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

(57) Abstract: A method for producing a metal-ceramic composite coating with increased hardness on a substrate includes adding a sol of a ceramic phase to the plating solution or electrolyte. The sol may be added prior to and/or during 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. The ceramic phase may be 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. The coating, other than the ceramic phase may comprise Ni, Ni-P, Ni-W-P, Ni-Cu-P, Ni-B, Cu, Ag, Au, Pd.

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## **“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, and a battery or rectifier supplies direct current. In one method the anode is of the plating metal and metal molecules of the anode are oxidised and dissolved into the electrolyte and at the 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 Ni-P or Ni-B onto a substrate which may be a metal or plastic substrate.

25      Electroless plating may also be used to form a metal-ceramic composite coating on a substrate, such as an Ni-P-TiO<sub>2</sub> coating for example. TiO<sub>2</sub> nanoparticles are added to the electroless plating solution and co-deposit on the substrate with the Ni-P in an Ni-P-TiO<sub>2</sub> matrix. The TiO<sub>2</sub> particles can tend to agglomerate together in solution and thus distribute non-uniformly on the substrate thus giving uneven properties to the coating, and with the objective of reducing this the solution is  
30      continuously stirred and/or a surfactant is added to assure good dispersion of the TiO<sub>2</sub> particles through the solution.

35      Ni-P- TiO<sub>2</sub> coatings may also be formed on a substrate or item by first forming a coating of Ni-P on the item by electroplating and then dipping the item into a TiO<sub>2</sub> sol to deposit TiO<sub>2</sub> on/in the coating by the sol-gel process.

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

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## SUMMARY OF INVENTION

In one aspect, the present invention provides a plating or coating method for producing a metal-ceramic composite coating on a substrate, which includes adding a ceramic phase to the plating solution or electrolyte as a sol in an amount controlled to be sufficiently low that nanoparticles of the ceramic phase form directly onto or at the substrate, and continuously stirring the plating solution or electrolyte.

5 In another aspect, the present invention provides a plating or coating method for producing a metal-ceramic composite coating on a substrate which includes adding a ceramic phase to the plating solution as a sol in an amount 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, and continuously stirring the plating solution or electrolyte.

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Described herein is a method for producing a metal-ceramic composite coating on a substrate which includes adding a sol of a ceramic phase to the plating solution or electrolyte.

Also described is a plating or coating method for producing a metal-ceramic composite coating on a substrate, which includes 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. Also described is a plating or coating method for producing a metal-ceramic composite coating on a substrate which includes 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.

Also described is a plating or coating method for producing a metal-ceramic composite coating on a substrate which includes 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.

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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

5 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 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 0 250 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

5 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 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 0 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.

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

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.

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, Pd.

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

35 The term 'sol' in this specification means a solution of the ceramic phase. It is believed that molecules of the ceramic phase such as molecules of  $TiO_2$  exist in a net-structure in the sol, and

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5 during the plating process react at the surface with to form a crystalline metal – ceramic composite coating.

10 The plating process may be an electroless plating or coating process or alternatively be a galvanic plating process. Where the plating process is a galvanic plating process the plating current may be in the range 10 mA/cm<sup>2</sup> to 300 mA/cm<sup>2</sup> preferably 20 mA/cm<sup>2</sup> to 100 mA/cm<sup>2</sup>.

15 In this specification plating and coating are used interchangeably.

20 0 In another aspect the invention comprises an item or surface plated or coated by a process of the invention as described above.

25 5 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.

## BRIEF DESCRIPTION OF THE FIGURES

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

25 Figure 1 is a schematic diagram of apparatus used in the experimental work subsequently described in some examples,

30 Figure 2 shows surface morphologies of (a) a conventional Ni-P coating, and novel Ni-P-TiO<sub>2</sub> composite coatings prepared at TiO<sub>2</sub> sol dripping rates of (b) 0.02 ml/s, (c) 0.007 ml/s and (d) 0.004 ml/s,

35 Figure 3 shows cross-sectional morphologies and elemental distributions of (a1, a2) a conventional Ni-P coating, and novel Ni-P-TiO<sub>2</sub> composite coatings prepared at TiO<sub>2</sub> sol dripping rates of (b1, b2) 0.02ml/s, (c1, c2) 0.007ml/s, and (d1, d2) 0.004ml/s,

Figure 4 shows XRD spectra of Ni-P-TiO<sub>2</sub> composite coatings prepared at different sol dripping rates of (a) 0.004ml/s, (b) 0.007ml/s and (c) 0.02ml/s, and of (d) a conventional Ni-P coating,

Figure 5 shows microhardness of Ni-P-TiO<sub>2</sub> composite coatings prepared at different sol dripping rates,

5 Figure 6 shows wear track images for (a) a conventional Ni-P coating, and novel Ni-P-TiO<sub>2</sub> composite coatings prepared with the TiO<sub>2</sub> sol dripping rates of (b) 0.02ml/s, (c) 0.007ml/s and (d) 0.004ml/s,

0 Figure 7 shows surface morphologies of (a) a conventional Ni-P coating, and novel Ni-P-TiO<sub>2</sub> composite coatings prepared at different concentrations of TiO<sub>2</sub> sol of (b) 30 ml/L, (c) 60 ml/L, (d) 90 ml/L, (e) 120 ml/L, (f) 150 ml/L, and (g) 170 ml/L,

5 Figure 8 shows XRD spectra of (a) a conventional Ni-P coating, and novel Ni-P-TiO<sub>2</sub> composite coatings prepared at TiO<sub>2</sub> sol concentrations of: (b) 30 ml/L, (c) 60 ml/L, (d) 90ml/L, (e) 120 ml/L, (f) 150 ml/L, and (g) 170 ml/L,

Figure 9 shows microhardness of the novel Ni-P-TiO<sub>2</sub> coatings prepared at different concentrations of TiO<sub>2</sub> sol,

0 Figure 10 shows wear tracks of (a) a conventional Ni-P coating, and novel Ni-P-TiO<sub>2</sub> coatings prepared at TiO<sub>2</sub> sol concentrations of (b) 30 ml/L, (c) 60 ml/L, (d) 90 ml/L, (e) 120 ml/L, (f) 150 ml/L, and (g) 170 ml/L,

25 Figure 11 shows surface morphologies of (a) a conventional electroplating Ni coating, and Ni-TiO<sub>2</sub> composite coatings prepared at different concentrations of TiO<sub>2</sub> sol: (b) 1.25 ml/L, (c) 2.5 ml/L, (d) 7.5 ml/L, (e) 12.5 ml/L, (f) 50 ml/L.

30 Figure 12 shows micro-hardness results of Ni-TiO<sub>2</sub> composite coatings prepared at different concentrations of TiO<sub>2</sub> sol,

Figure 13 shows wear volume loss of Ni-TiO<sub>2</sub> composite coatings prepared at different concentrations of TiO<sub>2</sub> sol,

35 Figure 14 shows the surface morphologies of Ni-TiO<sub>2</sub> composite coatings prepared at different plating currents: (a) 10 mA/cm<sup>2</sup>, (a) 50 mA/cm<sup>2</sup>, (a) 100 mA/cm<sup>2</sup>.

Figure 15 shows micro-hardness results of Ni-TiO<sub>2</sub> composite coatings prepared at different plating currents,

5 Figure 16 shows wear volume loss of Ni-TiO<sub>2</sub> composite coatings prepared at different currents,

Figure 17 shows the surface morphologies of ultra-black surfaces of Ni-P-TiO<sub>2</sub> composite coatings prepared with dripping rates of TiO<sub>2</sub> sol of (a) 0.007 ml/s and (b) 0.004 ml/s.

0 Figure 18 shows the cross-sectional morphologies of ultra-black surfaces of Ni-P-TiO<sub>2</sub> composite coatings prepared with dripping rates of TiO<sub>2</sub> sol of (a) 0.007 ml/s and (b) 0.004 ml/s.

Figure 19 shows the reflectance of ultra-black surfaces of Ni-P-TiO<sub>2</sub> composite coatings prepared with dripping rates of TiO<sub>2</sub> sol of 0.007 and 0.004ml/s,

5 Figure 20 shows the surface morphologies of ultra-black surfaces of Ni-P-TiO<sub>2</sub> composite coatings prepared with concentrations of TiO<sub>2</sub> sol at (a)50 ml/L, (b)90 ml/L, (c)120 ml/L and (b)150 ml/L.

0 Figure 21 shows the cross-sectional morphologies of ultra-black surfaces of Ni-P-TiO<sub>2</sub> composite coatings prepared with concentrations of TiO<sub>2</sub> sol at (a)50 ml/L, (b)90 ml/L, (c)120 ml/L and (b)150 ml/L.

Figure 22 shows the reflectance of ultra-black surfaces of Ni-P-TiO<sub>2</sub> composite coatings prepared with concentrations of TiO<sub>2</sub> sol at 50, 90, 120 and 150ml/L.

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Figure 23 shows the surface morphologies of (a) a conventional electroless plated Ni-P coating, (b) a conventional Ni-P-ZrO<sub>2</sub> composite coating, and (c) a novel Ni-P-ZrO<sub>2</sub> composite coating with the sol concentration of 120 ml/L.

30 Figure 24 shows the XRD spectra of (a) a conventional electroless plated Ni-P coating, (b) a conventional Ni-P-ZrO<sub>2</sub> composite coating, and (c) a novel Ni-P-ZrO<sub>2</sub> composite coating with the sol concentration of 120 ml/L.

Figure 25 shows the microhardness of (a) a conventional electroless plated Ni-P coating, (b) a conventional Ni-P-ZrO<sub>2</sub> composite coating, and (c) a novel Ni-P-ZrO<sub>2</sub> composite coating with the sol concentration of 120 ml/L.

5 Figure 26 shows surface second-electron morphologies of (a) a conventional Ni-TiO<sub>2</sub> composite coating, and (b) a novel sol-enhanced Ni-TiO<sub>2</sub> composite coating. The insets in (a) and (b) are locally magnified backscattered electron images.

0 Figure 27 shows the variation of microhardness as a function of the annealing temperature for a conventional Ni-TiO<sub>2</sub> composite coating and a novel sol-enhanced Ni-TiO<sub>2</sub> composite coating.

5 Figure 29 shows wear tracks on (a) a conventional Au coating, and (b) a novel sol-enhanced Au coating.

5 Figure 30 shows wear tracks on (a) a conventional Au coating, and (b) a novel sol-enhanced Au coating.

Figure 31 shows the effect of Al<sub>2</sub>O<sub>3</sub> sol concentration on the microhardness of coatings.

## DETAILED DESCRIPTION OF EMBODIMENTS

Described herein is a method for producing a metal-ceramic composite coating on a substrate which includes adding a sol of a ceramic phase to the plating solution or electrolyte.

25 The sol may have a concentration such that the sol is transparent (particles of the ceramic phase are not visibly present in the sol), and may in certain embodiments have a concentration of the ceramic phase of between about 10 to about 200g/litre, or about 20 to about 100g/litre.

30 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 an amount of the sol may also be added to the solution or electrolyte prior to the commencement of plating or coating.

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In certain embodiments the sol may be added at a rate of less than about 0.02ml/litre of the plating solution or electrolyte, and may be added at a rate of less than about 0.01ml/litre, and preferably less than about 0.07ml/litre, and in the range about 0.001 to about 0.005ml/litre. 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.

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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 Ti, W, Si, Zr, Al, Y, Cr, Fe, Pb, Co, or a rare earth element.

5 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.

0 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.

25 By the process of the invention we have been able to achieve Ni-P- TiO<sub>2</sub> coatings having microhardness of about 1025HV. In a conventional electroplating process in which TiO<sub>2</sub> 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.

30 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.

35 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.

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.

## 5 EXAMPLES

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

### 0 Example 1 - Ni-P-TiO<sub>2</sub> composite coating on Mg alloy by electroless plating, at different sol rates

A transparent TiO<sub>2</sub> sol was prepared in the following way: 8.68 ml of titanium butoxide (0.04 g/ml) was dissolved in a mixture solution of 35 ml of ethanol and 2.82 ml diethanolamine. After magnetic stirring for 2 hours, the obtained solution was hydrolyzed by the addition of a mixture of 0.45 ml deionized water and 4.5 ml ethanol dropwise under magnetic stirring. After stirring for 2 hours, the TiO<sub>2</sub> sol was kept in a brown glass bottle to age for 24 hours at room temperature.

The transparent TiO<sub>2</sub> sol was added into 150 ml of a conventional Ni-P electroless plating (EP) solution by dripping at a controlled rate during plating (1 drop = 0.002 ml approx). During plating the solution was continuously stirred by magnetic stirring at the speed of ~200r/min. The solution temperature was kept at 80-90°C and the plating time was ~90 min. Figure 1 shows the experimental apparatus used. In Figure 1 the following reference numerals indicate the following parts:

- 25 1. Separatory funnel
2. TiO<sub>2</sub> sol outlet
3. Lids
4. Erlenmeyer
5. Beaker
- 30 6. Water
7. Electroless plating solution
8. Samples
9. Bracket
10. Magnetic stirrer
- 35 11. Siderocradle

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12. Funnel stand

The plating process was repeated at different sol dripping rates and sol concentrations.

5 On analysis the coatings were found to be mainly crystalline, and to have micro-hardness up to 1025 HV<sub>0.2</sub>, compared to ~590 HV<sub>0.2</sub> for conventional Ni-P coatings and ~700 HV<sub>0.2</sub> for conventional Ni-P-TiO<sub>2</sub> composite coatings. The width of the wear tracks of the coating was reduced to about 160  $\mu\text{m}$  in some cases, compared to the corresponding width for the conventional composite coating of about 500  $\mu\text{m}$ .

0 Figure 2 shows surface morphologies of the Ni-P-TiO<sub>2</sub> composite coatings produced at sol dripping rates of 0.004, 0.007, 0.02ml/s, at a concentration of TiO<sub>2</sub> sol 120 ml/L.

5 Referring to Figure 2a the conventional EP Ni-P coating has a typical “cauliflower-like” structure with some pores caused by formation of H<sub>2</sub> in the EP process as shown by the arrows.

With TiO<sub>2</sub> sol dripped into the EP Ni-P solution at a rate of 0.02ml/s, the “cauliflower” structure became smaller – see Figure 2b. Clusters of micro-Ni crystals formed in the interfaces, indicating that the TiO<sub>2</sub> sol addition promoted the nucleation of Ni crystals and prevented the growth of Ni 0 crystals.

Figure 2c shows the coating produced at a sol dripping rate of 0.007ml/s. It was compact and smooth coating of Figure 2a. Well-dispersed white nano-particles were distributed on the surface as shown by the arrows on the right top inset in Figure 2c. It is believed that these particles are TiO<sub>2</sub> 25 nano-particles.

At a TiO<sub>2</sub> sol dripping rate of 0.004ml/s, the coating was also compact and smooth – see Figure 2d. Loose TiO<sub>2</sub> particles congregated in the interfaces between Ni crystals as shown by the arrows in the Figure 2d.

30 Figure 3 shows cross-sectional morphologies and elemental distributions of an Ni-P coating, and of Ni-P-TiO<sub>2</sub> composite coatings prepared at the different dripping rates of TiO<sub>2</sub> sol.

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The conventional Ni-P coating is compact with a thickness of  $\sim 25 \mu\text{m}$  – see Figure 3a1, and good adhesion to the Mg substrate. The Ni and P elements have homogeneous distributions along the coating – see Figure 3a2.

5 Figures 3b1 and 3b2 show the microstructure and elemental distributions of the Ni-P-TiO<sub>2</sub> composite coating prepared with a sol dripping rate of 0.02ml/s. The coating was thinner than the Ni-P coating. The thickness further decreased, from about 23  $\mu\text{m}$  to around 20  $\mu\text{m}$  at a sol dripping rate of 0.007ml/s - Figures 3c1 and 3c1, and to 18  $\mu\text{m}$  at a dripping rate of 0.004ml/s – see Figure 3d1.

0 Figures 4a-c show the XRD spectra for the Ni-P-TiO<sub>2</sub> composite coatings prepared at the different dripping rates, and Figure 4d for the Ni-P coating. The conventional EP medium P content coating possesses a typical semi-crystalline structure, i.e. mixture of amorphous phase and crystallized phase, while the Ni-P-TiO<sub>2</sub> composite coatings possess fully crystalline phase structures.

5 The composite coatings produced by the process of the invention possess hardness up to about 1025 HV<sub>200</sub>, compared to about 710 HV<sub>200</sub> for composite coatings prepared by powder methods and about 570HV<sub>200</sub> for conventional Ni-P coatings. Figure 5 shows the microhardness of the Ni-P-TiO<sub>2</sub> composite coatings prepared at sol dripping rates of from 0.004ml/s to 0.02ml/s. Greatest hardness 0 was obtained at the dripping rate of 0.007ml/s.

25 In Figure 6a the width of wear track of the conventional Ni-P coating was about 440  $\mu\text{m}$ . Many deep plough lines are observed. In contrast, the novel Ni-P-TiO<sub>2</sub> composite coatings possessed better wear resistance as seen from Figures 6b, c and d. The wear track of the composite coatings had a narrower width of about 380  $\mu\text{m}$  at 0.02ml/s, 160  $\mu\text{m}$  at 0.007ml/s, and 340  $\mu\text{m}$  at 0.004ml/s. The novel composite coatings also had very few plough lines compared with the conventional Ni-P coatings.

30 **Example 2 – Ni-P TiO<sub>2</sub> composite coatings on Mg by electroless plating, at different sol concentrations**

The effect of TiO<sub>2</sub> concentration in the sol was also studied. Ni-P-TiO<sub>2</sub> composite coatings were prepared as described in Example 1 but with a constant sol dripping rate of 0.007ml/s and at sol concentrations of TiO<sub>2</sub> sol at 30, 60, 90, 120, 150 and 170 ml/L (1.2, 2.4, 3.6, 4.8, 6.0, 6.8 g/L).

Figure 7 shows surface morphologies of a conventional Ni-P coating and the novel Ni-P-TiO<sub>2</sub> composite coatings prepared at different TiO<sub>2</sub> sol concentrations.

Figure 7a shows the typical “cauliflower”-like structure of the conventional Ni-P coating with some pores on the surface due to the formation of H<sub>2</sub> in the EP process as shown by the arrows.

Figures 7b and 7c show the surface morphologies of the composite coatings with TiO<sub>2</sub> sol dripped into the EP solution at concentrations of 30 ml/L and 60 ml/L, respectively. No white TiO<sub>2</sub> particles were observed in the EP solution during the process. Many micro-sized Ni crystallites formed and congregated on the big Ni grains or in the low-lying interfaces between Ni grains – see Figure 7b. At a sol concentration of 60 ml/L, many well-dispersed and micro-sized Ni crystallites formed on the surface with no congregation – see Figure 7c, and the Ni crystallites became smaller with a smoother surface. White TiO<sub>2</sub> particles were formed in the EP solution as the sol concentration increased.

Figure 7d shows the surface morphology of the coating produced at a sol concentration of 90 ml/L. Micro-sized Ni crystallites are smaller with good dispersion. Large-scale Ni crystals were observed with many small and well-dispersed Ni crystallites on them as shown by the arrows in Figure 7d. At a sol concentration of 120 ml/L, micro-sized Ni crystals almost disappeared – see Figure 7e, and nano-sized TiO<sub>2</sub> particles were observed on the surface with good dispersion as shown by the arrows in the inset of Figure 7e.

Figure 8 shows XRD spectra of the conventional Ni-P coating and the novel Ni-P-TiO<sub>2</sub> composite coatings at the different concentrations of TiO<sub>2</sub> sol. The conventional EP Ni-P coating has a typical semi-crystallized structure, i.e. a mixture of amorphous and crystalline phases – see Figure 5a, while the novel Ni-P-TiO<sub>2</sub> composite coatings have different phase structures with better crystallinity at the lower concentrations of TiO<sub>2</sub> sol as shown in Figures 8b, 8c, 8d and 8e. The coatings have a semi-crystalline structure at higher sol concentrations of 150 and 170 ml/L - see Figures 8f and 8g.

The effect of sol concentration on the microhardness of the composite coatings is shown in Figure 9. At relatively low TiO<sub>2</sub> sol concentrations of 30 – 60 ml/L, the microhardness was about 700 HV<sub>200</sub>. No white TiO<sub>2</sub> particles were observed. At sol concentrations of from 60 to 120 ml/L white TiO<sub>2</sub> particles were observed in the EP solution, and the microhardness increased to a peak of about 1025 HV<sub>200</sub>.

Images of wear tracks on the conventional Ni-P coating and the novel Ni-P-TiO<sub>2</sub> composite produced at different concentrations of TiO<sub>2</sub> sol are shown in Figure 10.

At sol concentrations of 30-60 ml/L the wear tracks became discontinuous as shown in Figures 10b and 10c, and almost no plough lines are observed. At sol concentrations of 90-120ml/L the tracks became narrower (but more continuous) - the width of tracks decreased from ~240  $\mu\text{m}$  to ~160  $\mu\text{m}$ . Figures 10d and 10e show the wear tracks on coatings produced at sol concentrations of 150 and 170 ml/L.

We observed that when the sol was dripped into the EP solution it fast diluted under stirring. The solution was kept transparent and no white particles could be seen by the naked eye, implying that the TiO<sub>2</sub> particles are very small. The TiO<sub>2</sub> nano-particles have no opportunity to agglomerate together to form clusters. Therefore nano-sized TiO<sub>2</sub> particles are deposited together with Ni, forming a metal/nano-oxide composite coating. The nano-particle dispersion also contributes to the improved hardness and wear resistance.

### Example 3 – Ni-TiO<sub>2</sub> coating on mild steel by electroplating, at different sol concentrations

A Ni-TiO<sub>2</sub> electroplating coating was formed on carbon steel by adding a TiO<sub>2</sub> sol prepared as described in example 1 into a traditional Ni electroplating solution at the commencement of electroplating. The bath composition and electroplating parameters are listed in the table below. 12.5ml/l of transparent TiO<sub>2</sub> sol solution prepared as described in example 1 was added to the electroplating solution, and then Ni-TiO<sub>2</sub> composite coatings were formed on carbon steels with a current of 50 mA/cm<sup>2</sup>. Ni and Ni-TiO<sub>2</sub> coatings were prepared without sol addition for comparison. The Ni-TiO<sub>2</sub> coating was prepared with a concentration of TiO<sub>2</sub> nano-particles (diameter < 25 nm) of 10 g/L.

Bath composition/parameters	Quantity
NiSO <sub>4</sub> •6H <sub>2</sub> O	300 g/L
NiCl <sub>2</sub> •6H <sub>2</sub> O	45 g/L
H <sub>3</sub> BO <sub>3</sub>	40 g/L
TiO <sub>2</sub> sol	12.5 mL/L
pH	3.8
Temperature	Room temperature (20°C)
Current <i>i</i>	50 mA/cm <sup>2</sup>
Time	10 min

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The Ni-TiO<sub>2</sub> composite coating formed had a micro-hardness of 428 HV<sub>100</sub>, compared to 356 HV<sub>100</sub> for the Ni-TiO<sub>2</sub> composite coating formed conventionally and 321 HV<sub>100</sub> for the Ni coating.

5 Coatings were prepared at TiO<sub>2</sub> sol concentrations of 0, 1.25, 2.5, 7.5, 12.5 and 50ml/L (0, 0.05, 0.0625, 0.3, 0.5, 2 g/L).

0 Figure 11 shows surface morphologies of the Ni-TiO<sub>2</sub> composite coatings prepared at sol concentrations of 0, 1.25, 2.5, 7.5, 12.5 and 50ml/L.

5 Figure 12 shows microhardness of the Ni-TiO<sub>2</sub> composite coatings prepared at sol concentrations of 0, 1.25, 2.5, 7.5, 12.5 and 50ml/L. The microhardness of the Ni coating was nearly 320HV<sub>100</sub>. The Ni-TiO<sub>2</sub> composite coatings had increased microhardness, up to 428HV<sub>100</sub>, at the sol concentrations of 1.25ml/L to 12.5ml/L.

Referring to Figure 13 the Ni coating had the worst wear volume loss at about  $8 \times 10^{-3}$  mm<sup>3</sup>. The Ni-TiO<sub>2</sub> composite coatings had better wear resistance.

#### 0 **Example 4 – Ni-TiO<sub>2</sub> coating on mild steel by electroplating, at different currents**

Coatings were prepared as in Example 3 but at different plating currents. Figure 14 shows the surface morphologies of Ni-TiO<sub>2</sub> composite coatings prepared with 12.5ml/L TiO<sub>2</sub> sol addition at currents of 10, 50, 100mA/cm<sup>2</sup>.

25 Figure 15 shows the microhardness of Ni-TiO<sub>2</sub> composite coatings prepared with 12.5ml/L TiO<sub>2</sub> sol addition at currents of 10, 50, 100mA/cm<sup>2</sup>. At 10mA/cm<sup>2</sup> the coating had a microhardness of about 300HV<sub>100</sub>, the microhardness increased to 428HV<sub>100</sub> at 50mA/cm<sup>2</sup>, and the microhardness was about 380HV<sub>100</sub> at current of 100mA/cm<sup>2</sup>.

30 Figure 16 shows wear volume loss of the Ni-TiO<sub>2</sub> composite coatings. The coating had best wear resistance at 50mA/cm<sup>2</sup>, with a wear volume loss of about 0.004mm<sup>3</sup>.

#### 35 **Example 5 – Ultra-black Ni-P-TiO<sub>2</sub> composite coating on carbon steel, by electroless plating**

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An Ni-P-TiO<sub>2</sub> electroless coating with ultra-black surface was formed on carbon steel through adding TiO<sub>2</sub> sol prepared as in example 1 into a conventional Ni electroless solution at a controlled rate. When 90ml/L (3.6 g/L) transparent TiO<sub>2</sub> solution was added at a rate of 0.007ml/s to a plating solution of 150 ml, a Ni-P-TiO<sub>2</sub> electroless coating with an ultra-black surface with the lowest reflectance at 0.1-0.5% of visible light was formed.

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Figure 17 shows the surface morphologies of Ni-P-TiO<sub>2</sub> composite coatings prepared at different sol addition rates of 0.007 and 0.004ml/s.

Figure 18 shows the cross-sectional morphologies of Ni-P-TiO<sub>2</sub> composite coatings prepared at different sol addition rates.

Figure 19 shows the reflectance of the ultra-black surfaces of Ni-P-TiO<sub>2</sub> composite coatings prepared at different sol addition rates, in the range of visible light. Lower reflectance was obtained when the TiO<sub>2</sub> sol was added at 0.007ml/s.

Figure 20 shows the surface morphologies of Ni-P-TiO<sub>2</sub> composite coatings prepared at different sol concentrations of 50, 90, 120 and 150 ml/L.

Figure 21 shows the cross-sectional morphologies of Ni-P-TiO<sub>2</sub> composite coatings prepared at different sol concentrations.

Figure 22 shows the reflectance of ultra-black surfaces of Ni-P-TiO<sub>2</sub> composite coatings in the range of visible light prepared at different sol concentrations.

#### **Example 6 - Cu-TiO<sub>2</sub> coatings on carbon steel, by electroplating**

A small amount of TiO<sub>2</sub> sol prepared as in example 1 was added into a conventional electroplating Cu solution, leading to the *in situ* synthesis of Cu-TiO<sub>2</sub> composite coatings. This novel Cu-TiO<sub>2</sub> composite coating had a micro-hardness of 210 HV, compared to 150 HV of the traditional Cu coating, showing 40% increase.

#### **Example 7 - Ni-P-ZrO<sub>2</sub> composite coating on Mg alloy, by electroless plating**

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A transparent  $ZrO_2$  sol was prepared in the following way: 45 ml of zirconium propoxide was dissolved in a mixture solution of 124 ml of ethanol and 11.3 ml diethanolamine. After magnetic stirring for 2 hours, the obtained solution was hydrolyzed by the addition of a mixture of 1.84 ml deionized water and 16.2 ml ethanol dropwise under magnetic stirring. After stirring for 2 hours, the  $ZrO_2$  sol was kept in a brown glass bottle to age for 24 hours at room temperature. The transparent  $ZrO_2$  sol was added into a conventional Ni-P electroless plating (EP) solution by dripping at a controlled rate during plating (1 drop = 0.002 ml approx). During plating the solution was continuously stirred by magnetic stirring at the speed of  $\sim 200$  r/min. The solution temperature was kept at 80-90°C and the plating time was  $\sim 90$  min.

Figure 23 shows surface morphologies of the Ni-P- $ZrO_2$  composite coatings produced at sol dripping rates of 0.007 ml/s, at a concentration of  $ZrO_2$  sol 120 ml/L.

Figure 24 show the XRD spectra of the Ni-P- $ZrO_2$  composite coatings produced at sol dripping rates of 0.007 ml/s, at a concentration of  $ZrO_2$  sol 120 ml/L.

The traditional electroless plated Ni-P and Ni-P- $ZrO_2$  coatings possessed a typical semi-crystallization, i.e. the mixture of crystallization and amorphous state, as shown in Figure 24 a and b. In contrast, the Ni-P- $ZrO_2$  composite coating had a fully crystallized state as shown in Figure 24c.

Figure 25 shows the mechanical properties of the Ni-P- $ZrO_2$  composite coatings produced at sol dripping rates of 0.007 ml/s, at a concentration of  $ZrO_2$  sol 120 ml/L.

The microhardness of the Ni-P- $ZrO_2$  composite coating was increased to 1045 HV<sub>200</sub> compared to 590 HV<sub>200</sub> of the conventional Ni-P coating and 759 HV<sub>200</sub> of the conventional Ni-P- $ZrO_2$  composite coating.

#### **Example 8 - Ni-TiO<sub>2</sub> composite coatings on mild carbon steel**

A Ni-TiO<sub>2</sub> electroplating coating was deposited on mild carbon steel by adding a TiO<sub>2</sub> sol prepared as described in example 1 into a traditional Ni electroplating solution during electroplating and at a low and controlled rate. 12.5 ml/l of transparent TiO<sub>2</sub> sol solution was added into the electroplating solution, and then Ni-TiO<sub>2</sub> composite coatings were formed on carbon steels with a current of 50 mA/cm<sup>2</sup>. Ni-TiO<sub>2</sub> coatings were prepared with solid TiO<sub>2</sub> nano-particles (diameter < 25 nm) of 10 g/L for comparison.

Figure 26 shows surface second-electron morphologies of: (a) a conventional Ni-TiO<sub>2</sub> composite coating, and (b) the sol-enhanced Ni-TiO<sub>2</sub> composite coating. The insets in (a) and (b) are locally magnified backscattered electron images. The traditional Ni-TiO<sub>2</sub> coating exhibited a quite rough and uneven surface (Figure 26a). Large spherical Ni nodules with the size of ~4  $\mu\text{m}$  were clearly seen, on which there were many superfine Ni nodules (~300 nm) as shown in the inset in Figure 1a. Large clusters of TiO<sub>2</sub> nano-particles (~400 nm) were incorporated in the Ni nodules, as pointed by the arrows in the inset (BSE image). In contrast, the sol-enhanced Ni-TiO<sub>2</sub> composite coating had a much smoother surface (Figure 26b). Two shapes of Ni nodules, i.e. spherical and pyramid-like, were displayed on the surface. The pyramid-like Ni nodules with ~1.5  $\mu\text{m}$  size were relatively uniformly distributed in the spherical Ni nodules. It can be clearly seen from the inset in Figure 1b that the size of the spherical Ni nodules was quite small, ~200 nm.

Figure 27 shows the variation of microhardness as a function of the annealing temperature: ■ - conventional Ni-TiO<sub>2</sub> composite coating; ● - sol-enhanced Ni-TiO<sub>2</sub> composite coating. The as-deposited sol-enhanced coating possessed a high microhardness of ~407 HV<sub>50</sub> compared to ~280 HV<sub>50</sub> of the conventional coating. The microhardness of the conventional coating was ~280 HV<sub>50</sub> after low-temperature annealing (up to 150°C), followed by a relatively steady decline to ~180 HV<sub>50</sub> when the coating was annealed at 400°C for 90 min. In contrast, for the sol-enhanced coating, the high microhardness (~407 HV<sub>50</sub>) can be stabilized up to 250°C.

Figure 28 shows the engineering stress-strain curves for (A) the conventional and (B) the sol-enhanced Ni-TiO<sub>2</sub> composites tested at a strain rate of  $1 \times 10^{-4} \text{ s}^{-1}$ . The sol-enhanced composite shows a significantly increased tensile strength of ~1050 MPa with ~1.4% strain, compared to ~600 MPa and ~0.8% strain of the traditional composite.

#### Example 9 - Au-TiO<sub>2</sub> composite coating on Ni-coated brass

A small amount of TiO<sub>2</sub> sol prepared as described in example 1 was added into the a conventional 1 electroplating Au solution, leading to the synthesis of Au-TiO<sub>2</sub> composite coatings. The 30 microhardness and wear resistance were greatly improved as summarised in the table below.

Microhardness of traditional Au and sol-enhanced Au-TiO<sub>2</sub> composite coatings

Group I	Group II
Condition: 10 mA/cm <sup>2</sup> , 6.5 min	Condition: 50 mA/cm <sup>2</sup> , 2.5 min

	Microhardness (HV <sub>10</sub> )	Wear volume loss ( $\times 10^{-3}$ mm <sup>3</sup> )	Microhardness (HV <sub>10</sub> )	Wear volume loss ( $\times 10^{-3}$ mm <sup>3</sup> )
Conventional Au	242 ± 6	1.58 ± 0.02	248 ± 4	1.62 ± 0.02
Novel sol-enhanced Au	269 ± 7	1.43 ± 0.02	293 ± 10	0.82 ± 0.03
Improvement	11%	10.5% or reduced to 90%	18%	98% or reduced to 50.6%

Figure 29 shows the wear tracks on (a) the conventional Au coating, and (b) the sol-enhanced Au coating. The electroplating was carried out with a current density of 10 mA/cm<sup>2</sup> for 6.5 min. The wear volume loss was measured and calculated from the width of the wear track. It was found that the wear volume loss of the conventional Au coating was  $\sim 1.58 \times 10^{-3}$  mm<sup>3</sup>, compared to  $\sim 1.43 \times 10^{-3}$  mm<sup>3</sup> of the sol-enhanced Au coating.

Figure 30 shows the wear tracks on (a) the conventional Au coating, and (b) the sol-enhanced Au coating. The electroplating was carried out with a current density of 50 mA/cm<sup>2</sup> for 2.5 min. It was calculated that the wear volume loss of the conventional Au coating was  $\sim 1.62 \times 10^{-3}$  mm<sup>3</sup>, compared to  $\sim 0.82 \times 10^{-3}$  mm<sup>3</sup> of the sol-enhanced Au coating, indicating that the wear resistance of sol-enhanced coatings was significantly improved.

## 15 Example 10 - Cu-ZrO<sub>2</sub> composite coating on carbon steel

ZrO<sub>2</sub> sol prepared as described in example 7 was added into a conventional electroplating Cu solution, leading to the synthesis of Cu-ZrO<sub>2</sub> composite coatings. Cu and Cu-ZrO<sub>2</sub> (solid-particle mixing) coatings were also prepared with a concentration of ZrO<sub>2</sub> nano-particles (diameter < 25 nm) of 10 g/L. The table below lists the microhardness and electrical resistance of the Cu, conventional (solid-particle mixing) and sol-enhanced Cu-ZrO<sub>2</sub> composite coatings. The sol-enhanced Cu-ZrO<sub>2</sub> composite coating had a significantly increased microhardness of  $\sim 153$  HV<sub>50</sub> compared to  $\sim 133$  HV<sub>50</sub> of the conventional Cu-ZrO<sub>2</sub> coating.

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Electrical resistance ( $\mu\Omega \cdot \text{cm}$ )	Microhardness (HV <sub>50</sub> )
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Cu	1.76	123
Conventional Cu-ZrO <sub>2</sub>	2.92	133
sol-enhanced Cu-ZrO <sub>2</sub>	2.33	153

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### Example 11 - Cu-Al<sub>2</sub>O<sub>3</sub> composite coating on carbon steel

Cu-Al<sub>2</sub>O<sub>3</sub> composite coating was prepared by adding Al<sub>2</sub>O<sub>3</sub> sol into a conventional electroplating Cu solution. The Al<sub>2</sub>O<sub>3</sub> sol was synthesized with Al tri-sec-butoxide ((C<sub>2</sub>H<sub>5</sub>CH(CH<sub>3</sub>)O)<sub>3</sub>Al) as the precursor. A small amount of absolute ethanol was added to 1.7017 g of 97% Al tri-sec-butoxide in a beaker and the increment of mass of 8.0630 g was recorded as the weight of absolute ethanol. The mol ratio of aluminium iso-propoxide and water was 0.01 : 12.4. Under magnetic stirring, 158 mL of de-ionized water was slowly added into the mixture of Al tri-sec-butoxide and ethanol and a few drops of 30% nitric acid were added into the solution to adjust the pH value to 3.5. At this stage, the solution contained white precipitate and it was stirred on a hot plate of 60°C, until all white precipitate dissolved. Finally, a clear aluminium oxide sol was prepared.

Figure 31 shows the effect of Al<sub>2</sub>O<sub>3</sub> sol concentration on the microhardness of coatings. The sol-enhanced Cu-Al<sub>2</sub>O<sub>3</sub> coating has a peaking microhardness of ~181 HV<sub>50</sub> compared to ~145 HV<sub>50</sub> of the Cu coating, indicating ~25% improvement.

In the description in this specification reference may be made to subject matter which is not within the scope of the claims of the current application. That subject matter should be readily identifiable by a person skilled in the art and may assist in putting into practice the invention as defined in the claims of this application.

In this specification where reference has been made to patent specifications, other external documents, or other sources of information, this is generally for the purpose of providing a context for discussing the features of the invention. Unless specifically stated otherwise, reference to such external documents is not to be construed as an admission that such documents, or such sources of information, in any jurisdiction, are prior art, or form part of the common general knowledge in the art.

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 scope hereof as defined in the accompanying claims.

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**CLAIMS:**

1. A plating or coating method for producing a metal-ceramic composite coating on a substrate, which includes adding a ceramic phase to the plating solution or electrolyte as a sol in an amount controlled to be sufficiently low that nanoparticles of the ceramic phase form directly onto or at the substrate, and continuously stirring the plating solution or electrolyte.
2. A plating or coating method for producing a metal-ceramic composite coating on a substrate which includes adding a ceramic phase to the plating solution as a sol in an amount 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, and continuously stirring the plating solution or electrolyte.
3. A plating or coating method according to claim 1 or 2, wherein the metal-ceramic coating forms on the substrate with a predominantly crystalline structure.
4. A plating or coating method according to any one of claims 1 to 3 comprising adding the sol at a rate of less than about 0.02ml/litre of the plating solution or electrolyte.
5. A plating or coating method according to any one of claims 1 to 4 comprising adding the sol by dripping the sol into the plating solution.
6. A plating or coating method according to any one of claims 1 to 5 wherein the sol has a concentration such that the sol is transparent whereby particles of the ceramic phase are not visibly present in the sol.
7. A plating or coating method according to any one of claims 1 to 6 wherein the sol has a sol concentration of 20 to 250 grams of the ceramic phase per litre of the sol.
8. A plating or coating method according to any one of claims 1 to 7 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.
9. A plating or coating method according to any one of claims 1 to 7 wherein the ceramic phase comprises  $TiO_2$ ,  $AlO_2$ ,  $ZrO_2$ , or  $SiC$ .

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10. A plating or coating method according to any one of claims 1 to 9 wherein the coating, other than the ceramic phase comprises Ni, Ni-P, Ni-W-P, Ni-Cu-P, Ni-B, Cu, Ag, Au, Pd.

5 11. A plating or coating method according to any one of claims 1 to 10 wherein the substrate comprises steel, Mg, Al, Zn, Sn, Cu, Ti, Ni, Co, Mo, Pb or an alloy thereof.

12. A plating or coating method according to any one of claims 1 to 10 wherein the substrate comprises a mild steel, alloy steel, or carbon steel.

0 13. A plating or coating method according to any one of claims 1 to 10 wherein the substrate comprises Mg or Al or an alloy thereof.

5 14. A plating or coating method according to any one of claims 1 to 13 wherein molecules of the ceramic phase exist in a net-structure in the sol.

15. A plating or coating method according to any one of claims 1 to 14 wherein the molecules of the ceramic phase exist in oxy-hydroxide form.

0 16. A plating or coating method according to any one of claims 1 to 15 which is an electroless plating or coating process.

25 17. A plating or coating method according to any one of claims 1 to 15 which is a galvanic plating process.

18. An item or surface plated or coated by a process according to any one of claims 1 to 19.

19. An item according to claim 18 wherein the substrate is a carbon steel and the substrate plated or coated substrate has very low light reflectivity.

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20. An item according to claim 18 wherein the plated or coated substrate is electrically conductive.

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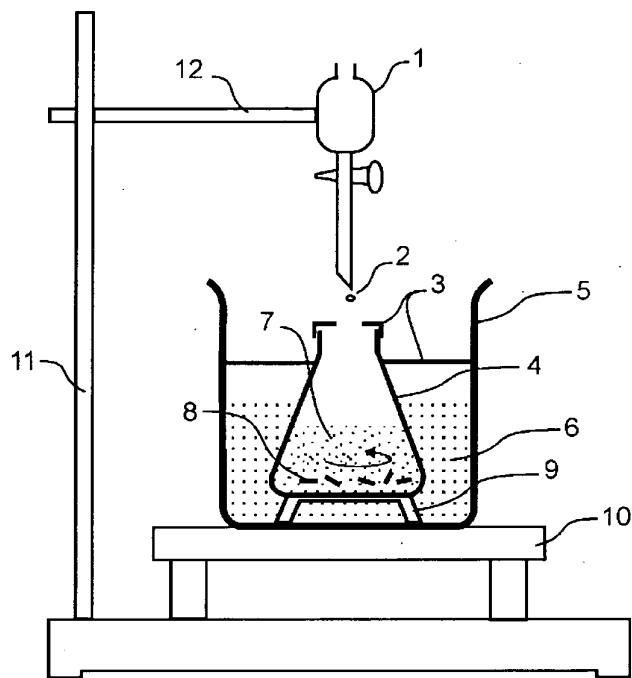


Figure 1

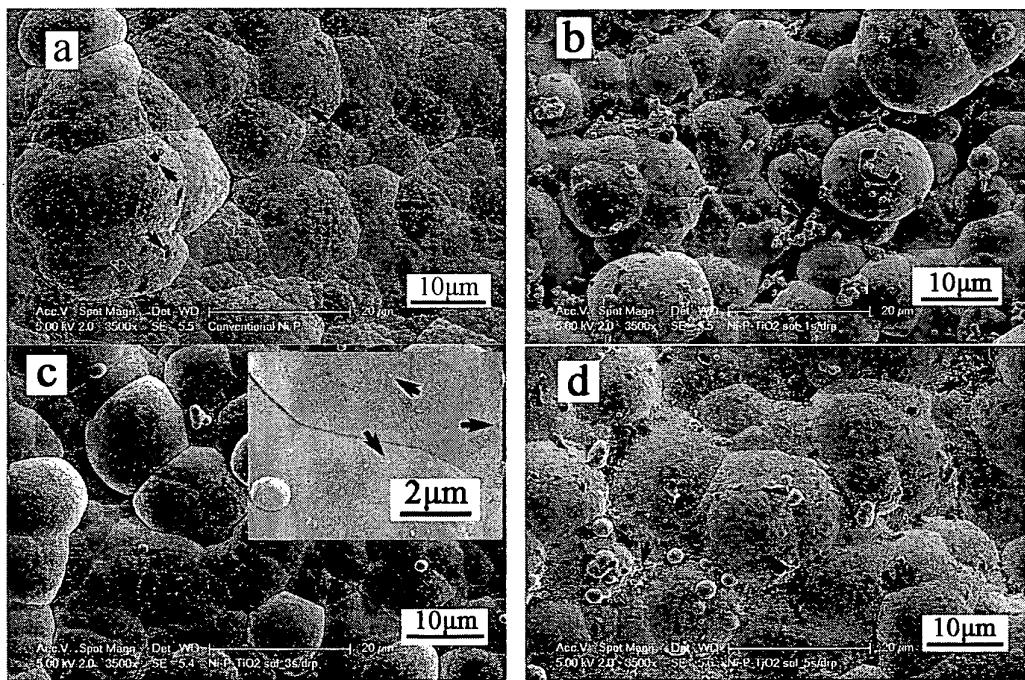


Figure 2

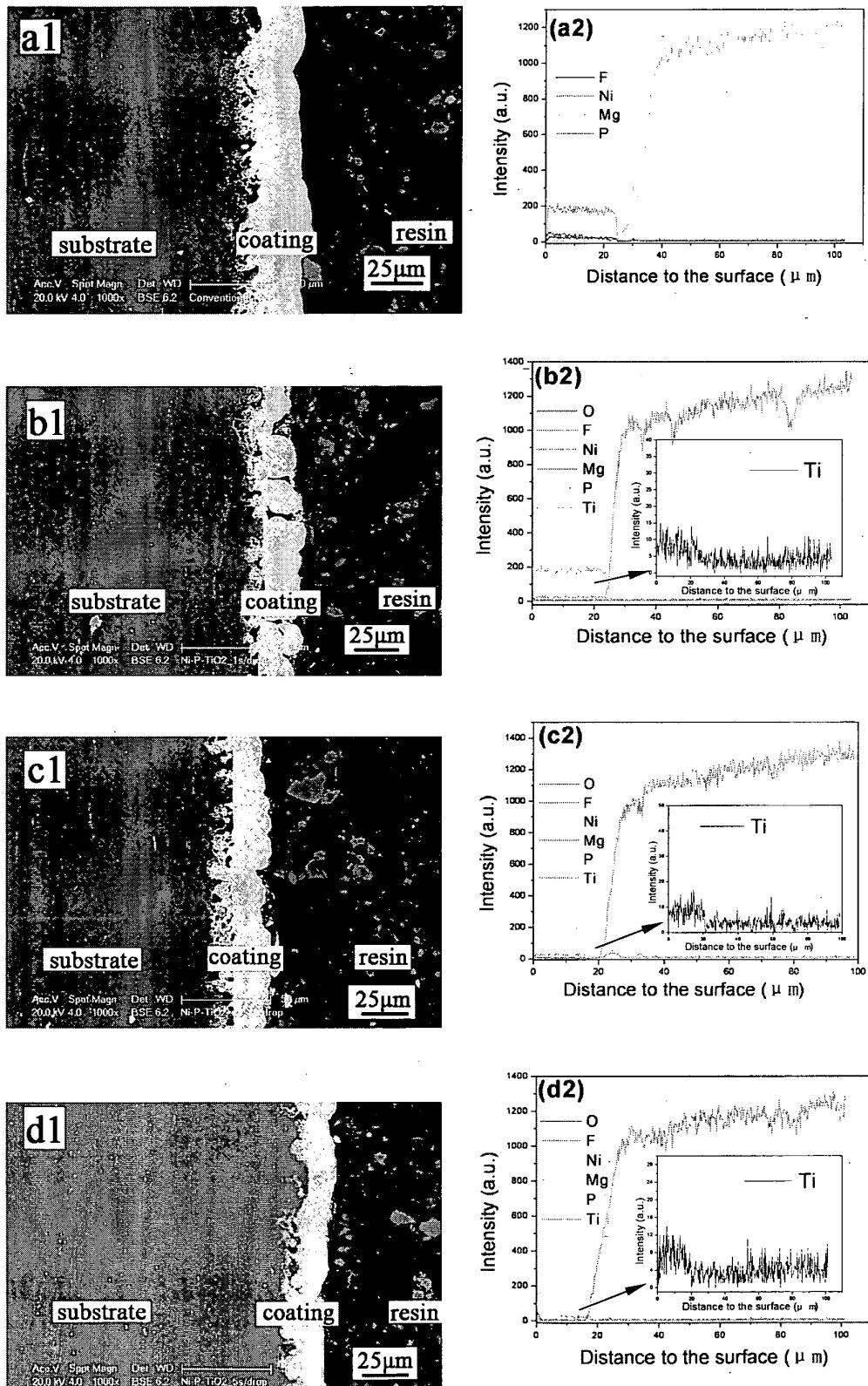


Figure 3

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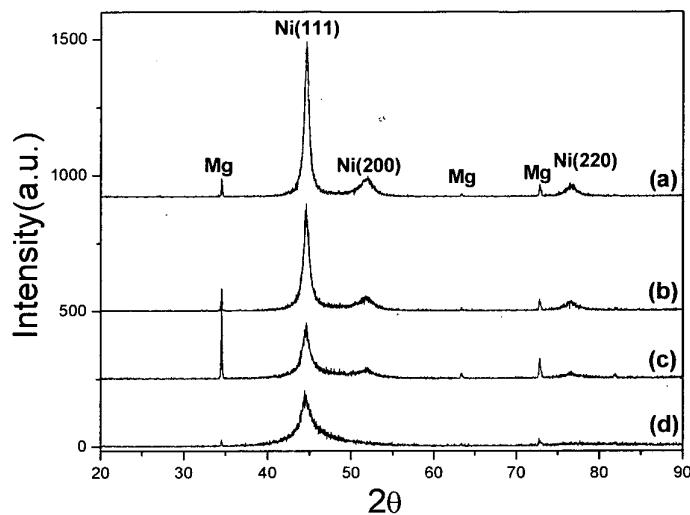


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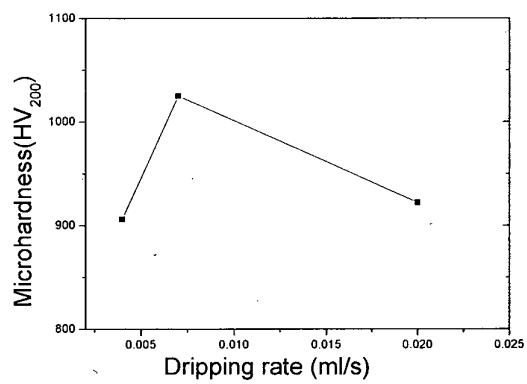


Figure 5

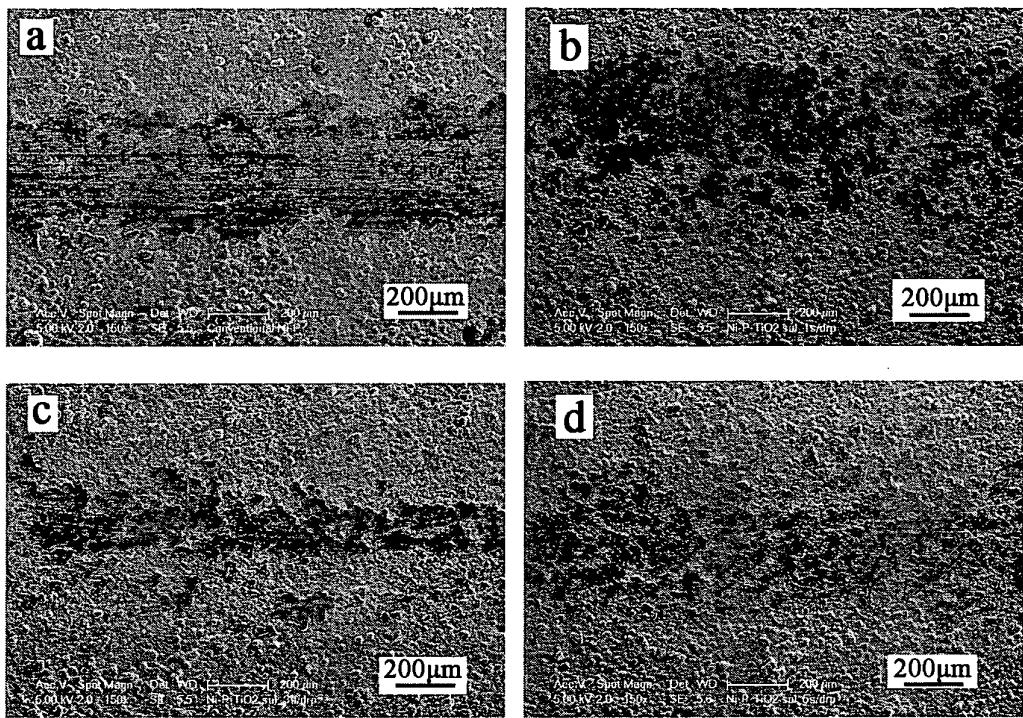


Figure 6

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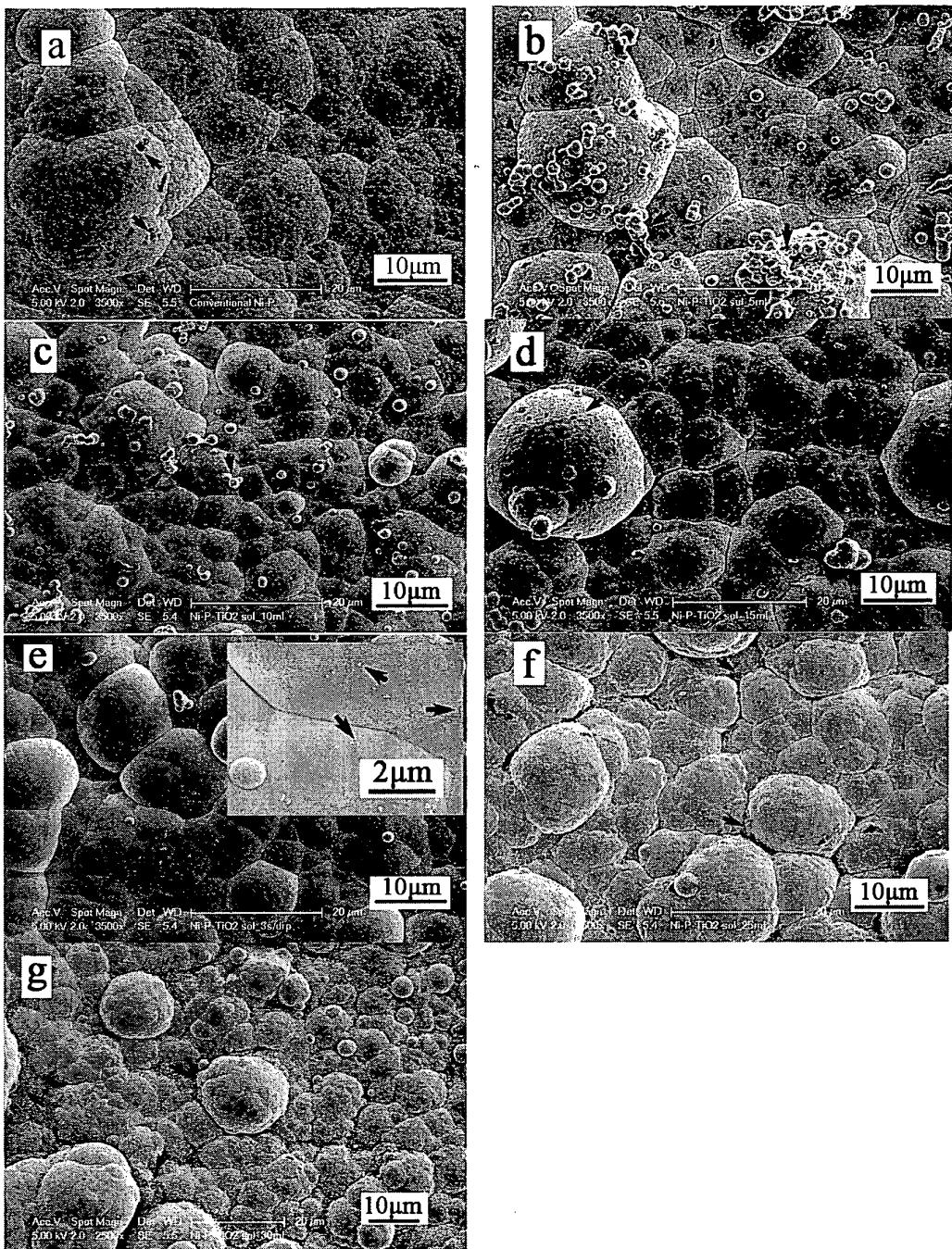
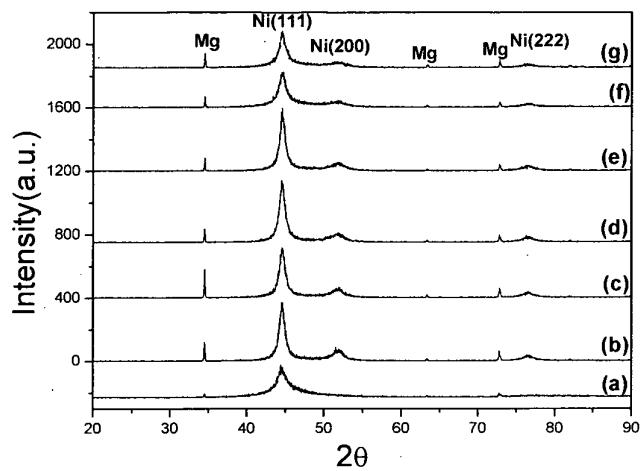
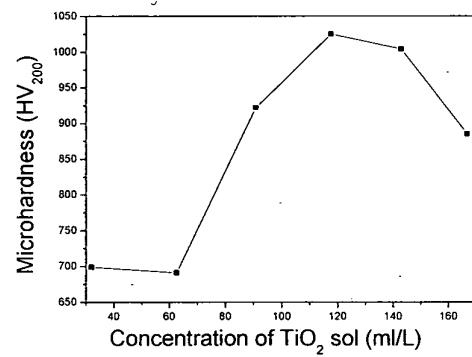


Figure 7

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**Figure 8****Figure 9**

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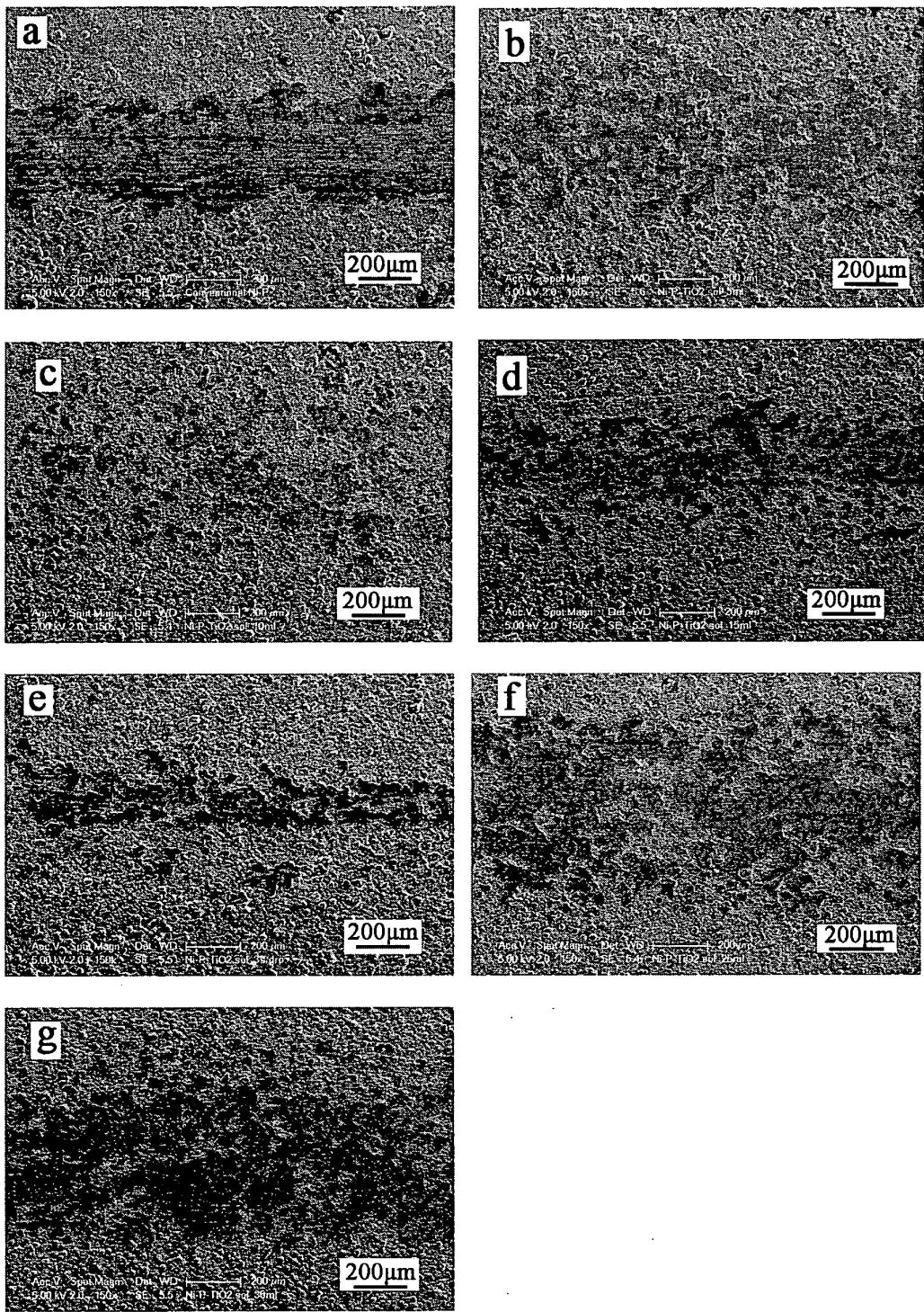


Figure 10

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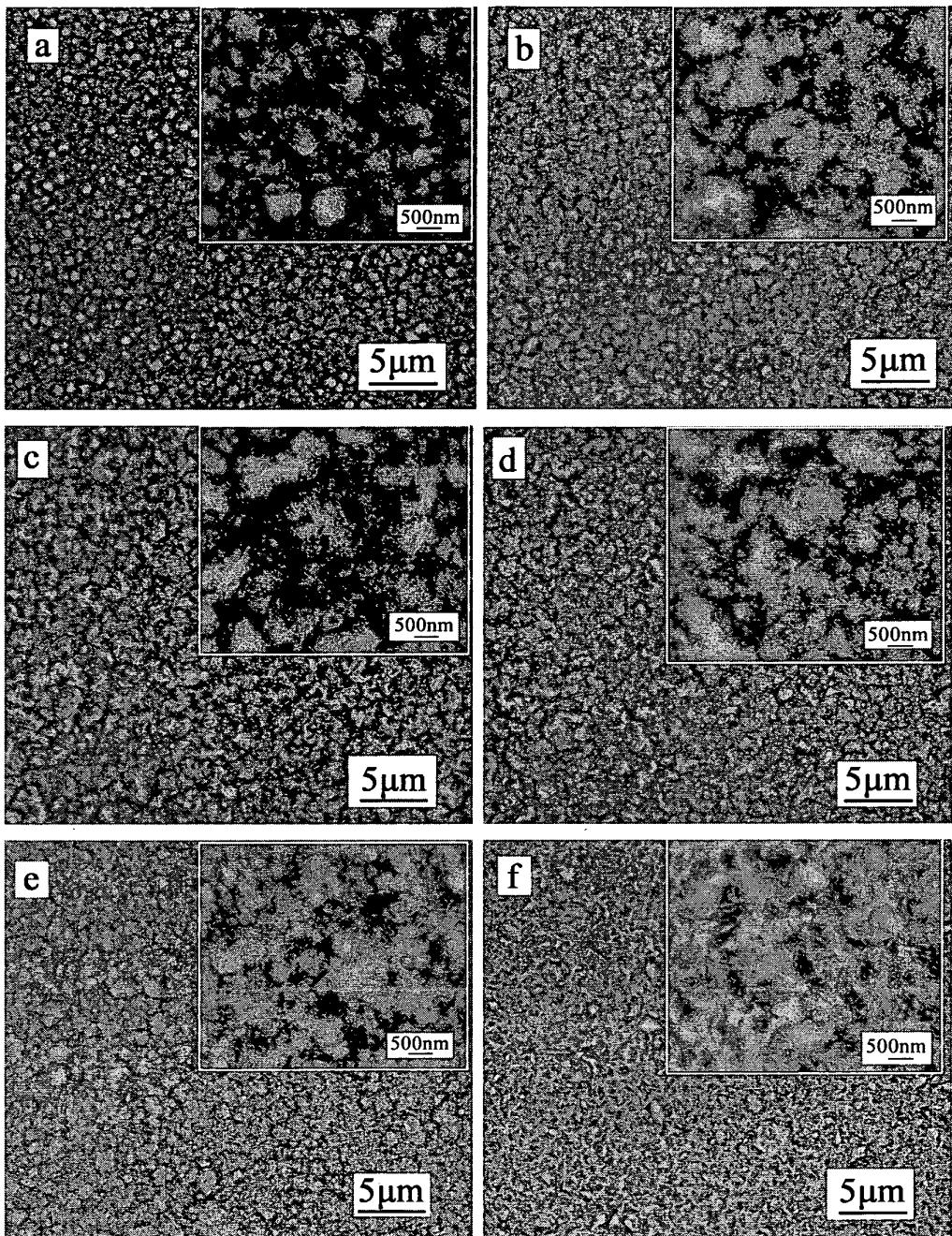


Figure 11

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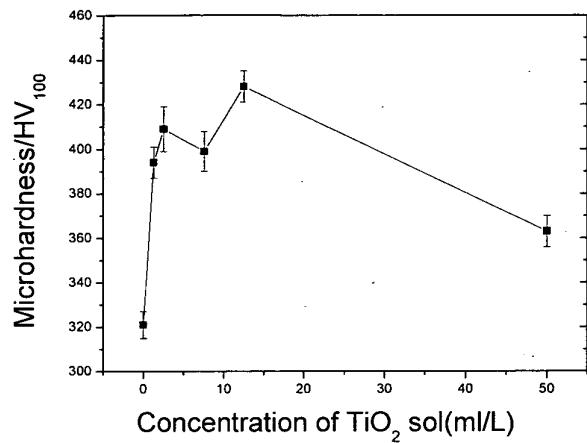


Figure 12

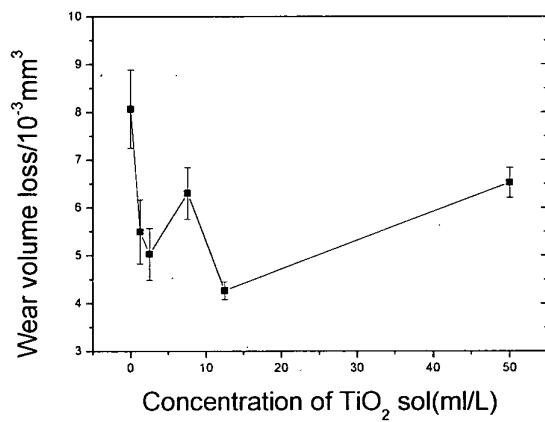


Figure 13

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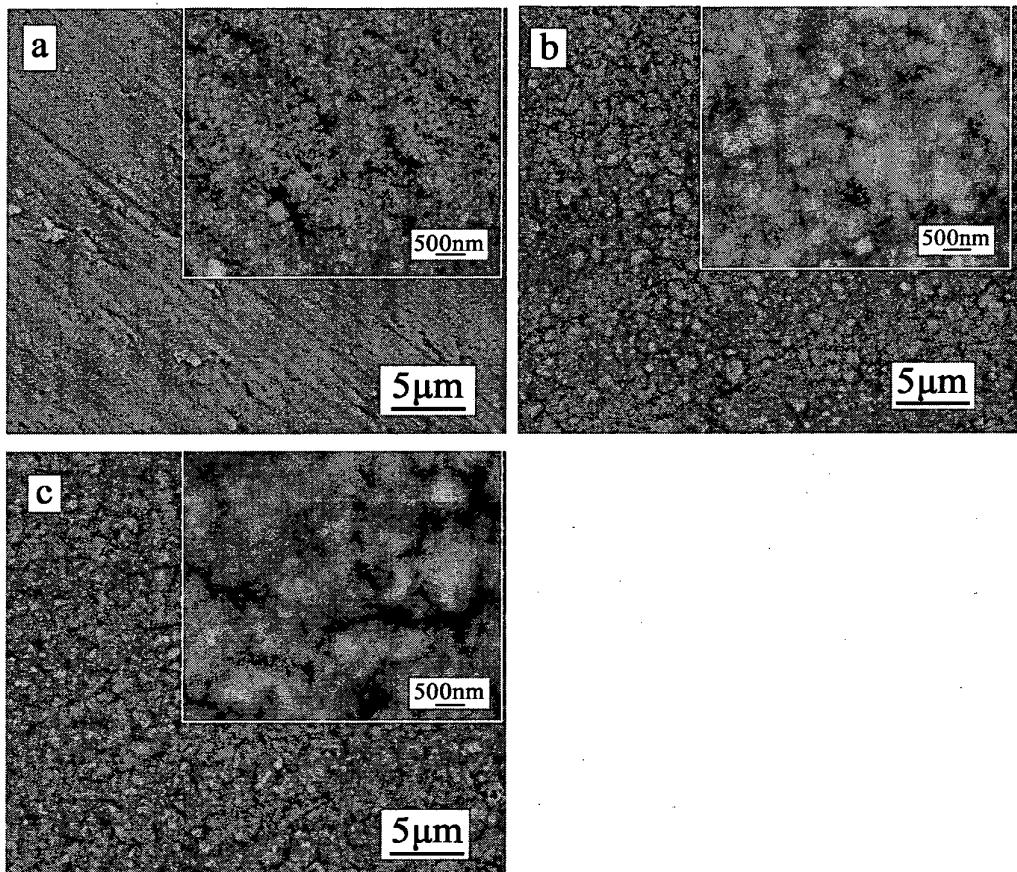
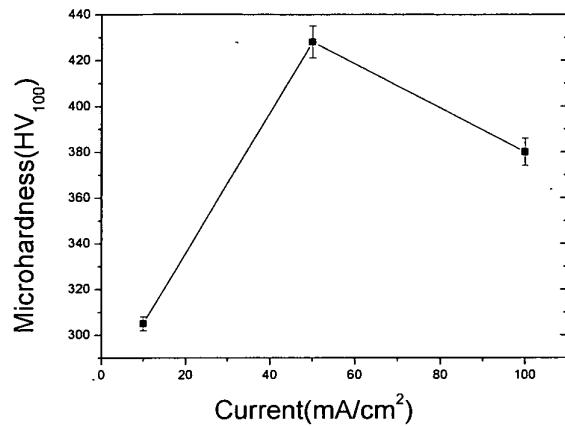
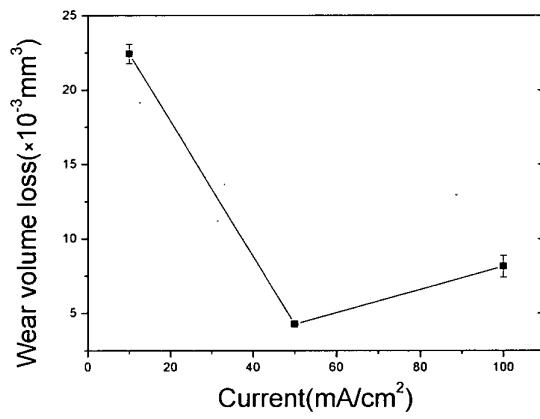


Figure 14

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**Figure 15****Figure 16**

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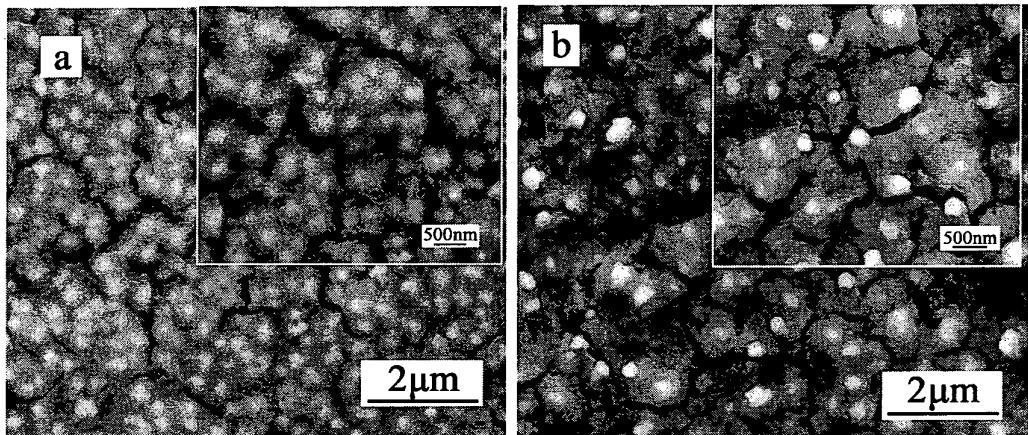


Figure 17

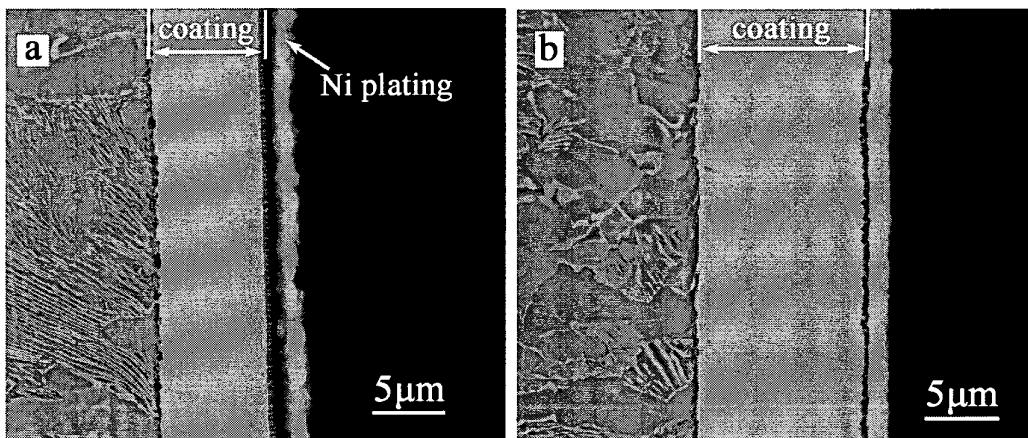


Figure 18

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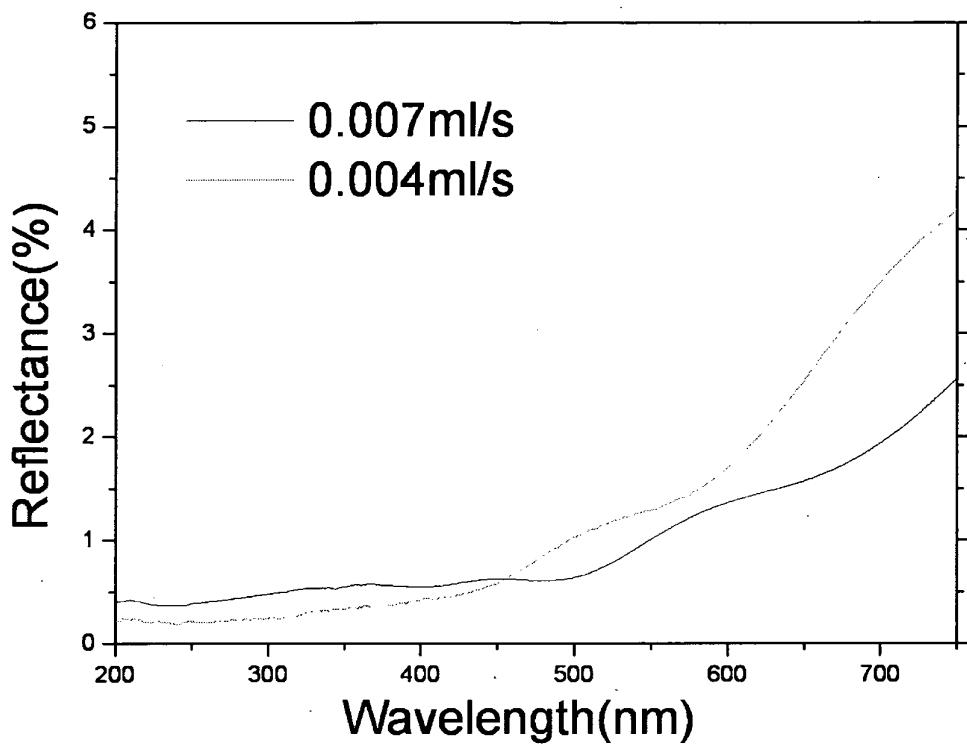
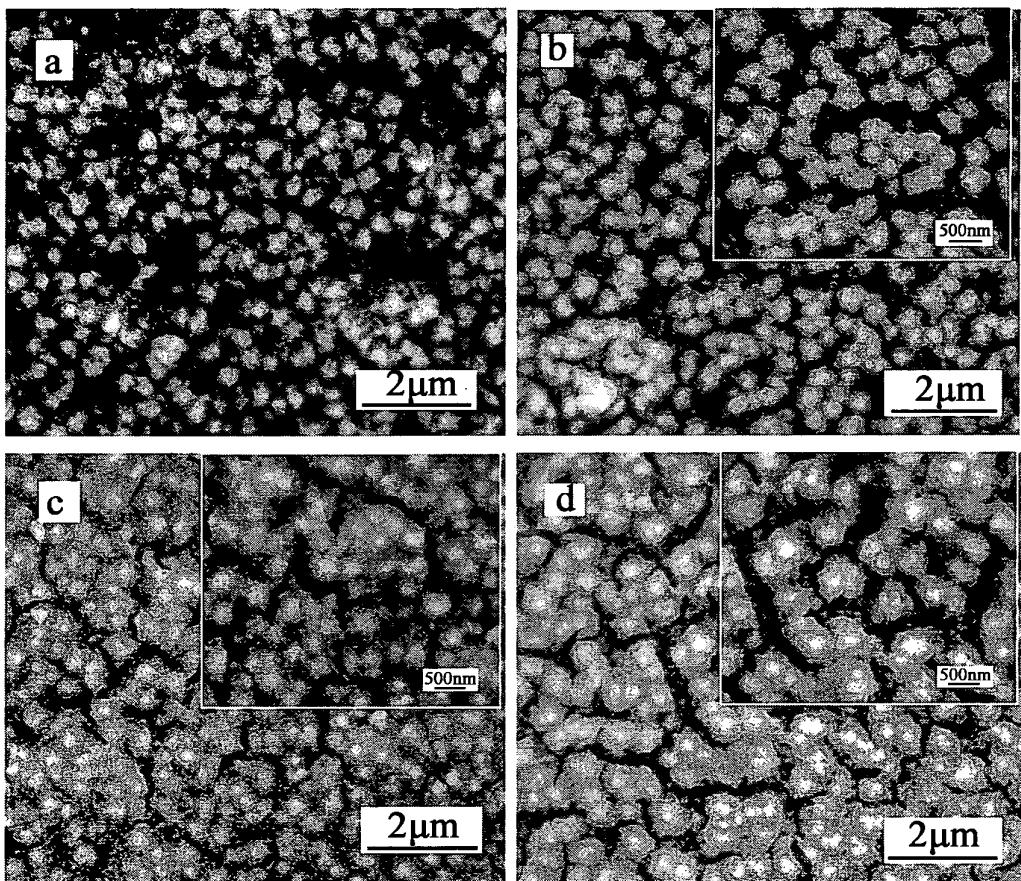


Figure 19

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**Figure 20**

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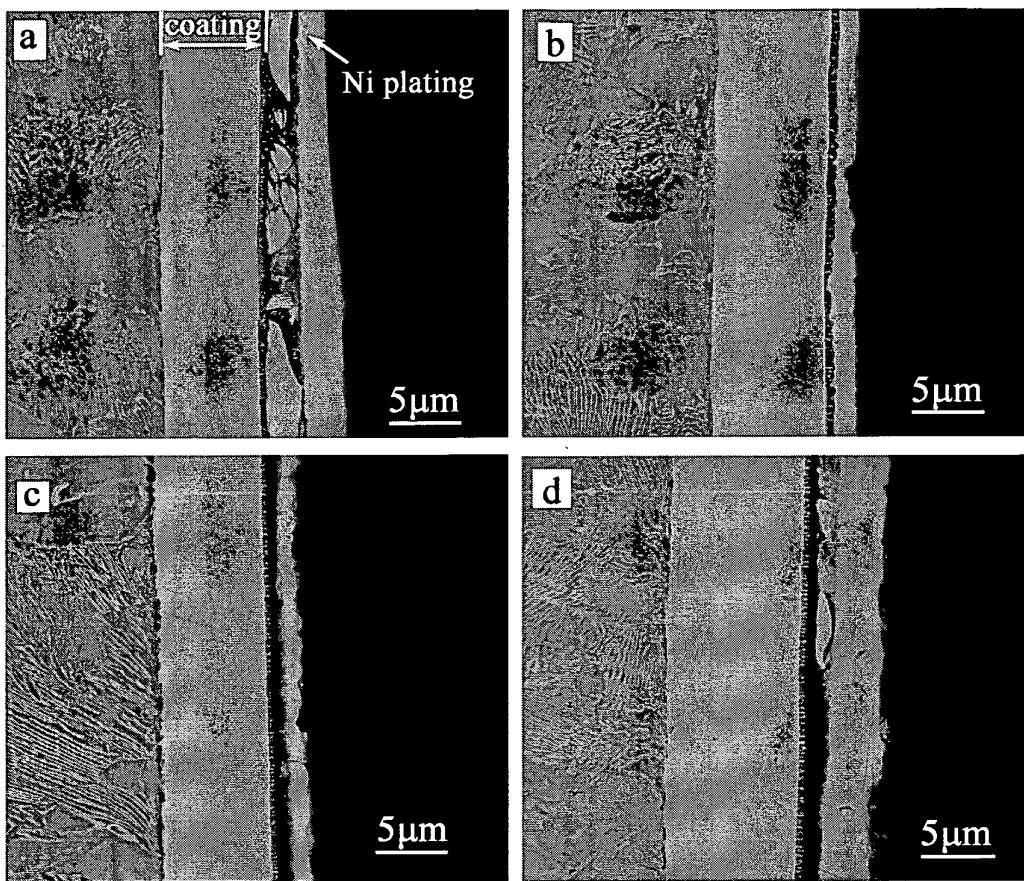


Figure 21

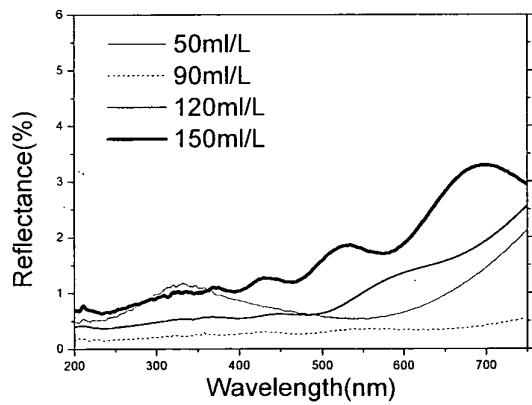


Figure 22

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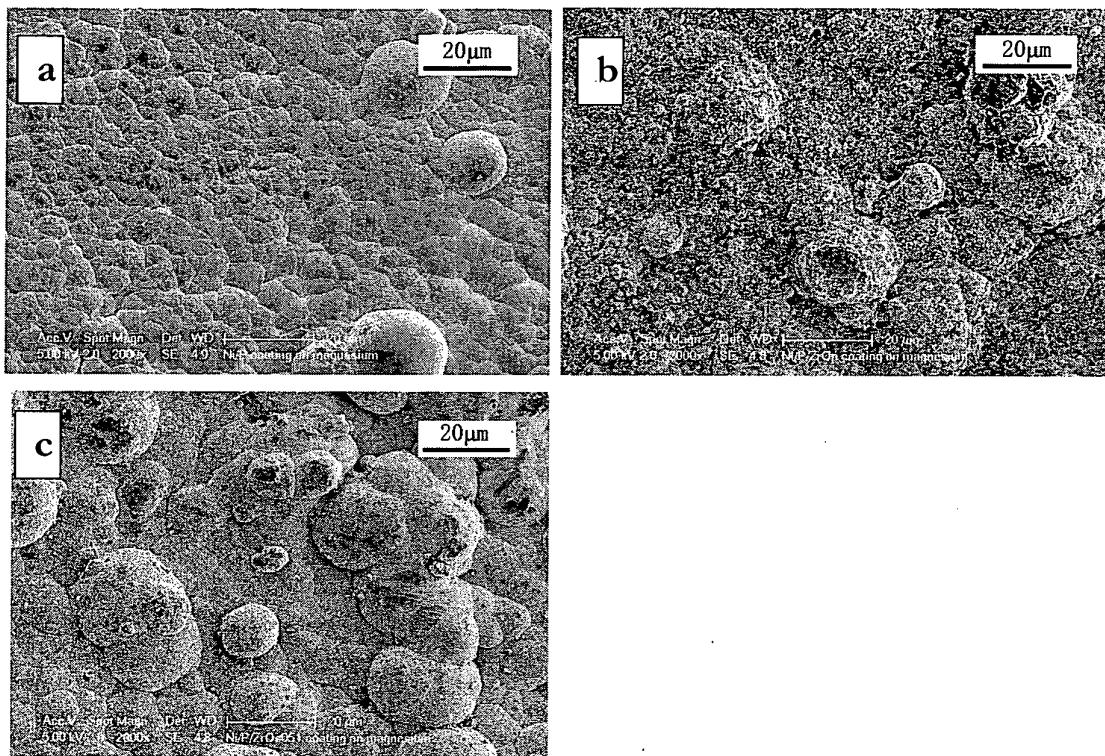
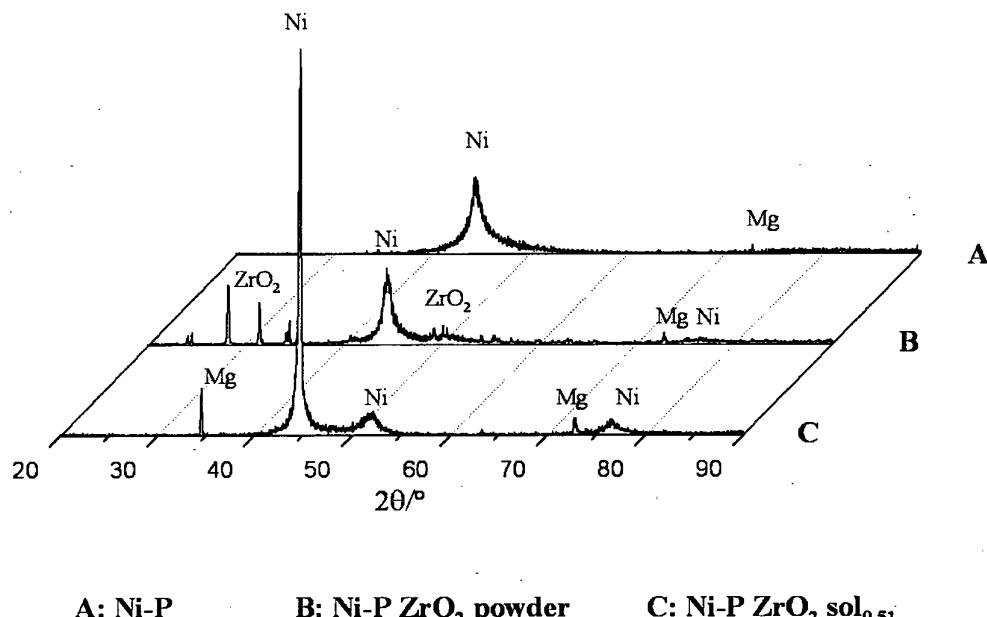


Figure 23

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A: Ni-P

B: Ni-P  $\text{ZrO}_2$  powderC: Ni-P  $\text{ZrO}_2$  sol<sub>0.51</sub>

Figure 24

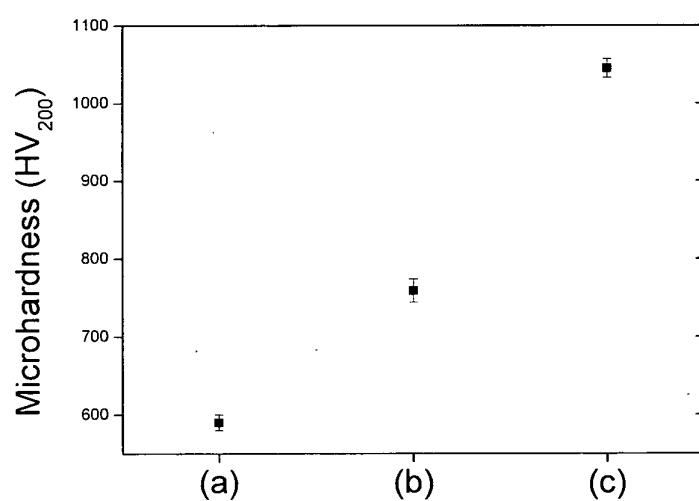


Figure 25

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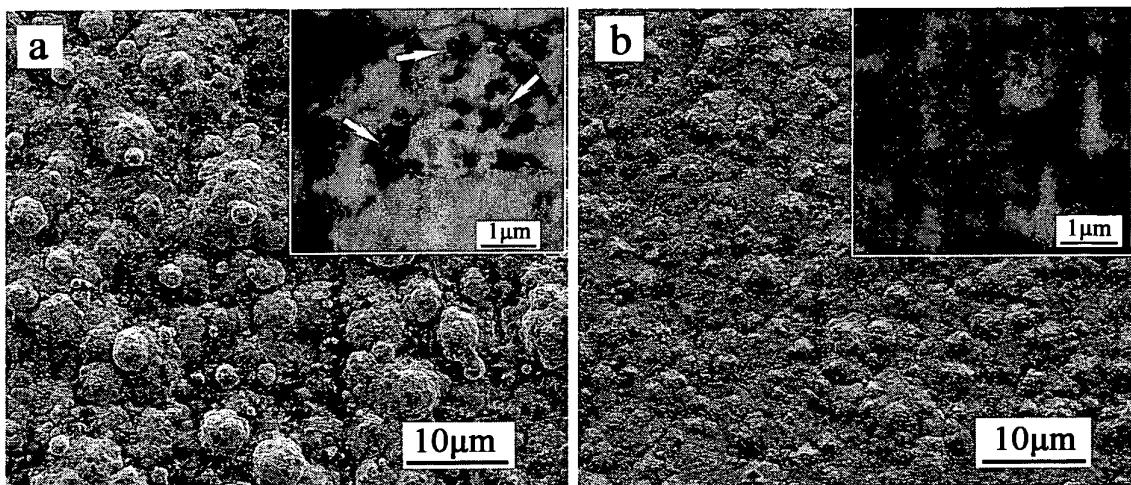


Figure 26

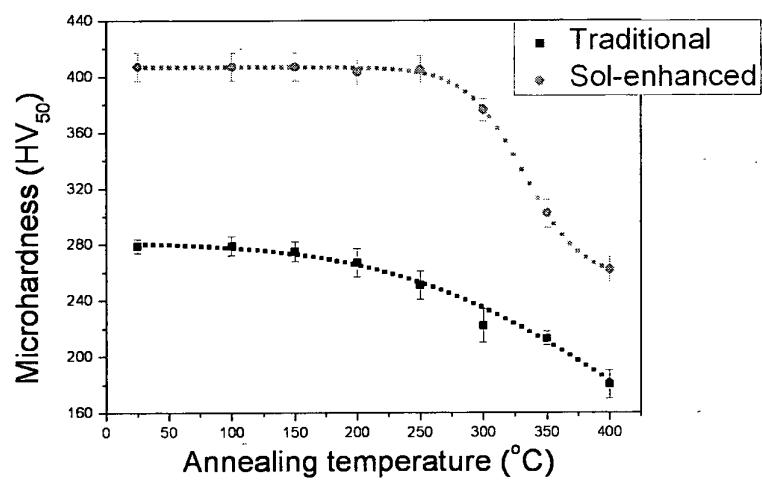


Figure 27

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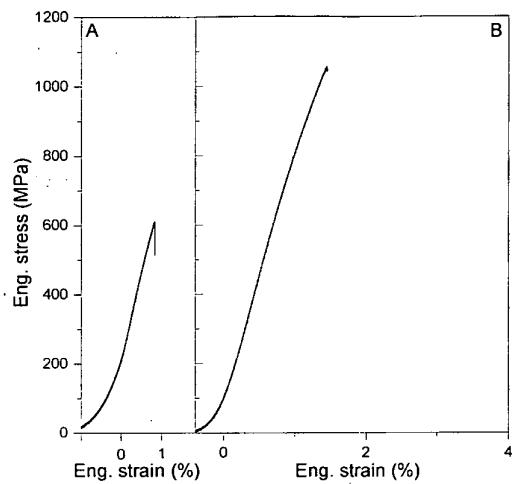


Figure 28

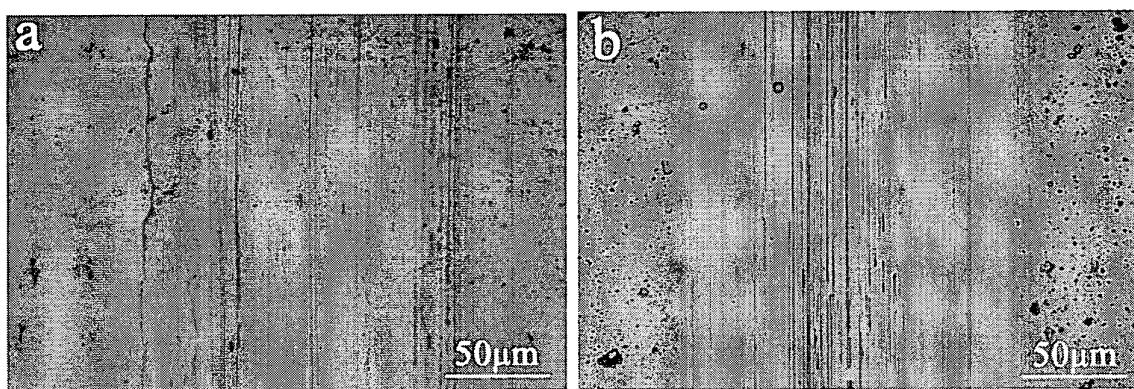


Figure 29

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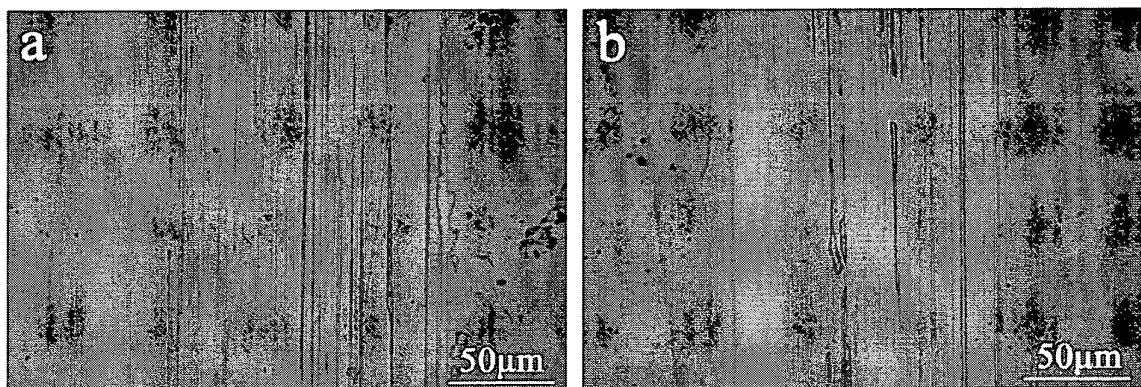


Figure 30

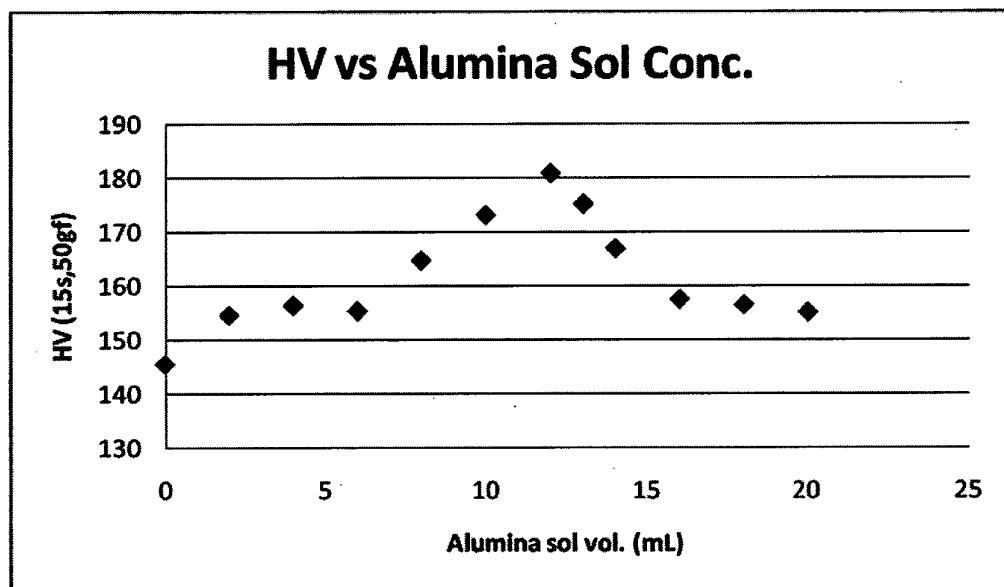


Figure 31