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(57) Abstract: A method of producing graphene on a metallic substrate, the method comprising (i) depositing a layer of carbon barrier material on a metallic substrate, (ii) depositing a layer of chemical vapour deposition (CVD) catalyst on the layer of carbon barrier material, and (iii) forming graphene on the layer of CVD catalyst by CVD.



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GRAPHENE COATING

FIELD OF THE INVENTION

- 5 The present invention relates generally to methods of producing graphene on a metallic substrate, and specifically to methods of producing graphene on a metallic substrate by chemical vapour deposition (CVD), and so formed layered composites.

BACKGROUND OF THE INVENTION

10

The reliability and long-term durability of metallic components is critical in many industrial sectors, such as aerospace, marine, transportation, construction, energy, and manufacturing. Protecting metallic substrates from corrosion is therefore vital to ensure useful component and system lifetimes, thus preventing economic loss and mechanical failure, while reducing
15 negative impact on the environment.

A well-established strategy for corrosion mitigation is to apply coatings on metallic substrates of interest. These may include barrier coatings or sacrificial coatings, and conventionally include metallic coatings, oxide coatings, and polymer coatings. However,
20 conventional coatings are use-specific, in that they must be engineered around the intended use of the substrate.

Efforts have therefore been made to develop alternative coating materials that are durable and ensure protection over a wide range of environmental conditions. However, there are
25 still several issues with existing coating methodologies that prevent the practical and large-scale implementation of alternative coatings for long term corrosion protection.

There remains therefore an opportunity to provide methods that can address and possibly ameliorate one or more problems associated with conventional corrosion prevention
30 methodologies.

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SUMMARY OF THE INVENTION

The present invention provides a method of producing graphene on a metallic substrate, the method comprising (i) depositing a layer of carbon barrier material on a metallic substrate,
5 (ii) depositing a layer of chemical vapour deposition (CVD) catalyst on the layer of carbon barrier material, and (iii) forming graphene on the layer of CVD catalyst by CVD.

Graphene, being highly impermeable to gases and chemically inert, is a promising candidate as a physical barrier to protect metallic substrate from corrosion under a wide range of
10 environmental conditions. High quality graphene is very challenging to grow on many commercially relevant metallic substrates, such as steel. For that reason, conventional procedures involve the initial formation of graphene on a suitable growth substrate and subsequent transfer of the preformed graphene on the metallic substrate of interest.

15 However, preformed graphene coatings only provide limited corrosion protection due to the inherent defects and discontinuities in the coatings, galvanic corrosion issues introduced by noble graphene, and/or direct corrosion attack at sites in which graphene has structural defects and discontinuities. In the context of conventional deposition procedures, that of the present invention can advantageously provide formation of high quality graphene on
20 metallic substrates of any shape and on a large scale. In that regard, each deposition step in the method of the invention ensures that the graphene which is ultimately formed on the metallic substrate can provide effective and durable corrosion protection.

For example, the deposition of a layer of carbon barrier material on the metallic substrate
25 provides a variety of benefits in the context of formation of graphene by CVD. In particular, presence of a layer of carbon barrier material minimises carbon diffusion away from the deposition area. This optimizes the amount of carbon available for graphene formation and improves control over the formation process.

30 Also, the layer of carbon barrier material impedes carbon diffusion into the metallic substrate during CVD. This is particularly advantageous when the metallic substrate is sensitive to

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carbon, as in the case of steel substrates. In those instances, presence of a layer of carbon barrier material prevents the modification of the carbon content in the metallic substrate during CVD. This advantageously ensures that the mechanical and chemical characteristics of the substrate are preserved.

5

In addition, the deposition of a layer of CVD catalyst can advantageously facilitate formation of multi-layer graphene, which can minimise the deleterious influence of defects in CVD graphene. Such layers have been shown to offer excellent protection due to low permeability to gas and ions.

10

In that context, the combined deposition of a layer of carbon barrier material and a layer of CVD catalyst offers an advantageous combination of the required degree of catalysis for graphene formation and suppression of carbon diffusion for substrate protection and controlled formation of graphene.

15

The method of the invention is particularly suitable for the development of graphene on metallic substrates on an industrial scale. To that effect, CVD can be adapted to promote formation of graphene on large areas. Also, since CVD is an omnidirectional process the method of the invention has the potential of being implemented in processes for the formation of protective layers of graphene on metallic substrates with complex shapes.

20

In addition, the combined use of a layer of carbon barrier material and a layer of CVD catalyst makes it advantageously possible to form graphene by CVD on metallic substrates that would not be otherwise suitable for use in CVD deposition of graphene. For example, the method of the invention is particularly advantageous for the provision of graphene by CVD on metallic substrates that have limited or no catalytic action towards hydrocarbon dissociation.

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In some embodiments, the metallic substrate comprises an engineering alloy, such as steel.

30

In those instances, the method of the invention is particularly advantageous to ensure durable

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corrosion mitigation for engineering alloys, such as steel, while preserving their desired characteristics of elasticity, strength, ductility, toughness, and resistance to fatigue.

In some embodiments, the carbon barrier material comprises copper. Copper is
5 advantageous in that it combines effective carbon barrier characteristics and, when the metallic substrate is an iron alloy such as steel, provides for a layer which thickness can be tailored to prevent iron diffusion from the substrate.

In some embodiments, the CVD catalyst comprises nickel. Nickel is a particularly effective
10 catalyst for hydrocarbon dissociation during CVD of graphene, and advantageously promotes formation of multi-layer graphene. Formation of multi-layer graphene is particularly advantageous in that it can negate the deleterious influence of defects in single layer graphene, which may compromise corrosion protection of the substrate. The discontinuities/uncovered areas in the single graphene layer can be masked by immediate
15 upper layers in multi-layer graphene, thus providing a more efficient surface coverage which accounts for an effective and durable corrosion resistance.

Overall, the method of the invention can be successful in achieving formation of graphene on a metallic substrate, which can confer the substrate with remarkable corrosion resistance.
20 The term "corrosion" is used herein in accordance to its broadest meaning of chemical alteration and/or degradation of a metallic material as a consequence of a reaction between the material and its environment. As such, the term encompasses degradation by chemical (for example electrochemical) oxidation. Thus, by "corrosion resistance" used herein in relation to a material is meant the ability of the material to resist the alteration and/or
25 degradation of its chemical structure as a consequence of a reaction between the material and its environment, which may include alteration or degradation by chemical (including electrochemical) oxidation.

Accordingly, the present invention may also be said to provide a method of improving
30 corrosion resistance of a metallic substrate by formation of graphene on the substrate, the method comprising (i) depositing a layer of carbon barrier material on a metallic substrate,

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(ii) depositing a layer of chemical vapour deposition (CVD) catalyst on the layer of carbon barrier material, and (iii) forming graphene on the layer of CVD catalyst by CVD, wherein the metallic substrate with deposited graphene has improved corrosion resistance relative to the metallic substrate absent the graphene. Each of steps (i)-(iii) may be in accordance with
5 corresponding steps described herein.

The invention also relates to a layered composite comprising a metallic substrate having graphene produced thereon in accordance with the method disclosed herein.

10 In a further aspect, the invention relates to a layered composite comprising (i) a metallic substrate, (ii) a layer of carbon barrier material on the metallic substrate, (iii) a layer of CVD catalyst on the layer of carbon barrier material, and (iv) a graphene layer on the layer of CVD catalyst.

15 By the specific combination of layers, the layered composite is advantageously characterised by resistance to and/or immunity from chemical and electrochemical degradation in aggressive environments, effective resistance to permeation of fluids, and great mechanical integrity over the desired lifetime of the composite.

20 **BRIEF DESCRIPTION OF THE DRAWINGS**

Embodiments of the invention will be now described with reference to the following non-limiting drawings, in which:

25 Figure 1 shows Arrhenius plot for the diffusion coefficients of copper in nickel,

Figure 2 shows Arrhenius plot for the diffusion coefficients of nickel in copper,

Figure 3 shows a Scanning Electron Microscope (SEM) cross-sectional image of an
30 embodiment mild steel substrate following deposition of a layer of copper and a layer of nickel,

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Figure 4 shows Raman spectrum of an embodiment mild steel substrate comprising layers of copper and nickel, following CVD formation of graphene over the layer of nickel,

- 5 Figure 5 shows (a) potentiodynamic polarization (PDP) plots obtained using a bare mild steel substrate and a substrate having graphene formed on it in accordance with an embodiment method of the invention, and (b) EIS Bode plots (impedance vs frequency plots) comparing corrosion resistance of bare mild steel (MS), Cu and Ni coated mild steel (Ni_Cu_MS_2), and graphene coated Ni_Cu_MS_2 (Gr_Ni_Cu_MS_2), in 0.1M NaCl
10 aqueous solution, after pre-immersion in the solution for 2 hours,

- Figure 6 shows comparative long-term corrosion resistance over a 1008 hour test performed on (a) a bare mild steel substrate, (b) a mild steel substrate having a layer of copper and a layer of nickel deposited thereon, and (c) a mild steel substrate having a layer of copper, a
15 layer of nickel deposited thereon, and graphene formed on the layer of nickel,

Figure 7 shows long-term corrosion resistance of nickel and Monel 400 (i.e., a nickel-copper alloy) surfaces with and without formation of graphene,

- 20 Figure 8 shows time dependent phase angle vs frequency plots of (a) bare Ni, (b) graphene coated Ni, (c) bare Monel 400 alloy and (d) graphene coated Monel 400 alloy, after immersion in 0.5M H₂SO₄ for different durations up to 720 h,

- Figure 9 shows (a) potentiodynamic polarization (PDP) plots and (b) EIS Bode plots
25 (impedance vs frequency plots) comparing corrosion resistance of bare mild steel (MS), Ni coated mild steel (Ni_MS), and corresponding sample after CVD with carbon precursor gas (CVD_Ni_MS), measured during immersion of the samples in a 0.1M NaCl aqueous solution following pre-immersion in the solution for 2 hours, and

- 30 Figure 10 show Raman spectrum of the surface of the Ni-coated mild steel after CVD with carbon precursor gas (CVD_Ni_MS).

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a method of producing graphene on a metallic substrate. In particular, the method involves the sequential deposition of at least two functional layers on the metallic substrate, followed by the formation of graphene by CVD directly on the outermost functional layer (i.e. the layer of CVD catalyst). Accordingly, by graphene being produced "on" the metallic substrate is meant that graphene is produced indirectly on the substrate, as opposed to being produced directly on the substrate.

By the substrate being "metallic" is meant the substrate comprises at least one metal element. Thus, the expression "metallic substrate" embraces pure metal substrates (i.e. made of a single metal element) as well as alloy substrates (i.e. comprising at least two elements, one of which is a metal element). In particular, a metallic substrate suitable for use in the invention would be one that can be used under the specific CVD operative conditions adopted to form graphene. Typically, the metallic substrate would have a melting point higher than about 850 °C, for example higher than 1,000 °C.

In some embodiments, the metallic substrate comprises an alloy. For example, the metallic substrate may be made of an alloy. Examples of suitable alloys include engineering alloys. Accordingly, in these embodiments the metallic substrate is selected from a cast-iron substrate, a steel substrate, a titanium alloy substrate, a nickel alloy substrate, a zinc alloy substrate, and a copper alloy substrate.

In some embodiments, the metallic substrate comprises steel. The term "steel" is used herein according to its broadest meaning of an alloy of at least iron and carbon.

Examples of suitable steel includes carbon steel. By the expression "carbon steel" is meant steel with carbon content up to 2.1 wt.%.

Accordingly, in some embodiments the metallic substrate comprises low carbon steel (also known as "mild steel"). By the expression "low carbon steel" is meant herein steel containing

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an amount of carbon of about 0.3 wt.% or less, for example about 0.04% to about 0.30% wt.%. In some embodiments, the metallic substrate comprises mild steel containing about 0.15 to about 0.2 wt.% carbon. In those instances the substrate may be any substrate used as structural steel (e.g. universal beams), screws, drop forgings, case hardening steel, steel bar, steel rod, steel tube, angles and channels., etc. In some embodiments, the metallic substrate comprises mild steel containing about 0.2 to about 0.3 wt.% carbon. In those instances, the substrate may be one that is used in machine structures, gears, free cutting steel, shaft and forged components, etc.

10 In some embodiments the metallic substrate comprises medium carbon steel. By the expression "medium carbon steel" is meant herein steel containing an amount of carbon of more than about 0.30% wt.% to about 0.60 wt.%.

In some embodiments, the metallic substrate comprises high carbon steel (also known as "carbon tool steel"). By the expression "high carbon steel" is meant herein steel having an amount of carbon of about 0.60 wt.% to about 1.50 wt.%.

In some embodiments, the metallic substrate comprises ultra-high carbon steel. By the expression "ultra-high carbon steel" is meant herein steel having an amount of carbon of about 1.5 wt.% to about 2.1 wt.%.

In some embodiments, the metallic substrate comprises alloy steel. As used herein, the expression "alloy steel" means steel that contains at least one alloying element other than iron and carbon. Examples of alloy steel suitable for use in the invention include steel that contains chromium, nickel, molybdenum, vanadium, tungsten, manganese, phosphorous, sulphur, silicon, copper, titanium, aluminium, or a combination thereof.

In some embodiments, the metallic substrate comprises stainless steel. By "stainless steel" is meant herein steel that contains at least 11% chromium. Optionally, stainless steel may also contain nickel and/or molybdenum. Examples of suitable stainless steel include ferritic

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stainless steel, martensitic stainless steel, austenitic stainless steel, precipitation-hardened stainless steel, and duplex stainless steel (i.e. comprising ferrite and austenite phases).

In some embodiments, the metallic substrate is a non-alloy metallic substrate. By being
5 "non-alloy", the metallic substrate is made of a single metal as opposed to being an alloy. For example, the metallic substrate may be made of one of copper, iron, titanium, nickel.

The metallic substrate may be of any shape and/or dimensions that would be suitable for use in a CVD deposition process. For example, the metallic substrate may be selected from a
10 sheet, a beam, a valve component, a pipe, a piping component, a naval vessel component, a tank, or common structural components.

The method of the invention also comprises a step of depositing a layer of carbon barrier material on the metallic substrate.
15

The layer of carbon barrier material serves a number of purposes. On the one hand, it is aimed at preventing carbon diffusion away from the graphene deposition surface during formation of graphene by CVD. In doing so, the layer of carbon barrier material can also inhibit diffusion of carbon into the metallic substrate. Further advantageously, when the
20 metallic substrate itself contains carbon (as in the case of steel), the layer of carbon barrier material prevents carbon diffusion also away from the substrate through the layer of carbon barrier material. This assists with the preservation of the substrate microstructure and the control of carbon available for graphene formation.

25 Diffusion of carbon into the metallic substrate during CVD of graphene can be deleterious since it could compromise the mechanical integrity of the substrate and the effective deposition of graphene. This is particularly relevant when the metallic substrate presents high solubility to carbon (as in the case of steel). In those instances, in the absence of a layer of carbon barrier material a considerable fraction of carbon produced during CVD of
30 graphene will readily dissolve into the metallic substrate due to the high temperature conditions of CVD. As the solubility to carbon decreases rapidly with decreasing

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temperature, the dissolved carbon will be rejected rapidly when the substrate is cooled following CVD, leading to embrittlement of the substrate sub-surface (e.g. due to excessive formation of metal carbides in sub-surface region), and/or undesirable formation of carbon soot instead of graphene at the surface of the substrate.

5

The layer of carbon barrier material may be deposited directly on the metallic substrate, or on one or more further layer(s) of another material that may be interposed between the metallic substrate and the layer of carbon barrier material.

10 Accordingly, in the context of the present invention expressions such as "deposited on" or "depositing on" are used herein in their broadest sense to encompass either that a given layer is deposited directly on a substrate layer, or that one or more additional intermediate layers may be interposed between that given layer and the substrate layer.

15 In some embodiments, the layer of carbon barrier material is deposited directly on the metallic substrate.

The carbon barrier material may be any material that prevents diffusion of carbon through its volume. Typically, suitable carbon barrier materials would be characterised by low
20 solubility to carbon. In that context, examples of suitable carbon barrier materials include materials presenting solubility to carbon of about 0.05 wt.% or less, at about 1,000°C. Accordingly, in some embodiments the carbon barrier material presents solubility to carbon of about 0.025 wt.% or less, about 0.01 wt.% or less, or about 0.005 wt.% or less, at about 1,000°C.

25

One or more other factors may need to be taken into account when selecting an appropriate carbon barrier material. For example, a suitable carbon barrier material would be one that remains solid at CVD operative conditions. Typically, the carbon barrier material would have a melting point higher than about 850 °C, for example higher than 1,000 °C. In that
30 regard, a skilled person will be aware of such additional considerations when selecting suitable carbon barrier materials.

In some embodiments, the carbon barrier material is selected from a carbon barrier metal, a carbon barrier refractory oxide, a carbon barrier refractory carbide, or a combination thereof. Examples of suitable carbon barrier metals include copper, platinum, rhenium, zirconium, hafnium, titanium, vanadium, uranium, tantalum, niobium, and chromium. In some
5 embodiments, the carbon barrier material is selected from copper, rhenium, zirconium, hafnium, titanium, vanadium, uranium, niobium, and chromium.

In some embodiments, the carbon barrier material is copper. The selection of copper as the
10 carbon barrier material is particularly advantageous. The negligible solubility of copper to carbon (0.008 wt.% or less at about 1,000°C) makes it an effective barrier to carbon diffusion into and from the metallic substrate. As a result, the adoption of copper as the carbon barrier material advantageously allows the deposition of a thinner layer of CVD catalyst relative to other carbon barrier materials.

15 Further, in case the metallic substrate comprises iron (as in the case of the metallic substrate being steel), the thickness of copper layer can be tailored such that iron cannot reach the graphene deposition area during CVD formation of graphene. Since iron is a considerably inefficient catalyst for the dissociation of hydrocarbon, its diffusion to the graphene
20 deposition surface of the CVD catalyst would considerably hinder or prevent the formation of good quality defect-free graphene during CVD.

The layer of carbon barrier material may be deposited by any means known to a skilled person that would result in the formation of a continuous layer that is effective to prevent
25 carbon diffusion into the metallic substrate. Examples of suitable procedures include cold spray, electrodeposition and thermal evaporation.

In some embodiments, the layer of carbon barrier material is deposited by cold spray. A skilled person would be aware of suitable procedures and conditions for the successful
30 deposition of an effective carbon barrier layer. The adoption of cold spray and electrodeposition can be advantageous in that they are less infrastructure-intensive relative

to other deposition procedures that require, for example, the adoption of high temperatures and/or vacuum. In addition, the deposition of the layer of carbon barrier material by cold spray results in layer having high surface area due to the superficial features resulting from the sprayed material. This may advantageously translate in high surface area of the CVD catalyst, which can boost the efficiency of graphene formation by CVD.

The layer of carbon barrier material may be of any thickness that is effective in preventing (i) carbon diffusion into the metallic substrate during CVD of graphene, and (ii) diffusion of elements that can hinder or adversely affect the formation of graphene to the surface of the CVD catalyst onto which graphene is grown, for example from the metallic substrate and/or from any intermediate layer between the metallic substrate and the CVD catalyst.

For example, when the metallic substrate is an iron alloy the layer of carbon barrier material should also be sufficiently thick to impede diffusion of iron from the substrate to the surface of layer of CVD catalyst onto which graphene is formed. A skilled person would be aware of how to determine optimal thickness values for the layer of carbon barrier material in relation to the specific elements the layer is designed to block. An example of a suitable procedure for the determination of optimal thickness of the layer of carbon barrier material may be based on the determination of specific diffusion distance of a given element through the carbon barrier material at the intended CVD operative conditions, as described herein.

In some embodiments, the layer of carbon barrier material has a thickness of at least 5 μm . For example, the layer of carbon barrier material may have a thickness of from about 5 μm to about 100 μm , from about 10 μm to about 100 μm , from about 15 μm to about 100 μm , from about 20 μm to about 100 μm , from about 25 μm to about 100 μm , or from about 50 μm to about 100 μm . In some embodiments, the layer of carbon barrier material has a thickness of about 5 μm , about 10 μm , about 15 μm , about 25 μm , or about 50 μm . For a given deposition technique, a skilled person would be capable of devising suitable deposition conditions (e.g. temperature, duration, etc.) that would provide for the required thickness of the layer of carbon barrier material.

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The method of the invention also comprises the deposition of a layer of CVD catalyst on the carbon barrier. In the context of the invention, the CVD catalyst is one that facilitates decomposition of hydrocarbon for formation of graphene by CVD at a temperature that is lower than the temperature that would otherwise be required for hydrocarbon decomposition
5 in the absence of the catalyst.

In general, formation of graphene by CVD involves two steps, namely (i) the dissociation of hydrocarbon precursor gas to provide carbon atoms, and (ii) the formation of the carbon structure of graphene using the disassociated carbon atoms. Both stages require extreme
10 levels of energy to promote dissociation of the carbon precursor gas and effective formation of the graphene carbon structure. Accordingly, a suitable CVD catalyst for use in the method of the invention would be any material that allows stages (i) and (ii) to occur at lower temperature relative to the temperature that would otherwise be required in the absence of the catalyst.

15

In some embodiments, the CVD catalyst comprises a transition metal selected from nickel, cobalt, platinum, silver, ruthenium, iridium, palladium, and tantalum, or an alloy comprising one or more thereof. In some embodiments, the CVD catalyst comprises a transition metal selected from nickel, cobalt, silver, ruthenium, iridium, and palladium, or an alloy
20 comprising one or more thereof.

In some embodiments, the CVD catalyst is nickel. There are a number of advantages in using nickel as the CVD catalyst. Nickel is stable at the temperature of graphene formation by CVD, and is characterised by substantial solubility to carbon (0.6 wt. % at 1,326°C) that, in
25 turn, enables effective formation of multilayer graphene on its surface. In addition, the lattice constant of nickel makes it particularly suitable for near epitaxial formation of graphene. Specifically, the lattice constant of Ni is 3.52 Å and its first-neighbour distance in the bulk is 2.49 Å, which is almost identical to the lattice constant of graphene 2.46 Å.

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A particular advantage of using nickel as the CVD catalyst is that nickel maximises deposition of multi-layered graphene during CVD, which can provide improved protective characteristics over single-layered graphene.

- 5 Structural defects of single-layered graphene, if present, could adversely affect the corrosion protection ability of the graphene. In particular, the discontinuities may act as preferential corrosion sites. Undesired defects include irregularities in the graphene structure, lack of complete surface coverage, cracks, wrinkles, and/or presence of allotropic carbon other than graphene with high cathodic nature. However, defects of single-layer graphene, if present,
10 can be masked by a subsequent layer in the multi-layer structure.

The layer of CVD catalyst may be deposited by any means known to a skilled person that would result in the formation of a continuous layer that is effective to catalyse the formation of graphene by CVD. Examples of suitable procedures include electrodeposition, thermal
15 evaporation, plasma enhanced atomic layer deposition (PEALD), magnetron sputtering.

It was observed that formation of graphene (as opposed to other carbon allotropes) is facilitated by the availability of a surface of pure nickel throughout the duration of the CVD procedure. A skilled person would take this into account when devising the appropriate
20 thickness of the layer of CVD catalyst. In particular, the layer of CVD catalyst would have to be sufficiently thick to prevent diffusion of species from at least the metallic substrate and/or the layer of carbon barrier material to the exposed surface of the CVD catalyst onto which graphene forms. In other words, while a degree of diffusion of species through some of the thickness of the layer of CVD catalyst is inevitable (for example from the substrate or
25 from the layer of carbon barrier material), it is advantageous to ensure the diffusing species do not surface on the opposite side of the layer of CVD catalyst (i.e. on the surface of the CVD catalyst onto which graphene forms). This would ensure that graphene forms on a surface of pure CVD catalyst. By “surface” of pure CVD catalyst is meant herein up to 50 atomic layers of CVD catalyst from the atomic layer of CVD catalyst onto which graphene
30 forms.

Accordingly, the layer of CVD catalyst may have any thickness that is larger than the diffusion distance of an element the layer is intended to block. For a given set of deposition conditions (e.g. deposition temperature, deposition time, etc.), a skilled person would know how to determine the minimum thickness of the layer of CVD catalyst in relation to the diffusivity and solubility characteristics of a given element in the CVD catalyst. An example procedure in that regard is provided in the following paragraphs.

The distance that an element atom covers while diffusing in another substance depends on the specific diffusion coefficient of the element in the substance, which itself is temperature and time dependent. In that context, the diffusion distance of the element can be calculated by using equation (I) below:

$$x^2 = Q_i \times D \times t \dots\dots\dots (I)$$

In equation (I), x represents the average distance from a given starting point that an atom will have diffused in time t , Q_i is a numerical constant which depends on the dimensionality of the diffusion ($Q_i = 2, 4$, or 6 , for one-, two-, or three-dimensional diffusion, respectively), and D is the diffusion coefficient. In the context of this invention Q_i would be assumed to be 2, considering diffusion along one direction (i.e. that of the layer thickness).

Accordingly, for a given material to act as the carbon barrier layer, and given deposition temperature and time, the thickness of the layer of CVD catalyst should be larger than the value of x calculated using equation (I) using the diffusivity coefficient of that element in the CVD catalyst. The same procedure may also be adopted for the determination of the minimum thickness also of the layer of carbon barrier material, for example in relation to carbon and, in case the metallic substrate is steel, iron.

By way of example, assuming the carbon barrier material is copper and the CVD catalyst is nickel, the value of x relative to the copper/nickel system at 1,000°C for 6 hours is 7.5 μm (noting D for the copper/nickel system is about $1.3 \times 10^{-11} \text{ cm}^2/\text{s}$). Accordingly, to ensure that a surface of pure nickel is always available for graphene formation at 1,000°C during a 6-

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hour deposition, the layer of nickel should have a thickness larger than 7.5 μm . This would ensure that copper does not diffuse through the entire thickness of the nickel layer to reach the surface onto which graphene forms.

- 5 A skilled person would be aware that additional considerations may have to be made when optimising the thickness of the layer of CVD catalyst. For example, depending on the nature of the CVD catalyst, the thickness of the layer of CVD catalyst should not be such that it allows excessive amount of carbon solubilises into the CVD catalyst during formation of graphene. This is because excess carbon solubilised into the CVD catalyst would be expelled
10 upon cooling after CVD, resulting in formation of undesired soot instead of graphene.

In some embodiments, the layer of CVD catalyst has a thickness of at least 5 μm , for example at least 10 μm . For example, the layer of CVD catalyst may have a thickness of from about 5 μm to about 100 μm , from about 10 μm to about 100 μm , from about 15 μm to about 100
15 μm , from about 20 μm to about 100 μm , from about 25 μm to about 100 μm , or from about 50 μm to about 100 μm . In some embodiments, the layer of CVD catalyst has a thickness of about 5 μm , about 10 μm , about 15 μm , about 25 μm , or about 50 μm .

Provided a surface of pure CVD catalyst is available for graphene formation throughout
20 CVD of graphene, the layer of CVD catalyst may be deposited directly on the layer of carbon barrier material or on a layer of another material that is provided (either directly or not) on the layer of carbon barrier material. Accordingly, in some embodiments the layer of CVD catalyst is deposited directly on the layer of carbon barrier material.

25 In some embodiments, the CVD catalyst is monocrystalline. This is particularly advantageous in that it facilitates formation of defect-free graphene. For example, it is particularly advantageous to deposit a monocrystalline layer of CVD catalyst, for example nickel, exposing a (111) lattice surface for graphene formation. Also, in case the lattice constant of the exposed surface is similar to that of graphene, as in the case of nickel,
30 epitaxial formation of graphene is favoured.

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In some embodiments, the carbon barrier material is copper and the CVD catalyst is nickel. This combination is particularly advantageous, especially when the metallic substrate is steel. In addition to enabling CVD graphene formation on steel, which has limited or no catalytic activity towards hydrocarbon dissociation, the use of copper and nickel as the
5 carbon barrier material and CVD catalyst, respectively, is beneficial also to the mechanical properties of the overall composite. Thanks to the high compatibility of copper with both steel and nickel, the layer of copper will allow a certain degree of diffusion of iron and nickel into copper during CVD of graphene, thereby enhancing the mechanical strength of the substrate/copper and copper/nickel interfaces.

10

In some embodiments, the layer of carbon barrier material and the layer of CVD catalyst are compositionally different.

The deposition of compositionally different layers offers an advantageous combination of
15 efficiency and flexibility. In particular, by depositing compositionally different layers of carbon barrier material and CVD catalyst it is possible to ensure that each layer provides the required degree of catalysis for graphene formation and suppression of carbon diffusion, which in turn can maximise substrate protection and controlled formation of graphene. For example, the deposition of compositionally different layers enables to select, for each layer,
20 the material that can better perform the intended functions, thus optimising the functionality of each layer.

The method of the invention also comprises a step of forming graphene on the layer of CVD catalyst by CVD. A skilled person would be aware of suitable procedures for forming
25 graphene on the layer of CVD catalyst for the purpose of the invention. In a typical procedure, CVD is performed by placing a metallic substrate with the layer of carbon barrier material and CVD catalyst in a reaction chamber. The chamber is then optionally evacuated. Subsequently, the chamber is fluxed with a carbon precursor gas, which comprises a hydrocarbon gas that dissociates on the surface of the CVD catalyst to provide carbon atoms
30 for graphene formation.

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As a result of being formed, graphene is produced on the metallic substrate. Graphene that is produced typically adheres to the CVD catalyst to remain fixed on the substrate.

In this context, the nature of the CVD catalyst can dictate the mechanism of graphene formation during CVD. In a typical procedure, formation of graphene by CVD involves a two-step mechanism. First, a generation of nascent carbon atoms is effected by promoting catalytic dissociation of a gaseous hydrocarbon. The carbon atoms would then deposit on the exposed surface of the CVD catalyst and organise into the most thermodynamically favoured carbon allotrope. Depending on the solubility of carbon into the CVD catalyst, graphene may form according to a carbon segregation/precipitation mechanism (for CVD catalysts providing high solubility to carbon, such as nickel), or surface-catalysed growth mechanism (for CVD catalysts providing insignificantly low solubility to carbon). Where the solubility of carbon in the CVD catalyst is particularly high, graphene may also form during cooling of the CVD catalyst, during which carbon that dissolved at high temperature is rejected to the surface of the CVD catalyst during cooling to organise as graphene, for example as multilayer graphene.

Regardless of the growth mechanism, graphene nucleation and growth require carbon concentration near the CVD catalyst surface to exceed the equilibrium carbon solubility, that is, carbon supersaturation near the CVD catalyst surface. In this context, the nature of the CVD catalyst can also dictate the deposition parameters for formation of graphene by CVD. On the basis of at least the considerations outlined herein, a skilled person would be capable of devising suitable deposition conditions for the formation of graphene on the layer of CVD catalyst.

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The deposition temperature may be any temperature that ensures formation of graphene on the layer of CVD catalyst. By "deposition temperature" is meant herein the temperature at which the layer of CVD catalyst is exposed the carbon precursor gas. In some embodiments, formation of graphene is performed by CVD at a deposition temperature of from about 800 °C to about 1,100 °C. For example, formation of graphene is performed by CVD at a deposition temperature of from about 850 °C to about 1,100 °C, from about 900 °C to about

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1,100 °C, from about 950 °C to about 1,100 °C, or from about 1,000 °C to about 1,100 °C. In some embodiments, formation of graphene is performed by CVD at a deposition temperature of from about 1,050 °C to about 1,075 °C. For example, formation of graphene may be performed by CVD at a deposition temperature of about 1,060 °C.

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The carbon precursor gas is typically a mixture of a carrier gas and a hydrocarbon gas. By "carrier gas" is meant herein a gas that does not dissociate into carbon at the CVD operative conditions, and acts as a transport medium for the hydrocarbon gas. Examples of suitable carrier gases include argon.

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The hydrocarbon gas may be any hydrocarbon that presents in gas form at the deposition temperature, and that can dissociate into atomic carbon at that temperature. In some embodiments, the hydrocarbon is selected from hexane, cyclohexane, methane, ethanol, acetylene, and a combination thereof.

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The hydrocarbon gas may be provided in the carbon precursor gas at a flow rate that can generate carbon atoms at a rate that would be effective for graphene formation at the deposition conditions. Since formation of graphene on the layer of CVD catalyst may be limited by mass transport, the amount of hydrocarbon in the carbon precursor gas can
20 determine how much carbon would be available on the surface of the CVD catalyst for graphene formation. Suitable flow rate of hydrocarbon gas in the carbon precursor gas may be from about 0.4 sccm to about 1.4 sccm.

In a typical procedure, before introduction of the carbon precursor gas into the CVD
25 chamber, a reducing environment is created within the chamber by flowing a reducing gas, such as hydrogen along with the carrier gas (without the hydrocarbon gas). Hydrogen reduces with and removes any native oxide that is invariably present on the metallic substrate and thereby, provides a pristine metal surface for graphene deposition. The reducing environment also assists with preventing oxidation of carbon and graphene at the CVD
30 operative temperature.

- 20 -

The reaction chamber is typically evacuated ahead of graphene formation, such that CVD is conducted at sub-atmospheric pressure. In that regard, suitable pressure conditions for graphene formation may be from about 0.001 kPa to about 101 kPa. In some embodiments, formation of graphene is performed at a pressure of from about 1 Pa to about 1,500 Pa. In
5 some embodiments, formation of graphene is performed at atmospheric pressure.

Formation of graphene may be performed for any deposition time that would ensure formation of a continuous layer of graphene on the layer of CVD catalyst. By "deposition time" is meant herein the duration of the exposure of the layer of CVD catalyst to the carbon
10 precursor gas. For example, formation of graphene may be performed at a deposition time of from about 1 minute to about 120 minutes, for example from about 1 minute to about 90 minutes, from about 1 minute to about 60 minutes, from about 5 minutes to about 60 minutes, or from about 5 minute to about 45 minutes.

15 In some embodiments, formation of graphene is preceded by pre-heating the metallic substrate with the layer of carbon barrier material and the layer of CVD catalyst. This can assist with the formation of homogeneous and defect-free graphene. In some embodiments, formation of graphene is preceded by pre-heating the metallic substrate with the layer of carbon barrier material and the layer of CVD catalyst at the deposition temperature. For
20 example, formation of graphene is preceded by pre-heating the metallic substrate with the layer of carbon barrier material and the layer of CVD catalyst at a pre-deposition temperature of from about 800 °C to about 1,100 °C. In some embodiments, the pre-deposition temperature is from about 850 °C to about 1,100 °C, from about 900 °C to about 1,100 °C, from about 950 °C to about 1,100 °C, or from about 1,000 °C to about 1,100 °C. In some
25 embodiments, the pre-deposition temperature is from about 1,050 °C to about 1,075 °C, for example about 1,060 °C.

Formation of graphene may also require cooling the sample in a controlled manner following exposure to the carbon precursor gas. This is particularly useful when the CVD catalyst has
30 high solubility to carbon, and typically involves ensuring that the sample cools to room temperature (e.g. about 23°C) in a predetermined amount of time. For example, formation

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of graphene may comprise continuously cooling the metallic substrate with the layer of carbon barrier material and the layer of CVD catalyst from the deposition temperature to room temperature for a cooling time of from about 0.5 hours to about 6 hours. In some embodiments, the cooling time is from about 1 hour to about 6 hours, from about 2 hours to about 6 hours, from about 3 hours to about 6 hours, from about 4 hours to about 6 hours, or from about 5 hours to about 6 hours. For example, the cooling time may be about 4 hours.

In some embodiments, formation of graphene by CVD results in formation of defect-free graphene. In the context of the present invention, the degree of point defects can be determined by reference to the intensity of D peak ($1,350\text{ cm}^{-1}$) of the Raman spectrum (generated using laser of 514 nm excitation wavelength).

In some embodiments, the graphene is multi-layer graphene. Typically, Raman spectroscopy can be used as tool to determine whether the graphene that has formed on the layer of CVD catalyst is multi-layer graphene. By the expression "multi-layer graphene" is meant herein up to ten layers of graphene. More than ten layers of graphene would conventionally be regarded to be bulk graphite. In that regard, the relative intensity I_G/I_{2D} between the G-mode and the 2D-mode can be used to obtain an indication of whether the graphene is single layer graphene or multi-layer graphene. In that regard, I_G/I_{2D} ratio of <1 is indicative of a single layer of graphene, while I_G/I_{2D} ratio larger than 1 confirms multi-layer graphene. Accordingly, in some embodiments the graphene has a corresponding Raman spectrum characterised by a G-band and a 2D-band having relative intensity I_G/I_{2D} of at least 1.

By the nature of the CVD procedure, it will be understood that graphene forms directly on the layer of CVD catalyst. That is, while one or more additional layer(s) of other materials may be deposited between either (i) the metallic substrate and the layer of carbon barrier material, or (ii) the layer of carbon barrier material and the layer of CVD catalyst, the method of the invention provides for no intermediate layer(s) of other materials between the layer of CVD catalyst and the graphene.

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As explained herein, the method of the invention can be successful in developing multilayer graphene on a metallic substrate, which can confer the substrate with remarkable corrosion resistance. In a typical assessment for the purpose of the present invention, the corrosion resistance of a metallic substrate relative to the same substrate having graphene produced thereon may be quantified by electrochemical tests such as potentiodynamic polarization (PDP), and electrochemical impedance spectroscopy (EIS), for example of the kind described herein. A skilled person would nevertheless be capable of devising suitable procedures to perform comparative tests of the corrosion resistance of materials and composite materials of the kind described herein.

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The present invention also provides a layered composite comprising a metallic substrate having graphene produced thereon in accordance with the method described herein.

In a further aspect, the invention relates to a layered composite comprising (i) a metallic substrate, (ii) a layer of carbon barrier material on the metallic substrate, (iii) a layer of CVD catalyst on the layer of carbon barrier material, and (iv) a graphene layer on the layer of CVD catalyst.

The metallic substrate, the layer of carbon barrier material, and/or the layer of CVD catalyst may be a metallic substrate, a layer of carbon barrier material, or a layer of CVD catalyst of the kind described herein.

Also, the layer of carbon barrier material, and/or the layer of CVD catalyst may have a thickness as described herein in relation to each of those layers.

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As explained herein, by a given layer being "on" another substrate layer allow for one or more additional layer(s) being present between that given layer and the substrate layer.

In some embodiments, the layer of carbon barrier material is layered directly on the metallic substrate. That is, the layer of carbon barrier material is in direct contact with the metallic

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substrate as opposed of having one or more layers of another material interposed between the the layer of carbon barrier material and the metallic substrate.

In some embodiments, the layer of CVD catalyst is layered directly on the layer of carbon
5 barrier material. That is, the layer of CVD catalyst is in direct contact with the layer of carbon barrier material, as opposed of having one or more layers of another material interposed between the layer of CVD catalyst and the layer of carbon barrier material.

The graphene layer may be made of graphene of the kind described herein. In particular, the
10 graphene may be single-layer or multi-layer as disclosed herein.

By the specific combination of layers, the layered composite is advantageously characterised by resistance to and/or immunity from chemical and electrochemical degradation in aggressive environments, effective resistance to permeation of fluids, and great mechanical
15 integrity over the desired lifetime of the composite.

EXAMPLES

EXAMPLE 1

20 *Growth of layer of carbon barrier material and layer of CVD catalyst on metallic substrate*

The method of the invention was tested using a number of mild steel substrates. The method was performed by first depositing a layer of copper as the carbon barrier material, and a subsequent layer of nickel as the CVD catalyst. Graphene was then formed on the exposed
25 nickel surface by CVD.

The thickness of each of the copper and nickel layer was pre-determined based on the materials for each layer (i.e. copper and nickel) and the intended deposition temperature for the CVD of graphene, the latter being set to about 1,000°C. In essence, considerations on the
30 inter-diffusivity of copper into nickel at 1,000°C were made in order to select a thickness of

each layer that would be sufficient to ensure a surface of pure nickel would be available for formation of graphene during the entire CVD procedure at the deposition temperature.

Figures 1 and 2 show the relative diffusivity of copper and nickel. The data allow extrapolating corresponding diffusivity coefficient values at the intended reference temperature. Based on the data on Figures 1 and 2, diffusion coefficient values and corresponding diffusion distances for times of deposition of 4, 5 and 6 hours were determined using equation (I):

$$x^2 = Q_i \times D \times t \dots\dots\dots (I)$$

where, x represents the average distance from a given starting point that an atom will have diffused in time t , Q_i is a numerical constant which depends on the dimensionality of the diffusion ($Q_i = 2, 4$, or 6 , for one-, two-, or three-dimensional diffusion, respectively), and D is the diffusion coefficient. Q_i was taken to be 2 for mono-dimensional diffusion. Calculated values are reported in Table 1 below.

The maximum inter-diffusion distance for maximum time (6 hours) and maximum temperature (1,060 °C) was calculated to be 7.5 μm .

Table 1 – Values of diffusion distance of copper into nickel calculated using formula (I) at different reference temperatures and times.

Temperature (°C)	Time (hrs)	Diffusion coefficient (cm ² /sec)	Diffusion distance (μm)
1,060	6	1.3×10^{-11}	7.5
1,060	5	1.3×10^{-11}	6.9
1,060	4	1.3×10^{-11}	6.2
1,000	6	1.0×10^{-11}	6.6
1,000	5	1.0×10^{-11}	6.0
1,000	4	1.0×10^{-11}	5.4
900	6	5.5×10^{-12}	4.9
900	5	5.5×10^{-12}	4.4
900	4	5.5×10^{-12}	4.0

Ground and polished mild steel samples were coated with copper and nickel by electroplating. The layer of copper was deposited to be 13 μm to 20 μm . The layer of nickel was deposited to be 12 μm to 20 μm thick. Scanning Electron Microscopy (SEM) imaging taken on a cross-section of a sample confirms the intended thickness (Figure 3(a), relative to samples with 20 μm thick layers).

As the calculated highest diffusion thickness (7.5 μm) is significantly less than 12 μm or 20 μm , it was expected that a surface of pure nickel would be available at all times throughout graphene formation by CVD at 1,060 $^{\circ}\text{C}$ for all samples. To test the calculation, the samples were kept in a furnace for 6 h at 1,060 $^{\circ}\text{C}$. Energy dispersive x-ray (EDX) spectroscopy performed on the top surface of the all samples detected only nickel, confirming no copper or iron had diffused through the entire thickness of the nickel from the layer of copper and the metallic substrate, respectively.

EXAMPLE 2

Formation of graphene by CVD

Graphene growth on the mild steel substrate electroplated with Cu and then with Ni in accordance to the procedure described in Example 1 was carried out using a CVD quartz tube furnace. The procedure involved an initial pre-annealing of the samples for 40 minutes at 1,060 $^{\circ}\text{C}$ under a hydrogen/argon gas mixture (15/85 vol.%) atmosphere. Subsequently, hexane gas was flowed together with the hydrogen/argon gas mixture to provide a flow of carbon precursor gas into the chamber for 1 hour at the same temperature (1,060 $^{\circ}\text{C}$). Then, the chamber was cooled to room temperature at constant cooling rate for 4 hours.

Following CVD of graphene the samples were evaluated by Raman spectroscopy, which confirmed the layer formed on the nickel layer of all samples to be multilayer graphene with no significant defects (Figure 4). The greater intensity of G-mode peak at 1,584 cm^{-1} than that of 2D-mode peak at 2,682 cm^{-1} in each spectrum confirmed formation of multi-layer graphene over the entire surface of the sample. The ratio of G-mode and 2D-mode intensities ($I_{\text{G}}/I_{2\text{D}}$) was used to evaluate the number of graphene layers. The $I_{\text{G}}/I_{2\text{D}}$ ratio was found to

be about 1.5, which is suggestive of formation of a multilayer graphene over the entire surface of the tested sample. Furthermore, no significant D-mode peak was observed, which indicates low defect density and low disorder in the graphene. The measured spectra also show no presence of Raman peaks corresponding to Ni, Cu or Fe oxides, confirming the effectiveness of graphene in preventing post-CVD oxidation of the metals.

EXAMPLE 3

Evaluation of Corrosion Resistance of mild steel with graphene coating

The corrosion resistance of mild steel substrates with and without graphene was measured by electrochemical tests, i.e. potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS). The tests were designed to simulate the aggressiveness of seawater, and were carried out during immersion of the samples in a 0.1M aqueous solution of NaCl, after having pre-immersed the substrates in the solution for 2 hours. Mild steel with graphene produced thereon was found to be about two orders of magnitude more resistant to corrosion than mild steel absent the graphene.

Figure 5(a) shows PDP plots measured on a sample of bare mild steel compared to one with graphene coating in accordance with the procedure described herein. Figure 5(b) shows EIS Bode plots (impedance vs frequency plots) comparing the corrosion resistance of bare mild steel (MS), steel substrates coated only with copper and nickel (Ni_Cu_MS_2), and substrates having a copper layer, a nickel layer, and graphene formed on the nickel layer (Gr_Ni_Cu_MS_2).

The plot of Figure 5(a) allows appreciating that the corrosion rate (i.e., anodic current density at the open circuit potential (OCP)) of the graphene coated mild steel is about two orders of magnitude lower than that of the bare mild steel in 0.1M NaCl solution. Also, susceptibility of bare mild steel (MS) to corrosion was considerably suppressed due to the graphene coating, as evident of from the +500 mV higher E_{corr} of the sample with graphene compared to that of the bare steel sample.

The EIS plot in Figure 10(b) entirely supports the remarkable improvement in corrosion resistance of mild steel (MS) due to the multilayer graphene coating (Gr_Ni_Cu_MS_2) that was suggested by the PDP data in Fig. 10(a). The modulus of impedance ($|Z|$) at the lowest frequency (that is measure of corrosion resistance) is 2 orders of magnitude greater for Gr_Ni_Cu_MS_2 than that for MS, whereas it is only 17 times greater for mild steel with the nickel layer coated over the inner copper layer, i.e., without any graphene coating (Ni_Cu_MS_2).

EXAMPLE 4

10 *Long term corrosion resistance test*

The considerably improved corrosion resistance of mild steel with graphene coating was also found to be long lasting. EIS Bode plots were generated for bare mild steel (MS) and coated mild steel (Gr_Ni_Cu_MS_2) over immersion in a 0.1M NaCl solution for up to 1008 hours (Figure 6). The data clearly show that the remarkable resistance to corrosion of imparted by graphene remains constant over the entire duration of the test, relative to the poor resistance displayed by bare mild steel samples and bare steel samples with only a layer of copper and a layer of nickel thereon.

20 EXAMPLE 5

Tests were performed to evaluate the corrosion resistance imparted on different catalytic surfaces by CVD of graphene. Testes surfaces were those of a coper/nickel alloy (Monel 400) and pure nickel test substrate. Nickel was procured from Alfa Aesar (99.9945 Alfa Aesar no. 012043. FI) and Monel 400 alloy (175mm×100mm×2mm) was procured from VDM Metals Australia Pty Ltd. Their strips were machined into coupons (15mm×15mm×2mm). These coupons were ground with 180, 320, 800, 1200 and 2500 grade grinding papers successively. The coupons were subsequently polished with diamond polishing suspension, washed with acetone, and deionized water for 5 min in an ultrasonic bath and dried under compressed air. Composition of the Monel-400 alloy is given in Table 2 below.

Table 2 Composition (wt %) of the Monel-400 alloy used in the test

Elements	C	Ni	Mn	Si	Cu	Fe
Composition	0.1%	63.8%	1.0%	0.1%	32.8%	2.0%

CVD on ground and polished specimens was performed in a tube furnace (Lenton, UK) with
 5 a 25 mm diameter quartz tube. The specimens were loaded inside the furnace which was
 evacuated to 5 mtorr through a vacuum pump (Edwards, nXDS10i, Germany). A mixture of
 argon and hydrogen was introduced into the chamber with a flowrate of 250 sccm at 1.8 torr
 pressure to create a reducing atmosphere. The samples were held for 40 min at 1060 °C in
 the presence of Ar/H₂ flow. Subsequently, hexane was introduced into the chamber as the
 10 hydrocarbon gas for 60 min at 1060 °C with a flowrate of 1 sccm. Samples were then cooled
 down to the ambient temperature under the flow of Argon and H₂ mixture at 1.8 torr pressure.

Electrochemical tests were performed on the graphene-coated and bare samples of both
 nickel and Monel 400 using a Princeton applied research potentiostat (Model 2273) and a
 15 conventional three electrode electrochemical cell. Saturated calomel electrode was used as
 the reference electrode, platinum mesh as the counter electrode and the specimens were the
 working electrode. The exposed area of the working electrode was 0.785 cm². A 0.5 M
 aqueous solution of H₂SO₄ was used at room temperature as electrolyte for the
 electrochemical tests. The specimens were held at the open circuit potential (OCP) for 2
 20 hours prior to starting the electrochemical measurements for stabilizing the surface potential
 of the specimen. Potentiodynamic polarization tests were carried out over a voltage range of
 -250 mV to +250 mV vs OCP at a constant voltage scan rate of 0.5 mV/s. Electrochemical
 impedance spectroscopy (EIS) was performed over a frequency range of 1 MHz to 10 mHz,
 using 10 mV sinusoidal perturbation potential at OCP. All electrochemical experiments were
 25 repeated thrice using three different samples to examine the reproducibility.

Potentiodynamic polarization was carried out to evaluate the corrosion resistance of
 graphene coated nickel and Monel-400 alloy under proton exchange membrane fuel cell
 (PEMFC) condition. The anodic current density of graphene coated nickel at the open circuit
 30 potential is almost two orders of magnitude lower than that of the bare nickel in 0.5 M H₂SO₄

solution. The corrosion potential, E_{corr} (intercept of anodic and cathodic region, which is a measure of the corrosion susceptibility – the higher the E_{corr} , the lower the susceptibility) is around 80 mV higher for graphene coated nickel as compared to the bare nickel. The anodic dissolution rate of graphene coated Monel 400 alloy was observed to be about 1.5 orders of magnitude lower than the bare Monel 400 alloy, with a 50 mV higher E_{corr} . Therefore, a few atomic layer thick multi-layered graphene coating dramatically improved the corrosion resistance for both nickel and Monel 400 alloy in the PEMFC environment. In both cases, the anodic dissolution rate quickly accelerates beyond 0.1 V and merges with the curve for bare samples, indicating the breakdown of graphene coating at such high over potentials.

10

Metallic bi-polar plates slowly degrade under weakly acidic environment in PEMFC. Therefore, time dependent degradation of graphene coated nickel and Monel 400 alloy was worth investigating. As shown in Figure 7, electrochemical measurements were made every 48 h of immersion for 750 h, and impedance values at lowest frequency (which is a measure of corrosion resistance) are plotted. The impedance at lowest frequency for graphene coated nickel is $100 \pm 20 \text{ k}\Omega\text{-cm}^2$ after two hours of immersion, which is almost two orders of magnitude higher than that for the bare nickel ($1.17 \pm 0.63 \text{ k}\Omega\text{-cm}^2$).

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On the contrary, the impedance at lowest frequency for graphene coated Monel 400 is $22 \pm 7 \text{ k}\Omega\text{-cm}^2$ after two hours of immersion, which is only around one and half orders of magnitude higher than that for the bare alloy ($1 \pm 0.16 \text{ k}\Omega\text{-cm}^2$). However, the impedance values drop to $60 \pm 7 \text{ k}\Omega\text{-cm}^2$ and $15 \pm 1 \text{ k}\Omega\text{-cm}^2$ after initial period of immersion for graphene coated nickel and graphene coated Monel 400 respectively, and then remain largely unchanged for the rest of the test duration to 720 h. Initial drop of impedance (or less of corrosion resistance) can be attributed to the electrolyte penetration across the graphene layer through the defects and pores of graphene membrane along the lateral and perpendicular directions due to the capillary action.

25

As evident from Figure 7, both the nickel surface and Monel 400 surface show improved resistance to corrosion over their respective bare surfaces. The overall corrosion resistance for the graphene-nickel sample is found to be superior to that of the graphene-Monel 400

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- 30 -

alloy, testifying to the advantage of forming graphene on a pure surface of nickel. This phenomenon can be explained by the lower defect contents or structural imperfection of graphene plane in the graphene-nickel sample. The corrosion resistance that sustained during long term immersion for both metals can be attributed to the multi-layered graphene with low amount of defects. In the case of multilayer graphene, the discontinuities or defects of a graphene layer is consistently masked by the immediate upper layer, thus providing effective surface coverage and durable corrosion resistance.

Figures 8(a), 8(b), 8(c) and 8(d) show the time dependent phase angle vs frequency plots for bare nickel, graphene coated nickel, bare Monel 400 alloy and graphene coated alloy respectively. In these plots, different electrochemical processes are represented by different time constants at particular frequencies, e.g., charge transfer process or mass diffusion controlled reactions.

The phase angle vs frequency plots for bare nickel and bare Monel 400 alloy in Figures 8(a) and 8(c) show two overlapping time constants, one at around 2 Hz and another at the lowest frequency (<0.1 Hz), which are respectively believed to be due to the charge transfer controlled process at oxide/electrolyte interface and mass diffusion controlled reactions at metal/electrolyte interface.

In the case of bare Monel 400 alloy (Figure 8 (c)), these two time constants appear as partially overlapping time constants after 720 h of immersion; indicating the initiation of the breakdown of metal oxidehydroxide layer. In Fig. 8(a), two overlapping time constants remain unchanged even at 720 h of immersion indicating more uniform and robust nature of oxide layer on Ni surface compared to the Monel-400 alloy in Figure 8(c). On the contrary, time dependent phase angle evolutions for graphene coated nickel and graphene coated Monel 400 alloy (Figures 8(b) and 8(d)) show broader phase angle plots with two overlapping time constants, one for graphene coating/electrolyte interface in the high frequency range, and another for metal/electrolyte interface at lower frequency range.

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The broader nature of the curves gradually narrowed, and partial overlapping of the time constants started to appear, which reveals some degradation in the protective nature of the coating that become increasingly prominent with time, suggesting the evolution of ion transport kinetic across the metal/electrolyte interface. Two distinguished time constants
5 continued to appear for graphene coated alloy (Figure 8(d)) till 720 h of immersion, whereas two time constants started to merge again for graphene coated nickel (Figure 8(b)). The maximums at higher frequency range in case of both graphene coated Ni and alloy indicate the presence of graphene layer even after 720 h of immersion in 0.5M H₂SO₄ solution. However, the weak and strong maximums at low frequency range respectively in Figures
10 8(b) and (d) refer to less corrosion occurring at nickel surface compared to the alloy surface after 720 h of immersion in the acid solution.

Overall, the tests show that (i) multilayer graphene coated nickel and Monel 400 alloy respectively show 2 orders and 1.5 orders of improvement in corrosion resistance compared
15 to their bare counterparts in terms of anodic dissolution rate during potentiodynamic polarization test after 2 h of immersion in 0.5M H₂SO₄ solution; (ii) graphene-coated nickel withstands long term immersion in the acid solution and shows more than 20 times higher double layer resistance or charge resistance (R_{dl}) compared to uncoated metals even in 720 h of immersion; (iii) the graphene coating is largely un-attacked without showing any
20 significant coating delamination or blistering, while the bare metal/alloy suffer severe localised corrosion during immersion for 720 h; and (iv) the multilayer graphene-coated Ni possesses much superior corrosion resistance as bi-polar plates for proton exchange membrane fuel cell (PEMFC) than the graphene coated Cu.

25 COMPARATIVE EXAMPLE 1

Layered composites with no layer of carbon barrier material

A layer of nickel (CVD catalyst) was electroplated directly over the ground and polished surface of mild steel coupons. Graphene was formed on the layer of nickel in accordance to
30 the same procedure described in Example 2.

Potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) were carried out as described in Example 3 on the coupons of bare mild steel (MS), those with nickel layer (Ni_MS) only, as well as those subjected to CVD for graphene formation (CVD_Ni_MS), after pre-immersion in 0.1M NaCl for 2 hours.

5

PDP plots in Figure 9(a) suggest that Ni coating have somewhat decreased the susceptibility to corrosion of MS (since the E_{corr} of Ni_MS is 0.15 V less anodic to that of MS), whereas the CVD treatment for graphene on Ni_MS (CVD_Ni_MS) did not provide any further decrease in the susceptibility, rather it decreased the corrosion resistance. In fact, E_{corr} of CVD_Ni_MS was more anodic than Ni_MS. Corrosion current density (which is a measure of the corrosion rate) showed very little improvement in corrosion rate following either nickel coating (Ni_MS sample) or formation of graphene on the nickel layer by CVD (CVD_Ni_MS sample).

15 EIS plots in Figure 9(b) are consistent with the PDP data of Figure 9(a). The modulus of impedance ($|Z|$) at the lowest frequency (i.e., 0.1 Hz in this investigation), which a measure of corrosion resistance is somewhat greater for the Ni_MS sample compared to the MS sample, but it is lower for CVD_Ni_MS relative to the Ni_MS sample. This indicates that CVD treatment did not provide any improvement in corrosion resistance of Ni_MS.

20

In order to understand the inability of CVD graphene treatment to provide the corrosion resistance in the samples with no layer of carbon barrier material, the morphology and broad chemical characteristic of the samples were characterised by Raman spectroscopy, backscattered electron (BSE) image mode of scanning electron microscopy (SEM), and energy dispersive x-ray spectroscopy (EDX).

25

Raman spectroscopy performed on the surface of CVD_Ni_MS (Figure 10) suggests that a continuous layer of graphene had not formed on the surface of the nickel. In fact, the Raman spectrum is dominated by the resonance signals corresponding exclusively to nickel oxides. The data support the hypothesis that a considerable fraction of carbon might not have been available to diffuse out of the nickel layer during cooling of the sample for graphene

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formation, and that carbon might have diffused across the nickel-steel interface into the steel substrate to become unavailable for graphene formation.

In addition, BSE characterisation (not shown) indicated chemical inhomogeneity on the sample surface. EDX (not shown) revealed the presence of Fe on the surface in addition to Ni and C. The presence of Fe indicates that the temperature-time window of the CVD treatment allowed considerable amount of Fe to diffuse out of the steel substrate and through the Ni layer up to its surface. Microscopy of the cross-section of Ni_MS revealed the thickness of the nickel layer to be 15 μm . Fe is considerably soluble in Ni. A simple diffusivity calculation validates that a considerable amount of Fe should diffuse through a 15 μm thick Ni layer at the CVD deposition conditions. Since Fe is a considerably inefficient catalyst for dissociation of hydrocarbon, its considerable presence at the surface along with nickel seems to have hindered/prohibited development of a continuous layer of multilayer graphene during the CVD.

The characterisation of the samples with no layer of carbon barrier material allowed concluding that either graphene formed as a discontinuous layer, or carbon deposited on the surface of the nickel as another allotrope. In any event, either instance appear to have accelerated the tendency of the substrate to corrode due to the high cathodic nature of graphitic carbon.

In the preceding description, the inability of a thin nickel layer on mild steel to develop graphene upon CVD treatment has been attributed to the diffusion of Fe across the nickel layer that hinder formation of graphene, as well as to the likely loss of a considerable fraction of carbon due to diffusion across nickel-steel interface into steel matrix.

Throughout this specification and the claims which follow, unless the context requires otherwise, the word 'comprise', and variations such as 'comprises' and 'comprising', will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

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The reference in this specification to any prior publication (or information derived from it), or to any matter which is known, is not, and should not be taken as an acknowledgment or admission or any form of suggestion that that prior publication (or information derived from it) or known matter forms part of the common general knowledge in the field of endeavour

5 to which this specification relates.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS

1. A method of producing graphene on a metallic substrate, the method comprising:
depositing a layer of carbon barrier material on a metallic substrate,
depositing a layer of chemical vapour deposition (CVD) catalyst on the layer of carbon barrier material, and
forming graphene on the layer of CVD catalyst by CVD.
2. The method of claim 1, wherein the carbon barrier material presents a solubility to carbon of about 0.05 wt.% or less, at about 1,000°C.
3. The method of claim 1 or 2, wherein the carbon barrier material comprises one or more of copper, platinum, rhenium, zirconium, hafnium, titanium, vanadium, uranium, tantalum, niobium, and chromium.
4. The method of any one of claims 1-3, wherein the carbon barrier material is copper.
5. The method of any one of claims 1-4, wherein the CVD catalyst comprises a transition metal selected from one or more of nickel, cobalt, platinum, silver, ruthenium, iridium, palladium, and tantalum.
6. The method of any one of claims 1-5, wherein the CVD catalyst is nickel.
7. The method of any one of claims 1-6, wherein the metallic substrate comprises steel.
8. The method of any one of claims 1-7, wherein the layer of carbon barrier material has a thickness of at least 10 μm .
9. The method of any one of claims 1-8, wherein the layer of CVD catalyst has a thickness of at least 10 μm .

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10. The method of any one of claims 1-9, wherein a Raman spectrum measured on the formed graphene presents a G-mode band and a 2D-mode band with relative intensity I_G/I_{2D} of greater than 1.

11. The method of any one of claims 1-10, wherein the layer of carbon barrier material is deposited by cold spray, electrodeposition, or thermal evaporation.

12. The method of any one of claims 1-11, wherein the layer of CVD catalyst is deposited by electrodeposition, thermal evaporation, plasma enhanced atomic layer deposition (PEALD), or magnetron sputtering.

13. The method of any one of claims 1-12, wherein the graphene is formed by CVD at a deposition temperature of from about 800°C to about 1,100°C.

14. The method of any one of claims 1-13, wherein the layer of CVD catalyst is deposited directly on the layer of carbon barrier material.

15. A layered composite comprising a metallic substrate having graphene produced thereon in accordance with the method of any one of claims 1-14.

16. A layered composite, comprising:

- a metallic substrate,
- a layer of carbon barrier material on the metallic substrate,
- a layer of CVD catalyst on the layer of carbon barrier material, and
- a graphene layer on the layer of CVD catalyst.

17. The composite of claim 16, wherein the layer of carbon barrier material comprises one or more of copper, platinum, rhenium, zirconium, hafnium, titanium, vanadium, uranium, tantalum, niobium, and chromium.

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18. The composite of claim 16 or 17, wherein the carbon barrier material is copper.
19. The composite of any one of claims 16-18, wherein the CVD catalyst comprises a transition metal selected from one or more of nickel, cobalt, platinum, silver, ruthenium, iridium, palladium, and tantalum.
20. The composite of any one of claims 16-19, wherein the metallic substrate comprises steel.
21. The composite of any one of claims 16-20, wherein the layer of carbon barrier material has a thickness of at least 10 μm .
22. The composite of any one of claims 16-21, wherein the layer of CVD catalyst has a thickness of at least 10 μm .
23. The composite of any one of claims 16-22, wherein a Raman spectrum measured on the formed graphene presents a G-mode band and a 2D-mode band with relative intensity I_G/I_{2D} of greater than about 1.
24. The composite of any one of claims 16-23, wherein the layer of CVD catalyst is in direct contact with the layer of carbon barrier material.

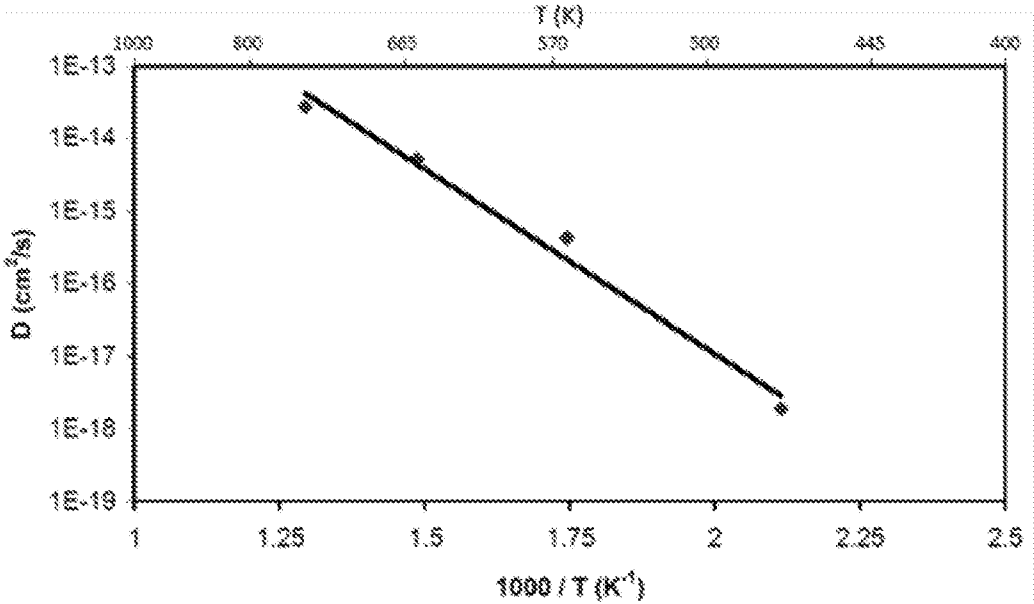


Figure 1

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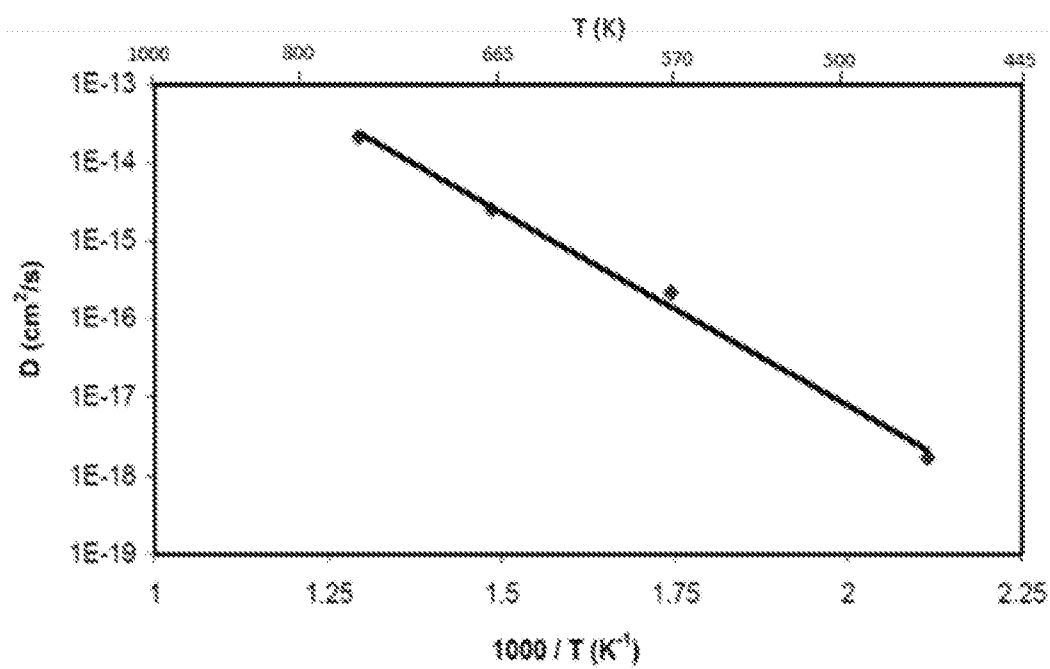


Figure 2

- 3/10 -

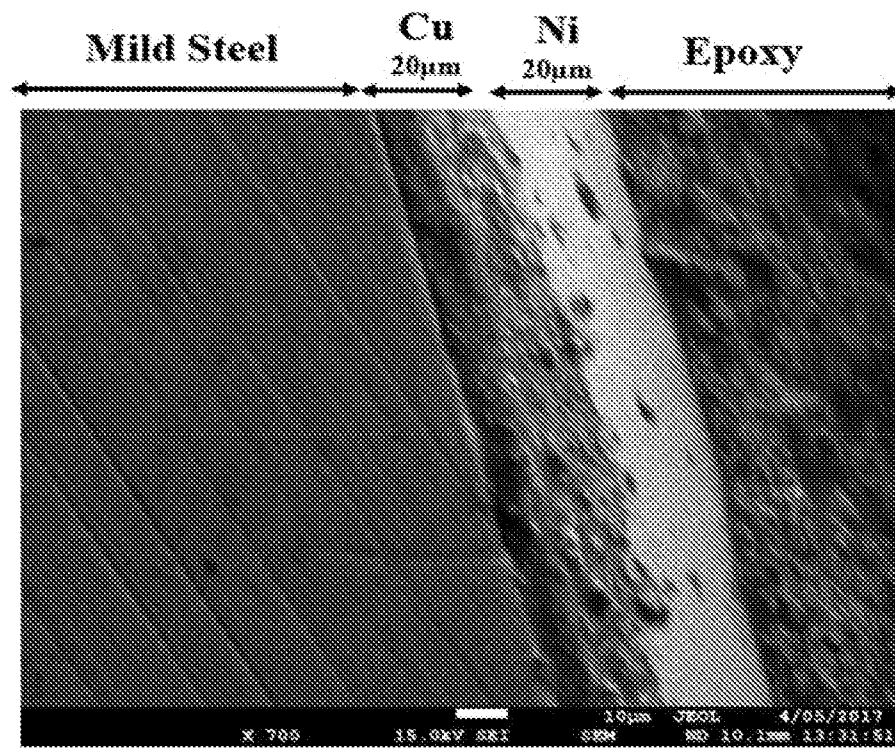


Figure 3

- 4/10 -

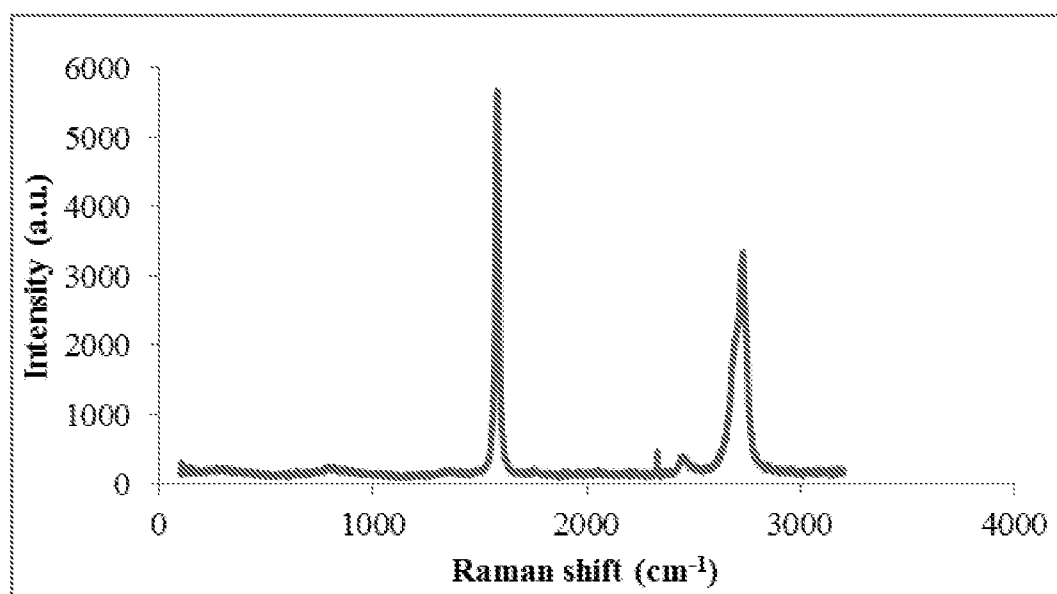


Figure 4

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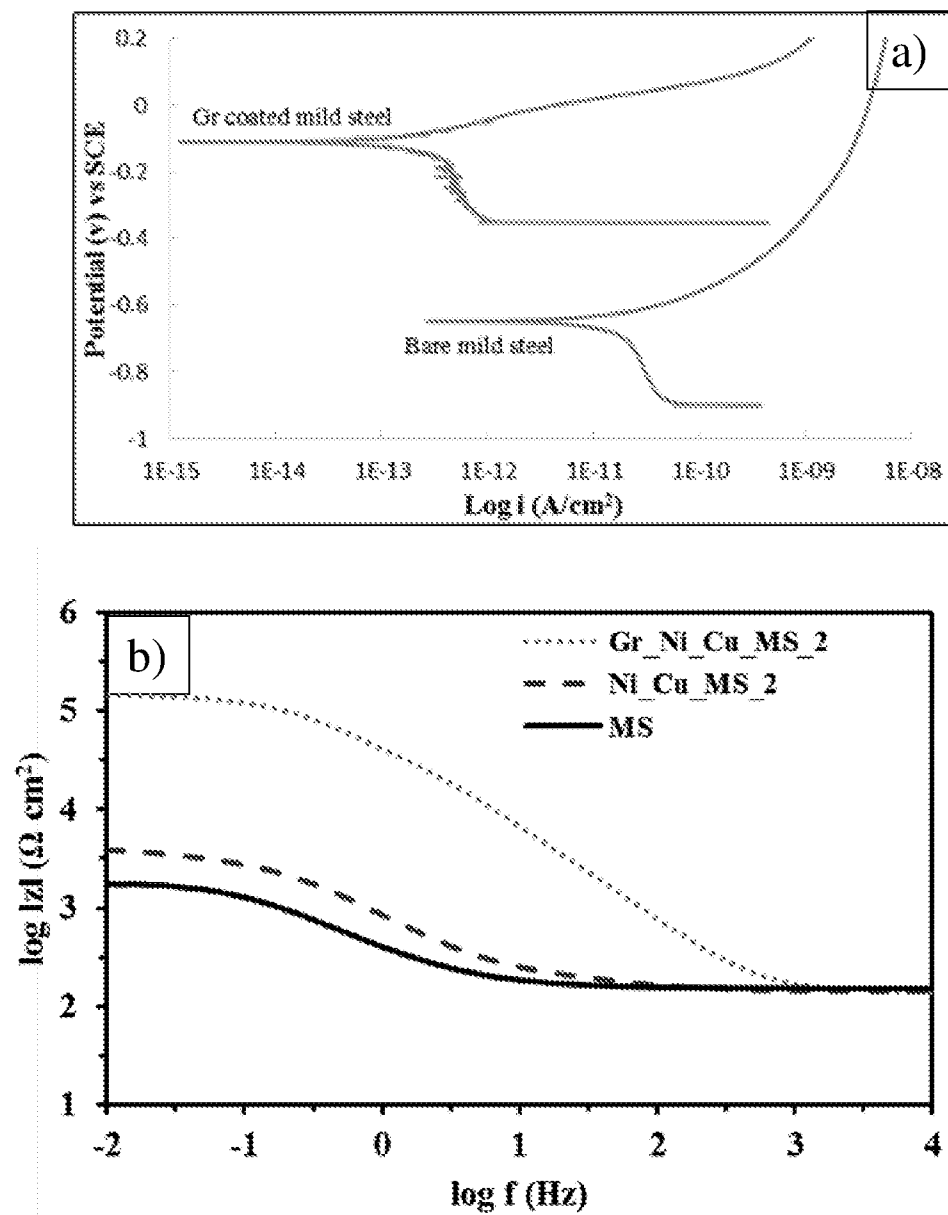


Figure 5

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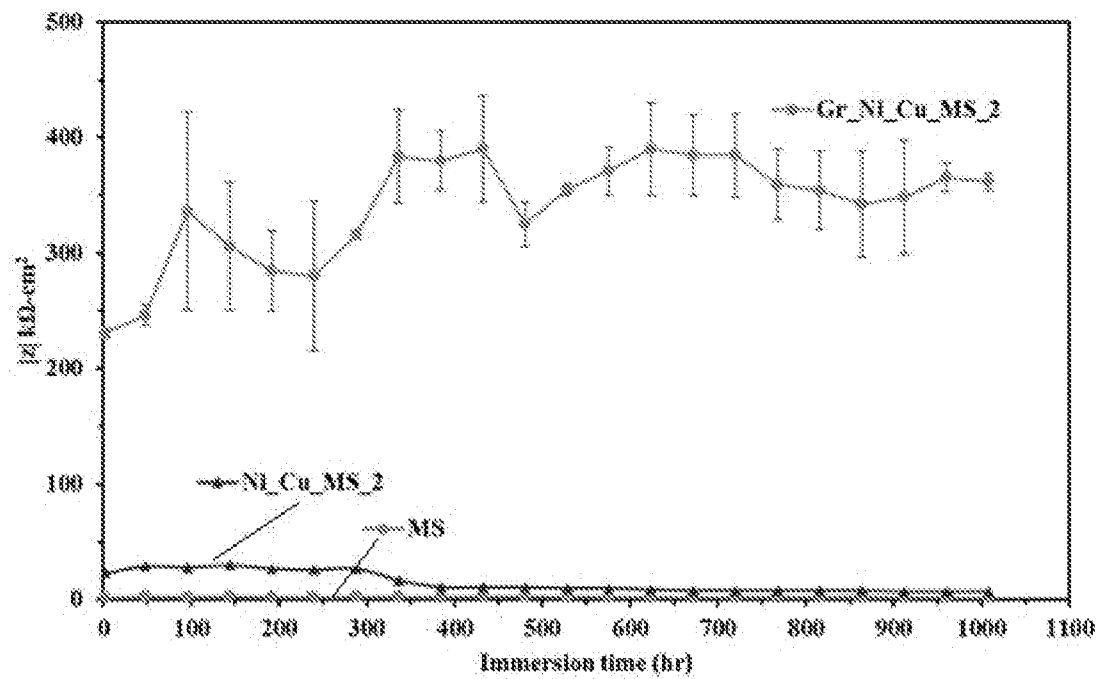


Figure 6

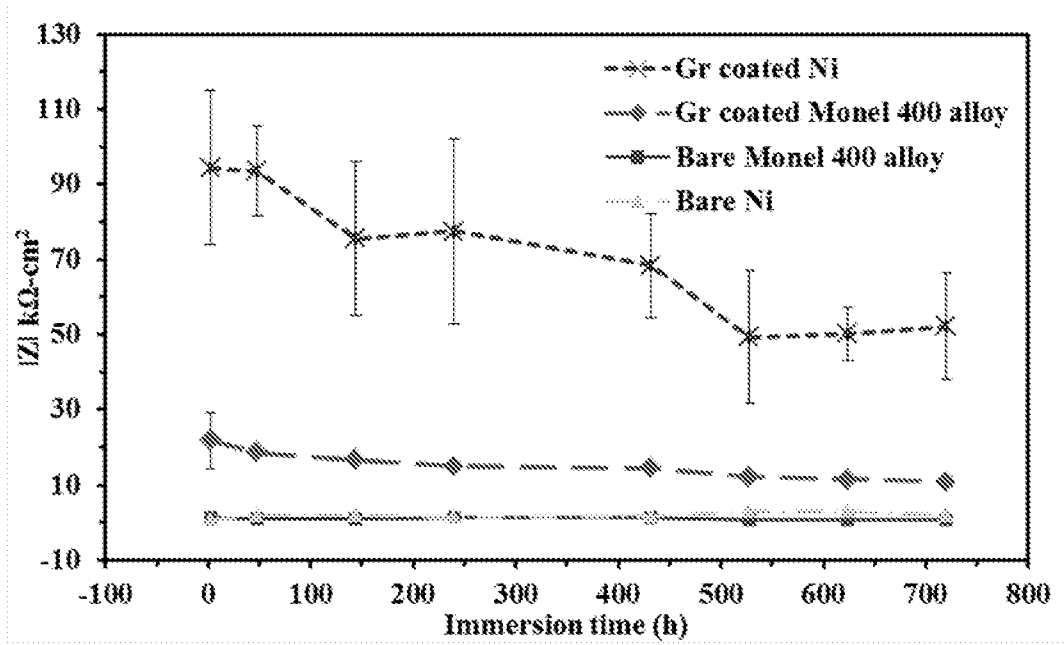
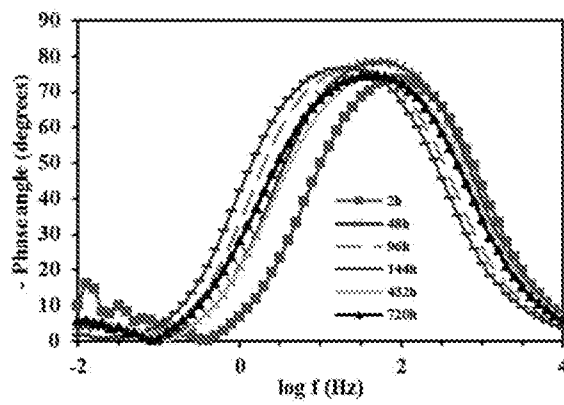
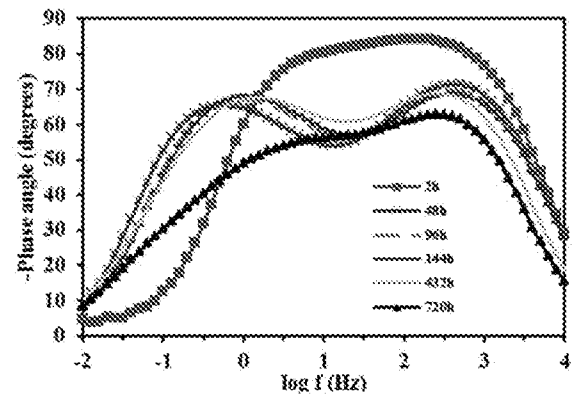


Figure 7

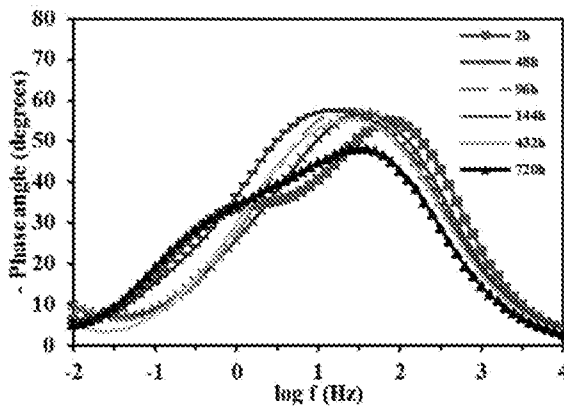
- 8/10 -



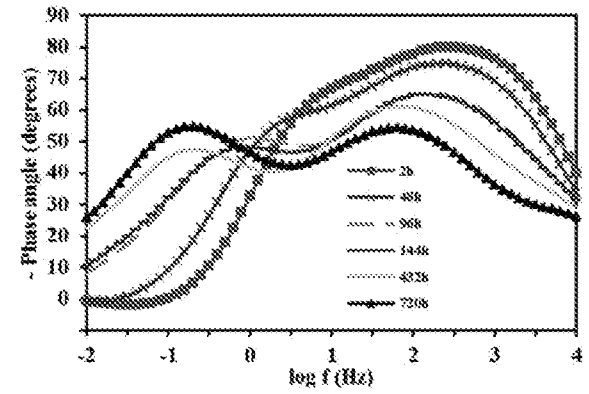
(a)



(b)



(c)



(d)

Figure 8

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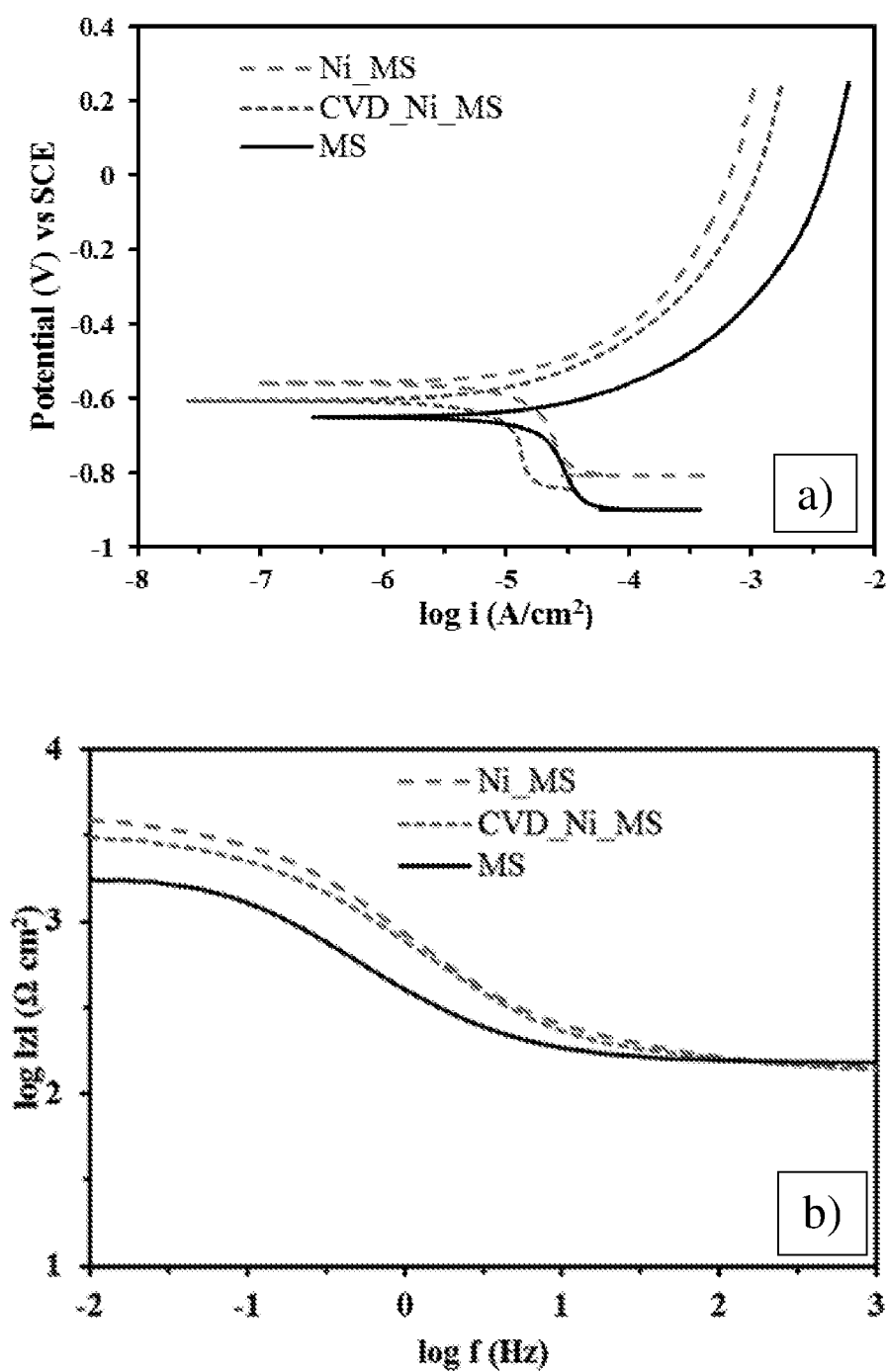


Figure 9

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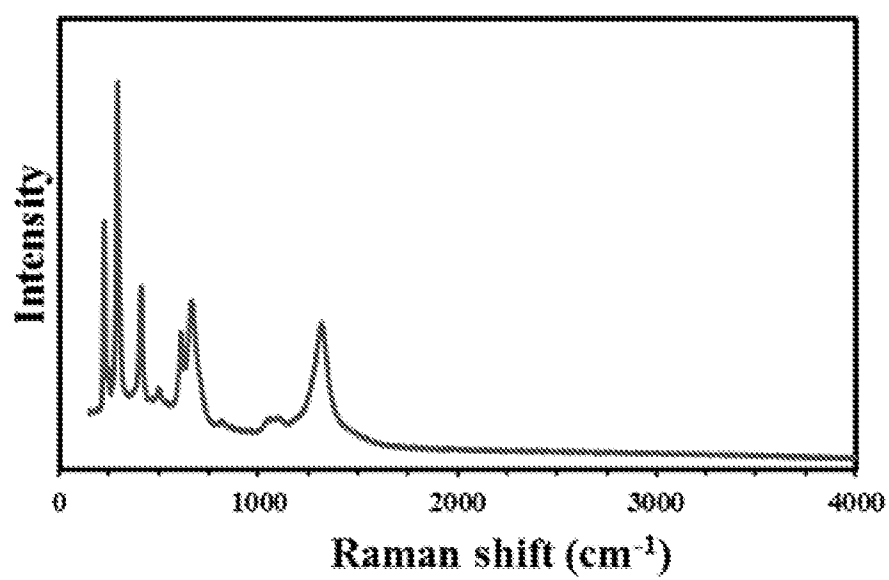


Figure 10

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2020/050186

A. CLASSIFICATION OF SUBJECT MATTER

C01B 32/186 (2017.01) B01J 23/755 (2006.01) B32B 15/04 (2006.01) C23C 28/02 (2006.01) C23C 16/02 (2006.01)
C23C 16/26 (2006.01)

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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

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

PATENW: IPC/CPC Marks (C23C 28/02/LOW, C23C 30/00/LOW, C01B 32/186, C01B 32/188, C23C 16/02/LOW, B32B 15/04/LOW, B32B 15/18, B32B 15/20) using keywords (INHBIT, CARBON, DIFFUSION, BARRIER, COPPER, PLATINUM, RHENIUM, ZIRCONIUM, HAFNIUM, TITANIUM, VANADIUM, URANIUM, TANTALUM, NIOBIUM, CHROMIUM, CATALYST, NICKEL, COBALT, SILVER, RUTHENIUM, IRIIDIUM, PALLADIUM, GRAPHENE, METALLIC, SUBSTRATE) and like terms; ESPACENET, GOOGLE SCHOLAR: using keywords (GRAPHENE, CHEMICAL, VAPOR, DEPOSITION, CARBON, DIFFUSION, BARRIER, CATALYST) and like terms; ESPACENET, AUSPAT, INTERNAL DATABASES provided by IP Australia: APPLICANT/INVENTOR(S) name searched

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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



Further documents are listed in the continuation of Box C



See patent family annex

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"D" document cited by the applicant in the international application	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search
4 May 2020

Date of mailing of the international search report
04 May 2020

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INTERNATIONAL SEARCH REPORT		International application No.
C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		PCT/AU2020/050186
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2013/0248229 A1 (TYCO ELECTRONICS CORPORATION) 26 September 2013 abstract; paragraphs [0008] – [0010], [0019] – [0028], [0040]; claims 1 – 2, 5, 7, 9, 11 – 12, 15, 19 – 20; figure 1	1 - 24
Y	US 2005/0069709 A1 (LEV et al.) 31 March 2005 abstract; paragraphs [0026] – [0028], [0033], [0040] – [0042]; claims 1, 9, 13, 15, 20 – 21, 25; figure 1	1 - 14, 16 - 24
X	JACOBBERGER M. ROBERT et al., “Simple Graphene Synthesis via Chemical Vapor Deposition”, Journal of Chemical Education, 31 July 2015, vol.92, pages 1903 – 1907 whole document	15
Y	whole document	1 - 14, 16 - 24
X	US 2016/0104640 A1 (INFINEON TECHNOLOGIES AG) 14 April 2016 abstract; paragraphs [0035], [0046], [0049], [0052], [0058] – [0059], [0065] – [0066], [0127]	15
A	abstract; paragraphs [0035], [0046], [0049], [0052], [0058] – [0059], [0065] – [0066], [0127]	
X	ZHANG YI et al., “Comparison of Graphene Growth on Single-Crystalline and Polycrystalline Ni by Chemical Vapor Deposition”, The Journal of Physical Chemistry Letters, 2010, vol. 1, pages 3101 – 3107 abstract; page 3102	15
A	abstract; page 3102	
Form PCT/ISA/210 (fifth sheet) (July 2019)		

INTERNATIONAL SEARCH REPORT		International application No.	
Information on patent family members		PCT/AU2020/050186	
This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.			
Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	Publication Date	Publication Number	Publication Date
US 2013/0248229 A1	26 September 2013	US 2013248229 A1	26 Sep 2013
		CN 104205241 A	10 Dec 2014
		CN 104205241 B	14 Nov 2017
		JP 2017106123 A	15 Jun 2017
		JP 6545207 B2	17 Jul 2019
		JP 2015518235 A	25 Jun 2015
		WO 2013142050 A1	26 Sep 2013
US 2005/0069709 A1	31 March 2005	US 2005069709 A1	31 Mar 2005
		US 7195817 B2	27 Mar 2007
		CN 1859985 A	08 Nov 2006
		EP 1677919 A2	12 Jul 2006
		WO 2005035818 A2	21 Apr 2005
US 2016/0104640 A1	14 April 2016	US 2016104640 A1	14 Apr 2016
		US 9627196 B2	18 Apr 2017
		CN 105513946 A	20 Apr 2016
		CN 105513946 B	01 Feb 2019
		DE 102015117176 A1	14 Apr 2016
End of Annex			
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.			