the ceramic phase is added to the plating solution or electrolyte in an amount of about 6 mL/L of plating solution or electrolyte.

In one embodiment, an additional coating comprising Ni-P is produced on the substrate prior to producing the metal-ceramic composite coating;

the metal-ceramic composite coating comprises Ni-P-ZrO₂;

30 the ceramic phase comprises ZrO₂;

the pH of the plating solution or electrolyte during addition of the sol, and optionally during plating or coating, is from about 5 to 7;

the temperature of the plating solution during addition of the sol, and optionally during plating or coating, is from about 70 to 90 °C; and

the sol of the ceramic phase is added to the plating solution or electrolyte in an amount from about 20 to about 30 mL/L of plating solution or electrolyte.

- 5 In one embodiment, an additional coating comprising Ni-P is produced on the substrate prior to producing the metal-ceramic composite coating;
- the metal-ceramic composite coating comprises Ni-P-ZrO₂;
 - the ceramic phase comprises ZrO₂;
 - the pH of the plating solution or electrolyte during addition of the sol, and optionally during plating or coating, is about 6;
- 10 the temperature of the plating solution during addition of the sol, and optionally during plating or coating, is about 80 °C; and
- the sol of the ceramic phase is added to the plating solution or electrolyte in an amount of about 25 mL/L of plating solution or electrolyte.
- 15 In one embodiment, the pH of the plating solution or electrolyte while producing the additional coating comprising Ni-P is from about 3 to 5; and
- the temperature of the plating solution or electrolyte while producing the additional coating is from about 70 to 90 °C.
- 20 In one embodiment, the pH of the plating solution or electrolyte while producing the additional coating comprising Ni-P is from about 4; and
- the temperature of the plating solution or electrolyte while producing the additional coating is from about 80 °C.
- 25 In one embodiment, the additional coating comprising Ni-P produced on the substrate prior to producing the metal-ceramic composite coating is produced by an electroless process; and
- the metal-ceramic composite coating comprising Ni-P-ZrO₂ is produced by an electroless process.
- 30 In one embodiment, the metal-ceramic composite coating comprises Ni-B-TiO₂;
- the ceramic phase comprises TiO₂;
 - the pH of the plating solution or electrolyte during addition of the sol, and optionally during plating or coating, is from about 3 to 4;
 - the temperature of the plating solution during addition of the sol, and optionally during
- 35 plating or coating, is from about 40 to 50 °C; and

the sol of the ceramic phase is added to the plating solution or electrolyte in an amount from about 10 to about 15 mL/L of plating solution or electrolyte.

In one embodiment, the metal-ceramic composite coating comprises Ni-B-TiO₂;

- 5 the ceramic phase comprises TiO₂;
 the pH of the plating solution or electrolyte during addition of the sol, and optionally during plating or coating, is about 3.5;
 the temperature of the plating solution during addition of the sol, and optionally during plating or coating, is about 45 °C; and
10 the sol of the ceramic phase is added to the plating solution or electrolyte in an amount of about 12.5 mL/L of plating solution or electrolyte.

In various embodiments, the metal ceramic coating comprises Ag-TiO₂;

- the ceramic phase comprises TiO₂;
15 the pH of the plating solution or electrolyte during addition of the sol, and optionally during plating or coating, is from about 11.5 to 13.5;
 the temperature of the plating solution during addition of the sol, and optionally during plating or coating, is from about 25 to about 35°C; and
 the sol of the ceramic phase is added to the plating solution or electrolyte in an amount
20 from about 5 to about 15 mL/L, for example 10 to about 15 mL/L, of plating solution or electrolyte.

In various embodiments, the metal ceramic coating comprises Ag-TiO₂;

- the ceramic phase comprises TiO₂;
25 the pH of the plating solution or electrolyte during addition of the sol, and optionally during plating or coating, is about 12.5;
 the temperature of the plating solution during addition of the sol, and optionally during plating or coating, is about 30°C; and
 the sol of the ceramic phase is added to the plating solution or electrolyte in an amount of
30 about 12.5 mL/L of plating solution or electrolyte.

In various embodiments, the metal-ceramic composite coating comprising Ag-TiO₂ is produced using a current density of about 10 mA/cm².

In certain embodiments, the item or surface comprises a metal-ceramic composite coating comprising a ceramic phase of dispersed amorphous particles having an average diameter from about 3 to about 30 nm.

5 In certain embodiments, the amorphous particles of the ceramic phase have an average diameter from about 1 to about 100, from about 3 to about 100, from about 1 to about 50, from about 3 to about 50, from about 1 to about 30, from about 3 to about 30, from about 1 to about 25, from about 3 to about 25, from about 1 to about 20, from about 3 to about 20, from about 1 to about 12, or from about 3 to about 12 nm.

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In certain embodiments, the amorphous ceramic particles are substantially uniformly dispersed throughout the metal-ceramic composite coating.

15 In certain embodiments, the inter-particle spacing between the amorphous ceramic particles is substantially the same throughout the metal-ceramic composite. In certain embodiments, the inter-particle spacing is from about 15 to about 50 nm.

In certain embodiments, the item or surface comprises at least one additional coating under or on top of the metal ceramic coating.

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In certain embodiments, the metal-ceramic composite coating has a grain size at least about 5% less than a corresponding coating prepared without the ceramic phase and/or a corresponding coating prepared without controlling the pH, degree of mixing, and/or temperature of the plating solution or electrolyte.

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In certain embodiments, the metal-ceramic composite coating has a Vickers microhardness at least about 10% greater than a corresponding coating prepared without the ceramic phase and/or a corresponding coating prepared without controlling the pH, degree of mixing, and/or temperature of the plating solution or electrolyte.

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In certain embodiments, the metal-ceramic composite coating has a wear loss volume at least about 10% less than a corresponding coating prepared without the ceramic phase and/or a corresponding coating prepared without controlling the pH, degree of mixing, and/or temperature of the plating solution or electrolyte.

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In certain embodiments, the metal-ceramic composite coating has an electrical resistivity and/or conductivity within about $\pm 3\%$ of a corresponding coating prepared without the ceramic phase and/or a corresponding coating prepared without controlling the pH, degree of mixing, and/or temperature of the plating solution or electrolyte.

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In certain embodiments, the metal-ceramic composite coating has a corrosion resistance substantially the same as or greater than a corresponding coating prepared without the ceramic phase and/or a corresponding coating prepared without controlling the pH, degree of mixing, and/or temperature of the plating solution or electrolyte.

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In certain embodiments, the item or surface comprises at least one additional coating under or on top of the metal-ceramic composite coating; and the combination of coatings has a corrosion resistance substantially the same or greater than a corresponding combination of coatings without the ceramic phase.

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In one embodiment, the coating has a thickness of at least about 5, 20, 80, 100, 200, 400, 600, 800, or 1000 μm , and useful ranges may be selected between any of these values (for example, from about 5 to about 1000, from about 20 to about 1000, from about 80 to about 1000, from about 200 to about 1000, from about 2 to about 600, 80 to about 600, or from about 200 to about 600 μm). In one embodiment, the thickness is from about 20 to 600 μm .

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In one embodiment, the coating has a thickness of at least about 20 μm , and a Vickers hardness of at least about 750 kg/mm^2 .

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In various embodiments the Vickers hardness may be at least about 750, at least about 800, at least about 850, at least about 900, at least about 950, at least about 1,000, at least about 1,050, at least about 1,100, at least about 1,150, at least about 1,200, or at least about 1,250 kg/mm^2 , and useful ranges may be selected between any of these values (for example, from about 750 to about 1,250, from about 800 to about 1,250, from about 850 to about 1,250, from about 900 to about 1,250, from about 950 to about 1,250, from about 1,000 to about 1,250, from about 850 to about 1,200, from about 900 to about 1,200, from about 950 to about 1,200, or from about 1,000 to about 1,200 kg/mm^2).

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In one embodiment, the coating, other than the ceramic phase, comprises Ni-P or Ni-B; has a Vickers hardness from about 800 to about 1,250; and a thickness of about 20 to 600 μm .

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In certain embodiments, the metal-ceramic composite coating has greater smoothness than a corresponding coating prepared without the ceramic phase and/or a corresponding coating prepared without controlling the pH, degree of mixing, and/or temperature of the plating solution or electrolyte.

In this specification plating and coating are used interchangeably.

The term “comprising” as used in this specification means “consisting at least in part of”. When interpreting each statement in this specification that includes the term “comprising”, features other than that or those prefaced by the term may also be present. Related terms such as “comprise” and “comprises” are to be interpreted in the same manner.

As used herein “(s)” following a noun means the plural and/or singular forms of the noun.

As used herein the term “and/or” means “and” or “or” or both.

It is intended that reference to a range of numbers disclosed herein (for example, 1 to 10) also incorporates reference to all rational numbers within that range (for example, 1, 1.1, 2, 3, 3.9, 4, 5, 6, 6.5, 7, 8, 9 and 10) and also any range of rational numbers within that range (for example, 2 to 8, 1.5 to 5.5 and 3.1 to 4.7) and, therefore, all sub-ranges of all ranges expressly disclosed herein are hereby expressly disclosed. These are only examples of what is specifically intended and all possible combinations of numerical values between the lowest value and the highest value enumerated are to be considered to be expressly stated in this application in a similar manner.

This invention may also be said broadly to consist in the parts, elements and features referred to or indicated in the specification of the application, individually or collectively, and any or all combinations of any two or more said parts, elements or features, and where specific integers are mentioned herein which have known equivalents in the art to which this invention relates, such known equivalents are deemed to be incorporated herein as if individually set forth.

Although the present invention is broadly as defined above, those persons skilled in the art will appreciate that the invention is not limited thereto and that the invention also includes embodiments of which the following description gives examples.

The embodiments and preferences described herein may relate alone or in any combination of any two or more to any of the above aspects.

BRIEF DESCRIPTION OF THE FIGURES

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In the subsequent description the following figures are referred to, in which:

Figure 1 shows surface morphologies of (a) a monolayer Ni-P coating; (b) a duplex Ni-P/Ni-P coating; (c) a duplex Ni-P/Ni-P-25ZrO₂ coating; and (d) a duplex Ni-P/Ni-P-50ZrO₂ coating.

10 Figure 2 shows cross-sectional morphologies of (a) a duplex Ni-P/Ni-P coating; (b) a duplex Ni-P/Ni-P-5ZrO₂ coating; (c) a duplex Ni-P/Ni-P-20ZrO₂ coating; (d) a duplex Ni-P/Ni-P-25ZrO₂ coating; (e) a duplex Ni-P/Ni-P-50ZrO₂ coating, and; (f) an elemental line scan of a Ni-P/Ni-P-50ZrO₂ coating.

Figure 3 shows XRD spectra of a monolayer Ni-P coating and a duplex Ni-P/Ni-P coating.

15 Figure 4 shows XRD spectra of a duplex NiP/Ni-P coating and Ni-P/Ni-P-XZrO₂ coatings deposited using different sol concentrations.

Figure 5 shows microhardness of duplex Ni-P/Ni-P-XZrO₂ coatings as a function of sol concentration.

20 Figure 6 shows electrochemical polarization curves of a AZ31 Mg alloy substrate, a monolayer Ni-P coating, a duplex Ni-P/Ni-P coating and duplex Ni-P/Ni-P-XZrO₂ coatings in 3.5 wt.% NaCl aqueous solution at room temperature.

Figure 7 shows porosity and thickness of an inner layer Ni-P coating with varying coating time.

Figure 8 shows microhardness and Ni content of Zn-Ni coatings deposited using different sol concentrations.

25 Figure 9 shows a representative XRF spectrum of a Zn-Ni coating.

Figure 10 shows XRD spectra for Zn-Ni coatings deposited at different sol concentrations.

Figure 11 shows Ni content of Zn-Ni coatings deposited using different sol concentrations and agitation speed.

Figure 12 shows microhardness of Zn-Ni coatings prepared using different sol concentrations and agitation speed.

Figure 13 shows XRD spectra for Zn-Ni coatings deposited at an agitation speed of 1200 rpm using different sol concentrations.

- 5 Figure 14 shows ESEM images depicting the surface morphology of Zn-Ni coatings deposited using the following sol concentrations in the bath: a) 0; b) 2; c) 6; d) 12, and; e) 20 mL/L. Electroplating parameters: $i = 80 \text{ mA/cm}^2$, 600 rpm, 40 °C and 10 min.

Figure 15 shows cross-sectional morphologies of Zn-Ni coatings deposited using the following sol concentrations in the bath: a) 0; b) 2; c) 6; d) 12, and; e) 20 mL/L.

- 10 Figure 16 shows ESEM images of the surface morphology of Zn-Ni coatings deposited at two agitation speeds at sol concentrations of a) 0; b) 2; c) 6; d) 12, and; e) 20 mL/L.

Figure 17 shows the wear track of Zn-Ni coatings deposited using sol concentrations of: a) 0; b) 2; c) 6; d) 12, and; e) 20 mL/L.

- 15 Figure 18 shows OCP test data for Zn-Ni coatings deposited at different sol concentrations and an agitation speed of 1200 rpm.

Figure 19 shows polarization curves for Zn-Ni coatings deposited at different sol concentrations and an agitation speed of 1200 rpm.

Figure 20 shows Nyquist plots and equivalent electrical circuit for Zn-Ni coatings deposited using different sol concentrations.

- 20 Figure 21 shows a representative XRF spectrum for a Zn-Ni coating after salt spray test.

Figure 22 shows an XRD result for a corroded coating after salt spray test.

Figure 23 shows XRD patterns of sol-enhanced Au-Ni-TiO₂ nano-composite coatings at different sol concentration.

- 25 Figure 24 shows cross-sectional morphologies of: (a) Au-Ni, and; (b) sol-enhanced Au-Ni-TiO₂ nano-composite coatings.

Figure 25 shows surface morphologies of sol-enhanced Au-Ni-TiO₂ nano-composite coatings: (a) Au-Ni, (b) Au-Ni-12.5mL/L TiO₂ and (c) Au-Ni-50mL/L TiO₂.

Figure 26 shows the following nanoindentation analysis of sol-enhanced Au-Ni-TiO₂ nano-composite coatings: (a) nano-hardness, (b) scratch displacement.

Figure 27 shows the electrical resistivity and electrical conductivity of sol-enhanced Au-Ni-TiO₂ nano-composite coatings.

- 5 Figure 28 shows TEM images and grain size distributions for the following coatings: a) 22CT Au-Ni; b) 22CT Au-Ni coating with TiO₂ powder added to an equivalent volume as the sol; c) 22CT Au-Ni with 12.5 mL/L TiO₂ sol.

- Figure 29 shows TEM diffraction images for the following coatings: a) 22CT Au-Ni; b) 22CT Au-Ni coating with TiO₂ powder added to an equivalent volume as the sol; c) 22CT Au-Ni with 12.5 mL/L
10 TiO₂ sol.

Figure 30 shows TEM images for the following coatings: a) 22CT Au-Ni coating with TiO₂ powder added to an equivalent volume as the sol; and b) 22CT Au-Ni with 12.5 mL/L TiO₂ sol.

Figure 31 shows surface morphologies of (a) an "undoped" Ni-B coating; and (b) a "doped" Ni-B coating.

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Figure 32 shows XRD spectra of Ni-Co and sol-enhanced Ni-Co-TiO₂ nano-composite coatings.

Figure 33 shows the cross-sectional morphology of Ni-Co and sol-enhanced Ni-Co-TiO₂ nano-composite coatings: (a) Ni-Co, (b) Ni-Co-12.5 mL/L TiO₂, and (c) Ni-Co-50 mL/L TiO₂.

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Figure 34 shows TEM images of (a) a Ni-Co coating and (b) a sol-enhanced Ni-Co-12.5 mL/L TiO₂ coating. The arrows in (b) indicate TiO₂ nano-particles.

- Figure 35 shows wear track images Ni-Co and sol-enhanced Ni-Co-TiO₂ nano-composite coatings:
25 (a) Ni-Co, (b) Ni-Co-12.5 mL/L TiO₂, and (c) Ni-Co-50 mL/L TiO₂.

Figure 36 shows potentiodynamic polarization curves: (a) Ni, (b) Ni-Co, (c) Ni-Co-12.5 mL/L TiO₂, and (d) Ni-B-50 mL/L TiO₂ in 3.5% NaCl aqueous solution.

- 30 Figure 37 shows XRD patterns of sol-enhanced nano-composite Ag-TiO₂ coatings.

Figure 38 shows cross-sectional morphologies of the coatings: (a) pure Ag coating, (b) Ag-12.5 mL/L TiO₂ composite coating, and (c) Ag-20 mL/L TiO₂ composite coating.

Figure 39 shows a bright field image of sol-enhanced Ag-TiO₂ nano-composite coating.

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Figure 40 shows a HAADF image of sol-enhanced Ag-TiO₂ nano-composite coating.

DETAILED DESCRIPTION OF EMBODIMENTS

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The invention comprises a method for producing a metal-ceramic composite coating on a substrate, the method comprising adding a sol of a ceramic phase to a plating solution or electrolyte, and controlling the pH, degree of mixing, and/or temperature of the plating solution or electrolyte. The inventors have found that by adding a sol of a ceramic phase to a plating solution or electrolyte, and controlling the pH, degree of mixing, and/or temperature of the plating solution or electrolyte it is possible to provide metal-ceramic composite coatings having desirable properties, such as hardness, wear resistance, chemical inertness, and corrosion resistance, for example.

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The sol may have a concentration of the ceramic phase such that the sol is transparent (particles of the ceramic phase are not visibly present in the sol). In one embodiment, the sol has a concentration of the ceramic phase such that the sol is substantially free of visible particles and/or agglomerates of the ceramic phase. In one embodiment, the sol is substantially free of particles of the ceramic phase having an average diameter of more than 2 nm.

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In certain embodiments the sol may have a concentration of the ceramic phase of about 10 g/L, about 20 g/L, about 35 g/L, about 40 g/L, about 50 g/L, about 75 g/L, about 100 g/L, about 125 g/L, about 150 g/L, about 175 g/L, about 200 g/L, about 225 g/L, about 250 g/L of the sol, about 300 g/L, about 350 g/L, or about 400 g/L, and useful ranges may be selected between any of these values (for example, from about 10 to about 400 g/litre, from about 10 to about 300 g/litre, from about 10 to about 250 g/litre, 10 to about 200 g/litre, about 10 to about 175 g/litre, about 10 to about 150 g/litre, about 10 to about 125 g/litre, about 10 to about 100 g/litre, from about 20 to about 400 g/litre, from about 20 to about 300 g/litre, about 20 to about 250 g/litre, about 20 to about 200 g/litre, about 20 to about 175 g/litre, about 20 to about 150 g/litre, about 20 to about 125 g/litre, from about 20 to about 100g/litre of the sol, from about 25 to about 400 g/litre, from about 25 to about 300 g/litre, about 25 to about 250 g/litre, about 25 to about 200 g/litre, about 25 to

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about 175 g/litre, about 25 to about 150 g/litre, about 25 to about 125 g/litre, or from about 25 to about 100g/litre of the sol).

5 The sol may be added to the plating solution or electrolyte in an amount and under conditions effective to provide a substantially uniform dispersion of particles having an average diameter from about 1 to about 100 nm of the ceramic phase in the metal-ceramic composite coating, while substantially avoiding precipitation of the ceramic phase in the plating solution or electrolyte.

10 The sol may added at a rate of 0.5 to 250 mls of sol per litre of the plating solution. In some embodiments, the sol is added at a rate or in a ratio of about 0.5, 0.75, 1, 1.25, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5, 8, 9, 9.5, 10, 10.5, 11, 11.5, 12, 12.5, 13, 14, 15, 20, 25, 30, 40, 50, 75, 100, 125, 150, 200, or 250 mls of sol per litre of the plating solution, and useful ranges may be selected between any of these values (for example, from about 0.5 to about 250, from about 0.5 to about 200, from about 0.5 to about 150, from about 0.5 to about 100, from about 0.5 to about 75, from 15 about 0.5 to about 50, from about 0.5 to about 25, from about 0.5 to about 20, from about 0.5 to about 15, 0.5 to about 12.5, from about 0.5 to about 10, from about 0.5 to about 8, from about 0.5 to about 6, from about 1 to about 250, from about 1 to about 200, from about 1 to about 150, from about 1 to about 100, from about 1 to about 75, from about 1 to about 50, from about 1 to about 25, from about 1 to about 20, from about 1 to about 15, 1 to about 12.5, from about 1 to about 10, 20 from about 1 to about 8, from about 1 to about 6, from about 1.25 to about 250, from about 1.25 to about 200, from about 1.25 to about 150, from about 1.25 to about 100, from about 1.25 to about 75, from about 1.25 to about 50, from about 1.25 to about 25, from about 1.25 to about 20, from about 1.25 to about 15, 1.25 to about 12.5, from about 1.25 to about 10, from about 1.25 to about 8, from about 1.25 to about 6, from about 2 to about 250, from about 2 to about 200, from about 2 to about 150, from about 2 to about 100, from about 2 to about 75, from about 2 to about 50, from 25 about 2 to about 25, from about 2 to about 20, from about 2 to about 15, 2 to about 12.5, from about 2 to about 10, from about 2 to about 8, from about 2 to about 6, from about 3 to about 250, from about 3 to about 200, from about 3 to about 150, from about 3 to about 100, from about 3 to about 75, from about 3 to about 50, from about 3 to about 25, from about 3 to about 20, from 30 about 3 to about 15, 3 to about 12.5, from about 3 to about 10, from about 3 to about 8, from about 3 to about 6, from about 5 to about 250, from about 5 to about 200, from about 5 to about 150, from about 5 to about 100, from about 5 to about 75, from about 5 to about 50, from about 5 to about 25, from about 5 to about 20, from about 5 to about 15, 5 to about 12.5, from about 5 to about 10, from about 5 to about 8, from about 5 to about 6, from about 6 to about 250, from about 35 6 to about 200, from about 6 to about 150, from about 6 to about 100, from about 6 to about 75,

from about 6 to about 50, from about 6 to about 25, from about 6 to about 20, from about 6 to about 15, 6 to about 12.5, from about 6 to about 10, from about 6 to about 8, from about 10 to about 250, from about 10 to about 200, from about 10 to about 150, from about 10 to about 100, from about 10 to about 75, from about 10 to about 50, from about 10 to about 25, from about 10 to about 20, from about 10 to about 15, 10 to about 12.5, from about 15 to about 250, from about 15 to about 200, from about 15 to about 150, from about 15 to about 100, from about 15 to about 75, from about 15 to about 50, from about 15 to about 25, from about 15 to about 20, from about 20 to about 250, from about 20 to about 200, from about 20 to about 150, from about 20 to about 100, from about 20 to about 75, from about 20 to about 50, or from about 20 to about 25 mls of sol per litre of the plating solution).

The sol may be aqueous or organic. Where an organic sol is added to the plating solution or electrolyte, organic solvent may accumulate in the plating solution or electrolyte and may be removed during method by any suitable method known in the art. In some embodiments, the sol is organic and is added to the plating solution or electrolyte at a rate of about 12.5 mL/L plating solution or electrolyte. In some embodiments, the sol is aqueous and is added to the plating solution or electrolyte at a rate of about 6 mL/L plating solution or electrolyte.

The sol of the ceramic phase may be added to the plating solution or electrolyte prior to and/or during the plating or coating process. Where the sol of the ceramic phase is added to the solution or electrolyte during the plating process it may be added throughout the plating or coating process, or in certain embodiments for less than all of the duration of the plating process but at least 80% or at least 70% or at least 60% or at least 50% of the duration of the plating process. Optionally, in such embodiments, an amount of the sol may also be added to the solution or electrolyte prior to the commencement of plating or coating.

The sol may be added to the plating solution or electrolyte at a rate sufficient to provide the desired concentration of the ceramic phase in the metal-ceramic coating, while not impacting on the plating or coating process.

In certain embodiments the sol may be added at a rate of less than about 0.02ml per second/litre of the plating solution or electrolyte, and may be added at a rate of less than about 0.01ml per second/litre, and preferably less than about 0.007ml per second/litre, and in the range about 0.001 to about 0.005ml per second/litre. In some embodiments, the rate of sol addition is less than about 0.02, 0.015, 0.01, 0.009, 0.008, 0.007, 0.006, 0.005, 0.003, 0.002, or 0.001 mL per second/litre of the

plating solution, and useful ranges may be selected between any of these values (for example, from about 0.02 to about 0.001, from about 0.015 to about 0.001, from about 0.01 to about 0.001, from about 0.009 to about 0.001, from about 0.008 to about 0.001, from about 0.007 to about 0.001, from about 0.006 to about 0.001, or from about 0.005 to about 0.001 mL per second/litre of plating solution). The sol may be added to the plating solution at the required slow rate by dripping or spraying the sol into the plating solution or by any other technique by which the sol can be added at the required slow rate.

It is believed in relation to some embodiments that if the ceramic phase is added as a sol during plating and at a sufficiently slow rate and low concentration, molecules of the ceramic phase from the sol form nanoparticles in situ on or at the surface of the substrate, and that a metal-ceramic composite coating having a largely crystalline rather than an amorphous structure is formed.

In certain embodiments the ceramic phase is a single or mixed oxide, carbide, nitride, silicate, boride of a metal or metalloid. The metal metalloid may be selected from periods 5 to 7 of groups 3 to 12, periods 2 to 6 of group 13, periods 3 to 6 of group 14, and periods 4 to 6 of group 15 of the periodic table, or a combination of any two or more thereof. For example, the ceramic phase may be single or mixed oxide, carbide, nitride, silicate, boride of Ti, W, Si, Zr, Al, Y, Cr, Fe, Pb, Co, or a rare earth element.

The pH, degree of mixing, and/or temperature of the plating solution or electrolyte is controlled in the method. The pH, degree of mixing, and/or temperature of the plating solution or electrolyte may be controlled prior to, during, or after addition of the sol to the plating solution or electrolyte, and may also be controlled during the plating or coating process.

In various embodiments the pH, degree of mixing, and/or temperature is controlled such that the amorphous particles of the ceramic phase in the metal-ceramic composite coating have an average diameter of about 1 nm, about 2 nm, about 3 nm, about 4 nm, about 5 nm, about 6 nm, about 7 nm, about 8 nm, about 9 nm, about 10 nm, about 11 nm, about 12 nm, about 13 nm, about 14 nm, about 15 nm, about 20 nm, about 25 nm, about 30 nm, about 40 nm, about 50 nm, about 60 nm, about 70 nm, about 80 nm, about 90 nm, or about 100 nm, and useful ranges may be selected between any of these values (for example, from about 1 to about 100, from about 3 to about 100, from about 1 to about 50, from about 3 to about 50, from about 1 to about 30, from about 3 to about 30, from about 1 to about 25, from about 3 to about 25, from about 1 to about 20, from about 3 to about 20, from about 1 to about 12, from about 3 to about 12 nm).

The pH, degree of mixing, and/or temperature of the plating solution or electrolyte may be monitored. In certain embodiments, the pH, degree of mixing, and/or temperature of the plating solution or electrolyte is maintained within a predetermined range during addition of the sol and, optionally, during plating or coating. The pH, degree of mixing, and/or temperature of the plating solution or electrolyte may be adjusted as necessary by any suitable method known in the art.

Without wishing to be bound by theory it is believed that by controlling the pH, degree of mixing, and/or temperature of during addition of the sol and, optionally, during plating or coating, the size of particles of the ceramic phase in the plating solution or electrolyte and incorporated into the metal-ceramic composite coating may be restricted.

The pH of the plating solution or electrolyte may be maintained within a predetermined pH range that is effective to maintain the ceramic phase in suspension during addition of the sol and, optionally, during plating or coating such that the plating solution or electrolyte substantially free of visible particles of the ceramic phase (or precursors thereof) and/or agglomerates.

The temperature at which the method is carried out is typically dependent on the coating to be produced and plating or method employed. Electroless plating methods are typically carried out at higher temperatures than galvanic methods. The sol may be added to the plating solution or electrolyte at a temperature suitable for carrying out the plating or coating method. Alternatively, the sol may be added to the plating solution or electrolyte at a temperature higher or lower than the temperature at which the plating or coating method is carried out, and the plating solution or electrolyte then heated or cooled to the temperature at which the plating or coating process is carried out. The temperature at which the plating or coating may be selected to achieve a plating reaction speed that provides a plated or coated surface of a quality suitable for its intended purpose.

The plating solution or electrolyte is mixed to effectively disperse the ceramic phase in the plating solution or electrolyte. Mixing may also prevent or reduce precipitation and/or agglomeration of particles of the ceramic phase in the plating solution or electrolyte. The degree of mixing may be controlled such that amorphous particles of the ceramic phase having an average diameter of from about 1 to 100 nm are substantially uniformly dispersed throughout the metal-ceramic coating.

The method of mixing may be selected based on the plating or coating method used. Examples include recirculation, aeration, stirring, and the like. Those skilled in the art will appreciate that

degree of mixing may affect the surface quality of the coating. For example, a high degree of mixing may be effective to prevent or reduce precipitation and/or agglomeration of particles of the ceramic phase in the plating solution or electrolyte, but may also prevent effective deposition of the plating or coating on the substrate.

5

An additional coating may be produced on the substrate prior to or after producing the metal-ceramic composite coating. In various embodiments, an additional coating is produced on the substrate prior to producing the metal-ceramic composite coating. The additional coating may, for example, enhance adhesion of the metal-ceramic coating or some other property of the coated substrate, such as corrosion resistance.

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In certain embodiments the substrate is a metal substrate such as mild steel, alloy steel, Mg, Al, Zn, Sn, Cu, Ti, Ni, Co, Mo, Pb or an alloy. In other embodiments the substrate is a non-metallic substrate such as a plastics and ceramic substrate.

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In certain embodiments the substrate is pretreated prior to contacting or immersing the substrate with plating solution or electrolyte.

In various embodiments the pretreatment process comprises one or more of the following steps: pre-coating, mechanical polishing, electro-polishing, alkaline washing, acid washing, degreasing, and electroactivation.

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In one embodiment the method comprises producing at least one additional coating on the substrate prior to producing the metal-ceramic composite coating. In one embodiment the substrate is stainless steel, Cu or brass and the additional coating is bright nickel.

25

In one embodiment the substrate is carbon steel and the carbon steel is subjected to a pretreatment process comprising the following steps:

- (a) polishing,
- (b) alkaline washing,
- (c) acid washing, and
- (d) washing in water.

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In another embodiment the substrate is aluminium and the aluminium is subjected to a pretreatment process comprising the following steps:

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- 5 (a) polishing,
(b) degreasing,
(c) acid washing,
(d) Zn immersion,
(d) acid washing, and
(e) Zn immersion.

In a further embodiment the substrate is magnesium and the magnesium is subjected to a pretreatment process comprising the following steps:

- 10 (a) polishing,
(b) degreasing,
(c) alkaline washing,
(d) acid washing,
(d) activation with a strong acid, and
15 (e) washing in water.

In one embodiment the substrate is stainless steel and the stainless steel is subjected to a pretreatment process comprising the following steps:

- 20 (a) polishing,
(b) alkaline washing,
(c) strong acid washing,
(d) plating with nickel, and
(d) washing in water.

25 In another embodiment the substrate is copper or brass and the copper or brass is subjected to a pretreatment process comprising the following steps:

- (a) polishing,
(b) alkaline washing,
(c) strong acid washing,
30 (d) electrochemical washing, and
(d) washing in water.

In various embodiments, the substrate is mild steel and the mild steel is subjected to a pretreatment process comprising the steps: (a) polishing, (b) degreasing, and (c) acid washing.

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In another embodiment, the pretreatment comprises depositing a Ni flash or strike. Flashing with Ni may, for example, improve surface smoothness and prevent diffusion, which may be useful for valuable coating, such as those comprising Au or Ag.

- 5 The plating or coating may be carried out to provide improved abrasion or wear resistance or corrosion resistance to an item or surface, to provide an electrically conductive coating on a surface or item, or to alter optical properties, for decorative purposes, for example.

10 By the process of the invention we have been able to achieve Ni-P- TiO₂ coatings having microhardness of about 1025HV. In a conventional electroplating process in which TiO₂ nanoparticles are added to the plating solution before the commencement of the plating and not in a sol, hardness of the order of 670-800HV is typically achieved.

15 In another particular embodiment where the substrate is mild carbon steel, the substrate plated or coated by the process of the invention has very low light reflection i.e. is ultra-black.

20 The plating process may be an electroless plating or coating process, in which the anode comprises the plating metal, the cathode the item to be plated or coated, and the ceramic phase is added as a sol to the solution comprising a reducing agent such as sodium hypophosphite, sodium borohydride, formaldehyde, dextrose, rochelle salts, glyoxal, hydrazine sulfate.

25 The plating process may alternatively be a galvanic plating process in which the anode comprises the plating metal, or ions of the plating metal are provided in the electrolyte, the cathode comprises the item to be plated, and the ceramic phase is added to the electrolyte as a sol.

In another aspect the invention comprises an item or surface plated or coated by a plating or coating method of the invention as described or defined herein.

30 In another aspect, the invention comprises an item or surface comprising a substrate and a metal-ceramic composite coating on the substrate, the metal-ceramic composite coating comprising a ceramic phase of dispersed amorphous ceramic particles having an average diameter of from 1 to 100 nm.

35 Without wishing to be bound by theory, it is believed that the formation of the ceramic particles in the coating disrupts the grain growth of the coating resulting in reduced grain size compared to a

corresponding coating prepared without the ceramic phase and/or a corresponding coating prepared without controlling the pH, degree of mixing, and/or temperature of the plating solution or electrolyte (for example, a coating prepared by substantially the same method, but without adding the ceramic phase either as a sol or otherwise and/or substantially the same coating prepared without a corresponding coating prepared without the ceramic phase and/or a corresponding coating prepared without controlling the pH, degree of mixing, and/or temperature of the plating solution or electrolyte).

In certain embodiments, the metal-ceramic composite coating has a grain size at least about 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 25, 30, 35, or 40 % less than a corresponding coating prepared without the ceramic phase and/or a corresponding coating prepared without controlling the pH, degree of mixing, and/or temperature of the plating solution or electrolyte, and useful ranges may be selected between any of these values (for example, from about 5 to about 40, from about 5 to about 35, from about 5 to about 30, from about 5 to about 25, from about 5 to about 20, from about 10 to about 40, from about 10 to about 35, from about 10 to about 30, from about 10 to about 25, from about 10 to about 20, from about 15 to about 40, from about 15 to about 35, from about 15 to about 30, from about 15 to about 25, from about 15 to about 20, from about 20 to about 40, from about 20 to about 35, from about 20 to about 30, from about 20 to about 25% less than a corresponding coating prepared without the ceramic phase and/or a corresponding coating prepared without controlling the pH, degree of mixing, and/or temperature of the plating solution or electrolyte).

The metal-ceramic composite coatings may have improved hardness compared to comparable coatings without the ceramic phase. For thick coatings hardness may be measured by, for example, Vickers microhardness. For thin coatings such as Au or Ag for example hardness may be measured by, for example, nano-indentation. The resulting nano-hardness value may be converted to a Vickers hardness value.

Hardness testing may be performed, for example, using nano or micro indenters, as is well known in the art. The testing parameters selected depend on to the coating material and coating thickness. For example, different tips may be used for testing different coatings.

Measurements may be performed on a Hysitron for nano indentation tests. The load and time is dependent on the coating thickness. The measurement directly provides a force displacement curve.

The resulting data may then be converted to a hardness measurement, for example by using appropriate software.

5 Vickers hardness measurements may also be using a MTS-XP nano indenter using, for example, a standard diamond pyramid tip. Again, the load is dependent on the coating thickness. The measurement directly provides a force displacement curve, which may then be converted to a hardness measurement.

10 In certain embodiments, the metal-ceramic composite coating has a Vickers microhardness at least about 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, or 60% greater than that of a corresponding coating prepared without the ceramic phase and/or a corresponding coating prepared without controlling the pH, degree of mixing, and/or temperature of the plating solution or electrolyte, and useful ranges may be selected between any of these values (for example, from about 10 to about 60, from about 10 to about 50, from about 10 to about 40, from about 10 to about 35, from about 10 to about 30, from about 10 to about 25, from about 10 to about 20, from about 15 to about 60, from about 15 to about 50, from about 15 to about 40, from about 15 to about 35, from about 15 to about 30, from about 15 to about 25, from about 15 to about 20, from about 20 to about 60, from about 20 to about 50, from about 20 to about 40, from about 20 to about 35, from about 20 to about 30, from about 20 to about 25, from about 25 to about 60, from about 25 to about 50, from about 25 to about 40, from about 25 to about 35, or from about 25 to about 30% greater than that of a corresponding coating prepared without the ceramic phase and/or a corresponding coating prepared without controlling the pH, degree of mixing, and/or temperature of the plating solution or electrolyte).

25 In certain embodiments, the coating has a Vickers microhardness of at least about 750, 775, 800, 810, 820, 825, or 850 HV when tested with a 50 g load for a holding time of 15 seconds. In certain embodiments, the metal-ceramic composite coating comprises Ni-P-ZrO₂; and the item or surface comprises an additional coating comprising Ni-P under the metal-ceramic composite coating. In certain embodiments, the metal-ceramic coating comprises Ni-Co-TiO₂.

30 In certain embodiments, the coating has a Vickers microhardness at least about 250, 260, 270, 280, 290, 300, or 310 HV₁₀₀ when tested with a 100 g load and a holding time of 15 seconds. In certain embodiments, the metal-ceramic coating comprises Zn-Ni-Al₂O₃.

In certain embodiments, the metal-ceramic composite coating has a nano-hardness at least about 5, 10, 15, 20, 30, 35, 40, 45, or 50% greater than a corresponding coating prepared without the ceramic phase and/or a corresponding coating prepared without controlling the pH, degree of mixing, and/or temperature of the plating solution or electrolyte, and useful ranges may be selected between any of these values (for example, from about 5 to about 50, from about 5 to about 40, from about 5 to about 30, from about 10 to about 50, from about 10 to about 40, or from about 10 to about 30% greater than that of a corresponding coating prepared without the ceramic phase and/or a corresponding coating prepared without controlling the pH, degree of mixing, and/or temperature of the plating solution or electrolyte).

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In certain embodiments, the coating has a nano-hardness of at least about 2.7. 2.8. 2.9. 3.0. 3.1. 3.2. 3.3, or 3.4 GPa. In certain embodiments, the metal-ceramic coating comprises Au-Ni-TiO₂.

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In various embodiments, the coating, for example a coating comprising Ag-TiO₂, has a nano-hardness of at least about 1.4, 1.45, 1.5, 1.55, or 1.6 GPa.

Certain metal-ceramic composite coatings also have improved wear properties, such as wear loss volume, scratch displacement, and/or wear track width, compared to corresponding coatings without the ceramic phase.

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In one embodiment, the metal-ceramic composite coating has a wear loss volume at least about 20, 25, 30, 35, 40, 45, 50, 60, 70, or 80% less than a corresponding coating prepared without the ceramic phase and/or a corresponding coating prepared without controlling the pH, degree of mixing, and/or temperature of the plating solution or electrolyte, and useful ranges may be selected between any of these values (for example, from about 20 to 80, from about 20 to 70, from about 20 to 60, from about 20 to 50, from about 20 to 40, from about 30 to 80, from about 30 to 70, from about 30 to 60, from about 30 to 50, from about 30 to 40, from about 40 to 80, from about 40 to 70, from about 40 to 60, or from about 40 to 50% less than a corresponding coating prepared without the ceramic phase and/or a corresponding coating prepared without controlling the pH, degree of mixing, and/or temperature of the plating solution or electrolyte). In one embodiment, the wear loss volume is measured according to ASTM G133.

30

Wear volume may be measured with a micro-tribometer (Nanovea, USA). The wear distance, tip formation and load depend on the coating type. The comparison is between measurements on two coatings with the same instrument under the same conditions.

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In one embodiment, the coating has a wear loss volume is less than about 6, 5, 4, 3, or $2 \times 10^{-3} \text{ mm}^3$.

In one embodiment, the coating comprises Zn-Ni- Al_2O_3 .

- 5 In one embodiment, the coating has a wear loss volume is less than about 225, 200, 175, 150, 125, 100, 95, 90, 85, or $80 \times 10^{-6} \text{ mm}^3$. In one embodiment, the coating comprises Au-Ni- TiO_2 .

In one embodiment, the coating has a wear loss volume is less than about 2.3, 2.0, 1.8, 1.6, 1.4, 1.2, 1.0, or $0.8 \times 10^{-13} \text{ M}^3$. In one embodiment, the coating comprises Ni-B- TiO_2 .

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In various embodiments, the coating, for example a metal-ceramic coating comprising Ni-Co- TiO_2 , has a wear loss volume of less than about 4, 3.5, 3, 2.5, 2.2, 2.0, 1.8, or $1.6 \times 10^{-13} \text{ M}^3$.

- 15 In one embodiment, the metal-ceramic composite coating has a wear track width at least about 5, 10, 15, 20, or 30% narrower than a corresponding coating prepared without the ceramic phase and/or a corresponding coating prepared without controlling the pH, degree of mixing, and/or temperature of the plating solution or electrolyte, and useful ranges may be selected between any of these values (for example, from about 5 to 30, from about 5 to 20, or from about 5 to 10%).

- 20 The wear track is formed with a load bearing on a wear tip, for example, a ceramic or plastic ball, repeatedly traversing a section of the coating for a set duration of time (typically 5 minutes) and a total distance travelled (typically about 20 m). The structure and width of the track is then measured.

- 25 In one embodiment, the coating has a wear track width of less than about 280, 270, 260, 250, 240, 230, 225, 220, or 210 μm . In one embodiment, the coating comprises Zn-Ni- Al_2O_3 .

In one embodiment, the coating has a wear track width of less than about 90, 80, 70, 65, 60, or 55 μm . In one embodiment, the coating comprises Au-Ni- TiO_2 .

- 30 In various embodiments, the coating, for example a metal-ceramic coating comprising Ni-Co- TiO_2 , has a wear track width of less than about 380, 360, 350, 340, 330, 320, or 310 μm .

- 35 In some embodiments, the electrical resistivity and/or conductivity of the metal-ceramic coatings is substantially the same as a corresponding coating prepared without the ceramic phase and/or a corresponding coating prepared without controlling the pH, degree of mixing, and/or temperature

of the plating solution or electrolyte. In certain embodiments, the metal-ceramic composite coating has an electrical resistivity and/or conductivity within about ± 3 , 2.5, 2, 1.5, or 1% of a corresponding coating prepared without the ceramic phase and/or a corresponding coating prepared without controlling the pH, degree of mixing, and/or temperature of the plating solution or electrolyte.

In certain embodiments, the metal-ceramic composite coating has a corrosion resistance substantially the same as or greater than a corresponding coating prepared without the ceramic phase and/or a corresponding coating prepared without controlling the pH, degree of mixing, and/or temperature of the plating solution or electrolyte.

In one embodiment, the metal-ceramic coating has a corrosion potential substantially the same as or greater than and/or a corrosion current density substantially the same as or less than a corresponding coating prepared without the ceramic phase and/or a corresponding coating prepared without controlling the pH, degree of mixing, and/or temperature of the plating solution or electrolyte.

In certain embodiments, the metal-ceramic coating has a corrosion potential greater than and/or a corrosion current density less than about 90, 95, 97, 98, or 99% of a corresponding coating prepared without the ceramic phase and/or a corresponding coating prepared without controlling the pH, degree of mixing, and/or temperature of the plating solution or electrolyte.

In certain embodiments, the metal-ceramic composite coating comprises a passivation layer on the surface of the coating.

The item or surface may comprise at least one additional coating under or on top of the metal-ceramic composite coating. Such additional coatings may be provided by producing the additional coating either prior to or after producing the metal-ceramic composite coating, as will be appreciated by those skilled in the art. The combination of coatings may have improved physical and/or chemical properties compared to a corresponding combination of coatings without the ceramic phase (i.e. the at least one additional coating under or on top of a coating corresponding to the metal-ceramic composite coating, but without the ceramic phase).

In certain embodiments, the item or surface comprising at least one additional coating under or on top of the metal-ceramic composite coating; and the combination of coatings has a corrosion

resistance substantially the same or greater than a corresponding combination of coatings without the ceramic phase and/or a corresponding combination of coatings prepared without controlling the pH, degree of mixing, and/or temperature of the plating solution or electrolyte.

- 5 In certain embodiments, the combination of coatings has a corrosion resistance substantially the same or greater than a corresponding combination of coatings without the ceramic phase and/or a corresponding combination of coatings prepared without controlling the pH, degree of mixing, and/or temperature of the plating solution or electrolyte; and a wear loss volume less than and/or a Vickers hardness greater than a corresponding combination of coatings without the ceramic phase
10 and/or a corresponding combination of coatings prepared without controlling the pH, degree of mixing, and/or temperature of the plating solution or electrolyte.

EXAMPLES

- 15 The following description of experimental work further illustrates the invention by way of example:

Example 1

- This example demonstrates sol-enhanced Ni-P-ZrO₂ coating of a magnesium alloy using electroless
20 plating, and investigates the microstructure, microhardness and corrosion properties of the coating.

Methods

Preparation of magnesium alloy plates

- 25 Magnesium alloy AZ31 plates of 40×25×3 mm³ were mechanically polished using SiC papers of grit #1200, cleaned at 60°C for 10 min in a 50 g/L NaOH and 10 g/L Na₃PO₄·12H₂O solution, acid-washed in 110 mL/L HNO₃ and 125 g/L CrO₃ solution for 40 sec at about 25°C, then activated by 38.5 vol.% HF for 10 min at about 25°C. Specimens were water-rinsed after each step.

- 30 *Electroless plating procedure*

Consecutive electroless processes were carried out in two plating baths. Bath composition and operating conditions are set out in Table 1. Specimens were first plated in Bath A to deposit the high phosphorus inner layer, then Bath B to deposit the ZrO₂ outer layer. Transparent ZrO₂ sol was prepared using the two step process described in Yang et al., 2011. *Applied Nanoscience* 1(1): 19-26.

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The nomenclature Ni-P/Ni-P-XZrO₂ is used to describe the duplex coating, where X refers to the amount of sol (mL/L) in the Bath B. "Ni-P/Ni-P coating" means that Bath B did not comprise any ZrO₂ sol when the specimen was coated.

Table 1: Bath composition and electroless plating parameters

Bath A (inner layer bath)			Bath B (outer layer bath)		
Bath constituents	Quantity	Conditions	Bath constituents	Quantity	Conditions
NiCO ₃ ·2Ni(OH) ₂ ·4H ₂ O	15 g/L	pH: 4.5-5.0	NiSO ₄ ·6H ₂ O	15 g/L	pH: 6.0-6.4
NaH ₂ PO ₂ ·H ₂ O	30 g/L	Agitation: 200rpm	NaH ₂ PO ₂ ·H ₂ O	14 g/L	Agitation: 200rpm
Lactic acid	10-20 mL/L	Temperature: 80 °C	NaCH ₃ COO	10-15 g/L	Temperature: 80 °C
Citric acid	10-20 g/L	Time: 120min	NH ₄ HF ₂	5-10 g/L	Time: 90min
HF (40%)	30-50 mL/L		Thiourea	1 mg/L	
Pb ²⁺	1 mg/L		ZrO ₂ sol	variable	

5 *Morphology, elemental composition and micro-hardness analysis*

The morphology and elemental composition of the duplex Ni-P/Ni-P-XZrO₂ coating was determined by FEI Quanta 200F FEG ESEM with energy dispersive spectroscopy (EDS) system. The crystal structure of the coating was examined using Bruker D₂ Phaser X-ray diffraction (XRD) with Cu target. The Vickers micro-hardness of the sample surface was measured using a load of 50 g with a loading time of 15 sec. The average value of nine measurements for each surface is reported.

Corrosion resistance evaluation

Electrochemical tests were carried out using a CHI604D electrochemical workstation using a classical three-electrode cell with platinum as the counter electrode, Ag/AgCl as the reference electrode, and the coating samples with a 1 cm² exposed area as the working electrode. Potentiodynamic polarization was measured at a scan rate of 1 mVs⁻¹ at about 25°C in 5 wt.% NaCl solution. All the potentials reported refer to the Ag/AgCl electrode.

A salt spray test was conducted according to the ASTM B117 standard (5 wt.% NaCl continuous spray at 35°C). The variation of porosity of the inner layer Ni-P coating with respect to coating time was tested by the method described in Zhang et al., 2007, *Applied Surface Science* 253(11):5116-5121 and Lian et al., 2006, *Surface and Coatings Technology* 200(20-21):5956-5962. Briefly, 1 cm² filter paper was soaked in solution comprising NaCl (10 g/L) and phenolphthalein (0.1 g/L). The filter paper was pasted onto the nickel coating for 10 min. The relative porosity of the coating was evaluated by determining the ratio of red spot area to the total area covered by the filter paper.

Results

Surface and cross-sectional morphologies of coatings

All coatings had a nodular surface morphology common to electroless Ni-P coatings as shown in Figure 1. The nodular size of the monolayer Ni-P coating was smaller than for the duplex coatings. A smaller nodular size was observed in the high phosphorus inner layer compared with the low phosphorus outer layer due to a smaller grain size and increased nucleation sites in the Ni grain. Small pores were observed on the surface of coatings deposited with a sol concentration >25 mL/L, possibly due to ZrO₂ particles being washed away.

The total thickness of the coating was approximately 40 μm comprising ~15 μm inner layer and ~25 μm outer layer as shown in Figure 2. The thickness of the coating was not affected by sol concentration in Bath B. The interface between the alloy substrate and inner layer coating was very rough due to grain boundary attack by acid pickling treatment (Bath A), which may enhance the coating adherence by improving mechanical interlocking between coating and substrate. The interface between the inner and outer layers was uniform and clean without any blended impurities. Mechanical breakage of duplex Ni-P/Ni-P-25ZrO₂ coatings demonstrated coating failure between the substrate and inner layer coating, indicating robust adherence between the two layers. No difference in cross-sectional morphology was observed between sol-free and sol-added coatings.

The EDS results presented in Figure 2 indicate that phosphorus (P) content of outer layer was not affected by sol doping. The phosphorus content of the inner and outer layers was 11.8 wt.% and 5.0 wt.%, respectively, as shown in Figure 2(f). The phosphorus gradient of the two layers is shown by the arrow in Figure 2f. Small black spots deposited in the coating were observed as shown in Figure 2c. Larger precipitate areas distributed throughout the coating were observed when the amount of added sol was increased to 50 mL/L (Figure 2e). The precipitate present in the coating comprised 19.1 wt.% Zr (Figure 2f).

Phase structures of coatings

A wide Ni (111) peak is present in the XRD spectrum for the monolayer Ni-P coating, which is indicative of amorphous structure (Figure 3). In contrast, a sharp intensity peak is seen in the XRD spectrum of the duplex Ni-P/Ni-P coating, indicating a crystal structure with Ni (111) texture of the outer layer. Coating layers with different P contents show different crystal structure, consistent with the EDS results of coating layers.

Although the amount of sol doping did not change the morphology of the deposit, it affected the crystallographic characteristics of the coatings as shown in Figure 4. The nickel grains are more randomly orientated with increasing sol addition. The phosphorus content of the coatings was unaffected by sol doping, consistent with the EDS analysis. The Ni (111) peak intensity (not shown in Figure 4) is similar for all deposits.

Coating hardness

The microhardness of the coating increased with increasing sol addition as shown in Figure 5 to a peak of ~820 HV with 25 mL/L sol. In contrast, the hardness of the coating without sol addition was only ~660 HV. When the sol content was increased to 50 mL/L, hardness decreased to ~730 HV, likely due to the agglomeration of ZrO₂ particles in the coating.

Corrosion performance

A large positive shift in corrosion potential and a decrease in corrosion current density in comparison with the uncoated AZ31 alloy substrate was observed for both monolayer and duplex coatings as shown in Figure 6 and Table 2. Monolayer Ni-P coating with high P content had the most positive potential and therefore the best corrosion resistance. Although the corrosion potential of the sol-enhanced coating was less than that of the sol-free coating, the passivation plateau of the sol-enhanced coating was much wider and the corrosion current density was decreased more in the passive state.

Table 2: Corrosion potential and corrosion current density obtained from polarization curves

Sample	E_{corr} (V) vs. Ag/AgCl	i_{corr} (A·cm ⁻²)
AZ31 substrate	-1.458	6.676×10^{-6}
Monolayer Ni-P coating	-0.178	1.243×10^{-6}
Duplex Ni-P/Ni-P coating	-0.242	1.054×10^{-6}
Duplex Ni-P/Ni-P-25ZrO ₂ coating	-0.321	3.741×10^{-7}
Duplex Ni-P/Ni-P-50ZrO ₂ coating	-0.303	1.028×10^{-6}

The results of the salt fog spray test for the substrate alone and coated substrate are shown in Table 3. The Ni-P/Ni-P duplex coatings demonstrated very good resistance to salt fog attack. Permeation into the substrate did not occur until the end of the salt spray test, and the duplex coating surface remained in good condition after more than 480 hours exposure. Only a single black corrosion spot

appeared on the surface of duplex Ni-P/Ni-P-15ZrO₂ coating after 220 hours, which may be due to H₂ release during plating.

Table 3: Results of salt spray test

Sample	Time (h)	Failure type
AZ31 substrate	24	Uniform corrosion with black and rough corrosion product
Monolayer Ni-P coating	86	Penetrating pitting corrosion with coating pilling off
Duplex Ni-P/Ni-P coating	480	Controlled pitting corrosion with substrate unaffected
Duplex Ni-P/Ni-P-15ZrO ₂ coating	480	Controlled pitting corrosion with substrate unaffected
Duplex Ni-P/Ni-P-25ZrO ₂ coating	480	Controlled pitting corrosion with substrate unaffected

The thickness of the coating increased linearly with longer coating time as shown in Figure 7.

- 5 Complete coverage of the substrate by the coating was only achieved after 80 minutes of plating. This is likely due to the low plating rate of this coating bath, which combines a low pH with the use of strong complexing agent to ensure a high phosphorous content of the coating is achieved. A single red spot was seen in the sample plated for 80 minutes. For coatings plated longer than 80 mins, no red areas were observed. When a second layer was applied the permeation of corrosive
10 media to the substrate was effectively blocked.

These results demonstrate that sol-enhanced Ni-P-ZrO₂ coating of a magnesium alloy provides effective corrosion resistance and desirable mechanical properties.

15 **Example 2**

This example demonstrates sol-enhanced Zn-Ni-Al₂O₃ coating of steel sheet using electrodeposition, and investigates the chemical and mechanical properties of the coating.

20 **Methods**

Preparation of coatings

- A 500 mL acidic sulphate bath was used to electroplate Zn-Ni and Zn-Ni-Al₂O₃ coatings. The composition and electroplating parameters are summarised in Table 4. After one hour magnetic
25 agitation, pH was adjusted by adding dilute H₂SO₄ from 4.8 to 2. The substrate was mild steel sheet of 25×25 mm, with two nickel plates as anodes at both sides. Samples were mechanically ground

down with 600-grit SiC paper and then electropolished in 95 vol.% acetic acid and 5 vol.% perchloric acid at 20 V for 3 min, followed by washing with distilled water and immediately placed into the electrolyte. After electrodeposition, the plated specimens were washed with distilled water and ethanol, and air-dried.

5 **Table 4: Composition and operational parameters of Zn-Ni deposition**

Constituent	Operational parameters
ZnSO ₄ ·7H ₂ O	pH = 2
NiSO ₄ ·6H ₂ O	T: 40°C
NaSO ₄ (80 g/l)	Time: 10 min
	i: 80 mA/cm ²
	Ni ²⁺ /Zn ²⁺ ion ratio: 1
	Agitation speed: 600 rpm

Transparent Al₂O₃ sol was prepared as follows. 97% Al tri-sec-butoxide (ATSB) and distilled water were used at a mol ratio of 0.01:12.4. A small amount of absolute ethanol was added to a beaker to solve the ATSB. Under magnetic stirring, deionized water was slowly added. 30% nitric acid was added to adjust the pH to 3.5 and peptize the solution. The solution was stirred at 60 °C until all white precipitate had dissolved resulting in clear sol. To investigate the effect of sol concentration on the properties of the Zn-Ni coating, different sol concentrations (2–20 mL/L) were added to the electrodeposition bath at 40 °C.

15 *Characterization of the coatings*

The morphology and composition of the coating were analysed using a field-emission scanning electron microscope with an energy-dispersive spectroscopy (EDS) system. A MiniPal 2 PW4025 X-ray spectrometer (XRF) with Rhodium tube and spinner was used for composition analysis. The phase structure of the coatings was examined using X-ray diffraction (XRD) with Cu K α radiation (U = 40 kV, I = 40 mA). Diffraction patterns were recorded in the 2 θ ranging from 20–90° at a scanning rate of 0.02°/s and step size 0.1 s/step. All chemical composition values are quoted in weight percentage using XRF and EDS representing the average of at least three measurements. Grain size measurement was conducted according to the Scherrer line broadening equation.

25 Microhardness was measured using a load of 100 g with a holding time of 15 s with a Vickers hardness tester. Linear reciprocating wear testing was conducted using a NANOVEA Tribometer. A ZrO₂ ball of diameter 6 mm was used as the abrasive ball, and the test was carried out at 0.5 N for 5 min and 100 rpm at room temperature with relative humidity of ~50%, with no lubrication

Electrochemical analysis

The galvanic performance of the coatings was evaluated based on open circuit potential (OCP). The corrosion resistance of the coatings was assessed by potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) measurements in 3.5 wt.% NaCl electrolyte using an electrochemical workstation at frequencies of 10^{-2} to 10^5 Hz at open circuit potential where the amplitude of the perturbation voltage was 10 mV. All corrosion tests were carried out at room temperature $\sim 25^\circ\text{C}$ using a standard flat cell with three-electrode system: platinum mesh as auxiliary, Saturated Calomel Electrode (SCE) as reference and coated specimen as working electrode. The polarization curves were measured at a constant scan speed of 0.01 mV/s. The corrosion current density and corrosion potential were determined based on Tafel's extrapolation. The exposed surface area of all samples was 1 cm^2 . The equivalent electrical circuit (EC) was determined using the ZVIEW program.

A salt spray test was conducted using 5 wt.% NaCl solution based on ASTM-B117 standard. Only $1.5 \times 1.5\text{ cm}^2$ area at the centre of the coating samples was exposed.

Results*Ni content and microhardness of coatings*

The Ni content of the coatings decreased when sol concentration was $>12.5\text{ mL/L}$ sol as shown in Figure 8. Figure 9 shows a representative XRF result. The Fe peaks are produced by the steel substrate. When sol concentration was increased up to 6 mL/L in the bath, hardness increased significantly from 208 HV_{100} to 293 HV_{100} . The addition of 12 and 20 mL/L decreased hardness to 244 HV_{100} and 200 HV_{100} , respectively.

Phase structures of coatings

As shown in Figure 10, coatings deposited using $< 6\text{ mL/L}$ sol remained as a single γ phase – a desirable phase structure for Zn-Ni coatings. When the amount of sol was increased up to 12 mL/L , a very low peak of low intensity corresponding to η phase appeared. However, when 20 mL/L sol is used, the phase structure comprised a mixture of two $\gamma\text{-Ni}_5\text{Zn}_{21}$ and η phases due to the reduced Ni content of the coatings. No Al_2O_3 peaks were detected by XRD, suggesting that the concentration of phases associated with Al_2O_3 is under the limit of detection for XRD.

When the sol concentration in the bath was increased up to 12 mL/L, a corresponding decrease in grain size was observed from 30 nm to 23 nm. The grain size of all coatings was on the nanometre scale, confirming the nanocrystalline structure of Zn-Ni and Zn-Ni-Al₂O₃ composite coatings.

5 *Effect of agitation speed*

The Ni content of the coatings decreased when the agitation speed was doubled from 600 rpm to 1200 rpm as shown in Figure 11, while the microhardness of the coatings was increased as shown in Figure 12. This indicates that more alumina sol is incorporated into the coating with increasing agitation speed. A peak broadening and decrease in peak intensity were more pronounced for Zn-Ni
10 coating deposited at higher agitation speed (1200 rpm) as shown in Figure 13. At a greater agitation speed, grain size decreased from 27 nm to 17 nm by increasing the sol concentration up to 12 mL/L. In addition, η phase peak intensities is higher for coatings deposited with 12 and 20 ml/l sol at 1200 rpm compared to the coatings deposited at 600 rpm, confirming decreased Ni content at increased agitation speed.

15
Surface and cross-sectional morphologies of coatings
Both the morphology and grain size Zn-Ni coatings were significantly affected by the addition of Al₂O₃ sol as shown in Figure 14. With no sol present (Figure 14a), relatively homogeneous hemispherical nodules with average size of 6 μ m were observed. For coatings deposited with sol, the
20 coating surface was smoother with more refined nodules of \sim 2 μ m. For coatings prepared with 6 mL/L sol, a cauliflower-like morphology was observed (Figure 14c).

The crystallization and growth of the electrodeposited layer was affected by the presence of sol in the bath. With increasing sol concentration in the bath (12 mL/L, Figure 14d), a decreased
25 cauliflower cluster size was observed. With 20 mL/L sol (Figure 14e), thin elongated platelets of crystals stacked on each other and hexagonal bars were observed. This morphology is similar to Zn coating with hexagonal columnar morphology.

The Zn-Ni coating exhibited cracks penetrating the costing to the substrate, which were almost non-
30 existent in the sol-enhanced coating as shown in Figure 15.

The surface morphology of coatings deposited with or without 2 mL/L sol at an agitation speed of 1200 rpm is similar to those prepared at 600 rpm as shown in Figure 16b. However, for coatings prepared with 6 or 12 mL/L sol, composites were observed at 1200 rpm (Figure 16c,d) that were

not observed at 600 rpm. This suggests that higher agitation speed reduces the nodule size of the coating, providing a smoother surface morphology.

Wear resistance of coatings

- 5 The wear track on the sol-enhanced Zn-Ni- Al_2O_3 composite coating deposited with sol present was narrower and shallower than for the Zn-Ni coating as shown in Figure 17a,c and Table 5. Wear resistance was shown to decrease with increasing sol concentration. This may be due to decreased microhardness as a result of reducing Ni content.

10 **Table 5: Wear track widths and wear resistance of Zn-Ni coatings deposited at 1200 rpm with varying alumina sol concentration.**

Al_2O_3 sol concentration in bath (ml/l)	Wear track (μm)	Wear loss volume (10^{-3} mm^3)	Microhardness (HV_{100})
0	292	7	237 ± 16
2	255	4	276 ± 14
6	225	3	312 ± 26
12	330	10	224 ± 26
20	391	17	184 ± 11

Corrosion resistance of coatings

- OCP values for the coatings shifted positively with increasing sol concentration, showing a trend towards decreasing corrosion current density as shown in Figure 18. The corrosion potential shifted positively, and the corrosion current density decreased with increasing sol up to 6 mL/L as shown in Figure 19 and Table 6. However, above 6 mL/L sol, an increase in corrosion current density and a decrease in the corrosion resistance was observed. This may be due to the decreasing Ni content and change of the structure of coatings with increased sol.

Table 6: Corrosion parameters extracted from polarization plots.

Al_2O_3 sol in bath (mL/L)	Corrosion potential (mV)	Corrosion current Density ($\mu\text{A}/\text{cm}^2$)
0	-1048	6
2	-1032	3.5
6	-1013	0.8
12	-1002	2
20	-971	10.5

20

The impedance plots of the coatings generated from EIS data exhibited two loops: a large capacitive loop at high frequency which is somewhat depressed, and an inductive loop at low frequency

characterised by decreasing Z_{real} and Z_{img} as shown in Figure 20. In the EC, CPE is the constant phase element, R_{ct} is the charge transfer resistance, R1 and L1 are elements associated with the inductive loop, and RS is the uncompensated solution resistance. The calculated values for circuit elements shown in Table 7 showed that the Zn-Ni coating with 6 mL/L sol in the bath possesses a maximum value of R_{ct} , and thus exhibits the best corrosion resistance of the coatings tested.

Table 7: Fitting values of the elements in equivalent circuit of the Zn-Ni alloy and composite coatings in 3.5% NaCl solution.

Al_2O_3 sol in bath (mL/L)	R_s ($\Omega \text{ cm}^2$)	CPE (F cm^{-2})	R_{ct} ($\Omega \text{ cm}^2$)	L1 (H)	R1 ($\Omega \text{ cm}^2$)
0	15	0.00085	45	15	150
2	11	0.00022	145	10	170
6	14	0.00001	365	20	850
12	17	0.0001	220	20	400
20	11	0.0009	52	38	150

White rust appeared on all coating surfaces after about 24 hours exposure to salt spray. The first red rust was observed on the Zn-Ni coating with 6 mL/L alumina sol in the bath after about 1560 hours, compared with about 1486 hours for Zn-Ni alloy coating without sol. The red rust formation time for both coatings was better than values reported in the literature for Zn-Ni coatings without passivation (Baldwin et al., 1993. *Corros Sci.* 35(5–8):1267-72; Ganesan et al., 2007. *Surface and Coatings Technology* 201(18):7896-904; Ramanauskas et al., 1997. *Surface and Coatings Technology* 6:92(1–2):16-21).

XRF and XRD tests were conducted on corroded samples after the salt spray test. For both coatings, Cl was detected in addition to Zn, Ni and Fe (Figure 21). XRD analysis revealed that the primary corrosion products were zinc hydroxide chloride hydrate ($\text{ZnCl}_2 \cdot 4\text{Zn}(\text{OH})_2 \cdot \text{H}_2\text{O}$), hydrozincite ($2\text{Zn}(\text{CO}_3) \cdot 3\text{Zn}(\text{OH})_2$) and zinc hydroxide (Figure 22).

These results demonstrate that sol-enhanced Zn-Ni- Al_2O_3 coating of steel sheet using by to 6 mL/L sol improved the corrosion resistance of the coating without affecting Ni content or the phase structure of the coating.

Example 3

This example demonstrates sol-enhanced Au-Ni- TiO_2 nano-composite coating of brass plates using electroplating, and investigates the chemical and mechanical properties of the coating.

Methods

Preparation of coatings

- 5 Au-Ni and sol-enhanced Au-Ni-TiO₂ composite coatings were electroplated onto brass plates substrates (20×15×0.6 mm³) comprising 64 wt.% Cu and 36% Zn. To prevent inter-diffusion between the Cu substrate and Au, a bright Ni layer of ~7 μm thick was deposited onto the substrate surface. Substrates were pretreated in alkaline solution at 80 °C for 30 sec at 10 mA/cm² current density, then electro-activated in HF solution at room temperature for 20 sec at 20 mA/cm².
- 10 Substrates were rinsed in distilled water before electroplating.

TiO₂ sol was prepared as described in NZ 578038. 8.68 mL of tetrabutylorthotitanate [Ti (OBu)₄] was dissolved into a solution of 35 mL ethanol and 2.82 mL diethanolamine. After magnetic stirring for 2 h, the solution was hydrolyzed by adding a mixture of 0.45 mL deionized water and 4.5 mL ethanol dropwise under magnetic stirring. The electrolyte composition and plating parameters are listed in Table 8.

15

Table 8: Electroplating bath composition and plating parameters

Bath composition and plating parameters	Value or Quantity
KAu(CN) ₂	2 g/L
NiSO ₄	2 g/L
C ₆ H ₈ O ₇	10 g/L
K ₃ C ₆ H ₅ O ₇ ·H ₂ O	13 g/L
TiO ₂ sol	0-50 mL/L
pH value	3.8±0.2
Plating time	10 min
Temperature	40±2°C
Current density	10 mA/cm ²
Agitation speed	200 rpm

20 *Morphology, composition and nano-hardness analysis*

The surface morphology and composition of the Au-Ni-TiO₂ coating was analysed as described in Example 1. The phase structure of the coatings was characterized by XRD with Cu Kα radiation (V = 30 kV, I = 15 mA). Diffraction patterns were recorded in the 2θ range from 20 to 80° at a scanning rate of 1° min⁻¹. Morphologies and distributions of TiO₂ nano-particles in the composite coating were studied by a transmission electron microscope (TEM) using a FEI Tecnai F20-ST field

25

emission gun microscope equipped with an energy dispersive X-ray (EDX) device, gatan imaging filter (GIF) and owning scanning transmission electron microscopy (STEM) capabilities.

Nano-indentation tests were conducted on a Nanoindenter (Hyston, USA). As the surface roughness was under the level of 10 nm, nine indents were performed on original coating specimens to a peak depth of 50 nm for nano-hardness measurements with a Berkeovich diamond tip. Nano-scratch resistance tests were performed with a conical tip with a 1000 μN constant load to 10 μm distance.

The wear properties of coatings were tested using a micro-tribometer (Nanovea, USA) with a ruby ball of 6 mm diameter as friction counterpart. A total sliding distance of 10 m with a load of 1 N and a sliding speed of 2 m/min were used. All wear tests were performed at $\sim 25^\circ\text{C}$ under dry, non-lubricated conditions. The wear track images on coatings were observed using a high-revolution optical microscope.

The electrical resistivity of the specimen was measured by four-point probe method using System Source Meter (Keithley 2602). During the test, the four-point probes were placed collinearly with equal spacing between them on the sample surface. Current was passed through the two outer probes and the potential between the two inner probes was measured. Considering the thickness of coating (d) was much shorter than the length, the electrical resistivity (ρ) was obtained using the following equation.

$$\rho = (\pi/\ln 2) (V/I) \times d$$

10 tests were performed per sample, and the electrical resistivity values were transferred to electrical conductivity values.

Results

Microstructure of sol-enhanced nano-composite Au-Ni-TiO₂ coatings

The XRD patterns for all Au-Ni coatings tested showed a typical semi-crystalline structure as shown in Figure 23. No TiO₂ peaks were seen for the composite coatings, probably due to the low quantity of TiO₂ particles and high intensity of other diffraction peaks. The predominant planes of the coatings were Au (111), Au (200), Ni (200), Au (220) and Au (311).

Analysis of the cross-sectional morphology of the coatings showed that the thickness of the Ni coating was approximately 7.2 μm as shown in Figure 24. A clear boundary between the coating and the substrate was present, and no abrasion or cracks were observed at the interface of the coating. All coatings were compact with a uniform thickness of $\sim 1.2 \mu\text{m}$, indicating a plating rate of ~ 0.125 5 $\mu\text{m}/\text{min}$. The sol-enhanced Au-Ni-TiO₂ composite coating exhibited a homogeneous structure with no visible TiO₂ particles.

The Au-Ni coating displayed typical granular morphology with a large protrusion size of $\sim 400 \text{ nm}$ as shown in Figure 25(a). The 12.5 mL/L TiO₂ sol-enhanced composite coating had a uniform 10 spherically nodular structure with a size of $\sim 300 \text{ nm}$ (Figure 25(b)). Many black dots $\sim 50\text{--}150 \text{ nm}$ in size were observed on the surface of the 50 mL/L TiO₂ sol-enhanced composite coating, as indicated by the white arrows in Figure 25(c). Some of the black dots can be attributed to clusters formed by TiO₂ nano-particles, as the Ti concentration in those areas was higher than other areas. Porous structure had formed in the areas around the clusters. Other black dots are voids likely 15 attributable to H₂ release during the electrodeposition process.

Mechanical properties of sol-enhanced nano-composite Au-Ni-TiO₂ coatings

At low sol concentration, nano-hardness increased and scratch displacement decreased with increasing TiO₂ concentration up to 12.5 mL/L TiO₂ as shown in Figure 26. The 12.5 mL/L TiO₂ 20 sol-enhanced composite coating had a nano-hardness of $3.20 \pm 0.15 \text{ GPa}$ and scratch displacement of $22.5 \pm 4.3 \text{ nm}$. When TiO₂ concentration was increased to 50 mL/L, nano-hardness was reduced to $2.66 \pm 0.12 \text{ GPa}$, and scratch displacement increased to $32.3 \pm 2.1 \text{ nm}$.

The Au-Ni coating exhibited the greatest wear damage with a track width of $95 \pm 3 \mu\text{m}$. In contrast, 25 the wear track widths of the TiO₂ sol-enhanced Au-Ni-TiO₂ coatings were narrower, with widths of 65 ± 4 and $82 \pm 4 \mu\text{m}$ for the 12.5 and 50 mL/L TiO₂ sol enhanced coatings, respectively.

The 12.5 mL/L TiO₂ sol-enhanced Au-Ni-TiO₂ composite coating exhibited the best wear resistance of the coatings tested with a wear volume loss of $76.3 \pm 4.2 \times 10^{-6} \text{ mm}^3$. The wear volume 30 loss of the Au-Ni coating and 50 mL/L composite coating were $238.2 \pm 8.3 \times 10^{-6} \text{ mm}^3$ and $153.2 \pm 7.7 \times 10^{-6} \text{ mm}^3$, respectively.

Electrical resistivity of sol-enhanced nano-composite Au-Ni-TiO₂ coatings

Electrical resistivity increased and electrical conductivity decreased with increasing TiO₂ sol content 35 as shown in Figure 27. For the 50 mL/L composite coating, the electrical resistivity was 3.38 ± 0.05

($\times 10^{-8} \Omega \cdot \text{m}$) and the electrical conductivity was 50.9 ± 0.8 (%IACS), compared with 3.25 ± 0.03 ($\times 10^{-8} \Omega \cdot \text{m}$) and 52.9 ± 0.5 (%IACS) for the Au-Ni coating.

Strengthening mechanism of the sol-enhanced Au-Ni-TiO₂ nano-composite coating

- 5 The improved strength of the sol-enhanced Au-Ni-TiO₂ nano-composite coating can be mainly attributed to two factors: (1) grain size refinement strengthening from nano-crystalline Au matrix, and (2) dispersion strengthening from the TiO₂ nano-particles.

10 The grain size of the sol-enhanced composite coating was calculated from the XRD spectra according to Scherrer's formula and the results are shown in Table 9. Grain size was lowest for the 12.5 mL/L sol-enhanced Au-Ni-TiO₂ nano-composite coating.

Table 9: Grain size of sol-enhanced Au-Ni-TiO₂ nano-composite coatings.

Composition and conditions	Grain size (nm)
Au-Ni coating	14.1 ± 0.4
Au-Ni-12.5 mL/L TiO ₂ composite coating	10.5 ± 0.3
Au-Ni-50 mL/L TiO ₂ composite coating	12.4 ± 0.3

15 Examination of the microstructure of sol-enhanced Au-Ni-TiO₂ nano-composite coatings imaged by high angle annular dark-field (HAADF) technique and analysed using nanoscale probe EDX analysis showed that TiO₂ nano-particles of 3–12 nm were uniformly dispersed in the coating matrix.

The average friction coefficient for the coatings is shown in Table 10. The 12.5 mL/L TiO₂ sol enhanced coating had the lowest friction coefficient.

20 **Table 10: Friction coefficient of sol-enhanced Au-Ni-TiO₂ nano-composite coating**

Composition and conditions	Average friction coefficient
Au-Ni coating	0.701
Au-Ni-12.5 mL/L TiO ₂ composite coating	0.663
Au-Ni-50 mL/L TiO ₂ composite coating	0.751

25 The wear rate of a coating is inversely proportional to the coating surface hardness and proportional to the friction coefficient (Hou and Chen, 2011. *Appl. Surf. Sci.* 257: 6340-6346). The results of this example show that the addition of 12.5 mL/L TiO₂ sol addition increased hardness and reduced the friction coefficient, indicating improved wear resistance.

These results demonstrate that sol-enhanced Au-Ni-TiO₂ coating of a brass substrate by electrodeposition provides enhanced mechanical properties, effective scratch and wear resistance, and similar electrical resistivity to a pure Au-Ni coating.

5 Example 4

This example examines the nano-structure of a sol-enhanced electroplated Au-Ni coating. A brass substrate pre-coated with approximately 7 µm bright nickel was subjected to electroplating using a commercial 22CT Au/Ni solution (6621). Electroplating was followed by pre-treatment and electro
10 activation. Plating parameters were identical for all coatings.

The grain refinement and distribution of particles in the coatings was characterised using transmission electron microscopy (TEM). TEM images of the coatings are shown in Figure 28. Grain distribution was measured from these images using automated particle size analysis. The
15 results presented in Figure 28 and Table 11 show that the inclusion of TiO₂ sol in the matrix significantly reduces grain size to a greater degree than TiO₂ powder.

Table 11: Grain size distribution of Au-Ni coatings

Coating	Grain size range (nm)	Average grain size (nm)	% reduction in grain size over Au-Ni
Au-Ni	22–27	28.8	
Au-Ni with TiO ₂ powder	19–34	26.4	8.3
Au-Ni with 12.5 mL/L TiO ₂ sol	16–31	22.2	22

The diffraction pattern for the Au-Ni containing TiO₂ sol is similar to that of the unreinforced
20 coating as shown in Figure 29 indicating that the TiO₂ was amorphous. In contrast, the diffraction pattern for the coating comprising TiO₂ powder indicates the presence of crystalline TiO₂.

Large TiO₂ particles were observed in the surface of the Au-Ni coating prepared with TiO₂ powder (Figure 30a), demonstrating agglomeration of the particles up to 200 nm in the bath at the relatively
25 low agitation speed required for electroplating. Particles of this size and number cannot contribute to dispersion strengthening, and have only a limited effect on grain refinement. In contrast, large quantities of ceramic particles were observed in the TiO₂ sol-enhanced coating (Figure 30b), providing a high number of grain disruption points. The apparent size range of the particles was 3–20 nm. Approximately 2% of the image comprises ceramic particles.

30

Example 5

This example examines the surface morphology and wear resistance of a sol-enhanced electroplated NiB coating.

5

A mild steel substrate was electroplated to deposit a NiB coating with or without the addition of 12.5 mL/L TiO₂ sol to the plating composition. The bath composition and conditions are described in Table 12.

10 **Table 12: Bath composition and electroplating parameters**

Bath components	Quantity	Conditions
Nickel Sulphate Hexahydrate	240 g/L	Temperature: 45 °C pH 3.5 ± 0.1
Nickel Chloride hexahydrate	45g/L	Current density: 10-20 mA/cm ² Time: 30-60 minutes
Boric acid	30 g/L	
Dimethylamine borane	3 g/L	

The sol-enhanced NiB coating had a considerably smoother surface than the NiB only coating (Figure 31). The sol-enhanced coating also had a 58% improvement in wear resistance under a 7N load compared with the unenhanced coating. The wear volume for the NiB coating was 2.46 x 10⁻¹³ M³ and 1.05 x 10⁻¹³ M³ for the sol-enhanced coating, a 50% improvement. In contrast, a powder doped coating had a wear volume of 1.05 x 10⁻¹³ M³ providing only a 21% improvement in wear volume loss.

20 **Example 6**

This example demonstrates sol-enhanced Ni-Co-TiO₂ coating of mild steel using electroplating, and investigates the chemical and mechanical properties of the coating.

25 **Methods**

Preparation of coatings

Ni-Co coatings and sol-enhanced Ni-Co-TiO₂ nano-composite coatings were electroplated using a modified watt's bath. The bath was prepared using Sigma analytical grade reagents and contained 250 g/L NiSO₄·6H₂O, 40 g/L NiCl₂·6H₂O, 30 g/L CoSO₄·7H₂O, 35 g/L H₃BO₃ and 0-50 mL/L

30

TiO₂ sol. The pH value of bath was adjusted by H₂SO₄ and NaOH to be around 3.5. TiO₂ sol was prepared as reported in NZ 578038.

5 The electroplating system consisted of a mild steel sample as the cathode and a Ni plate as the anode. The steel substrates were mechanically polished using SiC paper to a grit of #1200, then degreased ultrasonically in ethanol and pre-treated in 1 mol/L HCl solution for 2 min. The substrates were then rinsed thoroughly with distilled water, and electroplated by using a TENMA 72-8355 DC power supply. The electrolyte was magnetically stirred at a rate of 400 rpm and maintained at 55°C. The current density was set to 2 A/dm², and the coating was conducted for 30
10 min.

Coating characterization

The morphologies and compositions of the coatings were analyzed using a field emission scanning electron microscope (FEI Quanta 200) with an energy-dispersive spectroscopy (EDS) system. The
15 phase structure and preferred orientation of the coatings were determined by XRD using (D2 Bruker X-ray diffractometer) operated at 30 kV and 10 mA with the Cu-K α radiation. TEM analysis was conducted by using a FEI Tecnai T12 transmission electron microscope.

Vickers microhardness was measured using a load of 100 g with a holding time of 15 s. The results
20 for the hardness were the average of 5 measurements. The wear property of coatings was tested using a micro-tribometer (Nanovea, USA) in air at 25°C, relative humidity of ~50% and under dry, non-lubricated conditions. All wear tests were performed under a load of 5 N, a sliding speed of 2 m/min and a contact radius of 6 mm for a total sliding distance of 20 m. The electrochemical tests were conducted in an electrochemical workstation (CHI604D) using a classical three-electrode
25 system. Potentiodynamic polarization tests were carried out at a scan rate of 1 mVs⁻¹ at room temperature in a 3.5 wt.% NaCl solution.

Results

XRD spectrum of coatings

The X-ray diffraction (XRD) patterns of Ni-Co and sol-enhanced Ni-Co-TiO₂ nano-composite coatings are shown in Figure 32. All diffraction patterns are presented as a face centered cubic solid solution with peaks of Ni (111), Ni (200) and Ni (220). No TiO₂ peaks could be seen from the sol-enhanced Ni-Co-TiO₂ nano-composite coatings, probably due to the low quantity of the TiO₂ nano-
35 particles dispersed throughout the coating.

Cross-section of coatings

The cross-section morphology of Ni-Co coating and sol-enhanced Ni-Co-TiO₂ nano-composite coatings was analyzed by ESEM as shown in Figure 33. All coatings have a similar thickness of approximately 9 μm. The deposition rate of coatings remains substantially constant with an increasing sol content in the plating solution. No defects or cracks were observed at the interfaces of either the Ni-Co or the sol-enhanced Ni-Co-12.5 mL/L TiO₂ coatings (Figures 33(a) and 33(b)). This suggests good adhesion between the steel substrate and coating. No obvious TiO₂ particles were observed in the cross-section of Ni-Co-12.5 mL/L TiO₂ coating.

With a TiO₂ sol concentration of 50 mL/L in the bath, detachment and cracking lines can be seen in the coating – see Figure 33(c). There are small Ti enriched areas along the cracking lines, which were confirmed by the EDS probe. The addition of such quantities of TiO₂ sol tended to cause the agglomeration of TiO₂ nanoparticles, and create a porous structure at the grain boundaries, leading to a deterioration in coating adhesion.

Microhardness

Table 13 presents the microhardness value of the as-deposited Ni-Co-TiO₂ nano-composite coatings as a function of TiO₂ sol concentration in the bath. The microhardness of Ni-Co coating (no TiO₂ sol) was ~651 HV. At a low sol concentration, microhardness increases significantly with increasing sol addition. The microhardness increased to a peak value of ~834 HV when the TiO₂ sol concentration is 12.5 ml/L. Further increasing the concentration of the TiO₂ sol resulted in a decrease of coating microhardness. When the sol concentration is equal to or greater than 20 mL/L, the microhardness of coatings decreased to the same level as the pure Ni-Co coating.

The improvement of microhardness may be attributed to dispersion hardening due to the highly dispersed TiO₂ nanoparticles in the coating matrix.

Table 13: Microhardness of sol-enhanced Ni-Co-TiO₂ nano-composite coatings as a function of TiO₂ sol concentration.

TiO ₂ sol concentration (mL/L)	Microhardness (HV ₅₀)
0	650.6 ± 5
2.5	686.6 ± 6.5

5	739 ±10.2
10	798.2 ±11.4
12.5	833.8 ±12.1
15	736.4 ±6.9
20	657.2 ±8.7
50	655 ±6.8

Figure 34 shows the TEM images and electron diffraction patterns of Ni-Co and sol-enhanced Ni-Co-12.5 mL/L TiO₂ coatings. The Ni-Co coating shows a mixed crystal structure which confirmed by the inserted electron diffraction pattern in Figure 34(a). In the sol-enhanced coating highly dispersed TiO₂ nano-particles with an average size below 15 nm were distributed uniformly throughout the coating as shown in Figure 34(b). This result demonstrates that the addition of 12.5 mL/L TiO₂ sol to the electrolyte can effectively avoid particle agglomeration and produce a highly dispersed distribution of TiO₂ nano-particles in the coating matrix, significantly improving the mechanical properties of the coating, when coating under the conditions indicated above.

Wear resistance

Tribological and wear property of Ni-Co-TiO₂ coatings were studied. Table 14 below shows the average friction coefficient of the coatings.

Table 14: Friction coefficient of Ni-Co and Ni-Co-TiO₂ coatings

Coating	Average friction coefficient
Ni-Co coating	0.619 ±0.031
Ni-Co-12.5 mL/L TiO ₂ composite coating	0.547 ±0.027
Ni-Co-50 mL/L TiO ₂ composite coating	0.579 ±0.029

The Ni-Co coating possesses the highest friction coefficient (0.619) compared with the sol treated coatings. The coating produced with 12.5 mL/L sol showed an average friction coefficient of 0.547. The average friction coefficient of Ni-Co-50 mL/L TiO₂ increases to 0.579.

The decrease in friction coefficient of the Ni-Co-TiO₂ coatings is probably because the TiO₂ nanoparticles in the coating matrix can act as solid lubricant during the wear process.

Using 50 mL/L TiO₂ sol, compared to 12.5 mL/L TiO₂, led to a friction coefficient increase and a rougher coating surface. However, this friction coefficient was still lower than the Ni-Co coating.

The wear track images, wear track width and wear volume loss of the Ni-Co coating and sol-enhanced nano-composite Ni-Co-TiO₂ coatings are shown in Figure 35 and Table 15.

Table 15: Wear track widths, wear volume loss, and wear depth of Ni-Co and Ni-Co-TiO₂ coatings

TiO ₂ sol in bath (mL/L)	Wear track (μm)	Wear depth (μm)	Wear loss volume (10 ⁻¹³ m ³)
0	409	6.98 ± 0.349	4.59 ± 0.229
12.5	308	3.96 ± 0.198	1.47 ± 0.074
50	340	4.82 ± 0.241	2.19 ± 0.109

5

It can be observed that the Ni-Co coating has a relatively wide wear track with a width, depth and volume loss of ~409 μm, ~7.0 μm and ~4.59×10⁻¹³ m³, respectively. There are clear plowing lines and some large wear debris on the worn surface.

10 After adding TiO₂ sol into the plating solution, the worn area decreased and the plough lines became shallower and more uniform.

On the coating produced with 12.5 mL/L sol, the corresponding wear track width and wear volume loss decreased to ~308 μm, ~3.96 μm and ~1.47×10⁻¹³, respectively. The significant improvement of wear resistance is related to the increased hardness and reduced friction coefficient of the coating. Although the hardness of the Ni-Co-50 mL/L TiO₂ coating is at the same level as the Ni-Co coating, the wear resistance (~340 μm, ~4.82 μm and ~2.19×10⁻¹³) is significantly greater than that of the pure Ni-Co coating, due to its lower friction coefficient.

20 *Corrosion property of coatings*

Figure 36 presents the polarization curves of Ni, Ni-Co and TiO₂ sol-enhanced Ni-Co nano-composite coatings. The electrochemical properties obtained from potentiodynamic curves are listed in Table 16.

Table 16: Electrochemical parameters of potentiodynamic polarization curves calculated from the Tafel plots.

Sample	E _{corr} (V vs. SCE)	I _{corr} (×10 ⁻⁶ A/cm ²)
Ni	-0.385	3.112
Ni-Co	-0.488	7.064
Ni-Co-12.5 mL/L TiO ₂	-0.403	5.244

Ni-Co-50 mL/L TiO ₂	-0.454	5.903
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The corrosion potential E_{corr} and corrosion current density I_{corr} of Ni coating were ~ -0.385 V and $3.112 \mu\text{A}/\text{cm}^2$, while the E_{corr} and I_{corr} value obtained for Ni-Co coating were ~ -0.488 V and $7.064 \mu\text{A}/\text{cm}^2$, respectively. In principle, higher corrosion potential and lower corrosion current density indicate a better corrosion resistance. Ni deposit showed better corrosion resistance because of its dense nature and freedom from local defects compared to the Ni-Co deposits.

The corrosion potential E_{corr} and corrosion current density I_{corr} of sol-enhanced Ni-Co-12.5 mL/L TiO₂ coating was observed to be ~ -0.403 V and $\sim 5.244 \mu\text{A}/\text{cm}^2$, respectively, indicating an increased corrosion resistance compared to the Ni-Co coating. Increased sol addition caused a deterioration of the corrosion resistance of the composite coating, evidenced by the E_{corr} of -0.454 V and increased I_{corr} of $\sim 5.903 \mu\text{A}/\text{cm}^2$ for sol-enhanced Ni-Co-50 mL/L TiO₂ coating.

When 12.5 mL of TiO₂ sol was added, fine TiO₂ nano-particles were incorporated uniformly into the coating matrix as shown in Figures 33(b) and 34(b). The TiO₂ nano-particles were embedded in the Ni-Co matrix and filled in gaps, cracks and micro holes, resulting in a denser microstructure. Additionally, these nano-sized TiO₂ particles have high corrosion resistance themselves and can act as inert physical barriers to the initiation and development of defect corrosion, substantially improving the corrosion resistance of the coating.

When 50 mL/L TiO₂ sol was added into the electrolyte, the corrosion resistance decreased. However, the corrosion resistance was still greater than Ni-Co.

Example 7

This example demonstrates sol-enhanced Ag-TiO₂ coating of brass using electroplating, and investigates the chemical and mechanical properties of the coating.

Methods

Preparation of coatings

Pure Ag and sol-enhanced Ag-TiO₂ nano-composite coatings were electroplated onto brass substrates ($20 \times 20 \times 0.6 \text{ mm}^3$). The composition of the brass was 64 wt. % Cu and 36 wt. % Zn. In order to prevent inter-diffusion of Cu ions, a bright Ni layer of $\sim 7 \mu\text{m}$ thick was first deposited onto

the substrate surface. Before electroplating, the specimens were pretreated in alkaline solution at 80°C for 30 sec under 10 mA/cm² current density, then electro-activated in HF containing solution at room temperature for 20 sec under 20 mA/cm². These specimens were electroplated after cleaning by distilled water.

5

TiO₂ sol was prepared as reported in NZ 578038. The electrolyte composition and deposition parameters are listed in Table 17.

Table 17: Electroplating bath composition and plating parameters

Bath composition and plating parameters	Value or Quantity
Ag (metal)	30 g/L
KCN (free)	120 g/L
KOH	25 g/L
TiO ₂ sol	0-50 mL/L
PH value	12.5
Plating time	20 min
Temperature	30±1°C
Current density	10 mA/cm ²
Agitation speed	200 rpm

10

Characterization of the coatings

The phase structure of the coatings was characterized by X-ray diffraction (XRD) with Cu K α radiation ($V = 30$ kV, $I = 15$ mA). Diffraction patterns were recorded in the 2θ range from 20 to 80° at a scanning rate of 1° min⁻¹. The cross-section image of coatings was investigated using a field emission scanning electron microscope (FESEM) with an energy-dispersive spectroscopy (EDS) system.

15

Microstructure and phase distributions of the composite coating were studied by utilizing a transmission electron microscope (TEM). TEM analysis was conducted on a FEI Tecnai F20-ST field emission gun microscope (200kV) equipped with an energy dispersive X-ray (EDX) device, gatan imaging filter (GIF) and owning scanning transmission electron microscopy (STEM) capabilities.

20

The nano-indentation tests were conducted on a Nanoindenter (Hystron, USA). As the surface roughness was under the level of 10 nm and the thickness of Ag coating is around ~10 μ m, 9

25

indents were performed under a constant load of 2mN on original coating specimens to a peak depth of ~200 nm for nano-hardness investigation with a Berkeovich diamond tip.

Electrochemical analysis

- 5 The electrical resistivity of the specimen was measured by four-point probe method using System Source Meter (Keithley 2602). During the test, the four-point probes were placed collinearly with equal spacing between them on the sample surface. Current was passed through the two outer probes and the potential between the two inner probes was measured.
- 10 10 tests were performed on each sample and the as-obtained electrical resistivity values were transferred to electrical conductivity. In order to estimate the effect of sol addition on the conductivity of silver coatings, the electrical conductivity of composite coatings were tested and a ratio histogram was draw based on the conductivity of pure Ag coating.

15 **Results**

X-ray patterns of coatings

- Figure 37 shows the comparison of XRD spectra of pure Ag coating and sol-enhanced Ag-TiO₂ nano-composite coatings. The predominant planes of the coatings were Ag (111), Ag (200), Ag (220)
20 and Ag (311). No TiO₂ peaks could be seen in the Ag-TiO₂ composite coating, probably due to the low quantity of TiO₂ nano-particles and high intensity of Ag peaks.

Cross-section images of coatings

- Figure 38 shows the cross-sectional morphology of Ag and sol-enhanced Ag-TiO₂ coatings, which
25 were deposited onto the Ni coated brass substrates. The thickness of the Ni coating layer is ~7 μm. Both Ag (Figure 38(a)) and sol-enhanced Ag-TiO₂ have a similar thickness of ~10 μm, indicating a deposition speed of ~30 μm/hour. A clear boundary can be seen between the Ni layer and Ag layer. The coating exhibits a good adhesion as no cracks and abruption could be observed at the interface of coatings. No obvious TiO₂ nano-particles were seen in the cross-section of sol-enhanced Ag-12.5
30 mL/L TiO₂ coating (Figure 38(b)). However, with increasing the TiO₂ sol addition to 20 ml/L, agglomerated TiO₂ particles can be seen (boxed in Figure 38(c)) and voids were also observed in the coatings .

Mechanical property

Table 18 shows the nano-hardness of nano-composite Ag-TiO₂ coatings. The nano-hardness of Ag coating was ~1.33 GPa, a typical value of pure Ag coating. After adding a little amount of TiO₂ sol (5 mL/L), the nanohardness increased significantly to ~1.61 GPa. Then the nano-hardness of coating increases gradually with increasing sol addition and kept a stable value of above 1.60 GPa in the range of 5 mL/L to 15 mL/L. The 12.5 mL/L TiO₂ sol-enhanced composite coating possessed the highest nano-hardness of ~1.64 GPa, a 23.3% improvement compared to pure Ag. Further increasing the sol concentration to 20 mL/L led to a decrease of nano-hardness to ~1.30 GPa.

Table 18: Nanohardness of nano-composite Ag-TiO₂ coatings

TiO ₂ sol concentration in electrolyte (mL/L)	Hardness (GPa)
0	1.328 ±0.05312
5	1.608 ±0.06432
10	1.624 ±0.06496
12.5	1.635 ±0.0654
15	1.628 ±0.06512
20	1.302 ±0.05208

10

Table 19 shows the grain size calculated from the measured XRD patterns according to Scherrer's formula. It can be seen that the grain size of composite coatings shows a clear decrease when proper sol was added.

Table 19: Grain size of sol-enhanced Ag-TiO₂ nano-composite coatings

Coating	Grain size (nm)
Ag coating	38.5 ± 0.5
Sol-enhanced Ag-12.5 mL/L TiO ₂ composite coating	25.7 ± 0.4

15

Figures 39 and 40 present the bright field image and the high angle annular dark-field (HAADF) image of sol-enhanced Ag-TiO₂ nano-composite coating, respectively. Many white small nanoparticles (circled) can be seen in the grain boundaries and coating matrix as shown in Figure 39.

The HAADF image (Figure 40) presents a higher contrast and a better image. A lot of black dots (several circled) with a size of 10-25 nm were distributed uniformly in the grain boundaries and coating matrix (white color). By EDS probe, it was confirmed that these black dots are TiO₂ nano-

particles. The improved strength of the sol-enhanced Au-Ni-TiO₂ nano-composite coating can be mainly attributed to two factors: (1) grain size refinement strengthening from nano-crystalline Au matrix, and (2) dispersion strengthening from the TiO₂ nano-particles.

- 5 The strength of the sol-enhanced nano-composite Ag-TiO₂ coatings can be mainly attributed to two factors: (1) grain refinement strengthening and (2) dispersion strengthening.

When 12.5 mL/L of TiO₂ sol was added into the solution, the TiO₂ nano-particles were highly dispersed in the coating matrix and grain boundaries, resulting in a significant dispersion
 10 strengthening effect. When 20 mL/L TiO₂ sol was added into the electrolyte, TiO₂ nanoparticles started to agglomerate in the coating matrix and tended to cause a porous structure as shown in Figure 38(c), reducing the mechanical property of coating.

Conductivity

- 15 Being a good candidate of electronic material, the conductivity is an important parameter for silver. The electrical resistivity of the Ag and sol-enhanced Ag-TiO₂ coatings are shown in Table 20. The results show that the 12.5 mL/L TiO₂ sol-enhanced Ag-TiO₂ coating has an electrical resistivity only slightly greater than the pure Ag coating.

Table 20: Electrical resistivity of sol-enhanced Ag-TiO₂ coatings

Coating	Electrical resistivity (ratio to pure Ag coating)
Ag	1
Ag-12.5 mL/L TiO ₂ composite coating	1.012 ±0.01
Ag-20 mL/L TiO ₂ composite coating	0.991 ±0.02

- 20 The following paragraphs define aspects and embodiments of the invention:

1. A plating or coating method for producing a metal-ceramic composite coating on a substrate, the method comprising adding a sol of a ceramic phase to a plating solution or electrolyte, and controlling the pH, agitation, and/or temperature of the plating solution or electrolyte.

25

2. A plating or coating method according to paragraph 1, wherein the pH, agitation, and/or temperature is controlled such that nanoparticles of the ceramic phase form directly onto or at the substrate.

3. A plating or coating method according to paragraph 1 or 2, wherein the pH, agitation, and/or temperature is controlled such that the metal-ceramic coating forms on the substrate with a predominantly crystalline structure.
- 5
4. A plating or coating method according to any one of paragraphs 1 to 3, wherein the pH, agitation, and/or temperature is controlled to substantially avoid formation of nanoparticles or microparticles of the ceramic phase, and/or agglomeration of particles of the ceramic phase, in the plating solution or electrolyte.
- 10
5. A plating or coating method according to any one of paragraphs 1 to 4, wherein the pH, agitation, or temperature is controlled to reduce or prevent the formation of particles of the ceramic phase having an average diameter of more than 1000 nm in the plating solution or electrolyte.
- 15
6. A plating or coating method according to any one of paragraphs 1 to 5, wherein the pH, agitation, and/or temperature is controlled such that amorphous particles of the ceramic phase having an average diameter from about 1 to about 100 nm are incorporated into the metal-ceramic composite coating.
- 20
7. A plating or coating method according to paragraph 6, wherein the average diameter is from about 3 to about 30 nm.
8. A plating or coating method according to paragraph 6 or 7, wherein the amorphous particles are dispersed throughout the metal-ceramic composite coating.
- 25
9. A plating or coating method according to paragraph 8, wherein the amorphous particles are substantially uniformly dispersed throughout the metal-ceramic composite coating.
10. A plating or coating method according to any one of paragraphs 1 to 9, wherein the pH of the plating solution or electrolyte is monitored.
- 30
11. A plating or coating method according to any one of paragraphs 1 to 10, wherein the pH of the plating solution or electrolyte is maintained within a predetermined pH range during addition of the sol.
- 35

12. A plating or coating method according to paragraph 11, wherein the predetermined pH range is less than about 1 pH unit.
13. A plating or coating method according to paragraph 11 or 12, wherein the predetermined
5 pH range is suitable for plating or coating the substrate with the metal-ceramic composite coating.
14. A plating or coating method according to any one of paragraphs 1 to 13, wherein the pH of the plating solution or electrolyte is adjusted prior to, during, or after addition of the sol.
- 10 15. A plating or coating method according to paragraph 14, wherein the pH is adjusted by adding acid or base.
16. A plating or coating method according to any one of paragraphs 1 to 15, wherein the pH, agitation, and/or temperature of the plating solution or electrolyte is controlled during plating or
15 coating of the substrate.
17. A plating or coating method according to any one of paragraphs 1 to 16, further comprising controlling the rate of sol addition to the plating solution or electrolyte.
- 20 18. A plating or coating method according paragraph 17 comprising adding the sol at a rate of less than about 0.02ml per second/litre of the plating solution or electrolyte.
19. A plating or coating method according to paragraph 17 or 18 comprising adding the sol by dripping or spraying the sol into the plating solution.
- 25
20. A plating or coating method according to any one of paragraphs 1 to 19 wherein the sol has a concentration such that the sol is substantially free of visible particles and/or agglomerates of the ceramic phase.
- 30 21. A plating or coating method according to any one of paragraphs 1 to 20, wherein the sol has a sol concentration of 10 to 400 grams of the ceramic phase per litre of the sol.
22. A plating or coating method according to paragraph 21 comprising adding the sol at a rate of 0.5 to 250 mls of sol per litre of the plating solution.
- 35

23. A plating or coating method according to paragraph 21 or 22, wherein the sol is added at a rate of 1.25 to 50 mls of sol per litre of the plating solution.
24. A plating or coating method according to any one of paragraphs 1 to 23, wherein the sol is aqueous.
25. A plating or coating method according to any one of paragraphs 1 to 23, wherein the sol is organic.
26. A plating or coating method according to any one of paragraphs 1 to 25, comprising producing at least one additional coating on the substrate prior to or after producing the metal-ceramic composite coating.
27. A plating or coating method according to any one of paragraphs 1 to 26, wherein the ceramic phase is a single or mixed oxide, carbide, or nitride, of a metal or metalloid, or a combination of any two or more thereof.
28. A plating or coating method according to any one of paragraphs 1 to 27, wherein the ceramic phase is a single or mixed oxide, carbide, nitride, silicate, boride of a metal or metalloid selected from periods 5 to 7 of groups 3 to 12, periods 2 to 6 of group 13, periods 3 to 6 of group 14, and periods 4 to 6 of group 15 of the periodic table, or a combination of any two or more thereof.
29. A plating or coating method according to any one of paragraphs 1 to 28, wherein the ceramic phase is a single or mixed oxide, carbide, nitride, silicate, boride of Ti, W, Si, Zr, Al, Y, Cr, Fe, Pb, Co, or a rare earth element.
30. A plating or coating method according to any one of paragraphs 1 to 29, wherein the ceramic phase comprises TiO_2 , AlO_2 , Al_2O_3 , ZrO_2 , SiC , SiO_2 , SiC , CeO_2 , or ZnO .
31. A plating or coating method according to any one of paragraphs 1 to 30, wherein the coating, other than the ceramic phase comprises a metal or metalloid selected from periods 5 and 6 of group 3, periods 5 to 7 of groups 4 to 12, periods 3 to 6 of group 13, and periods 4 to 6 of groups 14 and 15, or an alloy of any two or more thereof.

32. A plating or coating method according to any one of paragraphs 1 to 31, wherein the coating, other than the ceramic phase comprises a metal or metalloid selected from Zn, Cd, Cu, Ni, Cr, Sn, Au, Ag, Pb, Ru, Rh, Pd, Os, Ir, Fe, Co, In, As, Sb, Bi, Mn, Re, Al, Zr, Ti, Hf, V, Nb, Ta, W, and Mo, or an alloy of any two or more thereof.
- 5
33. A plating or coating method according to any one of paragraphs 1 to 32 wherein the coating, other than the ceramic phase comprises Ni, Ni-P, Ni-W-P, Ni-Cu-P, Ni-B, Au-Ni, Ni-Zn, Ni-Co, Ni-W, Ni-Fe, Cr, Cu, Zn, Ag, Au, or Pd.
- 10
34. A plating or coating method according to any one of paragraphs 1 to 33 wherein the coating, other than the ceramic phase comprises Ni, Ni-P, Ni-B, Au-Ni, Ni-Zn, Ni-Co, or Au.
35. A plating or coating method according to any one of paragraphs 1 to 34, wherein the metal-ceramic composite coating comprises Ni-Co-TiO₂ or Ni-Zn-Al₂O₃.
- 15
36. A plating or coating method according to any one of paragraphs 26 to 35, wherein the coating, other than the ceramic phase comprises Ni-P.
37. A plating or coating method according to paragraph 36, wherein the additional coating comprises Ni-P, and the additional coating is produced prior to producing the metal-ceramic composite coating.
- 20
38. A plating or coating method according to paragraph 37, wherein the metal-ceramic composite coating comprises Ni-P-ZrO₂, and the phosphorus content of the metal-ceramic coating is greater than the phosphorus content of the additional coating.
- 25
39. A plating or coating method according to any one of paragraphs 1 to 38 wherein the substrate is a metal substrate.
- 30
40. A plating or coating method according to any one of paragraphs 1 to 39 wherein the substrate comprises steel, Mg, Al, Zn, Sn, Cu, Ti, Ni, Co, Mo, Pb or an alloy thereof.
41. A plating or coating method according to any one of paragraphs 1 to 40 wherein the substrate comprises mild steel, alloy steel, carbon steel, stainless steel, brass, or Mg, Cu, Al or an alloy thereof.
- 35

42. A plating or coating method according to any one of paragraphs 1 to 38 wherein the substrate is a non-metallic substrate.
- 5 43. A plating or coating method according to any one of paragraphs 1 to 38 wherein the substrate is a plastics or ceramic substrate.
44. A plating or coating method according to any one of paragraphs 1 to 43 which is an electroless plating or coating process.
- 10 45. A plating or coating method according to paragraph 44 wherein the solution comprises as a reducing agent sodium hypophosphite, sodium borohydride, formaldehyde, dextrose, rochelle salts, glyoxal, or hydrazine sulfate.
- 15 46. A plating or coating method according to any one of paragraphs 1 to 43 which is a galvanic plating process.
47. A plating or coating method according to paragraph 46 wherein the plating current is in the range 5 mA/cm^2 to 300 mA/cm^2 .
- 20 48. An item or surface plated or coated by a process according to any one of paragraphs 1 to 47.
49. An item or surface comprising a substrate and a metal-ceramic composite coating on the substrate, the metal-ceramic composite coating comprising a ceramic phase of dispersed amorphous ceramic particles having an average diameter of from 1 to 100 nm.
- 25 50. An item or surface according to paragraph 49, wherein the amorphous ceramic particles have an average diameter from 1 to 30 nm.
- 30 51. The item or surface according to paragraph 49 or 50, wherein the amorphous ceramic particles are substantially uniformly dispersed throughout the metal-ceramic composite coating.
52. The item or surface according to paragraph 49 or 51, wherein the metal-ceramic composite coating is as defined in any of the preceding paragraphs.
- 35

53. The item or surface according to any one of paragraphs 49 to 52, wherein the item or surface comprises at least one additional coating under or on top of the metal ceramic coating.

5 54. The item or surface according to any one of paragraphs 49 to 53, wherein the additional coating is as defined in any one of the preceding paragraphs.

55. The item or surface according to any one of paragraphs 49 to 54, wherein the metal-ceramic composite coating has a grain size at least about 5% less than a corresponding coating prepared without the ceramic phase and/or a corresponding coating prepared without controlling the pH, agitation, and/or temperature of the plating solution or electrolyte.

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56. The item or surface according to any one of paragraphs 49 to 55, wherein the metal-ceramic composite coating has a Vickers microhardness at least about 10% greater than a corresponding coating prepared without the ceramic phase and/or a corresponding coating prepared without controlling the pH, agitation, and/or temperature of the plating solution or electrolyte.

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57. The item or surface according to any one of paragraphs 49 to 56, wherein the metal-ceramic composite coating has a wear loss volume at least about 30% less than a corresponding coating prepared without the ceramic phase and/or a corresponding coating prepared without controlling the pH, agitation, and/or temperature of the plating solution or electrolyte.

20

58. The item or surface according to any one of paragraphs 49 to 57, wherein the metal-ceramic composite coating has an electrical resistivity and/or conductivity within about $\pm 3\%$ of a corresponding coating prepared without the ceramic phase and/or a corresponding coating prepared without controlling the pH, agitation, and/or temperature of the plating solution or electrolyte.

25

59. The item or surface according to any one of paragraphs 49 to 58, wherein the metal-ceramic composite coating has a corrosion resistance substantially the same as or greater than a corresponding coating prepared without the ceramic phase and/or a corresponding coating prepared without controlling the pH, agitation, and/or temperature of the plating solution or electrolyte.

30

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60. The item or surface according to any one of paragraphs 49 to 59, wherein the item or surface comprises at least one additional coating under or on top of the metal-ceramic composite coating; and the combination of coatings has a corrosion resistance substantially the same or greater than a corresponding combination of coatings without the ceramic phase and/or a corresponding
5 combination of coatings prepared without controlling the pH, degree of mixing, and/or temperature of the plating solution or electrolyte.

The foregoing describes the invention including embodiments and examples thereof. Alterations and modifications as will be obvious to those skilled in the art are intended to be incorporated in the
10 scope hereof as defined in the accompanying claims.

CLAIMS

1. A plating or coating method for producing a metal-ceramic composite coating on a substrate, the method comprising adding a sol of a ceramic phase to a plating solution or electrolyte,
5 and controlling the pH, degree of mixing, and/or temperature of the plating solution or electrolyte to reduce or prevent the precipitation of visible particles and/or agglomerates of the ceramic phase in the plating solution or electrolyte.
2. A plating or coating method according to claim 1, wherein the pH, degree of mixing,
10 and/or temperature is controlled such that the metal-ceramic coating forms on the substrate with a predominantly crystalline structure.
3. A plating or coating method according to claim 1 or 2, wherein the pH, degree of mixing,
15 and/or temperature is controlled to reduce or prevent the formation of particles and/or agglomerates of particles of the ceramic phase having an average diameter more than 100 nm in the plating solution or electrolyte.
4. A plating or coating method according to any one of claims 1 to 3, wherein the pH, degree
20 of mixing, and/or temperature is controlled such that amorphous particles of the ceramic phase having an average diameter from about 1 to about 100 nm are incorporated into the metal-ceramic composite coating.
5. A plating or coating method according to claim 4, wherein the amorphous particles are
25 dispersed throughout the metal-ceramic composite coating.
6. A plating or coating method according to any one of claims 1 to 5, wherein the pH of the
plating solution or electrolyte is monitored.
7. A plating or coating method according to any one of claims 1 to 6, wherein the pH of the
30 plating solution or electrolyte is maintained within a predetermined pH range during addition of the sol.
8. A plating or coating method according to any one of claims 1 to 7, wherein the pH, degree
35 of mixing, and/or temperature of the plating solution or electrolyte is controlled during plating or coating of the substrate.

9. A plating or coating method according to any one of claims 1 to 8, further comprising controlling the rate of sol addition to the plating solution or electrolyte.
- 5 10. A plating or coating method according claim 9 comprising adding the sol at a rate of less than about 0.02ml per second/litre of the plating solution or electrolyte.
11. A plating or coating method according to any one of claims 1 to 10, wherein the sol has a sol concentration of 10 to 400 grams of the ceramic phase per litre of the sol.
- 10 12. A plating or coating method according to claim 11 comprising adding the sol at a rate of 0.5 to 250 mls of sol per litre of the plating solution.
13. A plating or coating method according to any one of claims 1 to 12, comprising producing
15 at least one additional coating on the substrate prior to or after producing the metal-ceramic composite coating.
14. A plating or coating method according to any one of claims 1 to 13, wherein the ceramic phase is a single or mixed oxide, carbide, nitride, silicate, boride of Ti, W, Si, Zr, Al, Y, Cr, Fe, Pb,
20 Co, or a rare earth element.
15. A plating or coating method according to any one of claims 1 to 14, wherein the ceramic phase comprises TiO_2 , AlO_2 , Al_2O_3 , ZrO_2 , SiC, SiO_2 , SiC, CeO_2 , or ZnO.
- 25 16. A plating or coating method according to any one of claims 1 to 15, wherein the coating, other than the ceramic phase comprises a metal or metalloid selected from Zn, Cd, Cu, Ni, Cr, Sn, Au, Ag, Pb, Ru, Rh, Pd, Os, Ir, Fe, Co, In, As, Sb, Bi, Mn, Re, Al, Zr, Ti, Hf, V, Nb, Ta, W, and Mo, or an alloy of any two or more thereof.
- 30 17. A plating or coating method according to any one of claims 1 to 16 wherein the coating, other than the ceramic phase comprises Ni, Ni-P, Ni-W-P, Ni-Cu-P, Ni-B, Au-Ni, Ni-Zn, Ni-Co, Ni-W, Ni-Fe, Cr, Cu, Zn, Ag, Au, or Pd.
- 35 18. A plating or coating method according to any one of claims 1 to 17, wherein the metal-ceramic composite coating comprises Au-Ni- TiO_2 , Ni-Co- TiO_2 , Ni-Zn- Al_2O_3 , or Ni-B- TiO_2 .

19. A plating or coating method according to any one of claims 1 to 18, wherein the metal-ceramic composite coating comprises Ni-Co-TiO₂ or Ni-Zn-Al₂O₃.
- 5 20. A plating or coating method according to any one of claims 1 to 17, wherein the metal-ceramic composite coating comprises Ni-P-ZrO₂, the additional coating comprises Ni-P, and the additional coating is produced prior to producing the metal-ceramic composite coating.
- 10 21. A plating or coating method according to any one of claims 1 to 17, wherein the metal-ceramic composite coating comprises Ag-TiO₂.
22. A plating or coating method according to any one of claims 1 to 21 wherein the substrate is a metal substrate, plastics or ceramic substrate.
- 15 23. A plating or coating method according to any one of claims 1 to 22 which is an electroless plating or coating process, wherein the solution comprises as a reducing agent sodium hypophosphite, sodium borohydride, formaldehyde, dextrose, rochelle salts, glyoxal, or hydrazine sulfate.
- 20 24. A plating or coating method according to any one of claims 1 to 22 which is a galvanic plating process wherein the plating current is in the range 5 mA/cm² to 300 mA/cm².
- 25 25. An item or surface comprising a substrate and a metal-ceramic composite coating on the substrate, the metal-ceramic composite coating comprising a ceramic phase of dispersed amorphous ceramic particles having an average diameter of from 1 to 100 nm.
26. The item or surface according to claim 25, wherein the item or surface comprises at least one additional coating under or on top of the metal ceramic coating.

FIGURE 1

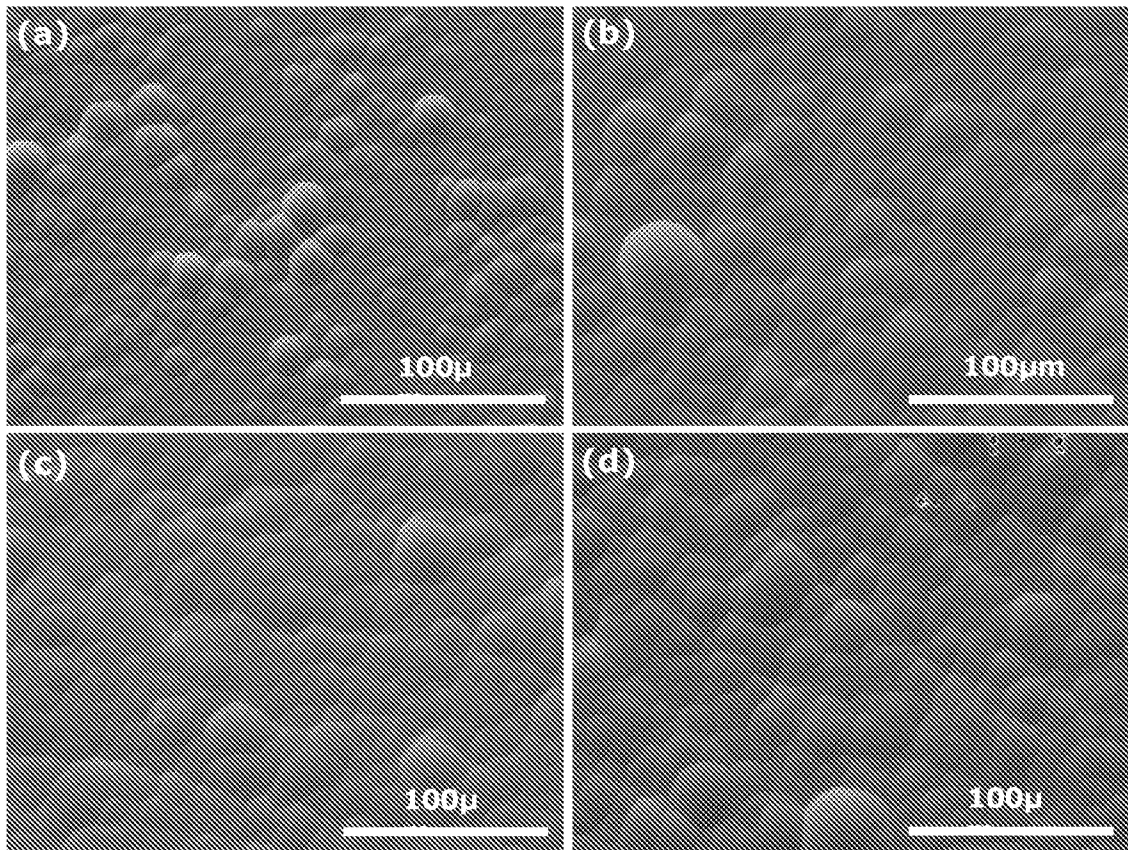


FIGURE 2

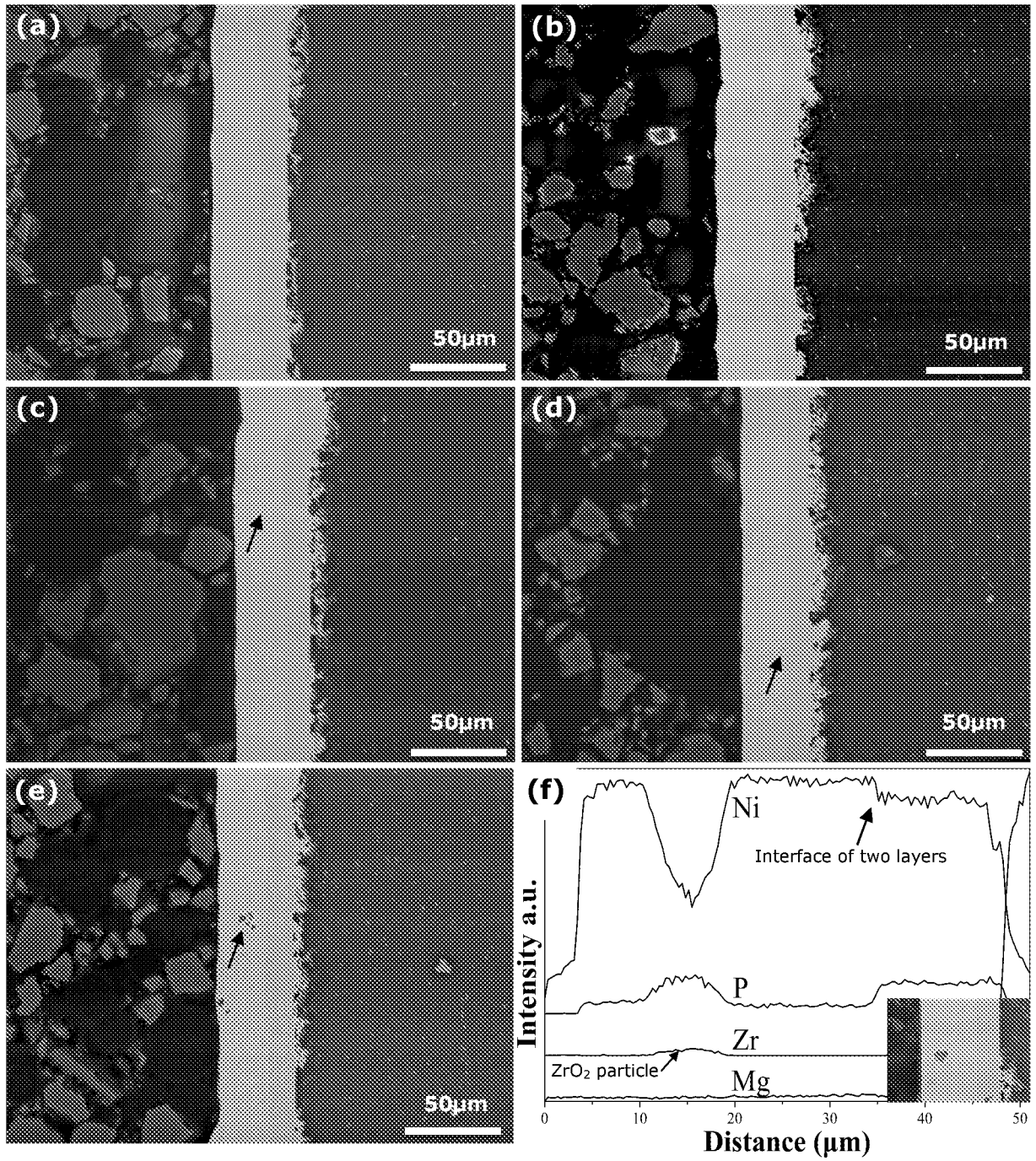


FIGURE 3

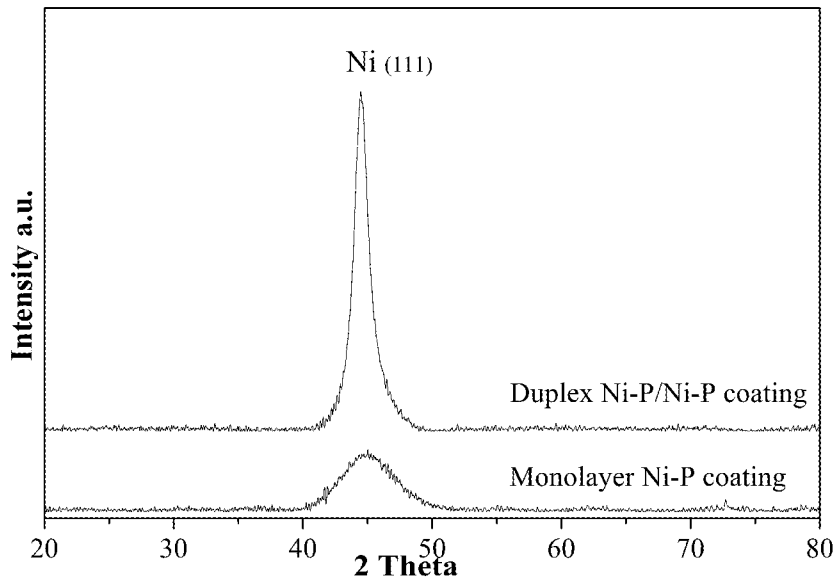


FIGURE 4

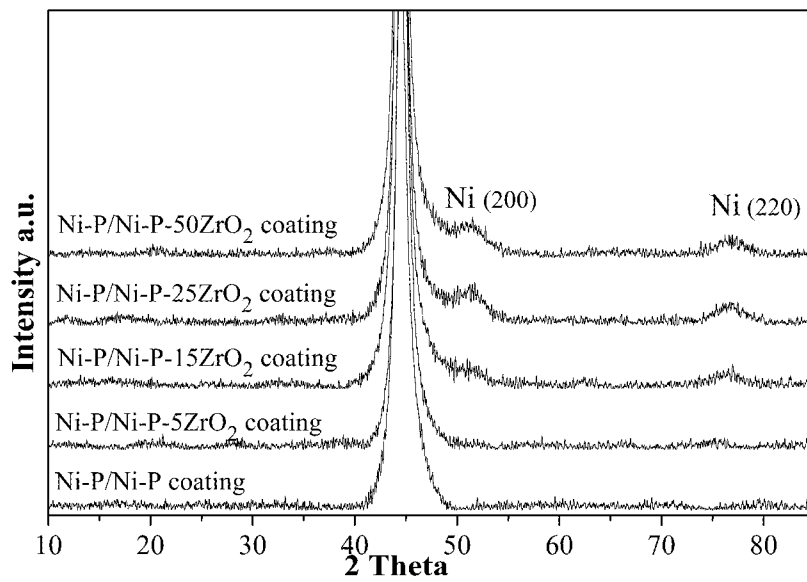


FIGURE 5

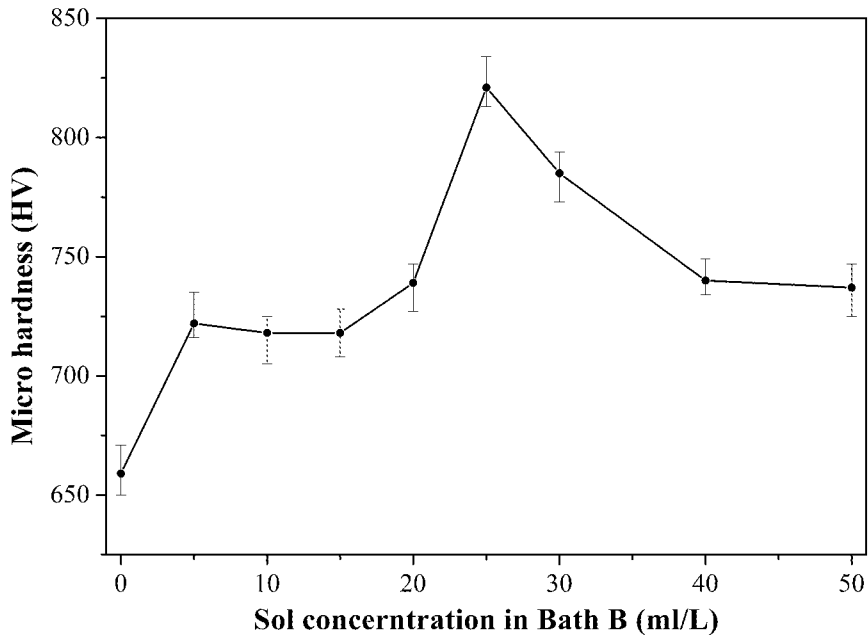


FIGURE 6

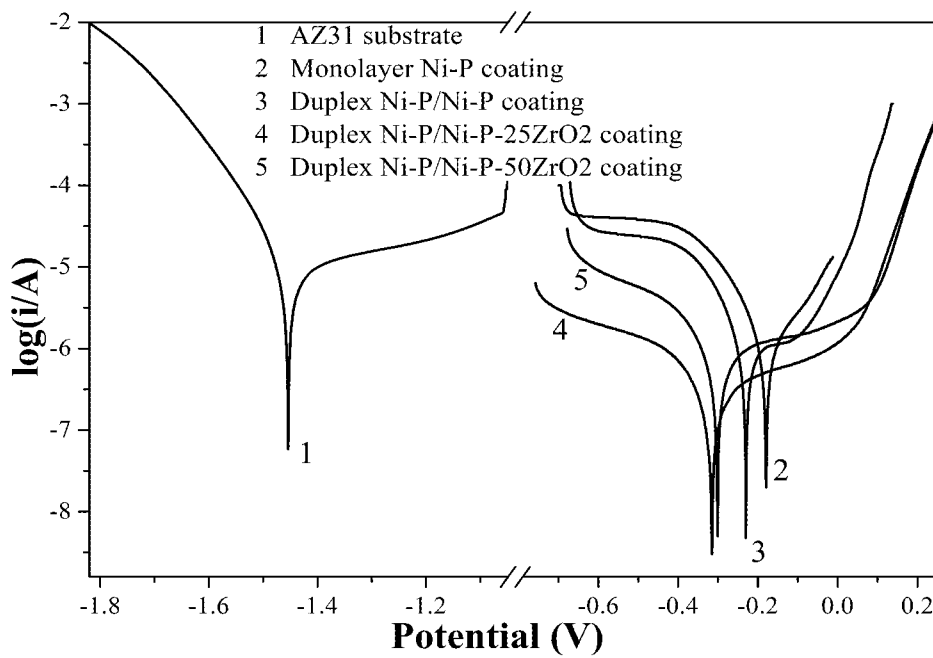


FIGURE 7

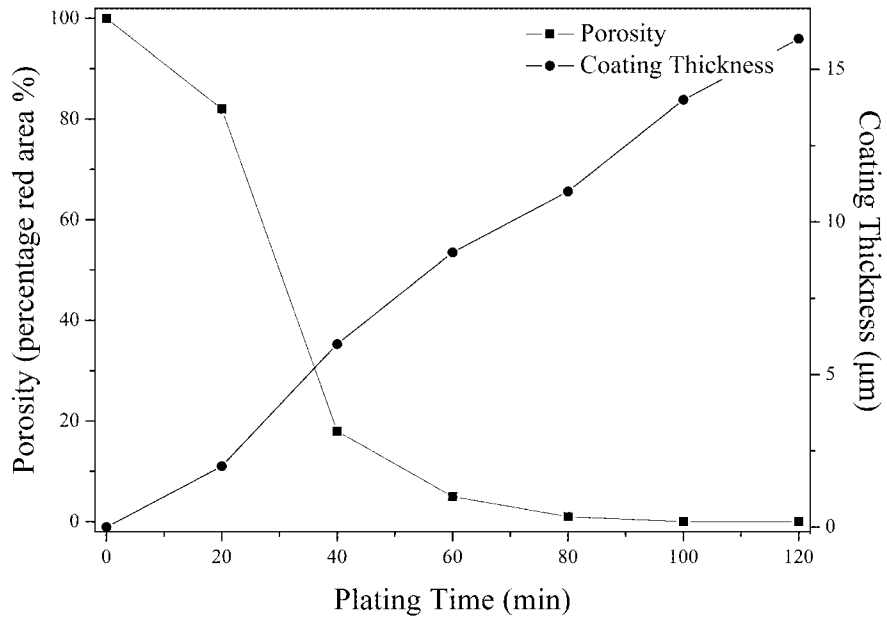


FIGURE 8

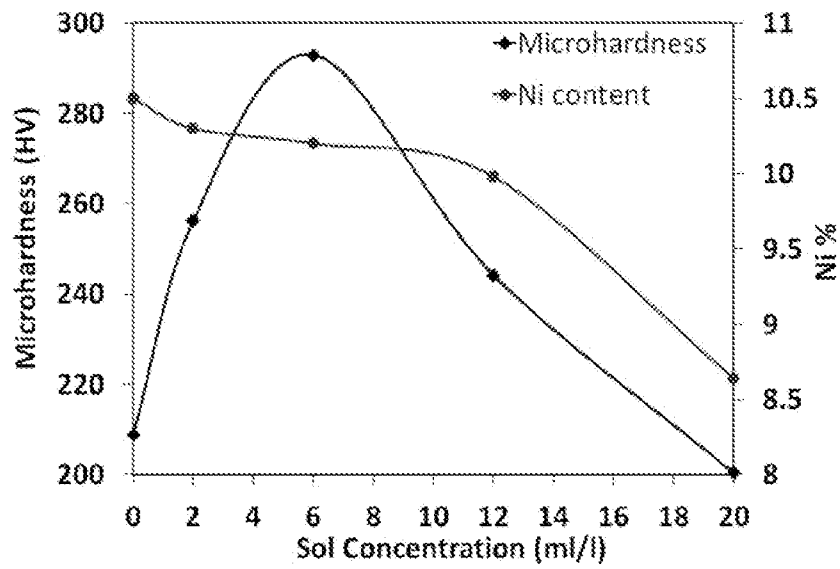


FIGURE 9

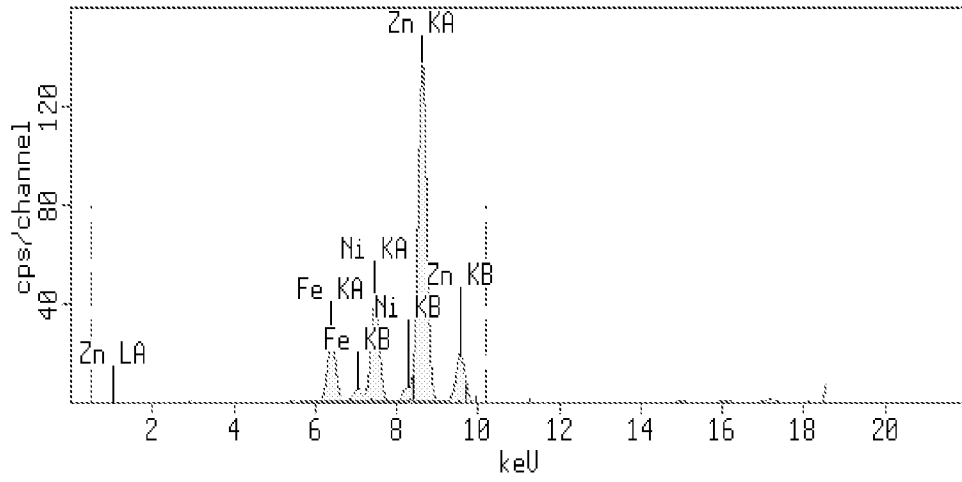


FIGURE 10

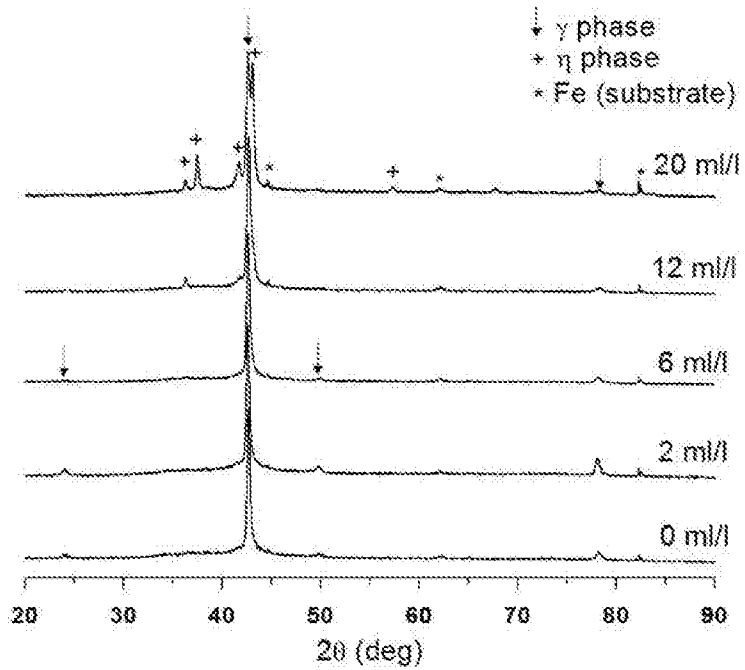


FIGURE 11

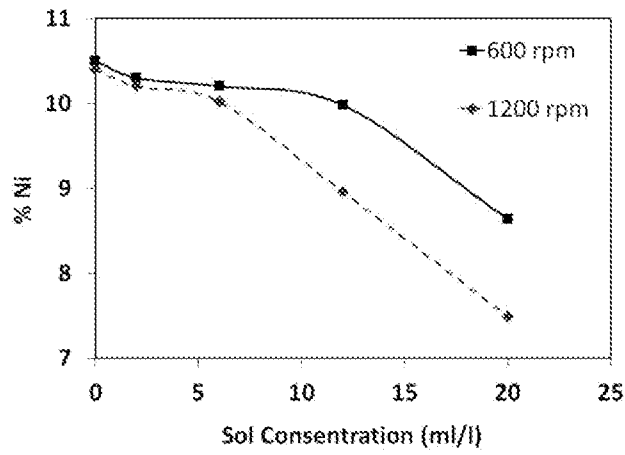


FIGURE 12

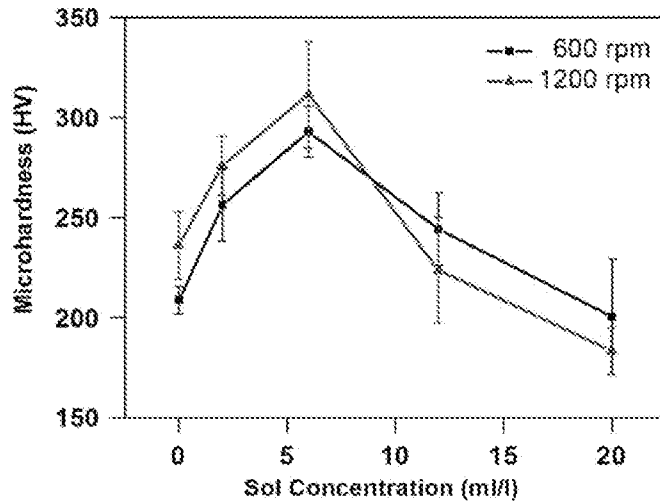


FIGURE 13

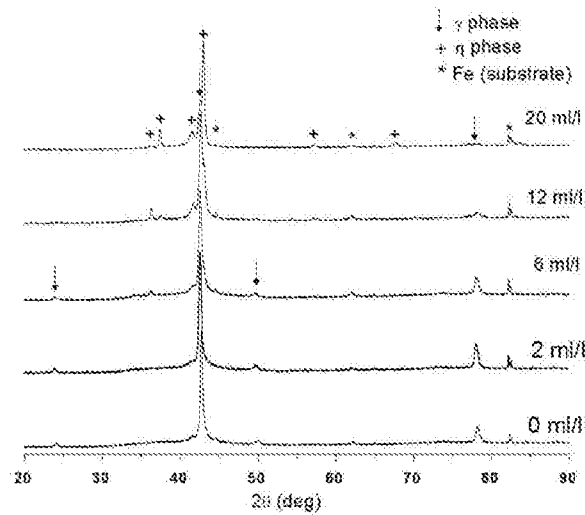


FIGURE 14

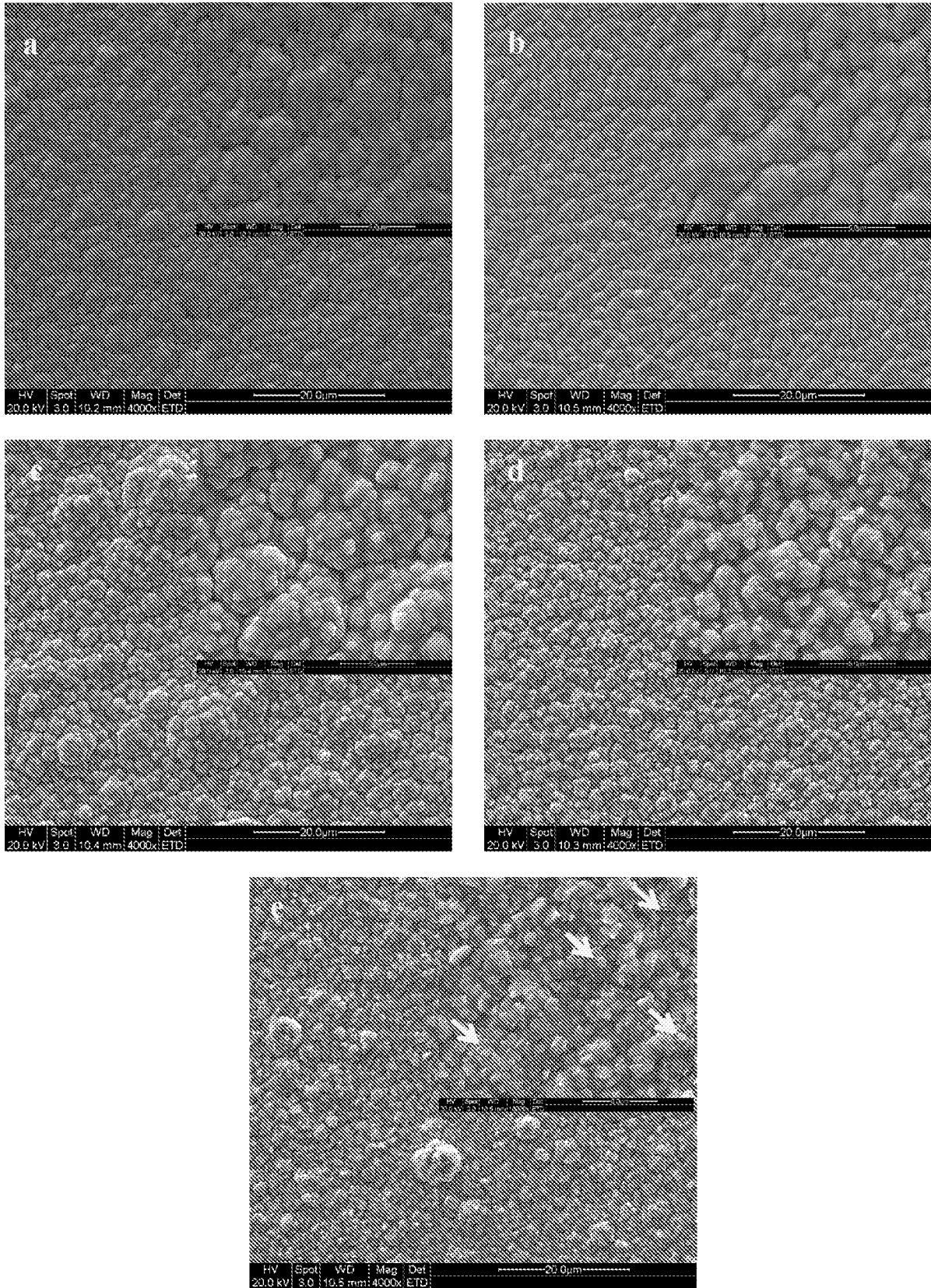


FIGURE 15

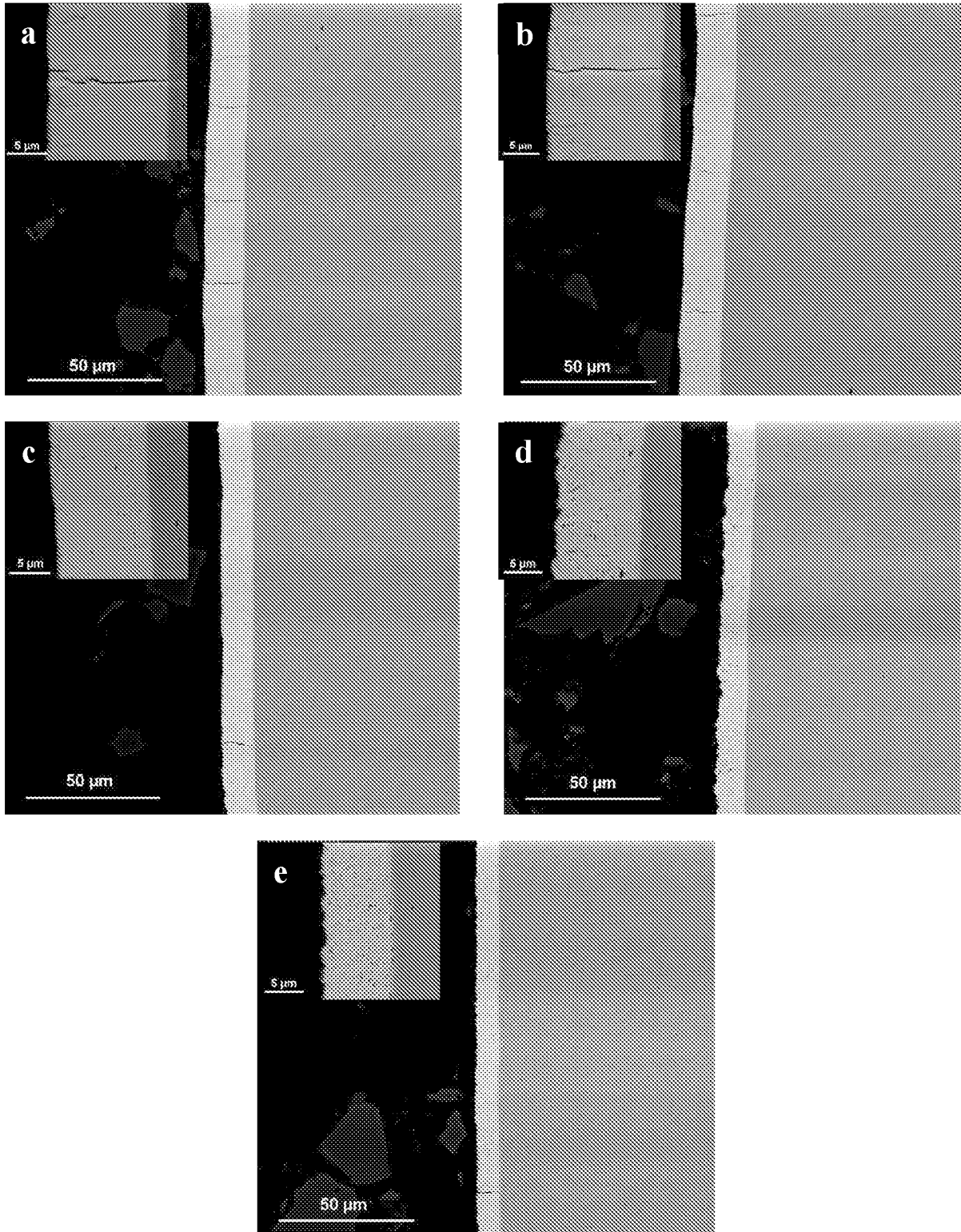
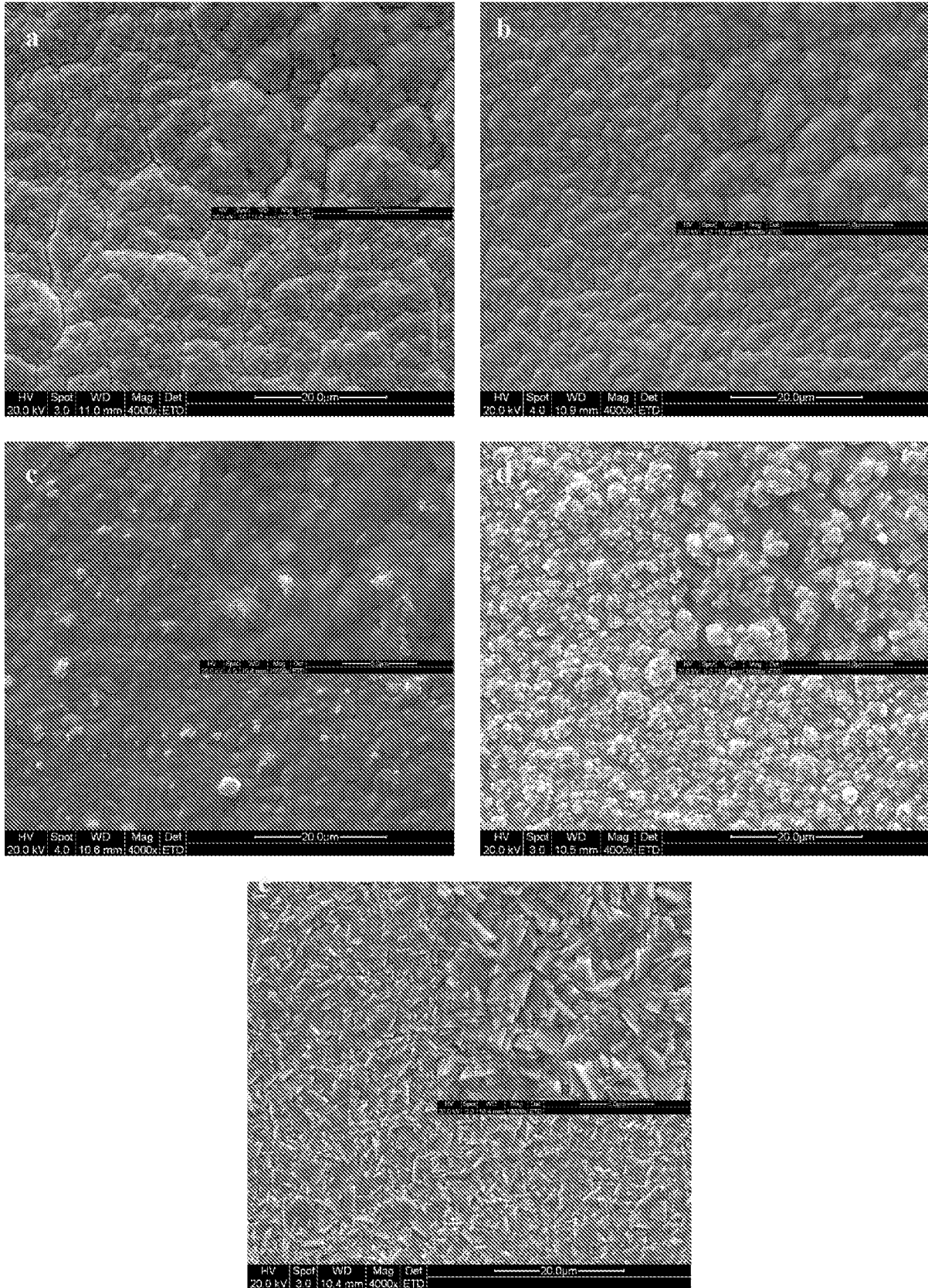


FIGURE 16



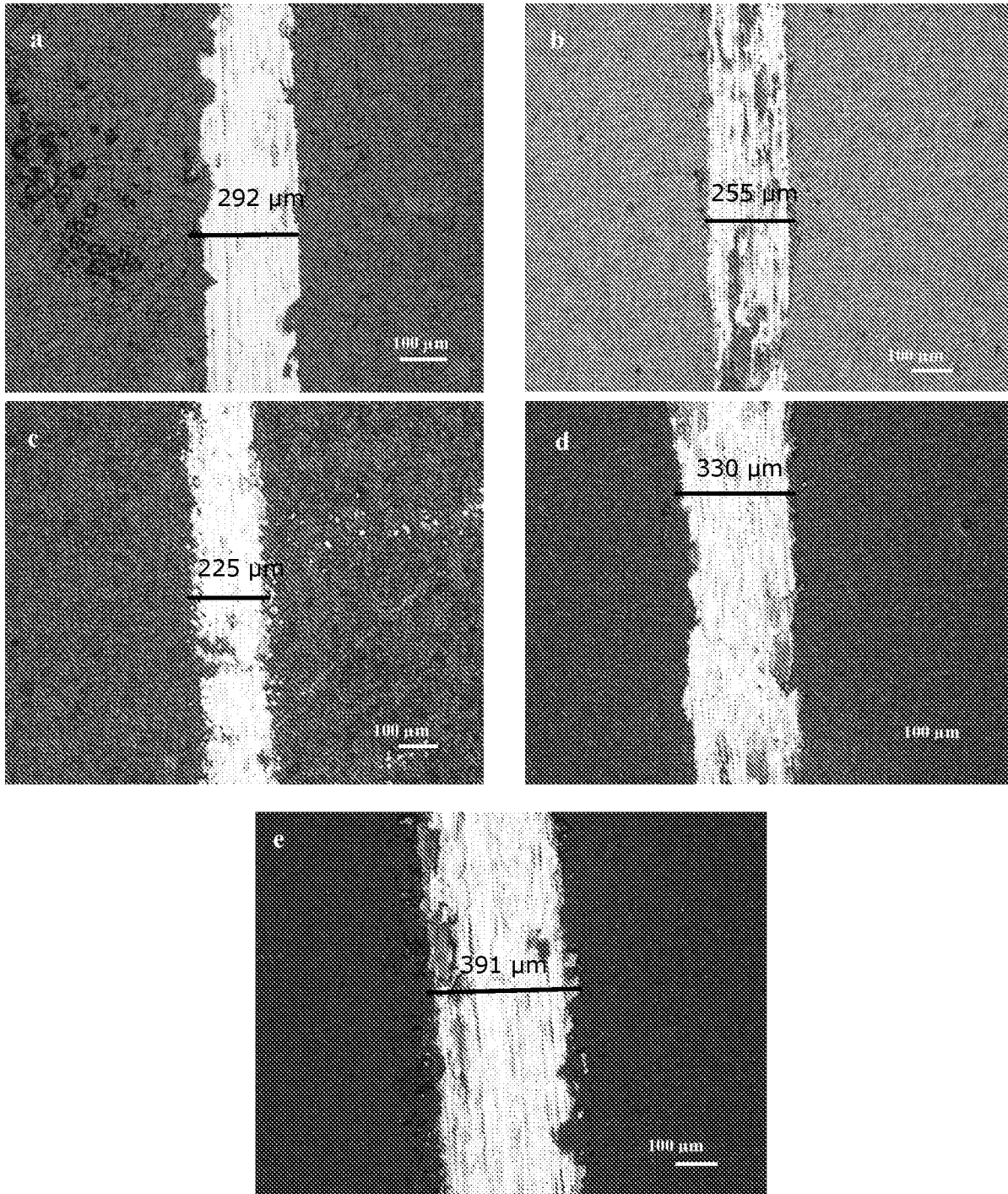


FIGURE 17

FIGURE 18

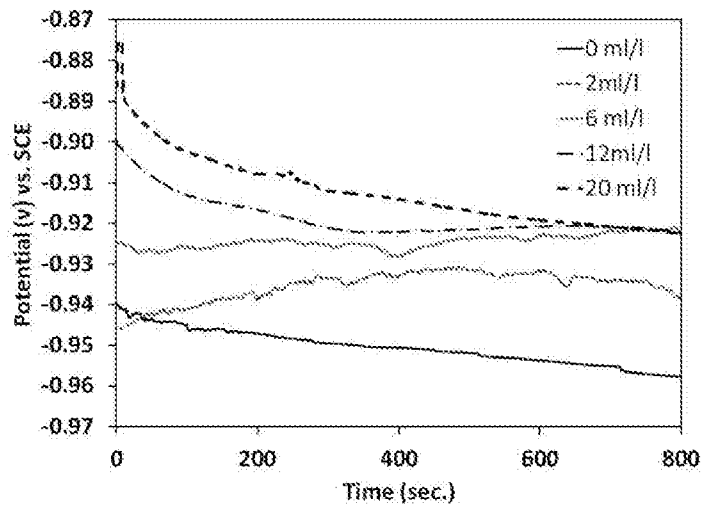


FIGURE 19

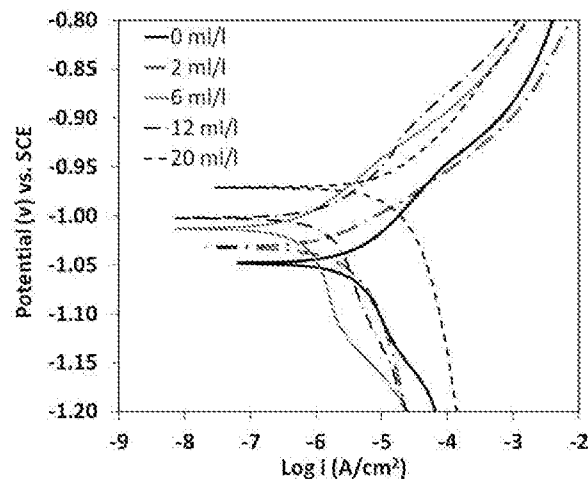


FIGURE 20

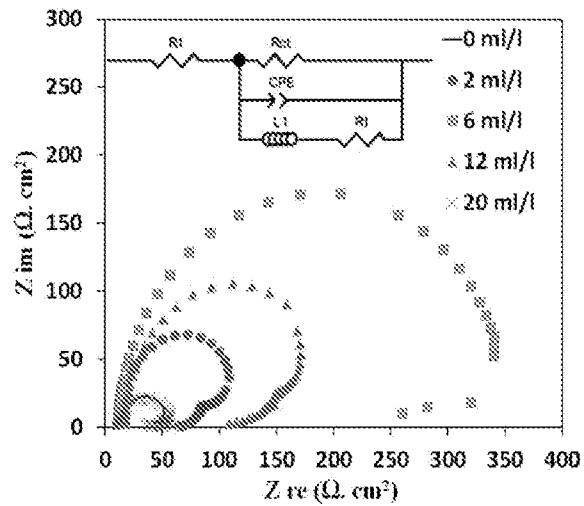


FIGURE 21

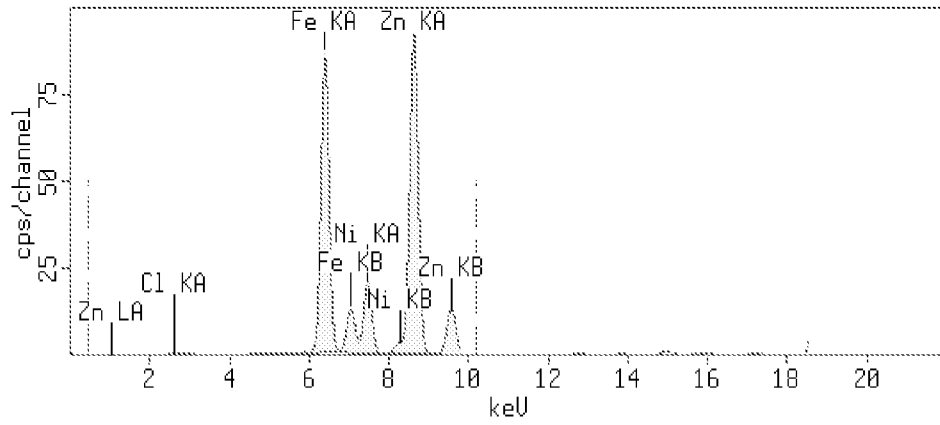


FIGURE 22

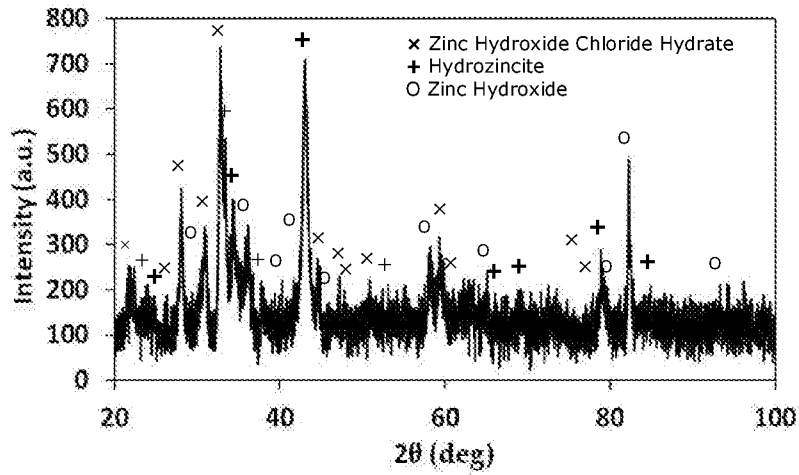


FIGURE 23

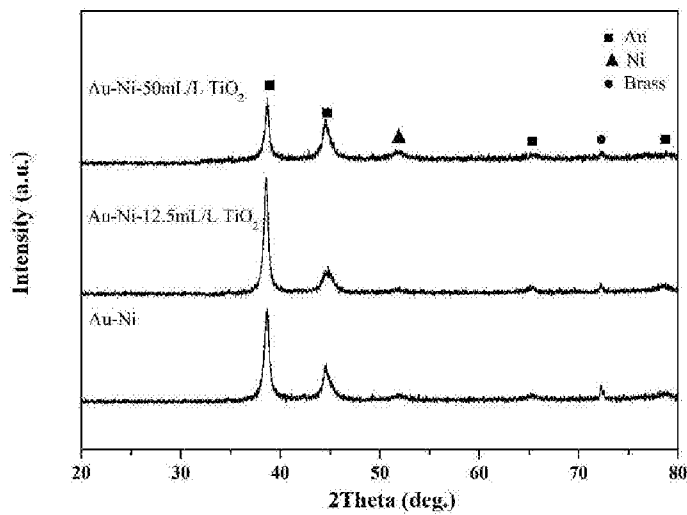


FIGURE 24

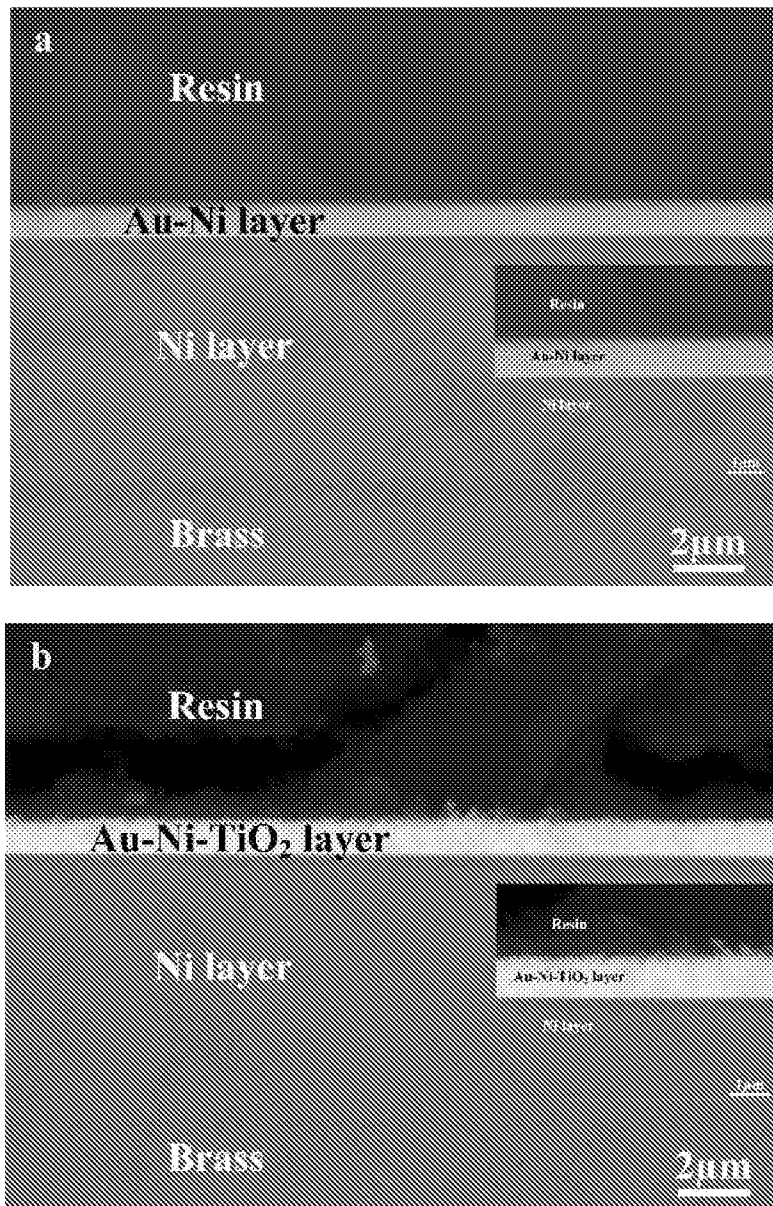


FIGURE 25

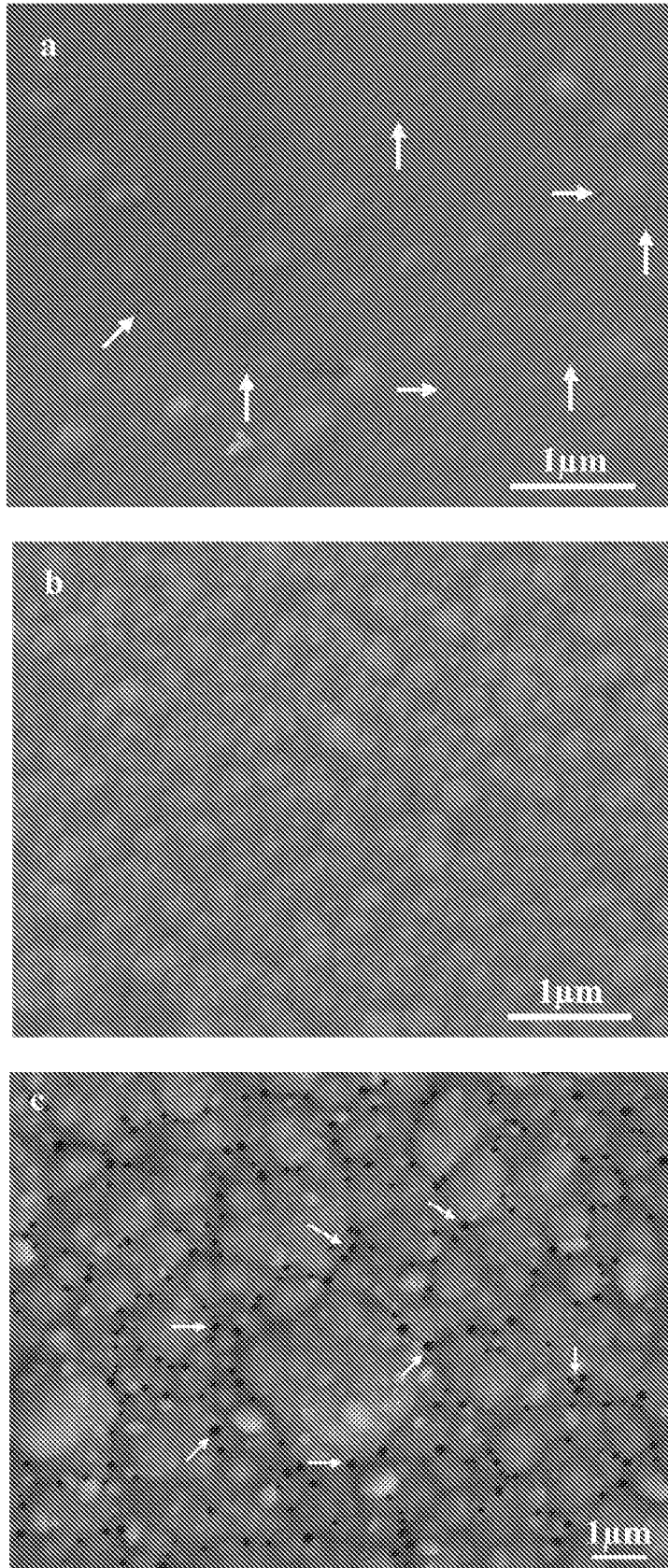
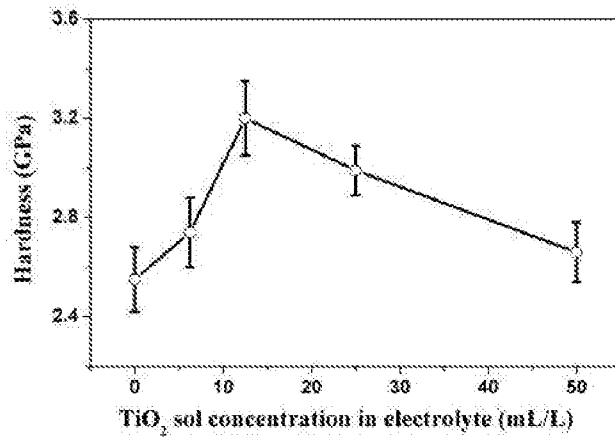
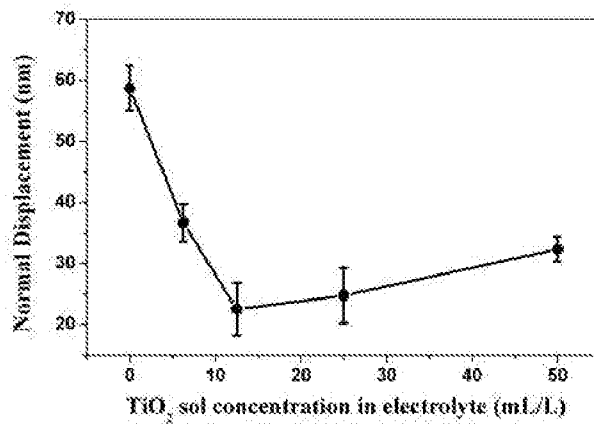


FIGURE 26



(a)



(b)

FIGURE 27

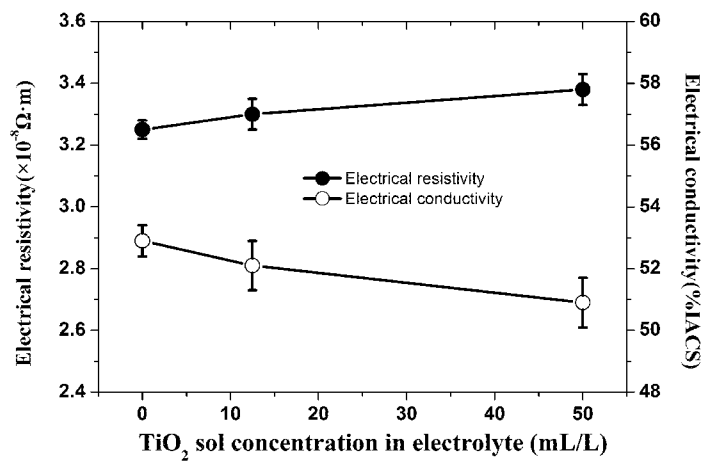
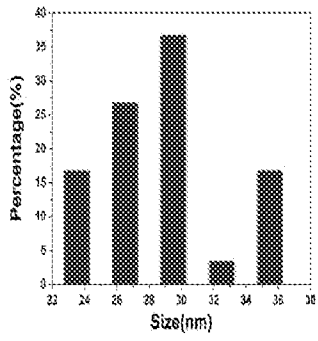
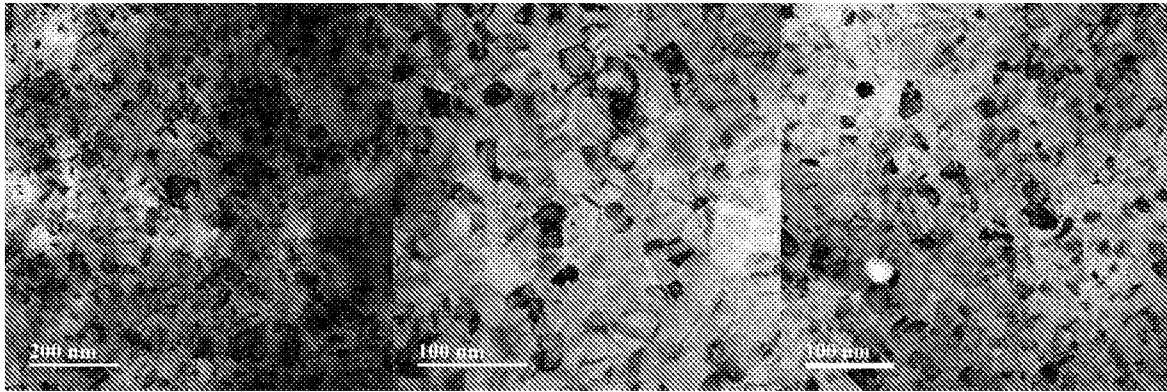
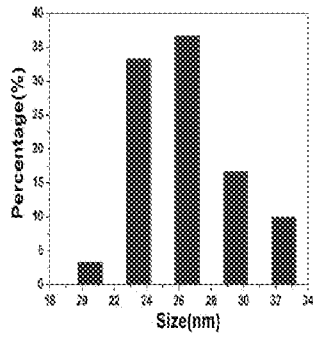


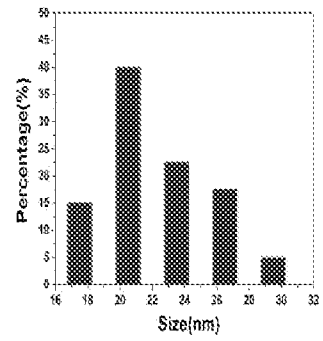
FIGURE 28



a

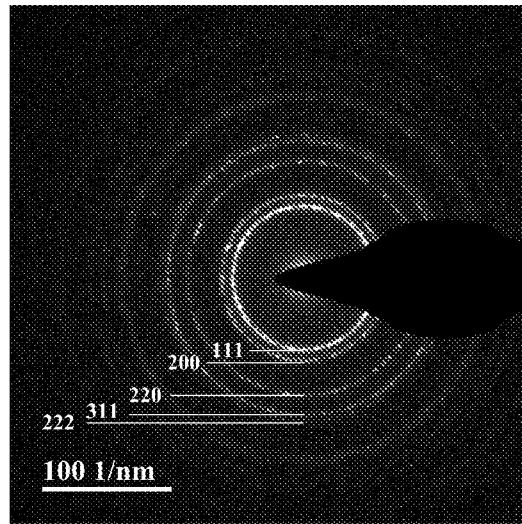


b

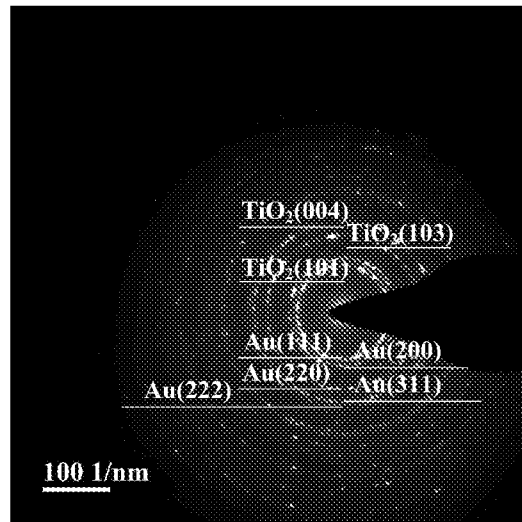


c

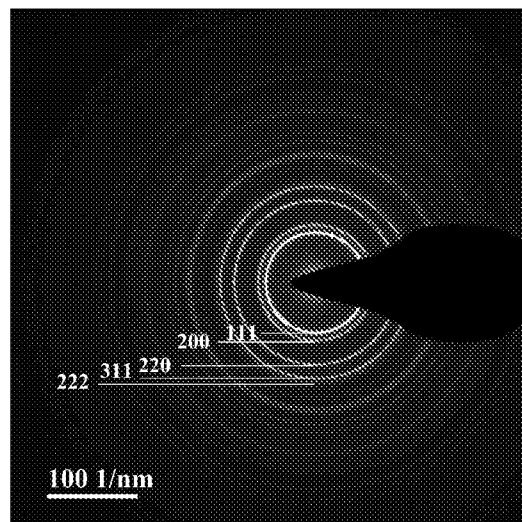
FIGURE 29



a

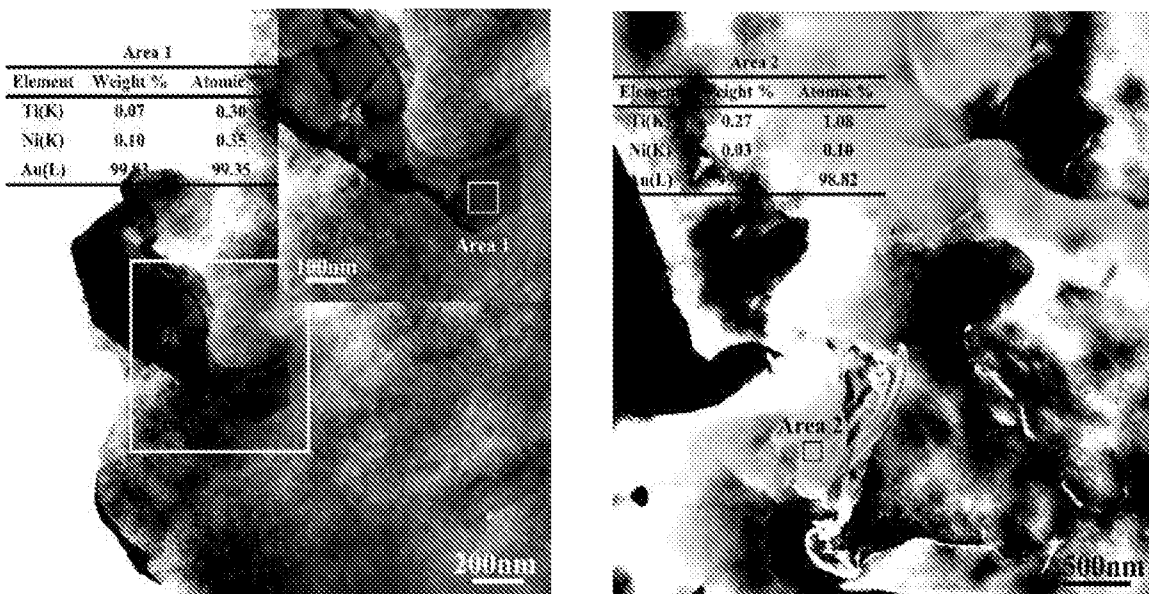


b

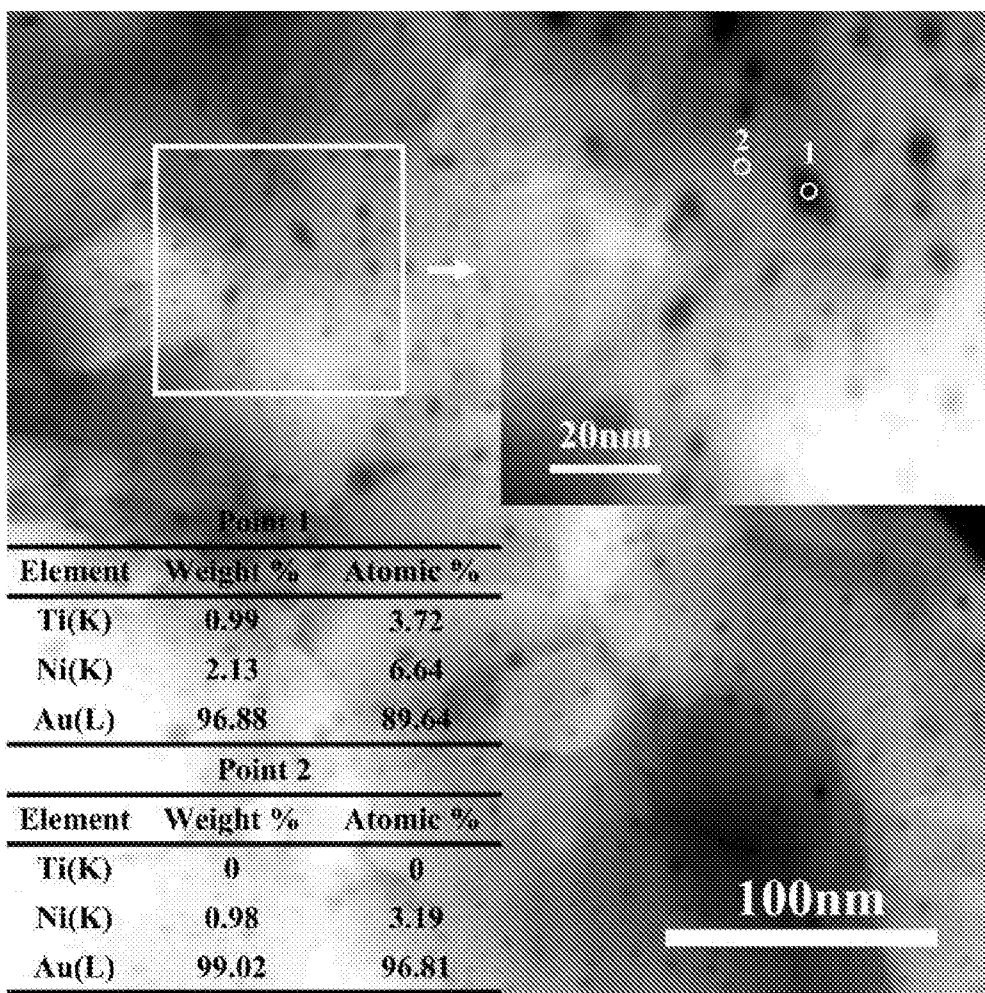


c

FIGURE 30



a



b

FIGURE 31

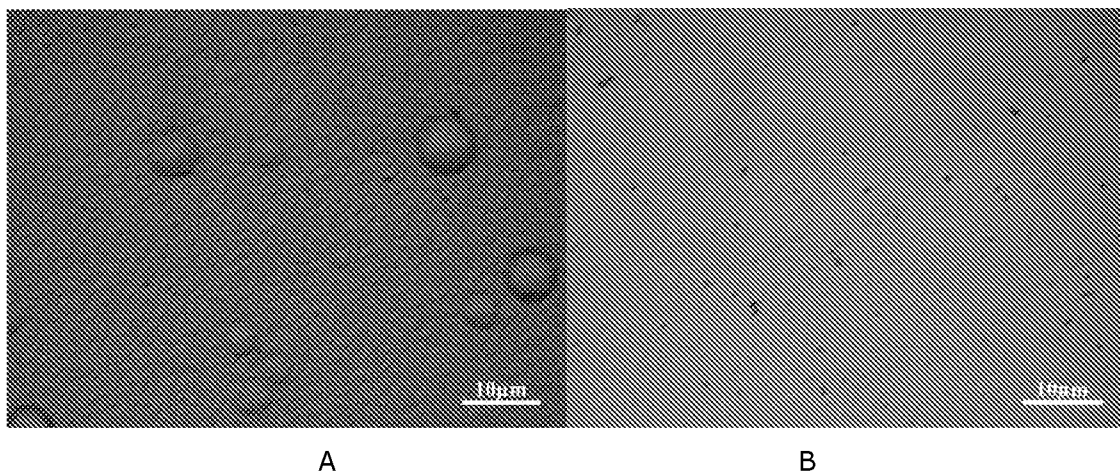


FIGURE 32

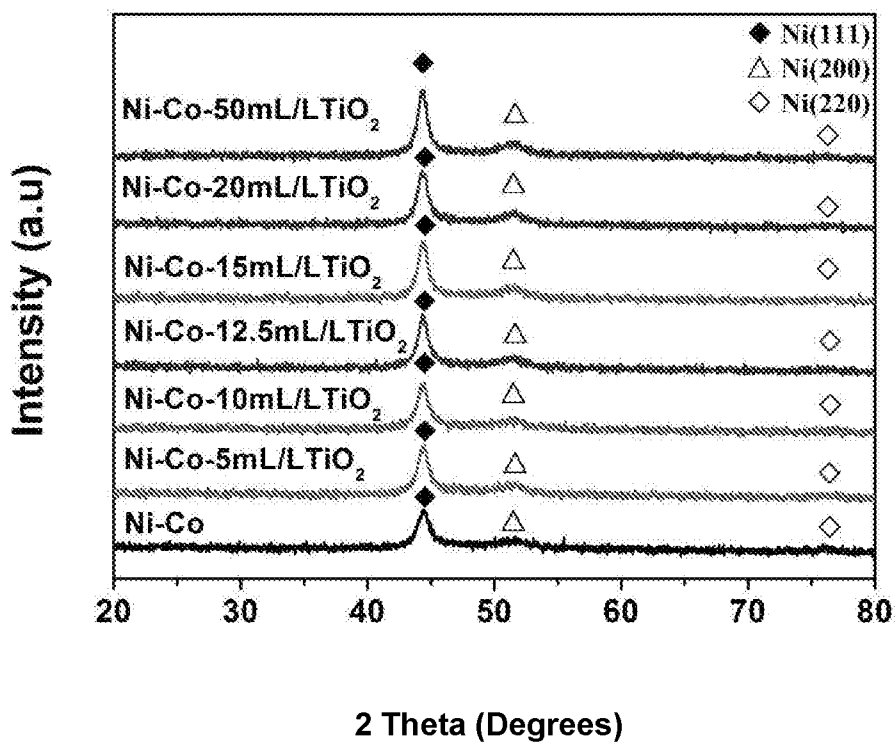


FIGURE 33

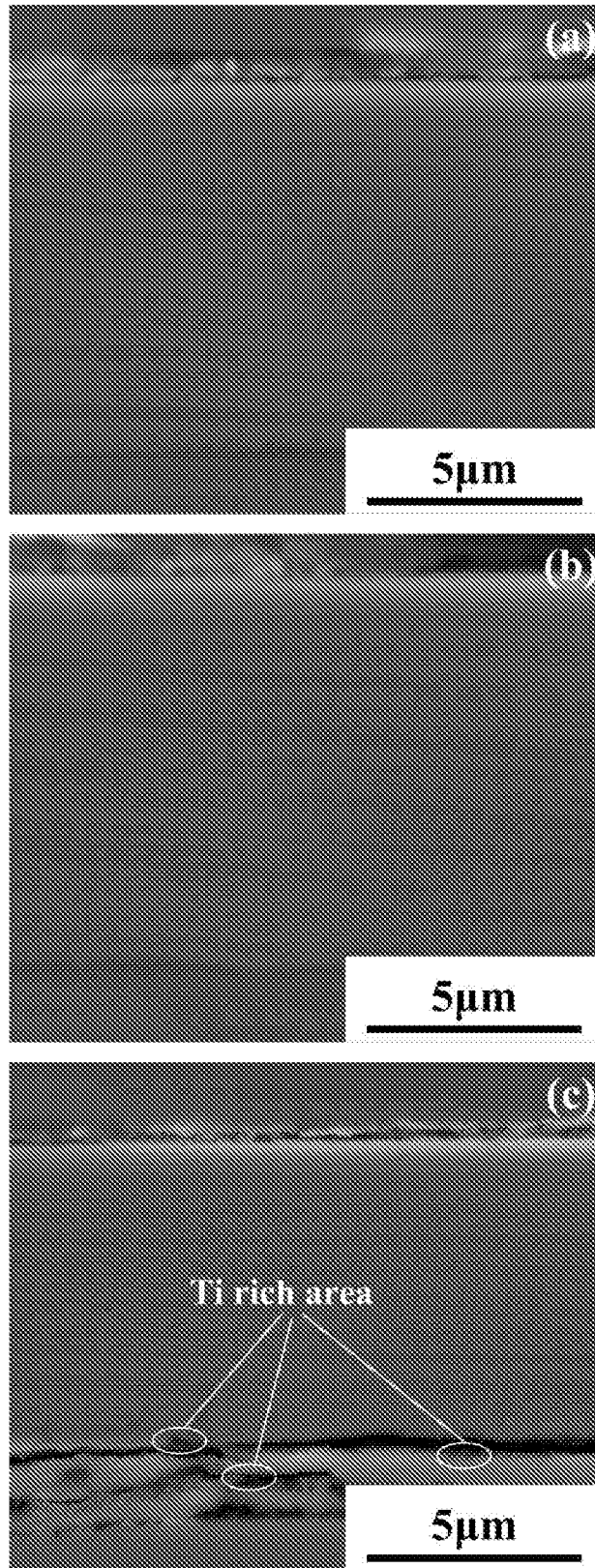


FIGURE 34

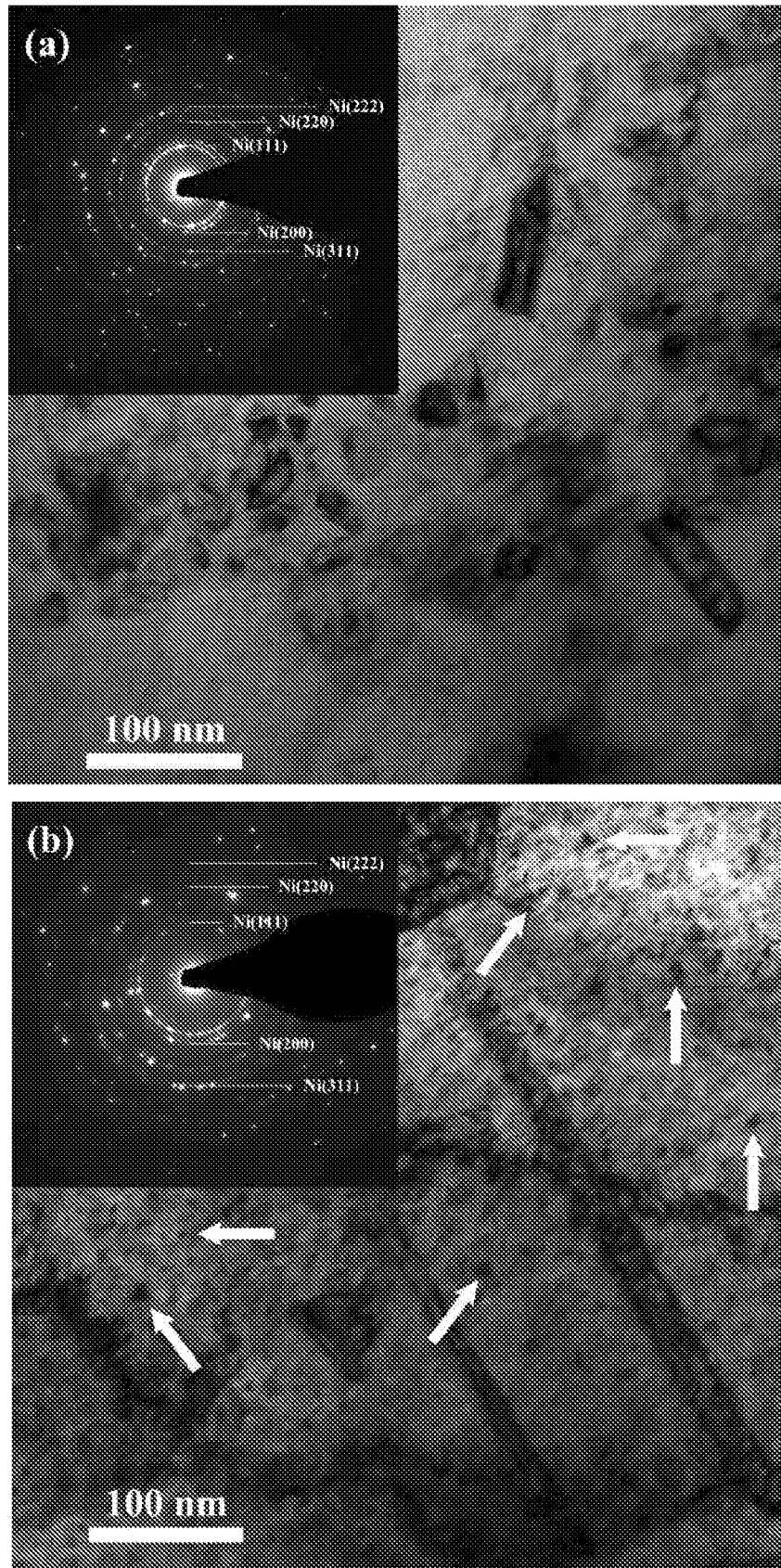


FIGURE 35

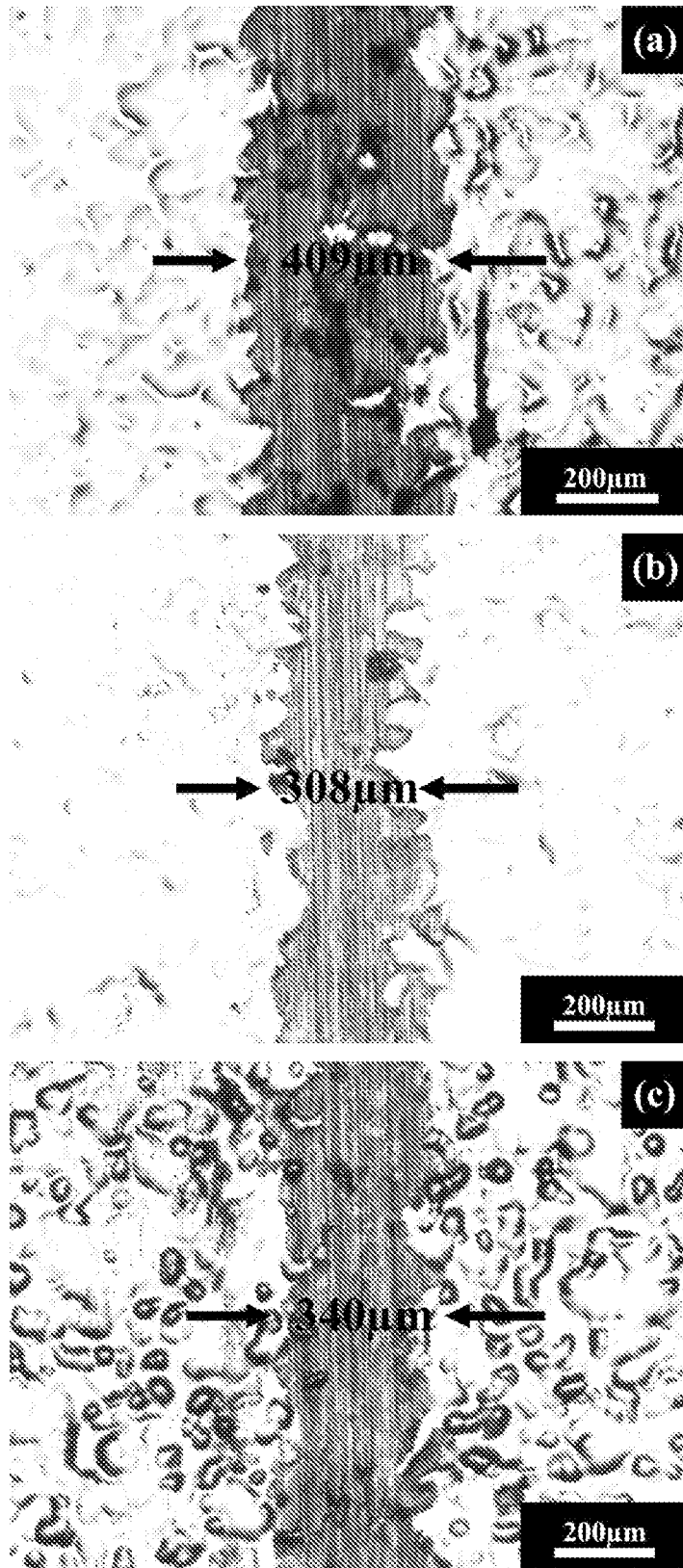


FIGURE 36

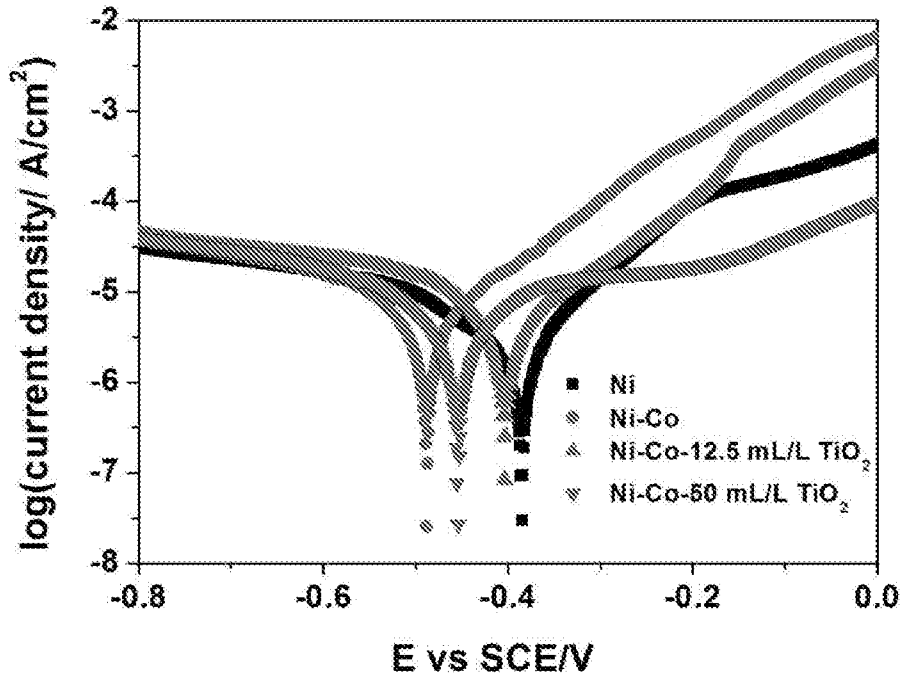


FIGURE 37

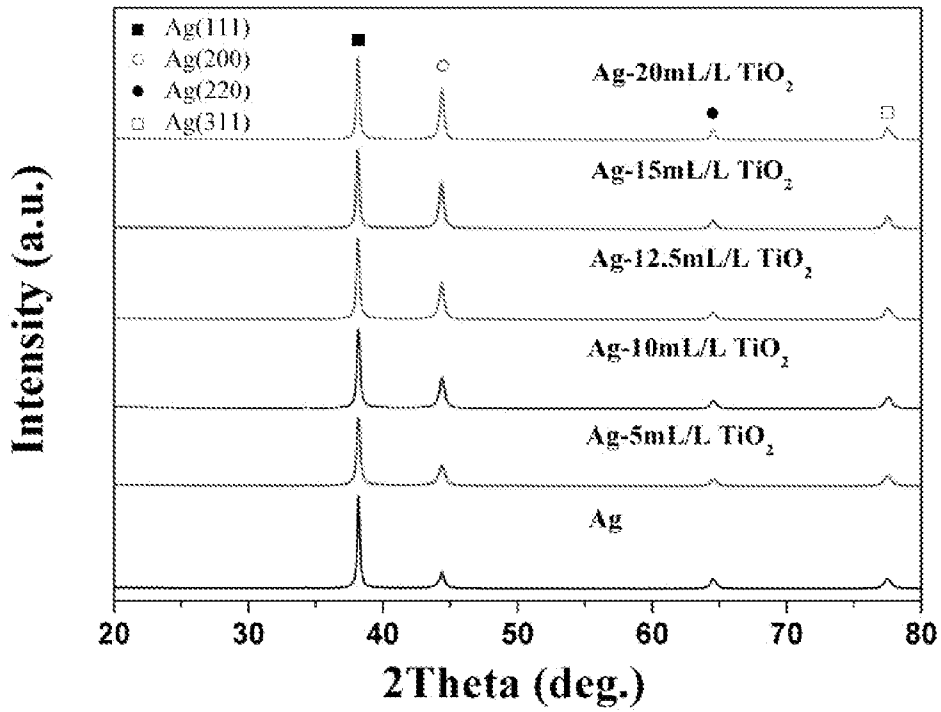


FIGURE 38

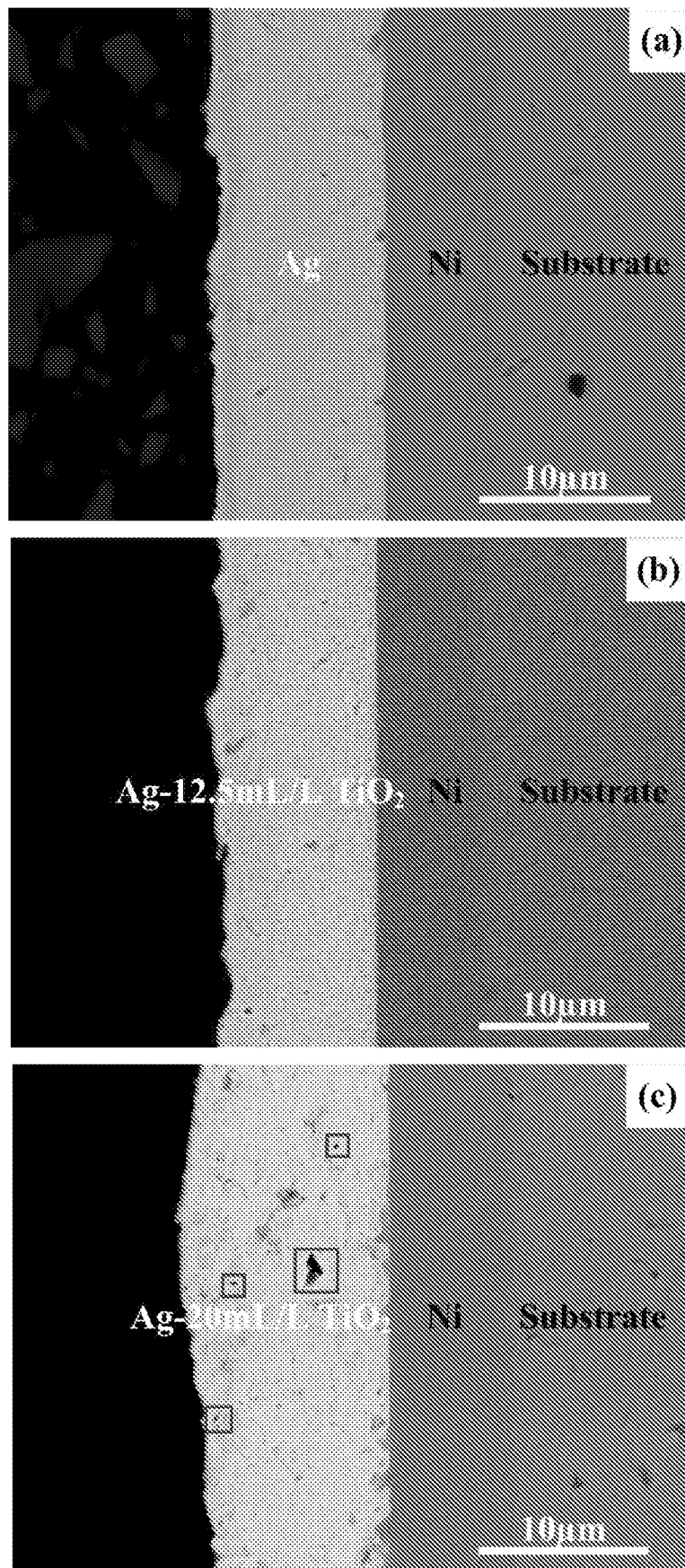


FIGURE 39

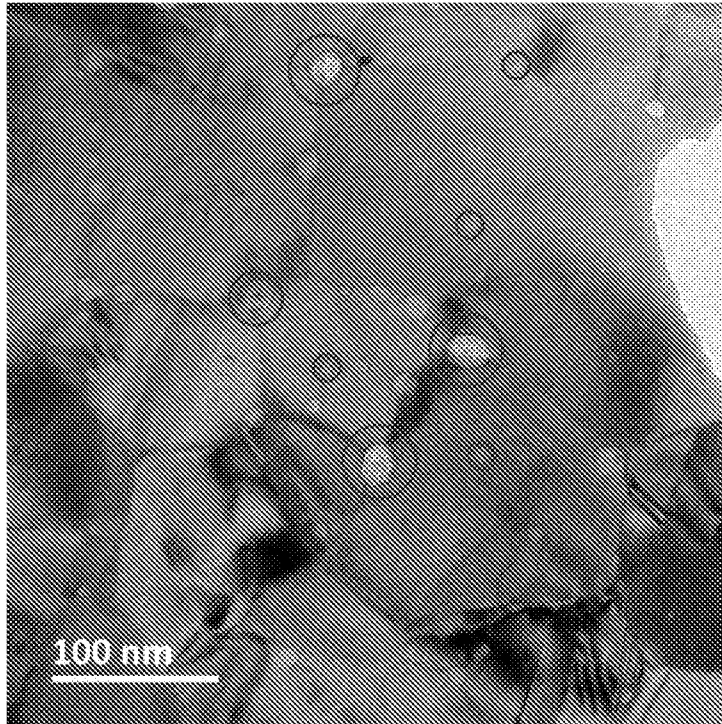
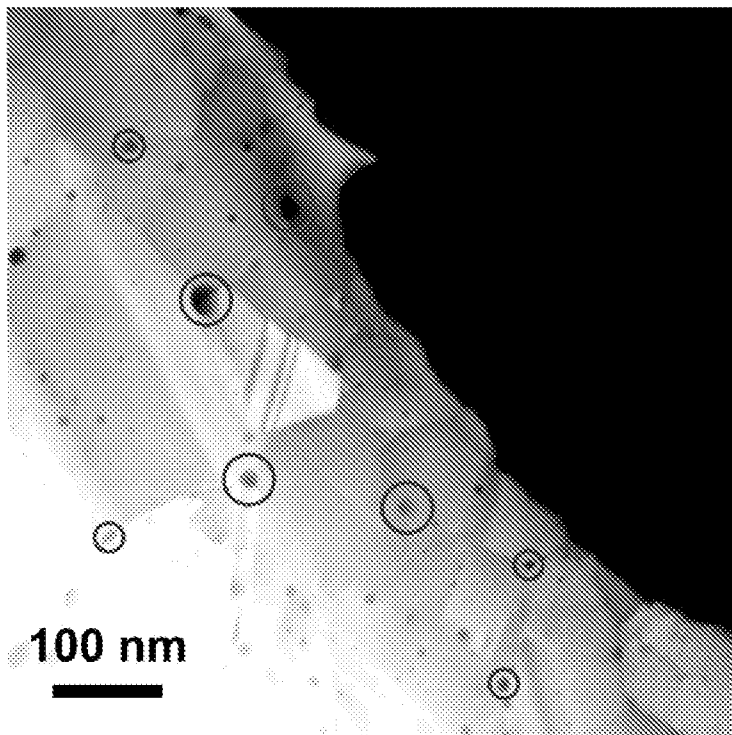


FIGURE 40



INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2015/053902

A. CLASSIFICATION OF SUBJECT MATTER

C23C 18/16 (2006.01) C25D 21/10 (2006.01) C25D 15/02 (2006.01) C25D 21/14 (2006.01) C25D 13/10 (2006.01)
C25D 21/02 (2006.01) C25D 1/00 (2006.01) C25D 5/00 (2006.01)

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)

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

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

EPODOC & WPIAP: IPC/CPC C25D13/02, C25D13/10, C23C18/16, C23C18/54, C23C20/02, C25D15/00/-, C25D21/02, C25D21/10, C25D21/14, C25D21/00/- C25D1/00/-, C25D5/00/-, C25D3/00/- & Keywords (ceramic, oxide, carbide, nitride, silicate, boride, metal+, alloy, zinc, cadmium, copper, nickel, chromium, tin, silver, gold, lead, ruthenium, rhodium, palladium, osmium, iridium, iron, cobalt, indium, arsenic, antimony, bismuth, manganese, rhenium, aluminium, titanium, hafnium, vanadium, niobium, tantalum, tungsten, molybdenum, control, pH, temperature, stir+, coat+, electroless, nano+, reduc+ & like terms)

Google Patents / Scholar: keywords: metal ceramic composite coating sol

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	



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	"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	
"E" earlier application or patent but published on or after the international filing date	"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	
"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)	"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	
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family	
"P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search
6 October 2015

Date of mailing of the international search report
06 October 2015

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AUSTRALIAN PATENT OFFICE
(ISO 9001 Quality Certified Service)
Telephone No. 0399359625

INTERNATIONAL SEARCH REPORT

International application No.

C (Continuation).

DOCUMENTS CONSIDERED TO BE RELEVANT

PCT/IB2015/053902

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2103718 A1 (NIHON PARKERIZING CO LTD) 23 September 2009 abstract; para 22, 25-28, 50, 52; examples; figure 1	1-17, 20-26
X	WO 2011/002311 A1 (AUCKLAND UNISERVICES) 06 January 2011 abstract; figures 2c, 7e; page 2, lines 26-35; page 3, lines 19-21, 28-30; page 8, lines 18-21	1-26
A	JP H05-171454 A (KANAI HIROYUKI) 09 July 1993 abstract	1-26
A	CN 103194784 A (JIANGSU UNIVERSITY) 10 July 2013 abstract	1-26
A	JP S59-123796 A (KAWASAKI STEEL CORP) 17 July 1984 abstract	1-26

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/IB2015/053902

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Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	Publication Date	Publication Number	Publication Date
EP 2103718 A1	23 September 2009	None	
WO 2011/002311 A1	06 January 2011	None	
JP H05-171454 A	09 July 1993	None	
CN 103194784 A	10 July 2013	None	
JP S59-123796 A	17 July 1984	None	

End of Annex

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

Form PCT/ISA/210 (Family Annex)(July 2009)