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- (71) **Applicant:** THE COURT OF EDINBURGH NAPIER UNIVERSITY [GB/GB]; Merchiston Tower, Colinton Road, Edinburgh EH10 5DT (GB).
- (72) **Inventors:** DAVIDSON, Alan MacDonald; c/o The Court of Edinburgh Napier University, Merchiston Tower, Colinton Road, Edinburgh EH10 5DT (GB). SHARP, John; c/o The Court of Edinburgh Napier University, Merchiston Tower, Colinton Road, Edinburgh EH10 5DT (GB).
- (74) **Agent:** MURGITROYD & COMPANY; Scotland House, 165-169 Scotland Street, Glasgow G5 8PL (GB).

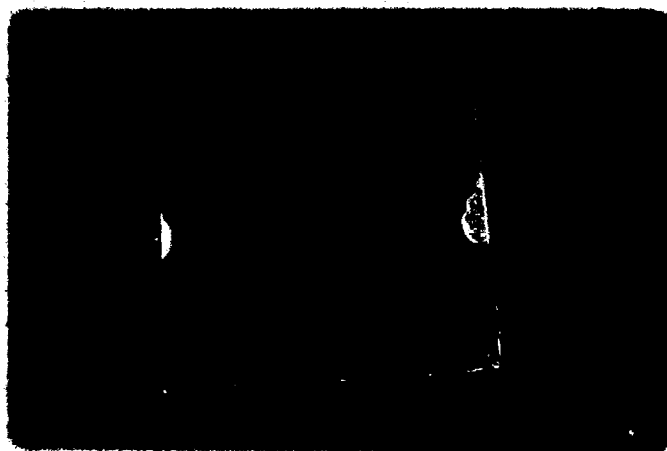
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(54) **Title:** METHOD FOR THE MANUFACTURE OF A COATED SUBSTRATE AND SUBSTRATE OBTAINED THEREBY

Figure 1



(57) **Abstract:** A method for the manufacture of a coated substrate and the substrate obtainable thereby, the method comprising at least the steps of: • - providing a substrate; • - contacting at least a part of the substrate with an electroless plating solution comprising a reducing agent, a metal precursor and a suspension of particulate material, wherein said particulate material is attracted to a magnetic field; • - generating a magnetic field around the substrate; and • - electrolessly plating metal from the metal precursor onto the contacted part of the substrate, thereby co-depositing the particulate material on the contacted part of the substrate to provide a coated substrate.



## METHOD FOR THE MANUFACTURE OF A COATED SUBSTRATE AND SUBSTRATE OBTAINED THEREBY

The present invention relates to a method for the manufacture of a coated substrate, such as an electrode or interconnect for a fuel cell, particularly a solid oxide fuel cell (SOFC), and a substrate manufactured according to the method.

Fuel cells are electrochemical devices which convert the chemical energy in fuels into electrical energy. Fuel cells comprise at least an electrolyte and two electrodes, namely an anode and a cathode, and may additionally comprise an interconnect. Fuel cells are typically constructed from an electrolyte sandwiched between two porous electrodes. A flow of a gaseous fuel – typically hydrogen – passes over the anode and an oxygen-containing gas passes over the cathode resulting in ionic transfer through the electrolyte and electronic transfer through an external load. In a SOFC, the ionic transfer occurs in the form of the diffusion of oxide ions into the electrolyte and their migration to the anode where they can combine with the fuel to liberate electrons which pass to an external circuit via an interconnect.

International Patent Application No. PCT/GB2008/003342 discloses a method of manufacturing an electrode for a fuel cell in which at least part of an electrode substrate is contacted with an electroless plating solution comprising a reducing agent, metal precursor and a suspension of particulate material to electrolessly plate metal from the metal precursor onto the contacted part of the electrode substrate and co-deposit the particulate material onto the electrode substrate.

The method of PCT/GB2008/003342 allows the deposition of a metal and particulate material onto a many substrate types, including non-conducting substrates. However, the deposition of the particulate material suspended in the plating solution relies upon its entrainment with the metal as the metal is being plated onto the substrate. Furthermore, the concentration of the particulate material at the substrate is dependent upon the concentration in the electroless

plating solution and the effectiveness of any mixing. This can lead to inadequate deposition of the particulate material onto the substrate.

5 It is an object of the present invention to provide a method for the manufacture of a coated substrate which addresses these problems. In particular, the present invention provides a method for the manufacture of a coated substrate which improves the deposition of the particulate material. This can provide higher densities of particular material on the coated substrate.

10 It is a further object of the present invention to provide a method which allows the selection of the properties of the coated substrate. The choice of particulate material can provide a variety of properties to the substrate, such a wear, corrosion or thermal resistance. Furthermore, by varying the proportion of the metal to particulate material deposited on the substrate, it is possible to alter the  
15 electrical conductivity and porosity of the coated substrate.

In a first aspect, the present invention provides a method for the manufacture of a coated substrate, the method comprising at least the steps of:

- providing a substrate;
- 20 – contacting at least a part of the substrate with an electroless plating solution comprising a reducing agent, a metal precursor and a suspension of particulate material, wherein said particulate material is attracted to a magnetic field;
- generating a magnetic field around the substrate; and
- 25 – electrolessly plating metal from the metal precursor onto the contacted part of the substrate, thereby co-depositing the particulate material on the contacted part of the substrate to provide a coated substrate.

The step of generating a magnetic field around the substrate can be carried out  
30 before or after the substrate is contacted with an electroless plating solution.

Consequently, the “contacting” and “generating” steps described above may also be provided in the reversed order to that given above, or simultaneously.

5 Preferably, the magnetic field is generated before the contacting step. It will be apparent that the benefits of the invention are achieved when the electroless plating step is carried out in the presence of a magnetic field.

10 The magnetic field may be one or both of a permanent magnetic field, such as the field generated by a permanent magnet, and an electromagnetic field, such as the field generated by an electromagnet. The magnetic field can be aligned to attract the particulate material to the substrate.

15 In order for the particulate material to be attracted to the magnetic field, and thereby deposit on the substrate in the field, the particulate material should exhibit a magnetic moment. The magnetic moment may be a permanent magnetic moment, such as that present in a ferrimagnetic or ferromagnetic materials or may be an induced magnetic moment, such as that present in a paramagnetic material in a magnetic field. Consequently, the particulate material may comprise one or more of the group selected from a ferrimagnetic material, a ferromagnetic material and a paramagnetic material.

20 The particulate material may also comprise a magnetic additive. The magnetic additive is attracted to a magnetic field and its presence increases the attraction of the particulate material to the magnetic field. The magnetic additive is selected from one or more of the group comprising a ferrimagnetic material, a ferromagnetic material and a paramagnetic material. It will be apparent that the magnetic additive should be a part of, i.e. unitary with, the particulate material, either within or on the surface of a particle of the particulate material.

30 Consequently, the particulate material may be attracted to the magnetic field by virtue of the magnetic additive. The magnetic additive is preferably a ferromagnetic material, such as nickel. Other magnetic additives include iron

and cobalt. Typically, the magnetic additive is present on the particulate material as a coating, such as a full or a partial coating. A partial coating does not cover the entire external surface area of the particle of particulate material. Coatings of nickel and/or cobalt are preferred.

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The magnetic additive, particularly a nickel, iron and/or cobalt magnetic additive, may be deposited on the particulate material by an electroless plating process. In this way, the magnetic additive may be provided as a metallic coating on the surface of the particles forming the particulate material. The deposition of the magnetic additive on the particulate material may be carried out in a pre-treatment step prior to the electroless plating step which co-deposits metal and particulate material onto the substrate. The pre-treating step comprises depositing a magnetic additive onto a particle to provide the particulate material; and forming an electroless plating solution with the particulate material, a reducing agent and a metal precursor.

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For instance, a metal such as nickel, may be deposited upon a particle to form the particulate material by a process similar to the electroless plating method for the manufacture of a coated substrate described herein. In this case, the particle to form the particulate material would take the place of the substrate, such that the electroless plating solution may comprise a reducing agent and a metal precursor and the plated metal is the magnetic additive. The pre-treatment may comprise at least the steps of providing a particle or plurality of particles, contacting the particles with an electroless plating solution comprising a reducing agent and a metal precursor and electrolessly plating metal on the particles to form the particulate material.

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Iron may be deposited on the particulate material in accordance with the method disclosed in *Chem. Mater.*, 2006, 18 (18), pp 4361–4368. Cobalt may be deposited on the particulate material in accordance with the method disclosed in IEEE Transactions on Magnetics, vol. 5, issue 3, pp. 314-317, 1969.

Alternatively, the magnetic additive may be in particulate form. In one embodiment, it can be deposited on the particles forming the particulate material by an electroless plating process, such as that described in PCT/GB2008/003342. In this case, the particle to form the particulate material would take the place of the substrate and the magnetic additive in particulate form would be the particulate material, such that the electroless plating solution may comprise a reducing agent, a metal precursor and a magnetic additive in particulate form. The magnetic additive in particulate form could be applied to the particle to form the particulate material in a pre-treatment step.

For instance, the deposition of the magnetic additive on the particulate material may be carried out in a pre-treatment step prior to the electroless plating step which co-deposits metal and particulate material onto the substrate. The pre-treatment may comprise at least the steps of providing a particle or plurality of particles to form the particulate material, contacting the particles with an electroless plating solution comprising a reducing agent, a metal precursor and a magnetic additive in particulate form and electrolessly plating metal from the metal precursor on the particles to form the particulate material, thereby co-depositing the magnetic additive in particulate form to provide a particulate material.

The inclusion of a magnetic additive in the particulate material is beneficial when the particle forming the particulate material (i.e. without the magnetic additive) is not attracted to the magnetic field, or is insufficiently attracted to the magnetic field to provide an acceptable coating on the substrate. In this way, the particulate material may comprise a particle which is a non-magnetic material i.e. which is not attracted to a magnetic field, or a material which is repelled by a magnetic field, such as a diamagnetic material, and the advantages described herein may still be obtained if a magnetic additive is present. The quantity of magnetic additive in the particulate material should be sufficient to enhance the attraction of the particulate material to the magnetic field, for instance to

overcome the repulsion of a component which is repelled by a magnetic field, so that a net attraction to a magnetic field is exhibited by the particulate material.

5 The generation of a magnetic field around the substrate increases the concentration of the particulate material near the substrate relative to those portions of the electroless plating solution experiencing a weaker or no applied magnetic field. In this way, the magnetic field can vary the concentration of the particulate material at different points in the solution. This can not only increase the concentration of the particulate material near the substrate compared to the  
10 average concentration of the particulate material in the electroless plating solution, leading to improved particulate material deposition, but also efficiently replace the suspended particulate material removed by deposition in the solution near the substrate from the rest of the solution experiencing a weaker or no applied magnetic field.

15 Furthermore, because of the attraction of the particulate material to the magnetic field, the concentration of the particulate material in the magnetic field can be increased in proportion with an increase with the intensity of the magnetic field in the solution, enabling real time adjustment of the deposition  
20 rate.

In contrast, in the method of PCT/GB2008/003342 in which co-deposition of the particulate material with the metal onto the substrate leads to a localised reduction in the concentration of the particulate material in the solution  
25 adjacent to the substrate, compared to that of the bulk solution, the mixing of the electroless plating solution is the main mechanism for replacing the particulate material adjacent to the substrate.

30 In a further embodiment, the method disclosed herein can be used to apply a particulate material imparting an advantageous property to a substrate. For instance, wear, thermal or corrosion resistant particulate material can be

deposited in order to provide such properties to the substrate. The method can be used with metallic substrates, such as alloys like steel, in which the particulate material would provide a resistant coating. Certain substrates, such as steel, may require pre-treating prior to the electroless plating. For instance, a pre-treatment step such as etching to remove the oxide coating from the surface of a steel substrate can be carried out. This provides improved adhesion of the coated layer.

The substrate may be electrically conducting, e.g. an electrode or an interconnect, such as a metal or alloy, or the substrate may be electrically non-conducting (i.e. an electrical insulator), such as a ceramic.

The method described herein can be particularly useful in coating an electrode, an interconnect, a membrane filter, a pipe, a joint, particularly tubular joints, a valve body, a turbine blade, or other items having a complex shape in which the surface to be coated may not be easily accessible. Such substrates having resistant coatings may have applications in the oil and gas industries, aviation and automotive industries, power generation such as heat exchangers and other fields operating in extreme environments.

In a preferred embodiment, the method described herein can be carried out to a substrate, such as a pipeline, *in situ* i.e. after the substrate has been placed in position for use. For instance, a resistant coating may be applied to the internal surface of a pipe in a pipeline, by passing the electroless plating solution through the pipe while generating a magnetic field around the pipe, for instance by applying external magnets or electromagnets to the outer surface of the pipe. The external magnets or electromagnets generate a magnetic field around the pipe, attracting the particulate material to its inner surface.

The coating may also be applied to a polymeric substrate, particularly a polymer membrane. Polymer membranes are often used in ion exchange and water

treatment. They can degrade over time and the application of a coating comprising a wear-resistant particulate material using the method described herein may extend the working life of the polymer membrane. The method is particularly advantageous because the porosity of the coating can be carefully controlled by varying the deposition rate of the particulate material. In a further embodiment, the coating may be provided to a polymeric substrate to provide a printed circuit board.

The method described herein may also be applied in the field of electronics, to provide nanomaterial aligned structures. A particulate material as disclosed herein will inherently align along the magnetic field lines of the magnetic field generated around the substrate. This effect can lead to the control of the spatial positioning of the particulate material co-deposited on the substrate, and/or control the alignment of a magnetically anisotropic particulate material co-deposited on the substrate.

The method of the present invention utilises a plating solution to electrolessly deposit a metal onto the substrate. The plating solution comprises a reducing agent, a metal precursor and a suspension of a particulate material. The suspended particulate material is co-deposited with the metal on the substrate during the electroless plating method.

In one embodiment, the metal to be deposited is one or more selected from the group consisting of: nickel, cobalt, platinum, rhodium, ruthenium, rhenium and palladium, or an alloy of more than one of these metals. The metal preferably comprises nickel. The metal to be deposited is provided by a metal precursor in the plating solution. The metal precursor is preferably a metal salt, and should be soluble in the plating solution to provide free metal ions.

The particulate material may be selected from a wide variety of solids depending upon the desired function. The particulate material may have a particle size in

the range from 0.2 to 40 micrometers, particularly if the particulate material is deposited on a substrate for use in a fuel cell. The particular particle size will be dependent on the application and the fuel cell design.

5 Alternatively, and/or additionally, the electroless plating solution may comprise a further particulate material. The further particulate material may be a non-magnetic material which is not attracted to a magnetic field. Such non-magnetic further particulate material would not comprise a magnetic additive and could be deposited by entrainment with the plated metal, as described in  
10 PCT/GB2008/003342.

The particulate material may comprise a plurality of particulate materials. Similarly, the further particulate material may comprise a plurality of further particulate materials. The particulate material and/or the further particulate  
15 material may comprise one or more of the group selected from a surfactant, a pore former, a lubricant, a smart material, a wear resistant material, a corrosion resistant material, a heat resistant material, an anti-microbial additive and a fuel cell electrode material. As discussed above, if the chosen material is not inherently attracted to a magnetic field, a magnetic additive may be added to  
20 provide the particulate material.

A surfactant deposited on the substrate as part of the electroless plating method may be used to improve the ceramic to metal ratio in the coating and also as a pore former. The coated substrate comprising deposited surfactant in the  
25 coating can be subjected, after the plating method, to a heating step in which the surfactant is burned off to form pores in the coating.

Apart from surfactants, other pore formers, such as graphite, may be present in the electroless plating solution. The pore former may be deposited on the  
30 substrate as part of the coating, by entrainment with the plated metal and is then removed. The removal process may be a heating operation to burn off the pore

former. In an alternative embodiment, the pore former may be a biocide which degrades over time to form pores in the parts of the coating which it previously occupied. The pore former may also be a polymer. In the case of polar polymers, these may be deposited on the substrate by electrostatic deposition. Under  
5 electrostatic deposition, the polar polymers deposit in alignment with an applied electrostatic field, and can subsequently be removed to form the pores in the coating, for instance by heating to burn off the polymers.

A lubricant may be present as a lubricant particle, such as a particle of  
10 polytetrafluoroethylene (PTFE). Such lubricant particles can provide a smooth surface to the coating, and may improve fluid flow over the coated surface of the substrate.

A smart material may be present in the electroless plating solution to impart  
15 particular properties to the coating on the substrate. For instance, the smart material may respond to light, heat, especially temperature, or other physical inputs to provide a smart coating on the substrate.

A wear, corrosion and/or temperature resistant material may be provided in the  
20 plating solution.

An anti-microbial additive may be present as an anti-microbial particle. Such  
particles may be provided as a soluble glass, which can dissolve out of the  
coating over time, when the coating is in contact with a suitable solvent, to  
25 produce pores in the coating.

The particulate material may be an electrode material, such as a SOFC electrode  
material. The particulate material may be a ceramic. The electrode material  
may be selected from one or more of the group comprising yttria stabilised  
30 zirconia (YSZ), ceria stabilised zirconia (CeSZ), cerium gadolinium oxide (CGO),  
samarium-doped ceria (SDC), lanthanum nickel ferrite (LNF) and mixed

lanthanum and gallium oxides. CeSZ, CGO, LNF and SDC are all particulate materials which are attracted to a magnetic field. YSZ and mixed lanthanum and gallium oxides are not attracted to a magnetic field and would therefore require the presence of a magnetic additive to be used as a particulate material. The co-deposition of the metal and the particulate material on the substrate can form the anode of the fuel cell.

The particulate material co-deposited with the metal can be lanthanum strontium manganite (LSM). The co-deposition of the metal and LSM particulate material on the substrate can form the cathode of the fuel cell. LSM is a preferred particulate material because it is attracted to a magnetic field. In particular, LSM is ferromagnetic at temperatures below 320 K. Consequently, LSM does not require the addition of a magnetic additive.

Should the inclusion of a magnetic additive in the particulate material be required, this may be provided within the particles forming the particulate material and/or as a coating on the particles. In one embodiment, if the magnetic additive is provided as a coating, it may be a partial coating to ensure that the 3-phase boundary required of the electrode is not lost, as would occur by fully coating the surface of the particles forming the particulate material. A partial coating can be achieved by partially masking the surface of the particles forming the particulate material, prior to depositing the magnetic additive as a coating. In this particular context, the term 'partially masking the surface of the particle' means masking less than 100% of the surface area of a particle, preferably in the range of from 25 to 75% of the surface area of a particle. Where the mask is present on the surface of the particle, coating of the magnetic additive is prevented. After coating of the magnetic additive on the unmasked areas of the surface of the particles forming the particulate material, the mask can then be removed to uncover the surface of the particles of the particulate material.

For instance, the mask may be applied to the particulate material during a pre-treatment step. If the magnetic additive is applied using an electroless plating method, such as a method discussed herein, a partial mask can be applied to the particles prior to contacting them with an electroless plating solution.

5 Preferably the partial mask is applied at the activation step during pre-treating of the particles.

It is preferred that the magnetic additive is not distributed uniformly throughout the particulate material. This allows the retention of the 3-phase boundary by  
10 ensuring that not all of the surface of the particulate material is composed of magnetic additive. This can be achieved by mixing the magnetic additive or a precursor thereof with the other components of the particulate material prior to particulate formation. The magnetic additive may be added as a precursor of the magnetic additive as long as this is transformed into the magnetic additive as  
15 part of the process of forming the particulate material.

A further particulate material, which does not comprise a magnetic additive, can be added to the electroless plating solution to provide the coated substrate in addition to the particulate material discussed above. If the further particulate  
20 material is an electrode material, it can be deposited on the substrate with the metal and particulate material as part of the plating process. This would provide regions of 3-phase boundary in the substrate coating, particularly when plated in combination with particulate material comprising a coating of magnetic additive.

25 The substrate may form the electrolyte or the interconnect of the fuel cell. Forming the electrode directly on the electrolyte or the interconnect simplifies the construction of the fuel cell. It is therefore preferred that the substrate is a continuous substrate, such as a monolith, rather than a particulate substrate. The substrate can take any shape. For example, it may be planar to conform to  
30 planar SOFC design, or it may be cylindrical to conform to tubular SOFC design.

In one embodiment, the substrate is selected from the group comprising lanthanum chromate, doped lanthanum chromate, doped lanthanum gallate, lanthanum manganate, doped lanthanum manganate, yttria stabilised zirconia (YSZ), ceria stabilised zirconia (CeSZ), cerium gadolinium oxide, samarium-doped ceria, lanthanum nickel ferrite and mixed lanthanum and gallium oxides. Alternatively the substrate may be a metallic substrate such as chromium-based, iron-based and/or nickel-based alloys or the substrate may be a polymeric substrate depending on the fuel cell design. Lanthanum chromate, doped lanthanum chromate, lanthanum manganate and doped lanthanum manganate are suitable substrate materials for the interconnect of the fuel cell. Yttria stabilised zirconia (YSZ), ceria stabilised zirconia (CeSZ), cerium gadolinium oxide, samarium-doped ceria and mixed lanthanum and gallium oxides are suitable substrate materials for the electrolyte of the fuel cell.

The reducing agent in the electroless plating solution should be capable of causing the reduction of the metal in the metal precursor to metal. It is preferred that the reducing agent comprises hypophosphite, but alternatives may be used depending on the metal to be deposited. The hypophosphite is preferably a hypophosphite salt, such as sodium hypophosphite.

The electroless plating solution also comprises a solvent. The solvent should be capable of dissolving the reducing agent and metal precursor. It is preferred that the solvent is water.

The electroless plating solution may further comprise a surfactant to assist in keeping the particulate material and any further particulate material in suspension in the plating solution.

In a further embodiment, the electroless plating solution is dosed with one or more of the group selected of: the particulate material, any further particulate material, the metal precursor and the reducing agent during the plating step.

In another embodiment, the concentration of one or more of the group selected of: the particulate material, any further particulate material, the metal precursor and the reducing agent in the plating solution is varied during the plating step.

5 In a further embodiment, the method of the invention comprises the step of pre-treating the substrate prior to the contacting step. The pre-treating step may comprise one or more steps selected from the group consisting of: degreasing, electrocleaning, etching, masking, activating and rinsing.

10 When the pre-treating step is an activating step, this may comprise depositing an electroless plating catalyst on the substrate. Preferably the electroless plating catalyst is palladium. The activating step may further comprise the step of sensitizing the substrate prior to or at the same time as the deposition of the electroless plating catalyst. This is particularly beneficial in those cases where  
15 the substrate is non-conducting, for instance when the substrate is the fuel cell electrolyte such as YSZ. The sensitizing step preferably comprises treating the substrate with a tin (II) chloride solution.

As the electroless plating process proceeds, a metallic element such as nickel is  
20 deposited on the substrate. This deposition can impart electrical conductivity to the coating. In a further aspect of the present invention, an electroplating step may be carried out when sufficient metal has been deposited on the substrate to provide an electrically conducting coating. A thickness of as little as 2 micrometers of the electrolessly plated metal coating on the substrate can  
25 provide sufficient conductivity for electroplating to then be carried out. Electroplating occurs at a higher rate than electroless plating and can therefore be used to increase the rate of deposition of the metal on the substrate after electroless plating has been used to provide an initial metal coating.

30 Embodiments of the invention will now be described by way of example only, and with reference to the accompanying non-limiting drawings.

Figure 1 shows an image of a coated substrate prepared by an electroless deposition process without the generation of a magnetic field;

5 Figure 2 shows a scanning electron micrograph of the surface of a coated substrate prepared by an electroless deposition process without the generation of a magnetic field;

10 Figure 3 shows an energy dispersive X-ray analysis spectrum of the highlighted area of the coated substrate shown in the micrograph of Figure 2;

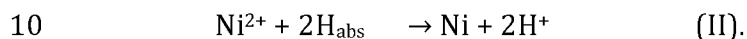
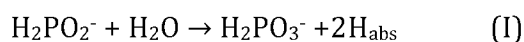
Figure 4 shows an image of a coated substrate and support wire prepared by an electroless deposition process carried out in a generated magnetic field;

15 Figure 5 shows an image of a coated substrate prepared by an electroless deposition process carried out in a generated magnetic field in which the support wire has been removed; and

20 Figure 6 shows the experimental set-up involving the generation of a magnetic field in the electroless co-deposition process.

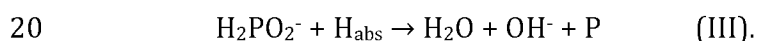
Electroless metal deposition refers to the chemical plating of a metal such as nickel, iron, copper or cobalt onto a substrate by chemical reduction in the absence of external electric current. Known electroless plating solutions generally comprise a metal precursor, such as a source of metal ions, and a  
25 reducing agent dissolved in a solvent. The solvent is typically water. The electroless plating solution may further comprise a buffer to provide the required solution pH and a complexing agent for the metal ions capable of preventing their precipitation from solution. Other additives such as stabilizers, brighteners, alloying agents, surfactants may also be present in the plating  
30 solution.

The metal deposition involves the reduction of the metal ions to the metallic form by the action of a reducing agent itself or a derivative of the reducing agent. The reducing agent may be a hypophosphite, an amine borane or a borohydride. Once initiated, deposition is autocatalysed by the metal deposited on the surface of the substrate. For example, nickel may be deposited onto a substrate from an aqueous solution of a nickel (II) and hypophosphite ions according to the following reactions:

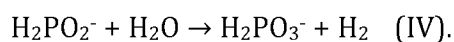


In this embodiment, the reaction product of the hypophosphite and water (absorbed hydrogen,  $\text{H}_{\text{abs}}$ ) reacts with the nickel (II) in the solution, rather than the reducing agent itself. It is preferred that the metal precursor is nickel (II) chloride. It is further preferred that the reducing agent is sodium hypophosphite. The solvent can be water.

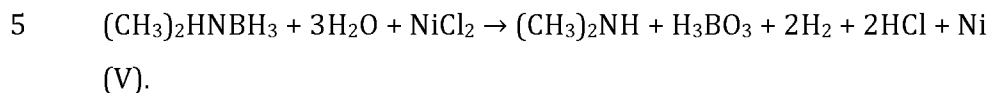
Concurrently, some of the hypophosphite may react with the absorbed hydrogen to deposit phosphorous onto the substrate, and produce water and hydroxyl ions as shown in reaction (III):



As a result, phosphorus may also be deposited with the nickel, forming a phosphorus alloy. Such deposits typically contain 2-14% by weight phosphorous, depending upon the precise nature of the plating solution. In addition to reaction (III), some of the hypophosphite may be oxidised by water to form phosphite with the liberation of gaseous hydrogen as shown in reaction (IV):



In an alternative embodiment, an amine borane may be used as the reducing agent. For example, the reduction of nickel (II) chloride by dimethylamine borane is shown in equation (V):



Depending upon the electroless plating bath conditions and bath composition, the conductive metal can be plated as either an amorphous or a crystalline metal.

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In the present invention, a suspension of a particulate material is also present in the plating solution. The particulate material has the property of being attracted to a magnetic field. The generation of a magnetic field around the substrate attracts the particulate material to the field and thereby the substrate, increasing the concentration of the particulate material near the substrate. The deposition of the nickel entrains the particulate material suspended in the plating solution resulting in the deposition of the particulate material with the nickel on the substrate. Agitation of the solution, for instance using a rotary stirrer, can aid in the mixing of the particulate material. It is preferred that magnetic stirring means is not used, as this may interfere with the magnetic field generated around the substrate to attract the particulate material.

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The magnetic field may be generated from a permanent magnet, such as a rare earth magnet, or from an electromagnet. The use of an electromagnet provides the advantage that the intensity of the magnetic field can be varied in proportion to the current flowing in the electromagnet. In some cases, the magnetic field may be intensified by the substrate itself, particularly if this is a ferromagnetic material.

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The magnetic field may produce graduated and/or directional growth of the deposited particulate material on the substrate because of the particulate

material's interaction with the field. In particular, deposition of the particulate material may follow the lines of magnetic flux, which is proportional to the number of lines of magnetic field on a surface. This can produce a coated substrate with anisotropic properties. For instance, conducting pathways of the deposited metal may be produced extending outwards from the substrate as the coating develops.

The deposited nickel and particulate material have an even uniform thickness, even in deep pores and recesses. The uniformity of the coating reproduces the substrate surface finish, which can be roughened to increase its surface area. This also means that the coating can be applied as a final production operation and can meet stringent dimensional tolerances.

It is apparent that as the plating step proceeds, the concentration of metal precursor, reducing agent, particulate material and any further particulate material in the plating solution will decrease as these components are consumed. Consequently, one or more of these components may be added to the plating solution during the plating step. The component may be added to the plating solution at regular or irregular intervals, or continuously. The component is preferably added in the solvent used for the plating solution.

The amount of any component added to the plating solution during the plating step may be sufficient to maintain the component at a given average concentration, such as the concentration at the start of the plating step. Alternatively, the amount of any component added to the plating solution during the plating step may be varied, or the time interval at which the component is added may be varied in order to adjust the concentration of the component at a particular depth in the co-deposited coating.

For instance, the concentration of the particulate material co-deposited with the metal may be greatest at the start of the plating step such that the proportion of

co-deposited particulate material to metal is greatest nearest to the substrate. In this case, if the coefficient of thermal expansion (CTE) of the particulate material and substrate are similar, for instance if both the substrate and particulate material comprise YSZ, the CTE of the coating adjacent to the substrate can be more closely matched to the substrate to minimise thermal stresses during cycling and operation. In this case, a magnetic additive is required to be added to the YSZ to provide a particulate material which is attracted to the magnetic field. The proportion of the metal co-deposited with the particulate material can be increased in the regions of the coating further from the substrate to provide the requisite electrical conductivity to the anode.

Furthermore, increasing the strength of the magnetic field can increase the concentration of particulate material drawn to the substrate, thereby altering the concentration of the particulate material deposited. This can also be used to compensate for a decrease in the total concentration of particulate material in the plating solution as plating progresses.

The plating step is typically carried out by immersing the substrate in a plating bath comprising the plating solution. In the embodiment in which nickel is to be plated from an aqueous plating solution, the plating bath is typically heated. It is preferred that the plating bath is heated to a temperature in the range of 80 to 100°C, more preferably 85 to 95°C, most preferably about 90°C to provide an optimum rate of deposition.

Alternatively, the plating step may be carried out by contacting only a part of the substrate with the plating solution, for example by immersing only a portion of the substrate in the plating solution.

Prior to carrying out the electroless plating step, one or more pre-treatment steps may be carried out. It is preferred that the substrate is degreased prior to

electroless plating, in either aqueous or non-aqueous cleaners utilising either ultrasonic or soak processes.

5 If the substrate is a conducting substrate, it can be electrocleaned by methods known in the art.

10 In another embodiment, only a part of the substrate is contacted with the plating solution by applying a mask, such as those known in the art of etching, to the substrate in a pre-treatment step. Consequently, the metal and particulate material is only co-deposited in those areas of the substrate not covered by the mask.

15 The operating properties of a fuel cell anode are closely related to the surface texture. In order to improve the efficiency of an anode, it should have a larger surface area to increase the rate of reaction. The surface area of the anode may be increased by one or both of providing a rougher surface texture and increasing porosity. Combining both of these methods allow the maximisation of the anode surface area to provide efficient reaction kinetics.

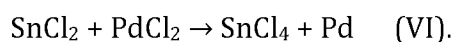
20 As discussed above, the co-deposited coating has a uniform thickness, even in deep pores and recesses. Therefore, the surface area of the anode may be increased by one or both of roughening the surface and increasing the porosity of the substrate. This can be achieved by the etching of the substrate surface, for example by wet-phase or dry-phase techniques.

25 Wet-phase etching utilises a liquid etchant, which may be agitated to achieve good process control. For example, solutions comprising one or both of sulphuric and hydrofluoric acid can be used to etch a YSZ substrate.

30 Dry-phase etching utilises a plasma or ion stream to remove the surface of the substrate. Plasma etching produces energetic free radicals which are neutrally

charged and react with and remove the surface of the substrate. Sputter etching bombards the substrate with a stream of energetic ions, typically of noble gasses, which knock atoms from the substrate surface. Alternatively abrasive blasting techniques may be employed to abrade the surface by utilising compressed air and abrasive media.

In order to initiate electroless plating on an insulating substrate, it is necessary to activate the substrate surface. This can be done by a sensitizing and catalysing process. Typically, palladium metal is employed as a catalyst. The catalyst allows the metal plating to proceed as an autocatalytic reaction, without the requirement of an external electrical current source. Palladium particles can be deposited on the insulator surface in a single, double or multi-step process. In the single-step process, the insulating substrate can be treated with a mixed acidic solution of  $\text{SnCl}_2$  and  $\text{PdCl}_2$  in the form of a hydrosol to deposit palladium in accordance with reaction (VI):



The metallic Pd is in colloidal form and is adsorbed onto the substrate surface. The adsorbed colloidal Pd particles act as a catalyst for the metal deposition during subsequent metal plating.

Alternatively, the insulating substrate can be consecutively sensitized with an acidified  $\text{SnCl}_2$  solution and then catalysed with a  $\text{PdCl}_2$  solution in a double-step process, with an optional intervening rinsing step. Substrate surface activation can be omitted if the substrate is a conducting substrate.

A further advantage of the method of the present invention is that the metal and particulate material can be co-deposited on insulating as well as conducting substrates, provided that any insulating substrate is activated as discussed above.

It is preferred that the substrate is rinsed between one or more of the pre-treating steps, or between the pre-treating and plating steps. Rinsing removes any residual contaminants from the pre-treating steps, providing a clean surface for the plating step. Rinsing may be carried out with a suitable analytical reagent grade solvent, or high purity deionised water.

Electroless plating, particularly with nickel, provides excellent corrosion, wear and abrasion resistance, ductility, lubricity, electrical properties, hardness and solderability.

The thickness of metal coating applied by electroless plating is dependent upon the time the substrate is immersed in the plating bath. A deposition rate of 16-20  $\mu\text{m}$  per hour is typical for a nickel plating process.

In order to show that the ceramic-metal ratio in a composite deposited on a substrate could be increased by the presence of a magnetic field, two coated substrates were prepared. The first – the control - was subjected to electroless co-deposition of nickel and yttria stabilised zirconia particulate material onto an alumina tile substrate. No magnetic field was applied during the co-deposition. The second involved the co-deposition of nickel and cobalt-coated yttria stabilised zirconia particulate material onto an identical alumina tile substrate similar bath conditions. A magnetic field was applied during the second co-deposition.

**Comparative Example 1: Electroless co-deposition of nickel and yttria stabilised zirconia onto an alumina substrate without generation of a magnetic field**

An alumina tile substrate (Unitec Ceramics Ltd) was suspended in 200ml of Cuprolite® solution (Alfachimici srl.), an alkaline cleaning agent, for 15 minutes

at 60°C in order to clean the substrate. The tile was then removed from the cleaning solution and dried.

5 The cleaned alumina tile substrate was then placed in a pre-catalyst solution of anhydrous stannous chloride (obtained from Schloetter Company Limited and manufactured by Alfachimici srl.) for 15 minutes at room temperature to sensitise the surface of the substrate. The sensitised substrate was then removed from the pre-catalyst solution.

10 The sensitised substrate was then suspended in a catalyst solution containing anhydrous palladium chloride (obtained from Schloetter Company Ltd and manufactured by Alfachimici srl.) for 15 minutes at 35°C. The substrate containing catalyst was separated from the catalyst solution by filtration and dried in an oven for 10 minutes at 80°C.

15 The dry substrate containing catalyst was then suspended in an electroless cobalt plating solution comprising Cobalt Chloride (Sigma-Aldrich Ltd), Sodium Hypophosphite (Sigma-Aldrich Ltd), Sodium Citrate (Sigma-Aldrich Ltd), Ammonium Chloride (Sigma-Aldrich Ltd) and 1L De-ionised Water to which  
20 was added 2 micrometer diameter YSZ powder (Unitec Ceramics Ltd). The resulting mixture had a pH of around 4.5. The pH of the mixture was then raised to 9.5 by the addition of ammonium hydroxide (Sigma-Aldrich Ltd) in order to initiate the electroless plating under the conditions shown in Table 1. During the electroless plating, the temperature was kept between 93 and 97°C for 45  
25 minutes and the mixture was continuously agitated with a magnetic stirrer.

**Table 1 – Non-magnetic electroless plating set-up**

| Parameter                   |              |
|-----------------------------|--------------|
| Bath loading                | 5g per 150ml |
| Agitation                   | 400rpm       |
| Electroless Deposition Time | 45 minutes   |
| YSZ Particle Size           | 2 micrometer |

An image of the control coated substrate is shown in Figure 1. Its surface was then analysed using a Cambridge S-90 scanning electron microscope (SEM) and an Oxford Instruments INCA Energy Dispersive X-Ray (EDX) analysis to determine concentrations of various elements. The elemental concentration was determined as the average value from 4 different sites on the surface of the substrate and provided the results shown in Table 2.

**Table 2 - Nickel/YSZ electroless co-deposition results**

| Element   | Weight% | Atomic% |
|-----------|---------|---------|
| Oxygen    | 06.45   | 22.18   |
| Nickel    | 68.75   | 63.28   |
| Yttrium   | 03.88   | 02.38   |
| Zirconium | 20.72   | 12.17   |

This plating showed a metal to ceramic ratio (by atomic %) of approximately 60:40, which is representative of the ceramic rate achievable without the generation of a magnetic field.

#### **Example 2: Electroless co-deposition of nickel and cobalt/yttria stabilised zirconia onto an alumina substrate in a generated magnetic field**

In order to compare the effect of a magnetic field on the co-deposition process, the YSZ particulate material was first electrolessly deposited with ferromagnetic

cobalt to provide a cobalt/YSZ particulate material which is attracted to a magnetic field. The cobalt deposition was carried out using the same electroless deposition method as described in Comparative Example 1.

5     Preparation of cobalt/YSZ particulate material

Ten grams of YSZ powder (Unitec Ceramics Ltd) was cleaned in a solution of Cuprolite® solution (Alfachimici srl.) for 15 minutes at 60°C as described for Comparative Example 1. The powder and solution were then filtered through a  
10     Buchner funnel under vacuum to separate the cleaned YSZ powder. The cleaned YSZ powder was then placed in a pre-catalyst solution of anhydrous stannous chloride (obtained from Schloetter Company Limited and manufactured by Alfachimici srl.) for 15 minutes at room temperature to sensitise the surface of the particulates. The sensitised particulates were then separated from the pre-  
15     catalyst solution by filtration with a Buchner funnel under vacuum.

The white sensitised particulates were then mixed into a catalyst solution containing anhydrous palladium chloride - obtained from Schloetter Company Ltd and manufactured by Alfachimici srl. - for 15 minutes at 35°C. The  
20     particulate containing catalyst was separated from the catalyst solution by filtration to reveal a brown powder which was then dried in an oven for 10 minutes at 80°C.

The dry particulate material containing catalyst was then added into an  
25     electroless cobalt plating solution prepared and treated as described in Comparative Example 1, and the electroless plating carried out under the conditions of Table 1.

The plated YSZ particulate material was black in colour and evidently magnetic  
30     because it was attracted to the magnetic stirrer and had to be rinsed off with de-ionised water prior to separation from the solution by filtration. The particulate

material was then dried in an oven for 1 hour at 80°C and analysed using a Cambridge S-90 scanning electron microscope (SEM) and Oxford Instruments INCA Energy Dispersive X-Ray (EDX) analysis.

5 Figure 2 shows a scanning electron micrograph of the surface of the cobalt-deposited YSZ particulate material. The area highlighted in the micrograph is that selected for the SEM analysis. Figure 3 shows the EDX spectrum from the highlighted area of the micrograph of Figure 2, in which the presence of cobalt on the surface of the YSZ particulate material can be seen.

10

Co-deposition of nickel and Co/YSZ particulate material on an alumina substrate in a generated magnetic field

The cobalt-deposited particulate material (2 g) was then used as a co-deposit with nickel onto an alumina tile substrate. The substrate was pre-treated as described in Comparative Example 1 and then suspended by a steel support wire in a 100 ml electroless nickel plating bath comprising the Co-deposited YSZ particulate material. The nickel plating bath was prepared and treated as described in Comparative Example 1. A magnetic field having a magnetic field strength of 65 millitesla was generated around the substrate. The process was similar to the non-magnetic co-deposition of Comparative Example 1 with the main difference being the addition of the magnetic field and the use of cobalt-deposited particulate material. The experimental set-up is shown in Figure 6.

25 After 45 minutes, the alumina tile substrate was removed from the bath. Figure 4 shows an image of the coated substrate and steel support wire. The darker areas of the tile indicate increased deposition of the Co-deposited YSZ particulate material and correspond to those areas of the tile substrate nearest the steel support wire. This implies that the wire itself had become magnetised and that there had been increased attraction of the cobalt-coated powder to those locations.

30

EDX analysis on non-wire contacting areas near to the wire was carried out and the results are shown in Table 3.

5 Table 3 confirms that electroless plating in a generated magnetic field was successful in reducing the relative proportion of Nickel with respect to the co-deposited particulate material (the co-deposited YSZ). The generation of a magnetic field around the substrate during electroless plating changed the Ni to particulate material ratio from approximately 60:40 to approximately 50:50 atomic%. Thus, the presence of a magnetic field increased the particulate  
10 material to metal ratio (atomic%) of electrolessly co-deposited coatings.

**Table 3** EDXA results for non-wire contacting areas

| Element | Transition | Weight % | Atomic % |
|---------|------------|----------|----------|
| O       | K          | 12.35    | 34.76    |
| Y       | L          | 1.82     | 0.93     |
| Ni      | K          | 65.66    | 50.45    |
| Zr      | L          | 16.07    | 8.01     |
| P       | K          | 4.06     | 5.86     |

15 The person skilled in the art will understand that the invention can be carried out in many various ways without departing from the scope of the appended claims. For instance, the invention encompasses the combination of one or more of the optional or preferred features disclosed herein.

**CLAIMS**

1. A method for the manufacture of a coated substrate, the method comprising at least the steps of:
  - providing a substrate;
  - contacting at least a part of the substrate with an electroless plating solution comprising a reducing agent, a metal precursor and a suspension of particulate material, wherein said particulate material is attracted to a magnetic field;
  - generating a magnetic field around the substrate; and
  - electrolessly plating metal from the metal precursor onto the contacted part of the substrate, thereby co-depositing the particulate material on the contacted part of the substrate to provide a coated substrate.
2. The method of claim 1 wherein the particulate material is chosen from one or more of the group selected from a paramagnetic material, a ferromagnetic material and a ferrimagnetic material.
3. The method of claim 2 wherein the particulate material is one or more of the group selected from a surfactant, a pore former, a lubricant (e.g. PTFE), a smart material, a wear resistant material (e.g. silicon carbide), a corrosion resistant material (e.g. aluminium oxide), a heat resistant material (e.g. YSZ), an anti-microbial additive and an electrode material.
4. The method of claim 3 wherein the particulate material is lanthanum strontium manganite.
5. The method of claim 1 or claim 2 wherein the particulate material comprises a magnetic additive which is attracted to a magnetic field.
6. The method of claim 5 wherein, prior to the step of contacting the substrate with an electroless plating solution, the steps of:

- depositing a magnetic additive onto a particle to provide the particulate material; and
  - forming an electroless plating solution with the particulate material, a reducing agent and a metal precursor.
7. The method of claim 4 wherein the magnetic component is nickel or cobalt.
8. The method of claim 5, claim 6 or claim 7 wherein the particulate material is selected from one or more of the group comprising yttria stabilised zirconia (YSZ), ceria stabilised zirconia (CeSZ), cerium gadolinium oxide, samarium-doped ceria, lanthanum nickel ferrite and mixed oxide of lanthanum and gallium.
9. The method one or more of the preceding claims wherein the magnetic field is one or both of a permanent magnetic field and an electromagnetic field.
10. The method of one or more of the preceding claims wherein the metal from the metal precursor is selected from one or more of the group consisting of: nickel, cobalt, platinum, rhodium, ruthenium, rhenium, copper and palladium.
11. The method of one or more of the preceding claims wherein the substrate is selected from the group comprising: a polymer, a metal, a metal alloy, lanthanum chromate, doped lanthanum chromate, doped lanthanum gallate, lanthanum manganate, doped lanthanum manganate, yttria stabilised zirconia (YSZ), ceria stabilised zirconia (CeSZ), cerium gadolinium oxide, samarium-doped ceria, lanthanum nickel ferrite and mixed lanthanum and gallium oxides.
12. The method of one or more of the preceding claims wherein the coated substrate is selected from the group comprising an electrode, an

interconnect, a membrane filter, a pipe, a valve body, a turbine blade and a joint.

13. The method of one or more of the preceding claims wherein the reducing agent comprises hypophosphite and/or formaldehyde.
14. The method of one or more of the preceding claims wherein the plating solution is dosed with one or more of the group comprising the reducing agent, the metal precursor, the particulate material and a further particulate material during the plating step.
15. The method of claim 14 wherein the concentration of one or more of the group consisting of: the reducing agent, the particulate material and the metal precursor in the plating solution is varied during the plating step.
16. The method of one or more of the preceding claims further comprising the step of pre-treating the substrate prior to the contacting step.
17. The method of claim 65 wherein the pre-treating comprises one or more steps selected from the group comprising degreasing, electrocleaning, etching, masking, activating and rinsing.
18. The method of claim 17 wherein the activating step comprises depositing an electroless plating catalyst on the substrate.
19. The method of claim 18 wherein the electroless plating catalyst is palladium.
20. The method of claim 18 or claim 19 further comprising the step of sensitizing the substrate prior to or at the same time as the deposition of the electroless plating catalyst.

21. The method of claim 20 wherein the sensitizing step comprises treating the substrate with a tin (II) chloride solution.
22. The method of claim 3, wherein said pore former is a surfactant which increases the ceramic to metal ratio in the deposit.
23. The method of claim 22, wherein once deposited said surfactant is subsequently dissolved or burned-off.
24. A coated substrate obtainable by the method of any one of claims 1 to 23.

1/4

Figure 1

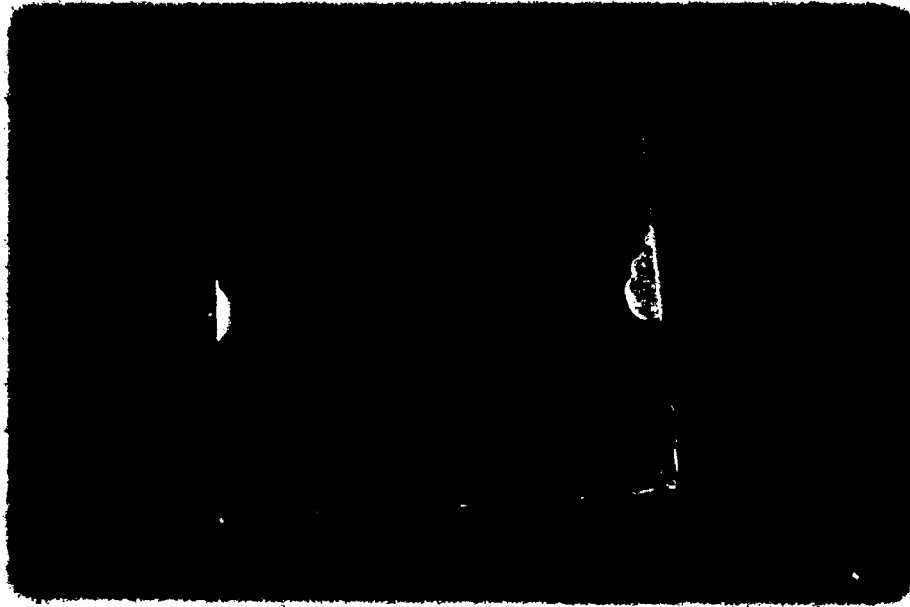
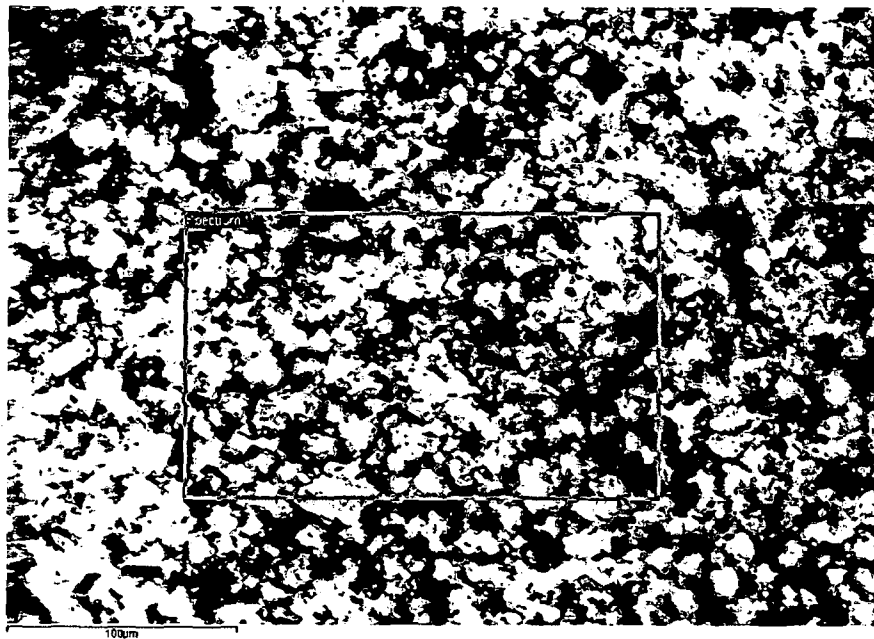
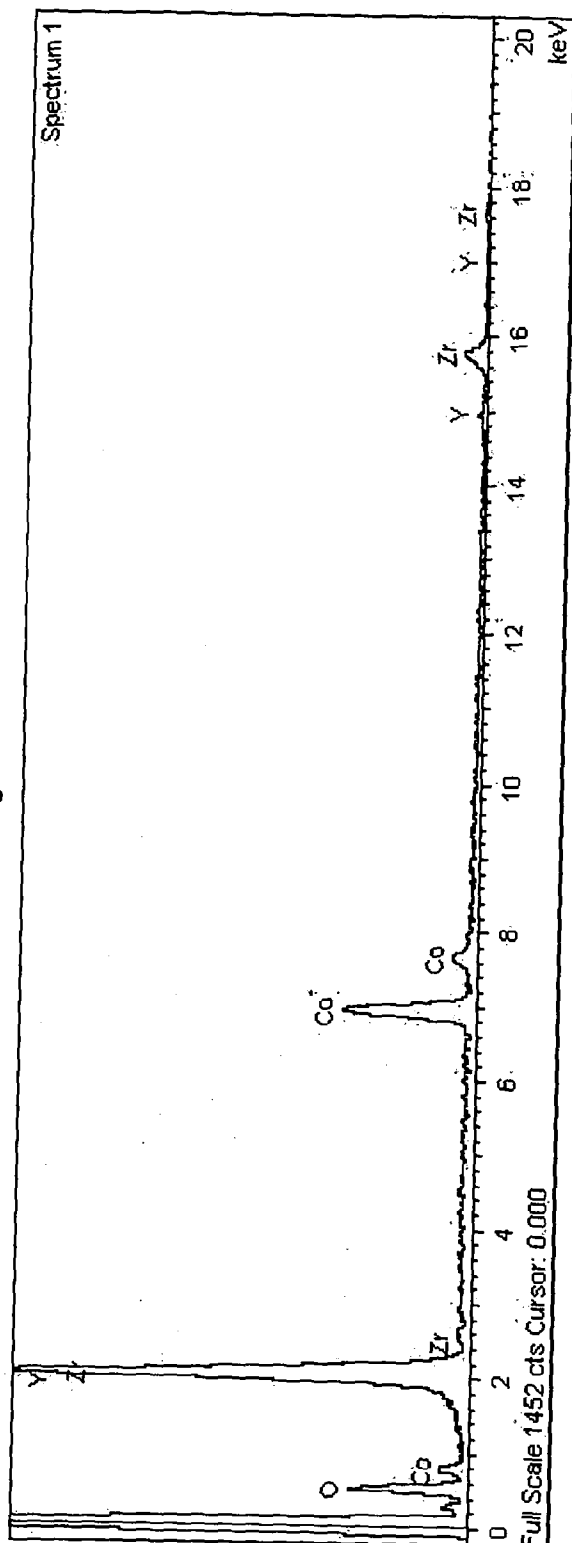


Figure 2



2/4

Figure 3

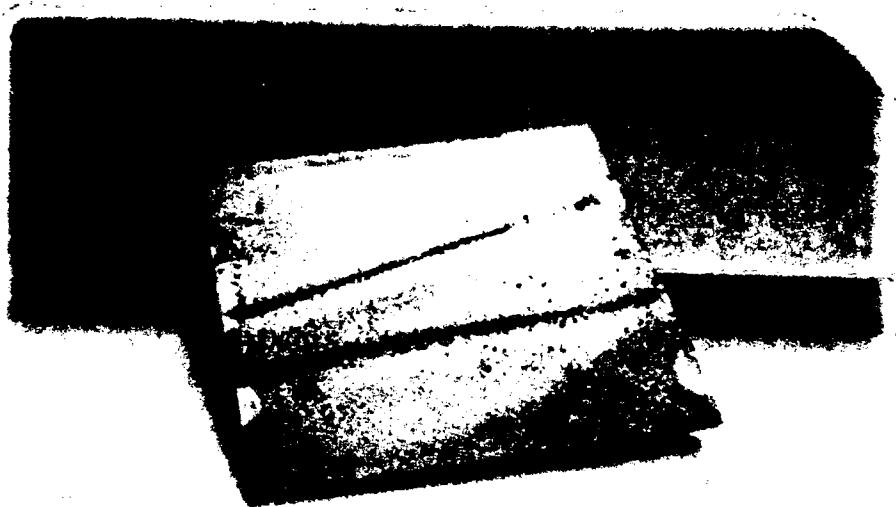


3/4

Figure 4

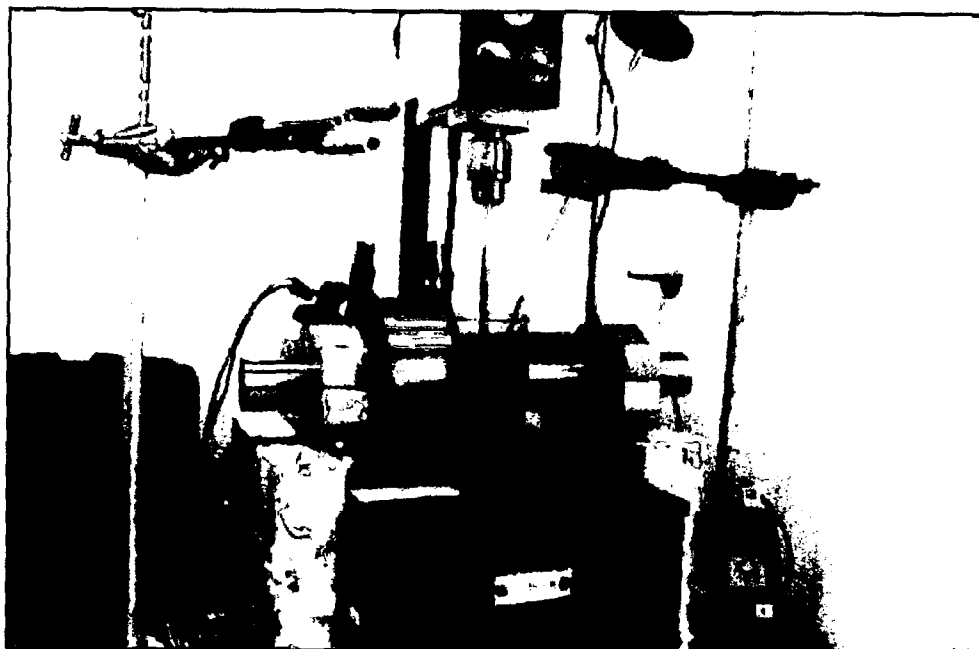


Figure 5



4/4

Figure 6



## INTERNATIONAL SEARCH REPORT

International application No  
PCT/GB2013/050496

A. CLASSIFICATION OF SUBJECT MATTER  
INV. C23C18/16 H01M4/88 C23C18/18  
ADD.

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)  
C23C H01M

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)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                                                      | Relevant to claim No. |
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| A         | abstract<br>paragraph [0002]<br>figure 1<br>paragraph [0004]<br><br>-----<br><br>-/--                                                                                                                                                                                                                                   | 1-23                  |



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

17 May 2013

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European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040,  
Fax: (+31-70) 340-3016

Authorized officer

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## INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2013/050496

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                                                                              | Relevant to claim No. |
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| A         | abstract<br>figure 1<br>paragraph [0004]                                                                                                                                                                                                                                                                                                        | 1-23                  |
| A         | -----<br>WO 2009/044144 A2 (COURT OF NAPIER<br>UNIVERSITY [GB]; WAUGH WILLIAM JOHN [GB];<br>DAVIDSON ALA) 9 April 2009 (2009-04-09)<br>abstract<br>example 1<br>claims<br>-----                                                                                                                                                                 | 1-24                  |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2013/050496

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
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