Title: ORGANIC-INORGANIC HYBRID COATINGS

Abstract: An organic-inorganic hybrid (ormosil) coating and method of preparing the same is provided. The method of coating preparation involves sol-gel processing techniques in which a first layer is formed from deposition of a sol comprising a curing agent followed by application of a second sol comprising at least one ormosil or ormosil hybrid onto the first layer. Dopant compounds or materials may be added to the curing agent sol to effect the chemical and/or mechanical properties of the coating. A thick and dense anticorrosion coating is provided.
For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.
ORGANIC-INORGANIC HYBRID COATINGS

Field of the Invention
The present invention relates to coatings formed on substrates and in particular, although not exclusively, to organically modified silane (ormosil) coatings.

Background to the Invention
Corrosion protection of metals, in particular aluminum alloys, is an important commercial and industrial field due to the extensive use of corrosion susceptible materials in construction, marine, automotive and aviation applications. Material corrosion is a significant problem as it significantly reduces structural integrity resulting in costly repair or if undetected for a significant length of time, irreparable damage and even loss of life.

One early and extensively used anticorrosion coating comprised chromate which whilst effective is highly toxic, carcinogenic and environmentally unfriendly. There was therefore a need for a more environmentally benign substrate treatment method.

A number of anticorrosion treatments have been proposed to address the above problems. One particular class of coatings known as organically modified silicates (ormosil) have found use in various high performance applications due to their good corrosion protection for various metal substrates.

Ormosils are hybrid organic–inorganic materials resulting from the hydrolysis and condensation of organically modified silanes with conventional alkoxide precursors. When formed as a coating, the organic component in the matrix offers the advantage of mechanical toughness and flexibility whilst the inorganic component provides the coating with its hardness and thermal stability.
US 2003/0012971 discloses an ormosil composite coating comprising a plurality of inorganic particles of a size greater than one micron entrapped within the ormosil structure. Inorganic particles are selected from oxides, nitrides, carbides and carbonitrides so as to provide ormosil films exhibiting enhanced abrasion and corrosion resistance.

The corrosion resistance behavior of ormosil thin films on aluminum substrates was investigated in *Progress in Organic Coatings* 44 (2002) 185-199; and *Progress in Organic Coatings* 50 (2004) 231-246. To prepare the coatings, at least one curing agent is added to the ormosil sol with the resulting sol mixture being allowed to stand for a short period of time prior to film deposition. The solutions are applied to a cleaned aluminum substrate via spray coating techniques.

One disadvantage with known ormosil films and associated substrate processing techniques is the required curing time. Typically, a conventional ormosil coating of approximately 6 to 16 micron thickness requires at least 24 hours to dry. Where thicker anticorrosion coatings are required, this drying time is significantly increased. The disadvantageous long drying time associated with known ormosil coatings increases the cost of treating the substrate in addition to lengthening manufacturing processes.

An additional disadvantage with conventional substrate treatment techniques involving ormosil films is the need to apply the prepared ormosil sol immediately or shortly after sol preparation. Following addition of the curing agent to the ormosil sol a curing process will begin and the sol will gradually solidify with the effect that the prepared sol cannot be stored for long periods prior to use. This introduces inconvenience to the manufacturer, as fresh solutions are required to be prepared immediately prior to substrate treatment.
Summary of the Invention

The inventors provide a method of treating a substrate in which the final curing time is significantly less than that of known techniques. Typically curing times of organic-inorganic hybrid coatings according to the present invention may be of the order of minutes and not hours as with prior art processing techniques.

By preparing a first sol comprising the curing agent being physically separate from a second sol comprising the ormosil or ormosil hybrid, a number of significant advantages are realised. Both solutions may be stored independently for long periods, of the order of months, prior to deposition on the substrate. Moreover, the inventors have found that by applying the curing agent containing sol directly onto the substrate followed by deposition of the ormosil or ormosil hybrid sol onto the layer formed by the curing agent sol, the drying time of the coating at ambient temperature, may be of the order of minutes.

According to specific implementations of the present invention, it is beneficial to incorporate dopant materials into the curing agent sol, for example granular particulates and/or nanoparticles, for example, to alter the chemical or mechanical properties of the coating. Additionally, it is possible to prepare dense thick coatings by including certain types of particulates within the curing agent sol. By preparing the coating via a two step process involving preparation of the separate curing agent sol and the ormosil or ormosil hybrid sol, it is possible to optimise stabilisation of the dopant material or dopant particulates within the curing agent sol without the stabilisation being effected by interaction between the ormosil and the stabilising agent.

Preferably, an organic polymer is used as stabilising agent, in particular polyvinylalcohol and/or triethylenetriamine.

According to a first aspect of the present invention there is provided a substrate having a sol-gel derived coating, said coating comprising a first layer
contact with said substrate, said first layer comprising at least one curing agent; and a second layer in contact with said first layer, said second layer comprising at least one ormosil or ormosil hybrid compound capable of being cured by said curing agent.

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Preferably, the curing agent comprises any one or a combination of the following set of triethylenetriamine (TETA); diethylenetriamine (DEA); tetaethylenepentamine (TEPA).

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Preferably, the ormosil or ormosil hybrid comprises any one or a combination of the following: tetramethoxysilane (TMOS); tetraethoxysilane (TEOS); 3-glycidoxypropylmethoxysilane (GLYMO).

The coatings of the present invention may be applied directly or indirectly onto any type of substrate material being in particular a metal, aluminium, aluminium alloy, in particular aluminium 2024-T3, glass, ceramic, stainless steel carbon, steel, galvanised steel or electroplated steel.

The other materials or chemicals that may be added to the curing agent sol may be configured to bind with the curing agent either by physical binding or chemical binding. The dopant material may comprise any desired material configured to alter the chemical and/or mechanical properties of the coating. The dopant material may comprise any one or a combination of the following: nanoparticles, γ-alumina, at least one biologically active molecule, at least one bacteria, at least one dopant metal ion, at least one dye compound, silicon carbide, metal carbide or alumina gel particulates.

According to a second aspect of the present invention there is provided a method of treating a substrate, said method comprising: applying a first sol comprising at least one curing agent to a substrate to form a coating; allowing said first sol to dry or partially dry; applying a second sol comprising at least one ormosil
or ormosil hybrid to said coating; and allowing said curing agent to cure said ormosil or ormosil hybrid.

Preferably, the first sol and the second sol are dried at room temperature, the drying time typically taking one to two minutes or preferably less than one minute.

According to a third aspect of the present invention there is provided a method of coating a substrate, said method comprising: preparing a first sol of at least one curing agent; preparing a second sol of at least one ormosil or ormosil hybrid; coating said substrate with said first sol; allowing the coating of said first sol to dry or partially dry; applying said second sol to the coating formed by said first sol; and allowing said curing agent to cure said ormosil or ormosil hybrid.

The drying time of the coating formed by deposition of the first sol and second sol, at ambient temperature, may be less than one hour, less than thirty minutes, less than five minutes or preferably less than one minute, depending upon the thickness and composition of the ormosil coating.

In order to achieve a substrate coating of required thickness, corrosion resistance and hardness the silanes, alkyl-silanes or alkyl-modified silanes of the present invention may be mixed with other organic, inorganic or hybrid polymers to obtain the desired ormosil or ormosil hybrid sol.

Metal atom or ion nanoparticles may be added to the curing agent sol prior to coating deposition. In particular zirconium may be added to the curing agent sol to effect the optical properties of the coating whereby the coating of the present invention may be configured as an anti-reflection coating.
Brief Description of the Drawings

For a better understanding of the invention and to show how the same may be carried into effect, there will now be described by way of example only, specific embodiments, methods and processes according to the present invention with reference to the accompanying drawings in which:

Fig 1 is a graph of potentiodynamic polarisation curves for a bare aluminum alloy substrate, a conventional chromic acid anodised coating, a hybrid sol-gel coating of the present invention cured at room temperature and a hybrid sol-gel coating of the present invention cured at 150°C incorporating silica gel particulates.

Detailed Description

There will now be described by way of example a specific mode contemplated by the inventors. In the following description numerous specific details are set forth in order to provide a thorough understanding. It will be apparent however, to one skilled in the art, that the present invention may be practiced without limitation to these specific details. In other instances, well known methods and structures have not been described in detail so as not to unnecessarily obscure the description.

The anticorrosion behaviour of organic-inorganic hybrid coatings cured at room temperature and 150°C has been studied using DC electrochemical and chemical exfoliation tests. It has been found that the surface treatment and hence the condition of the substrate, is an important factor to ensure good corrosion resistance. Removal of the substrate oxide layer prior to coating either by polishing or using a dilute acid etch gives rise to excellent corrosion resistance through improved substrate-coat bonding. The hardness of the hybrid coatings can be increased by doping the sol-gel with particulates.

Ormosil Preparation – Example 1

Preparation of the Curing Agent Sol (the first Sol)
The curing agent of 2 ml diethylenetriamine(DEA) was dissolved in an organic solvent of 80 ml 2-propanol and 20 ml methanol under vigorous stirring.

**Preparation of the Ormosil Sol (the second sol)**

10 ml 3-Glycidoxypropylmethoxysilane (GLYMO) and 10 ml tetraethoxysilane (TEOS) and 30 ml ethanol alcohol were mixed first, then 1 ml 10% HNO₃ water solution was added into the mixed solution to adjust the pH value. Finally, 10 ml water was added dropwise into the solution. The sol was allowed to age for 24 hours.

**Substrate Surface Preparation and Coating Methods**

Coupons of commercially wrought aluminium alloy 2024-T3 (AA) with a size of 2cm x 3cm were polished to a one micron surface finish and then ultrasonically cleaned in deionised water and methanol. The substrates were coated with the hybrid coating using a dip technique and dried at room temperature. The coatings were touch-dry after one hour. These samples were then used to conduct electrochemical polarisation curves and chemical exfoliation tests. They are listed in table 1 as the G0 group. A further five groups of coatings were applied to AA coupons of size 2.5cm x 5cm. Details of the preparation of these samples are given in Table 1. Sol-gel composite organic-inorganic hybrid coatings with particulate additions were also prepared and cured at 150°C for one hour (sample G4).

**Table 1. Details of sample preparation and coating procedure**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td>G0</td>
<td>Polished to a one micron surface finish and then ultrasonically cleaned in deionised water and methanol.</td>
</tr>
<tr>
<td>G1</td>
<td>Cleaned in soapy water, rinsed in deionised water and methanol. Sol-gel dip-coat and cured at room-temperature for 3 hrs.</td>
</tr>
<tr>
<td>G2</td>
<td>Polished to remove the oxide layer using carbimet paper with 400 grit. Ultrasonic clean in deionised water and methanol. Sol-gel dip-coat and cured at room-temperature for 3 hrs.</td>
</tr>
</tbody>
</table>
Samples G0, G1, G3 and G5 are substantially pure epoxy-silica coatings (silica and silica-epoxy). Sample G4 is also an epoxy-silica coating with the addition of silica gel particulates. Samples G0 to G5 differ from one another in the treatment of the original substrate material as detailed in table 1.

DC-polarisation tests of the coated AA substrates were performed using a conventional three-electrode electrochemical cell with a Saturated Calomel reference electrode (SCE) and Pt counter electrode. All measurements were conducted within aqueous, air-exposed, sodium chloride (3.5%) solution. The test area consisted of a 10 mm diameter circle. For comparison purposes equivalent data was obtained for the un-coated (bare) substrate. Exfoliation tests were performed by immersing both bare and coated samples in an air-exposed solution of 4M NaCl, 0.5M KNO₃ and 0.1M HNO₃ for 168 hours. Accelerated long term corrosion resistance was evaluated using the following cyclic method:

(1)  
(2)
immersion in aqueous, air-exposed, 3.5% NaCl solution for 2 hrs at room temperature → immersion in 100% relative humidity environment for 50 hrs at 50°C

A photographic record of the changes in surface condition was made over the duration of the test. The morphology of the coating and cross sections before and after corrosion testing was also studied using scanning electron microscopy (Philips XL40 or Joel 840A SEM). Thin sputtered carbon films were applied to some coatings in order to prevent surface charging in the standard SEM. Vickers hardness tests were carried out using a Mitutoyo MVK-H hardness tester using a 25 g load.

**Hardness and Film Thickness Measurements**

A Vickers hardness value of 145 kg/mm² was recorded for the polished bare Al 2024-T3 substrate while the room temperature cured hybrid film (sample G0) has a hardness of 51 kg/mm². The hybrid coating cured at 150°C for one hour was found to have a hardness 122 kg/mm². On addition of particulates to the coating (sample G4) the hardness was found to increase to 250 kg/mm². Thus, loading the coating with particulates has greatly increased the hardness of the coating by 60% above that of the bare substrate.

Film thicknesses were generally found to be in the range of 1-10 μm, which was dependent on the concentration of the hybrid sol. The average thickness of the films was found to be around 6 μm. The films obtained were very dense and uniform.

**Corrosion Resistance of the Coatings**

Figure 1 herein is a graph of Potentiodynamic polarisation curves recorded in aqueous 3.5% NaCl solution at 25°C for a bare polished room-temperature cured (AA) samples (curve 100); conventional chromic acid anodised coating (curve
200); a hybrid sol-gel coating cured at room temperature (curve 300); and a hybrid sol-gel coating comprising silica gel particulates, cured at 150°C (curve 400).

Curve (100) presents the polarisation behaviour of the polished bare AA alloy having an $I_{\text{corr}}$ value around 1.0 $\mu$A/cm$^2$ and $E_{\text{corr}}$ of $-600$ mV (SCE). The bare AA corroded rapidly on the application of small anodic potentials. As a comparison, curve (200) presents the AA substrate after chromic acid anodising. As can be seen this surface is less active having an $I_{\text{corr}}$ of around 3 nA/cm$^2$ and $E_{\text{corr}}$ $= -460$ mV. Curve (300) presents the results for the hybrid coat system on polished AA. This exhibits a significant improvement in corrosion resistance, when compared to the untreated Al alloy, with values of $I_{\text{corr}} = 10$ nA/cm$^2$ and $E_{\text{corr}} = -420$ mV. Curve 400 presents the hybrid sol-gel coat cured at 150°C with silica gel particulates. It shows an improvement in anticorrosion, when compared to the bare AA having an $I_{\text{corr}}$ of about 10 nA/cm$^2$ and $E_{\text{corr}} = -520$ mV.

**Accelerated Long Term Corrosion Resistance Testing**

Accelerated long term corrosion resistance was evaluated using the above cyclic corrosion method using original hybrid coated samples according to the present invention after a single corrosion test cycle.

After a single corrosion test cycle, it was observed that the anticorrosion coating of G1 group coated samples exhibited cracking. The reason for this may be attributed to the weak binding between the film and the bare AA. That is, the substrate was simply cleaned in soapy water and washed in deionised water, thereby leaving a loose oxide layer on the surface.

The samples prepared using the G2 procedure resulted in a film that exhibited good anticorrosion properties with little or no deterioration in the coating up to two test cycles (total: 4 hrs in 3.5% NaCl solution and 100 hrs in 50°C hot water humid environment). After three test cycles, some parts of the sample started to show signs of corrosion which further increased after 4 test cycles.
The G3 procedure produced samples that displayed similar behaviour to the G2 samples although it was noted that after 2 test cycles the G2 coating showed improved corrosion resistance over that of the G3 coating. Compared with G1 group samples, no cracking was found on the G2 and G3 samples. The reason for this is thought to be due to the removal of the substrate oxide film by either polishing or by the weak acid etch. Samples prepared via the G4 route exhibited good corrosion resistance after 2 tests cycles although after 3 test cycles the sample began to show signs of corrosion. The G5 procedure produced samples having the best corrosion resistance; only after five test cycles were signs of corrosion observed on the samples (total: 10 hrs in 3.5% NaCl solution and 250 hrs in 50°C hot water humid environment).

**Exfoliation Tests**

Coating sample G0 was examined before and after immersion in the exfoliation solution for 168 hours.

Substrates with a sol-gel coating were protected from corrosion showing no signs of spallation. The coating exhibited excellent anticorrosion properties providing an adherent protection film on the AA substrate. This result could be considered to be attributed to the surface finish polish, which improved the bonding between the film and the substrate.

**SEM Analysis**

The surface morphology of the bare AA substrate, chromic acid anodised (CAA) and hybrid coating (sample G0), were investigated following testing in the exfoliation solution.

Severe corrosion after 72 hrs immersion, was observed for the untreated substrate. Here a thick corrosion product was formed (oxide film formation) during immersion which, on drying, exhibited numerous cracks. Cracking and spalling of this film allows further oxidation of the substrate resulting in high corrosion rates.
Inspection of the CAA surface after 72 hrs immersion revealed good adhesion and that the surface was more resistant to corrosion.

However detailed examination of the surface of the untreated substrate identified the presence of numerous surface micro-pits. The thickness of the CAA coat was very thin (about one micron) and the occurrence of micro-pitting may be attributed to the presence of intermetallics within the microstructure of the AA material. By comparison the room temperature-cured organic-inorganic hybrid coat demonstrated excellent corrosion resistance and maintained adhesion even after 168 hrs in the exfoliation solution. Only at high magnification could any signs of damage (cracking) be observed. However such cracks were less than a micron in size and were not considered to be detrimental to the corrosion resistance of the coating.
Claims:

1. A substrate having a sol-gel derived coating, said coating comprising:

   a first layer in contact with said substrate, said first layer comprising at least one curing agent; and

   a second layer in contact with said first layer, said second layer comprising at least one ormosil or ormosil hybrid capable of being cured by said curing agent.

2. The substrate as claimed in claim 1 wherein said curing agent comprises any one or a combination of the following set of:

   triethylenetriamine (TETA);
   diethylenetriamine (DEA);
   tetraethylenepentamine (TEPA).

3. The substrate as claimed in claim 1 or 2 wherein said at least one ormosil or ormosil hybrid comprises any one or a combination of the following set of:

   tetramethoxysilane (TMOS);
   tetraethoxysilane (TEOS);
   3-glycidoxypropylmethoxysilane (GLYMO).

4. The substrate as claimed in any preceding claim wherein said substrate comprises any one of the following set of:

   - a metal;
   - aluminium;
   - an aluminium alloy;
   - a glass;
• a ceramic;
• stainless steel;
• carbon steel;
• galvanized steel;
• electroplated steel.

5. The substrate as claimed in any preceding claim further comprising an organic and/or inorganic dopant material dispersed within said first layer, said dopant material configured to alter the chemical and/or mechanical properties of said coating.

6. The substrate as claimed in claim 5 wherein said dopant material comprises nanoparticles.

7. The substrate as claimed in claim 5 wherein said dopant material is γ-alumina.

8. The substrate as claimed in claim 5 wherein said dopant material is at least one biologically active molecule.

9. The substrate as claimed in claim 5 wherein said dopant material is at least one species of bacteria.

10. The substrate as claimed in claim 5 wherein said dopant material is at least one dopant metal or metal ion.

11. The substrate as claimed in claim 5 wherein said dopant material is at least one dye compound.

12. The substrate as claimed in claim 5 wherein said dopant material is silicon carbide or a metal carbide.
13. The substrate as claimed in claim 5 wherein said dopant material comprises alumina gel particulates.

14. A method of treating a substrate, said method comprising:

applying a first sol comprising at least one curing agent to a substrate to form a coating;

allowing said first sol to dry or partially dry;

applying a second sol comprising at least one ormosil or ormosil hybrid to said coating; and

allowing said curing agent to cure said ormosil or ormosil hybrid.

15. The method as claimed in claim 14 wherein said first sol is dried at room temperature.

16. The method as claimed in claim 14 or 15 further comprising:

drying said second sol at room temperature.

17. The method as claimed in any one of claims 14 to 16 wherein said curing agent comprises any one or a combination of the following set of:

- triethylenetetramine (TETA);
- diethylenetriamine (DEA);
- tetraethylenepentamine (TEPA).

18. The method as claimed in any one of claims 14 to 17 wherein said at least one ormosil or ormosil hybrid comprises any one or a combination of the following set of:
tetramethoxysilane (TMOS);
tetraethoxysilane (TEOS);
3-glycidoxypropylmethoxysilane (GLYMO).

19. The method as claimed in any one of claims 14 to 18 wherein said substrate comprises any one of the following set of:

- a metal;
- aluminium;
- an aluminium alloy;
- a glass;
- a ceramic;
- stainless steel.

20. A method of coating a substrate, said method comprising:

preparing a first sol containing at least one curing agent;

preparing a second sol of at least one ormosil or ormosil hybrid;

coating said substrate with said first sol;

allowing the coating of said first sol to dry or partially dry;

applying said second sol to the coating formed by said first sol; and

allowing said curing agent to cure said ormosil or ormosil hybrid.

21. The method as claimed in claim 20 further comprising mixing said second sol with at least one dopant silane compound prior to said step of applying said second sol to said coating.
22. The method as claimed in claims 20 or 21 wherein a drying time of the coating formed by said first sol and said second sol, at ambient temperature, is less than one hour.

23. The method as claimed in any one of claims 20 to 21 wherein a drying time of the coating formed by said first sol and said second sol, at ambient temperature, is less than thirty minutes.

24. The method as claimed in any one of claims 20 to 21 wherein a drying time of the coating formed by said first sol and said second sol, at ambient temperature, is less than five minutes.

25. The method as claimed in any one of claims 20 to 21 wherein a drying time of the coating formed by said first sol and said second sol, at ambient temperature, is less than one minute.

26. The method as claimed in any one of claims 20 to 25 wherein said curing agent comprises any one or a combination of the following set of:

triethylenetriamine (TETA);
diethylenetriamine (DEA);
tetraethylenepentamine (TEPA).

27. The method as claimed in any one of claims 20 to 26 wherein said at least one ormosil or ormosil hybrid comprises any one or a combination of the following set of:

tetramethoxysilane (TMOS);
tetraethoxysilane (TEOS);
3-glycidoxypropylmethoxysilane (GLYMO).
28. The method as claimed in any one of claims 20 to 27 wherein said substrate comprises any one of the following set of:

- a metal;
- aluminium;
- an aluminium alloy;
- a glass;
- a ceramic;
- stainless steel.

29. The method as claimed in any one of claims 20 to 28 wherein the coating formed by said first sol and said second sol is generated at said substrate by a sol gel process.
Fig. 1