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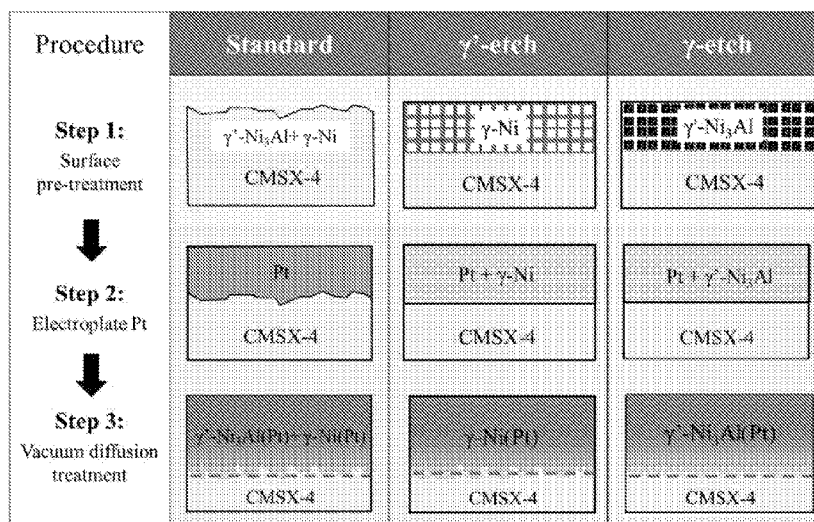
(54) **Title:** BOND COAT

Figure 1

(57) **Abstract:** The present invention relates to a platinum group metal-diffused bond coat with single gamma-prime phase of a nickel-based single crystal superalloy, which is suitable for use in thermal barrier coatings to protect components (e.g. turbine blades, augmentors, and exhaust and combustion chamber components) that are exposed to exceptionally high temperatures. The present invention also relates to methods of forming the platinum group metal-diffused gamma prime bond coat and to the use of this bond coat in thermal barrier coatings.

BOND COAT

INTRODUCTION

[0001] The present invention relates to a bond coat and, more specifically, to a platinum group metal-diffused bond coat. The platinum group metal-diffused bond coat of the present invention is suitable for use in thermal barrier coatings to protect nickel-based single crystal superalloy components (e.g. turbine blades, augmentors, and exhaust and combustion chamber components) that are exposed to exceptionally high temperatures during use. The present invention also relates to methods of forming the platinum group metal-diffused bond coat and to the use of this bond coat in thermal barrier coatings.

BACKGROUND OF THE INVENTION

[0002] Thermal-barrier coatings (TBCs) are widely applied to the hot sections of aero-plane engines in order to protect the turbine blade and improve the efficiency.

[0003] Thermal barrier coatings typically consist of four layers: the metal substrate, a metallic oxidation-resistant bond coat, a thermally grown oxide, and ceramic top coat.

[0004] The metal substrate is typically a nickel-based single crystal superalloy, such as CMSX-4. The thermally grown oxide layer is typically a layer of aluminium oxide and the ceramic top coat typically comprises yttria-stabilized zirconia (YSZ).

[0005] There are three major classes of bond coat in the aero-plane industry:

- (1) Overlay MCrAlY (M=Ni, Co) with beta-NiAl and gamma (or gamma prime) phase;
- (2) Platinum-modified nickel aluminide with beta-phase; and
- (3) Platinum-diffused bond coat with gamma and gamma-prime phase (as described in U.S. Patent No.s 5,942,337 and 5,981,091 to David S. Rickerby).

Compared with the former two classes, the platinum-diffused bond coat tends to have a longer thermal lifetime and can be prepared by a simplified fabrication procedure. This type of bond coat also exhibits negligible rumpling during thermal cycling due to its high creep resistance and a better compatibility with the CMSX-4 superalloy.

[0006] However, during a long-term oxidation, an inevitable depletion of platinum occurs due to its inward diffusion into the superalloy substrate. This represents a major performance concern, which results from a significant dilution of the beneficial effects of Pt. The beneficial effects for platinum include:

(a) The addition of platinum can substantially promote the formation of the thermal grown oxide (Al_2O_3) layer (as a protective scale) on the Pt-diffused bond coat and retain the oxidation resistance.

(b) The addition of platinum can inhibit the migration of deleterious elements (e.g. Ti, S, etc.) towards the surface, which may otherwise weaken the thermal grown oxide layer / bond coat interface.

[0007] In addition, Zhao et al. reported that the inward diffusion of platinum towards the CMSX-4 substrate after oxidation also caused the formation of a continuous γ -layer underneath of the thermal grown oxide (Al_2O_3) layer with dislocations and/or vacancies at the interface. These dislocations and vacancies degraded the bond coat/ Al_2O_3 interface coherency and can ultimately lead to the failure of TBCs.

[0008] As a result of this platinum depletion during thermal exposure, it is necessary to have a sufficiently high quantity of platinum in the bond coat so as to off-set the losses that will occur during use. This in turn adds greatly to the cost of these platinum-diffused bond coats because platinum is very expensive.

[0009] There is therefore a need for improved platinum group metal-diffused bond coatings in which the deleterious effects of platinum group metal depletion are minimised. In particular, there is a need for an improved platinum group metal-diffused bond coating in which the amount of platinum group metal retained at the bond coat / thermal grown oxide layer interface is maximised. The development of such a bond coat would significantly reduce the amount of platinum group metal required in the bond coat and this would in turn significantly reduce the cost if less platinum group metal could be utilized.

SUMMARY OF THE INVENTION

[0010] The inventors investigated the mechanism by which platinum diffusion occurs at high temperatures and this led to the design of a new bond coat in which the depletion of platinum from the bond coat is minimised.

[0011] Thus, according to a first aspect, the present invention provides a nickel-based single crystal superalloy substrate comprising a bond coating layer on a surface thereof, wherein the bond coating layer:

- (i) is a gamma-prime phase of the nickel-based single crystal superalloy;
- (ii) has a thickness of 10 to 100 micrometres; and
- (iii) further comprises a platinum-group metal.

[0012] According to a second aspect of the present invention there is provided a bond coat comprising a nickel-based single crystal superalloy, wherein said bond coat:

- (i) is a gamma-prime phase of the nickel-based single crystal superalloy;
- (ii) has a thickness of 10 to 100 micrometres; and
- (iii) further comprises a platinum group metal.

[0013] According to a third aspect of the present invention there is provided a thermal barrier coating comprising:

- (i) a nickel-based single crystal superalloy layer,
- (ii) a bond coat layer present on a surface of the nickel-based single crystal superalloy layer; and
- (iii) a ceramic top-coat layer contacting the opposing surface of the bond coat layer;

wherein the bond coat layer:

- (i) is a gamma-prime phase of the nickel-based single crystal superalloy;
- (ii) has a thickness of 10 to 100 micrometres; and
- (iii) further comprises a platinum group metal.

[0014] During use, a thermal grown oxide layer forms between the bond coat and the ceramic top-layer. Thus, in a fourth aspect, the present invention provides a thermal barrier coating comprising:

- (i) a nickel-based single crystal superalloy layer,
- (ii) a bond coat layer present on a surface of the nickel-based single crystal superalloy layer;
- (iii) a thermal grown oxide layer contacting the opposing surface of the bond coat layer; and
- (iv) a ceramic top-coat layer contacting the opposing surface of the thermal grown oxide layer.

wherein the bond coat layer:

- (i) is a gamma-prime phase of the nickel-based single crystal superalloy;
- (ii) has a thickness of 10 to 100 micrometres; and
- (iii) further comprises a platinum group metal.

[0015] In another aspect, the present invention provides a process for forming a nickel-based single crystal superalloy as defined in the first aspect of the present invention, the process comprising:

- (i) providing a nickel-based single crystal superalloy substrate;

- (ii) forming a layer of gamma-prime nickel-based single crystal superalloy having a thickness of 10 to 100 micrometres on a surface of the nickel-based single crystal superalloy substrate;
- (iii) infusing the layer of gamma-prime nickel-based single crystal superalloy with a platinum group metal.

[0016] In another aspect, the present invention provides a process for forming a bond coat as defined in the second aspect of the present invention, the process comprising:

- (i) providing a nickel-based single crystal superalloy substrate onto which the bond coat is to be formed;
- (ii) forming a layer of gamma-prime nickel-based single crystal superalloy having a thickness of 10 to 100 micrometres on a surface of the nickel-based single crystal superalloy substrate; and
- (iii) infusing the layer of gamma-prime nickel-based single crystal superalloy with a platinum group metal.

[0017] In another aspect, the present invention provides a process for forming a thermal barrier coating as defined in the third aspect of the present invention, the process comprising:

- (i) providing a nickel-based single crystal superalloy substrate;
- (ii) forming a layer of gamma-prime nickel-based single crystal superalloy having a thickness of 10 to 100 micrometres on a surface of the nickel-based single crystal superalloy substrate;
- (iii) infusing the layer of gamma-prime nickel-based single crystal superalloy with a platinum group metal; and
- (iv) applying a ceramic top-coat layer to the surface of the gamma-prime layer.

[0018] In another aspect, the present invention provides a nickel-based single crystal superalloy substrate obtainable by, obtained by or directly obtained by one of the processes defined herein.

[0019] In another aspect, the present invention provides a bond coat obtainable by, obtained by or directly obtained by one of the processes defined herein.

[0020] In another aspect, the present invention provides a thermal barrier coating obtainable by, obtained by or directly obtained by one of the processes defined herein.

[0021] In another aspect, the present invention provides a component for use in a gas turbine engine, said component comprising a nickel-based single crystal superalloy as defined in the first aspect of the invention, or a bond coat as defined in the second aspect of

the present invention, or a thermal barrier coating as defined in the third aspect of the invention.

DETAILED DESCRIPTION OF THE INVENTION

Bond coats

[0022] The inventors developed a novel and simple approach for producing a single phase of either gamma or gamma-prime platinum diffused bond coat on the surface of a nickel-based single crystal superalloy (CSMX-4 being used as a model substrate). The inventors surprisingly found that a gamma-prime platinum-diffused bond coat significantly impeded the depletion of platinum into the nickel-based single crystal superalloy (CSMX-4) during prolonged heating. Accordingly, the provision of a gamma-prime platinum diffused bond coat enables significantly less platinum to be used in the bond coat and this in turn provides a significant cost saving. In this regard, based on the data generated in the example section, the inventors believe the amount of platinum can be reduced by approximately 77%.

[0023] It has also been shown that the resultant thermal barrier coatings provide exceptional performance at elevated temperatures and have strong interfacial adhesion, high temperature yield strengths, and a remarkable effect on reducing the oxidation rate of the superalloy. Furthermore, the coating methodology needed to form the gamma-prime platinum diffused bond coat is simple to implement and reproducible.

[0024] As indicated above, the present invention relates to a nickel-based single crystal alloy provided with a bond coat layer (as defined in the first aspect of the present invention), the bond coat layer *per se* (as defined in the second aspect of the present invention), and a thermal barrier coating (as defined in the third aspect of the present invention).

[0025] Any suitable nickel-based single crystal superalloy, comprising gamma (γ) and gamma prime (γ') phases, may be used as the substrate and for the bond coat defined herein. Typically, such nickel-based single crystal superalloys comprise 50 to 70 weight% nickel and 1 to 7 weight% (more typically 4 to 6.5 weight %) aluminium. Suitably, such alloys further comprise the following main alloy elements (in weight%): chromium 0–10%, cobalt 0–15%, rhenium 0–7%, tantalum 0–12%, tungsten 0–10%, titanium 0–5%, molybdenum 0–4%, hafnium 0–2% (with the 50–70% nickel and 1 to 7% aluminium making up the balance).

[0026] Table 1 below shows the elemental composition of certain nickel-based single crystal superalloys. (Reference: Roger C. Reed, The superalloys: fundamentals and applications. Cambridge University Press, 2006)

Table 1 – elemental composition of nickel-based superalloys (weight percentage)

Alloy	Cr	Co	Mo	W	Al	Ti	Ta	Nb	Re	Ru	Hf	C	B	Zr	Ni
AM1	7	8	2	5	5	1.8	8	1	—	—	—	—	—	—	Bal
AM3	8	5.5	2.25	5	6	2	3.5	—	—	—	—	—	—	—	Bal
CM186LC	6	9.3	0.5	8.4	5.7	0.7	3.4	—	3	—	1.4	0.07	0.015	0.005	Bal
CM247LC	8	9.3	0.5	9.5	5.6	0.7	3.2	—	—	—	1.4	0.07	0.015	0.01	Bal
CMSX-2	8	5	0.6	8	5.6	1	6	—	—	—	—	—	—	—	Bal
CMSX-3	8	4.8	0.6	8	5.6	1	6.3	—	—	—	0.1	—	—	—	Bal
CMSX-4	6.5	9.6	0.6	6.4	5.6	1	6.5	—	3	—	0.1	—	—	—	Bal
CMSX-6	10	5	3	—	4.8	4.7	6	—	—	—	0.1	—	—	—	Bal
CMSX-10	2	3	0.4	5	5.7	0.2	8	—	6	—	0.03	—	—	—	Bal
EPM-102	2	16.5	2	6	5.55	—	8.25	—	5.95	3	0.15	0.03	—	—	Bal
GTD-111	14	9.5	1.5	3.8	3	5	3.15	0.07	—	—	—	0.1	0.014	0.007	Bal
GTD-222	22.5	19.1	—	2	1.2	2.3	0.94	0.8	—	—	—	0.08	0.004	0.02	Bal
IN100	10	15	3	—	5.5	4.7	—	—	—	—	—	0.18	0.014	0.06	Bal
IN-713LC	12	—	4.5	—	5.9	0.6	—	2	—	—	—	0.05	0.01	0.1	Bal
IN-738LC	16	8.5	1.75	2.6	3.4	3.4	1.75	0.9	—	—	—	0.11	0.01	0.04	Bal
IN-792	12.4	9.2	1.9	3.9	3.5	3.9	4.2	—	—	—	—	0.07	0.016	0.018	Bal
IN-939	22.4	19	—	2	1.9	3.7	—	1	—	—	—	0.15	0.009	0.1	Bal
Mar-M002	8	10	—	10	5.5	1.5	2.6	—	—	—	1.5	0.15	0.015	0.03	Bal
Mar-M246	9	10	2.5	10	5.5	1.5	1.5	—	—	—	1.5	0.15	0.015	0.05	Bal
Mar-M247	8	10	0.6	10	5.5	1	3	—	—	—	1.5	0.15	0.015	0.03	Bal
Mar-M200Hf	8	9	—	12	5	1.9	—	1	—	—	2	0.13	0.015	0.03	Bal
Mar-M421	15	10.8	1.8	3.3	4.5	1.6	—	2.3	—	—	—	0.18	0.019	0.04	Bal
MC2	8	5	2	8	5	1.5	6	—	—	—	0.1	—	—	—	Bal
MC-NG	4	—	1	5	6	0.5	5	—	4	4	0.1	—	—	—	Bal
MX4	2	16.5	2	6	5.55	—	8.25	—	5.95	3	0.15	0.03	—	—	Bal
Nasair100	9	—	1	10.5	5.75	1.2	3.3	—	—	—	—	—	—	—	Bal
PWA1422	9	10	—	12	5	2	—	1	—	—	1.5	0.14	0.015	0.1	Bal
PWA1426	6.5	10	1.7	6.5	6	—	4	—	3	—	1.5	0.1	0.015	0.1	Bal
PWA1480	10	5	—	4	5	1.5	12	—	—	—	—	—	—	—	Bal
PWA1483	12.2	9.2	1.9	3.8	3.6	4.2	5	—	—	—	—	0.07	—	—	Bal
PWA1484	5	10	2	6	5.6	—	9	—	3	—	0.1	—	—	—	Bal
PWA1487	5	10	1.9	5.9	5.6	—	8.4	—	3	—	0.25	—	—	—	Bal
PWA1497	2	16.5	2	6	5.55	—	8.25	—	5.95	3	0.15	0.03	—	—	Bal
Rene80	14	9	4	4	3	4.7	—	—	—	—	0.8	0.16	0.015	0.01	Bal
Rene125	9	10	2	7	1.4	2.5	3.8	—	—	—	0.05	0.11	0.017	0.05	Bal
Rene142	6.8	12	1.5	4.9	6.15	—	6.35	—	2.8	—	1.5	0.12	0.015	0.02	Bal
Rene220	18	12	3	—	0.5	1	3	5	—	—	—	0.02	0.01	—	Bal
ReneN4	9	8	2	6	3.7	4.2	4	0.5	—	—	—	—	—	—	Bal
ReneN5	7	8	2	5	6.2	—	7	—	3	—	0.2	—	—	—	Bal
ReneN6	4.2	12.5	1.4	6	5.75	—	7.2	—	5.4	—	0.15	0.05	0.004	—	Bal
RR2000	10	15	3	—	5.5	4	—	—	—	—	—	—	—	—	Bal
SRR99	8	5	—	10	5.5	2.2	12	—	—	—	—	—	—	—	Bal
TMS-75	3	12	2	6	6	—	6	—	5	—	0.1	—	—	—	Bal
TMS-138	2.9	5.9	2.9	5.9	5.9	—	5.6	—	4.9	2	0.1	—	—	—	Bal
TMS-162	2.9	5.8	3.9	5.8	5.8	—	5.6	—	4.9	6	0.09	—	—	—	Bal

[0027] Particular examples of suitable nickel-based single crystal superalloys include those listed in the Table 1 above. In a particular embodiment, the nickel-based single crystal superalloy is CSMX-4.

[0028] The bond coat layer is a gamma-prime phase of a nickel-based single crystal superalloy. By “a gamma-prime phase” we mean that all, or substantially all, of the gamma phase of the nickel-based single crystal superalloy has removed, so as to provide a layer which is all, or predominantly, the gamma-prime phase of the alloy.

[0029] Suitably, the bond coating comprises only the gamma-prime phase of the nickel-based single crystal superalloy.

[0030] As described further herein, the gamma phase of the nickel-based single crystal superalloy can be removed by the selective etching of a surface of a gamma/gamma-prime nickel-based single crystal superalloy substrate with a gamma etchant, or by the selective deposition of a gamma-prime nickel-based single crystal superalloy layer on to a substrate.

[0031] The gamma-prime bond coat layer has a thickness of 10 to 100 micrometres. Suitably, the thickness of the bond coat layer is 10 to 50 micrometres, more suitably 10 to 30 micrometres, even more suitably 10 to 25 micrometres, and most suitably 10 to 20 micrometres.

[0032] The bond-coat layer of the present invention comprises a platinum group metal. Examples of platinum group metals include platinum (Pt), ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os) and iridium (Ir). In an embodiment, the platinum group metal is platinum.

[0033] The amount of platinum group metal present in the bond coat will vary. Typically, it is anticipated that the amount of platinum group metal present will be within the range of 5 to 30 vol.%, suitably 10 to 27 vol.% and more suitably 20 to 25 vol.%. The volume fraction can be measured by a number of different techniques, such as taking cross-sectional SEM images and determining the amount of platinum group metal present using Image Pro plus 6.0 software or by measuring the weight gain of platinum group metal after electroplating. Both techniques are described further in the accompanying example section. The remainder of the bond coat layer is a gamma-prime phase of a nickel-based single crystal superalloy as defined herein.

[0034] In the thermal barrier coatings of the present invention, any suitable ceramic top coat material may be used.

[0035] In an embodiment, the ceramic top coat is formed from yttria-stabilised zirconia.

Process for forming the bond coat

[0036] As defined above, the present invention provides a process for forming a nickel-based single crystal superalloy as defined in the first aspect of the present invention, the process comprising:

- (i) providing a nickel-based single crystal superalloy substrate as defined herein;
- (ii) forming a layer of gamma-prime nickel-based single crystal superalloy having a thickness of 10 to 100 micrometres on a surface of the nickel-based single crystal superalloy substrate;
- (iii) infusing the layer of gamma-prime nickel-based single crystal superalloy with platinum group metal.

[0037] In another aspect, the present invention provides a process for forming a bond coat as defined in the second aspect of the present invention, the process comprising:

- (i) providing a nickel-based single crystal superalloy substrate onto which the bond coat is to be formed;
- (ii) forming a layer of gamma-prime nickel-based single crystal superalloy having a thickness of 10 to 100 micrometres on a surface of the nickel-based single crystal superalloy substrate;
- (iii) infusing the layer of gamma-prime nickel-based single crystal superalloy with platinum group metal.

[0038] In step (i) of these processes, the nickel-based single crystal superalloy substrate is provided.

[0039] In step (ii) the bond coat layer is formed on a surface of the nickel-based single crystal superalloy substrate. This can be achieved by carrying out a gamma etch of the surface to selective remove all, or substantially all, of the gamma phase present in a 10-100 micrometre layer of the substrate materials. Alternatively, it is possible to deposit a layer of gamma-prime nickel-based single crystal superalloy onto a surface of the nickel-based single crystal superalloy substrate.

[0040] Suitably, the bond coat layer is formed by gamma etching of the surface. Approaches for selectively etching gamma phase from the surface of a nickel-based single crystal superalloy are known in the art. Furthermore, suitable gamma etchants that selectively remove the gamma phase are also well known in the art.

[0041] The etching of the surface may be achieved by immersion of the surface of the nickel-based single crystal superalloy in a suitable gamma etchant solution, or by electrolytic etching techniques.

[0042] Suitably, electrolytic etching is used to remove the gamma phase and form the gamma-prime the layer of the bond coat.

[0043] A person skilled in the art will appreciate how to select suitable conditions for undertaking electrolytic gamma etching.

[0044] Suitably, a voltage of 2 to 10 V is used for the etching procedure and more typically, 0.5 to 6 V will be used.

[0045] Suitably, a current density of 50 to 300 mA/cm² is used for the etching procedure and more typically, 100 to 200 mA/cm² will be used.

[0046] Suitably, the etching is carried at room temperature for 0.5 to 20 minutes, with times of 1 to 10 minutes being more typical.

[0047] In an embodiment, the surface of the nickel-based single crystal superalloy is immersed in a gamma etchant solution and subject to a current density of 50 to 300 mA/cm² and/or a voltage of 2 to 10 V for a period of 0.5 to 20 minutes. In a further embodiment, the surface of the nickel-based single crystal superalloy is immersed in a gamma etchant solution and subject to a current density of 100 to 200 mA/cm² and/or a voltage of 2 to 6 V for a period of 1 to 10 minutes.

[0048] Suitably, the solution is stirred during the etching procedure.

[0049] The gamma etchant solution may be an acidic solution comprising 2 to 70 vol.% acid and 30 to 98 vol.% water. Particular examples of etchant solutions include the following:

- 8 vol.% H₃PO₄; 28 vol.% HNO₃; 32 vol.% H₂SO₄ and 32 vol.% H₂O
- 10 vol.% H₃PO₄; 90 vol.% H₂O
- 1 vol.% (NH₄)₂SO₄; 1 vol.% citric acid (C₆H₈O₇); 98 vol.% H₂O

[0050] Once the gamma-prime nickel-based single crystal superalloy layer has been formed, it is then infused with platinum group metal in order to form the bond coat. Any suitable technique currently used to make platinum group metal diffused bond coating may be used in order to infuse the platinum group metal into the gamma-prime nickel-based single crystal superalloy layer.

[0051] Suitably, the platinum group metal is electroplated into a pre-formed gamma-prime layer followed by heating at a temperature of 1000 to 1200 °C (and preferably 1100 to 1200 °C) for a time period of 0.5 to 4 hours (and preferably 1 to 2 hours) at a pressure of less than or equal to 10⁻³ mbar to form the platinum group metal diffused bond coat layer of the present invention. Suitably, the pressure is between 10⁻³ to 10⁻⁶ mbar, more suitably the pressure is 10⁻⁵ mbar or less and most suitably it is about 10⁻⁶ mbar.

[0052] A person skilled in the art will know how to electroplate a suitable quantity of platinum group metal into the gamma-prime nickel-based single crystal superalloy layer. Suitable electroplating techniques are commercially available.

[0053] In an embodiment, platinum P salt (diammine-dinitrito-platinum(II) solution, Sigma-Aldrich, UK) or platinum Q salt (platinum 5Q, $(\text{NH}_3)_4\text{Pt}(\text{HPO}_4)$, Johnson Matthey) solutions are used.

[0054] In a particular embodiment, a platinum Q salt (platinum 5Q, Johnson Matthey) solution is used.

[0055] Suitably, a current density of 2 to 30 mA/cm² is used for the electroplating of platinum group metal, and more typically 10 to 20 mA/cm² will be used.

[0056] Suitably, the electroplating is carried out for 5 to 120 minutes, with times of 10 to 30 minutes being more typical.

[0057] In another aspect, the present invention provides a process for forming a thermal barrier coating as defined in the third aspect of the present invention, the process comprising:

- (i) providing a nickel-based single crystal superalloy substrate;
- (ii) forming a layer of gamma-prime nickel-based single crystal superalloy having a thickness of 10 to 100 micrometres on a surface of the nickel-based single crystal superalloy substrate;
- (iii) infusing the layer of gamma-prime nickel-based single crystal superalloy with platinum group metal
- (iv) applying a ceramic top-coat layer to the surface of the gamma-prime layer.

[0058] Any suitable technique for applying the ceramic topcoat may be used, and more typically electron beam physical vapour deposition (EBPVD).

Applications

[0059] In another aspect, the present invention provides a component comprising a nickel-based single crystal superalloy as defined in the first aspect of the invention, or a bond coat as defined in the second aspect of the present invention, or a thermal barrier coating as defined in the third aspect of the invention.

[0060] Thermal barrier coatings are widely used in the automotive and aviation industries to provide protection to engine components that are exposed to excessively high temperatures.

Examples of such components, include turbine components (e.g. turbine blades), combustion chamber components and exhaust system components.

[0061] The thermal barrier coatings of the present invention therefore have utility in any situation where high temperatures are encountered and it is necessary to provide a protective coating to a nickel-based single crystal superalloy.

Brief Description of the Figures

[0062] An example of the invention will now be described by reference to the accompanying figures, in which:

Figure 1 Schematic illustration: the fabrication procedure and microstructure evolution of modified Pt-diffused bond coat by using selective etching.

Figure 2 Cross-sectional BSE images of standard Pt-diffused bond coat with EBPVD YSZ top coat: (A) as-received (B) after long-term diffusion treatment at 1150°C for 50 hours in vacuum; (C) after oxidation at 1150°C for 50 hours.

Figure 3 Concentration profile of Pt at the cross-section of standard Pt-diffused bond coat after heat treatments.

Figure 4 Surface and cross-sectional images of the etched substrate with different etching time by (A)+(C): γ' -etch; (B)+(D): γ -etch

Figure 5 Cross-sectional images of the as-electroplated (A) γ' -etched substrate and (B) γ -etched substrate with inset enlarged image at the substrate/coating interface.

Figure 6 Cross-sectional images of the γ -phase Pt-bond coat (A) as-received; (B) after diffusion at 1150°C for 50 hours in vacuum; (C) after oxidation at 1150°C for 50 hours.

Figure 7 Cross-sectional images of (A) the as-electroplated γ -etched substrate; (B) as-received bond coat after vacuum heat treatment at 1150°C for 2 hours; (C) after diffusion at 1150°C for 50 hours in vacuum; (D) after oxidation at 1150°C for 50 hours; (E~H): corresponding the bond coat/substrate interface with higher magnification.

Figure 8 Cross-sectional BSE images after oxidation at 1150°C for 50 hours of (A) the standard Pt-diffused bond coat and (B) the γ' -phase Pt-bond coat

Figure 9 Cross-sectional images of the TGO layer after oxidation at 1150°C for 50 hours on the (A) standard Pt-diffused bond coat (B) γ -phase Pt-bond coat; (C) γ' -phase Pt-bond coat; (D~F) EDX mapping of Pt at the bond coat layer beneath the TGO.

Figure 10: (a) Surface of the poorly electroplated sample; (c) Surface of the well electroplated sample; (b) and (d) corresponding images with higher magnification.

Figure 11: (a) Cross-sectional image of the porous thin Pt layer due to the excessive current density; (b) the dense and uniform thick Pt layer within the optimum range of current density; (c) Surface of the non-uniform electroplated sample due to the insufficient current density.

Figure 12: Electroplating rate as a dependency on the current density

Figure 13: Surface morphology of the overlay Pt layer and the composite Pt layer underneath with inset enlarged images

Figure 14: Cross-sectional images of the as-electroplated composite Pt layer (a) with overlay Pt layer (b) without overlay Pt layer.

Figure 15: Cross-sectional images of (a) as-electroplated composite coating; (b) two phases were highlighted by Image-Pro plus 6.0 software.

Figure 16: Cross-sectional images of a layer of (A) 100% Pt; (B) 77% γ' +23%Pt

Figure 17: (A) SEM images of the surface of the etched substrate and (B) enlarged images; (C) cross-sectional images of etched substrate and (D) enlarged images.

Figure 18: Cross-sectional images of the self-bonded γ' -coating after vacuum heat treatment for 2 hours at different temperatures: (A) 1100°C; (B) 1150°C; (C) 1200°C; (D~F) are the corresponding images at the coating/substrate interface with higher magnifications.

Figure 19: X-ray diffraction pattern of (A) γ' -coating and CMSX-4 substrate with inset figures of the enlarged peaks at (100) and (300); (B) γ' -precipitates (micro-cubes) obtained from CMSX-4 substrate.

Figure 20: Weight gain square as a function of oxidation time at 1150°C on the CMSX-4 substrate and γ' -coating (* pre-treated in vacuum for 2 hours at 1150°C)

Figure 21: SEM images of TGO fractured cross-sections after oxidation at 1150°C for 100 hours on (A) non-treated CMSX-4 substrate; (B) γ' -coating; (C) pre-treated CMSX-4 substrate; (D~F) are the corresponding enlarged images.

Figure 22: Amount of stable oxide as a function of oxygen partial pressure in the γ' -Ni₃Al system after long-term oxidation at 1150°C with the addition of Pt (at%): (A) 0; (B) 10; (C) 20; (D) 30; which is calculated by Thermo-Calc 3.1 software with TCNi6 database.

Figure 23: The activity of Ti or Ta (left Y) and the amount of phase (right Y) in the system of Ni₃(Ti, Ta) (1mol) with the addition of Pt (0~1.0at%) at 1150°C, which is calculated by Thermo-Calc 3.1 software with TCNi6 database.

EXAMPLES

Example 1

[0063] In this example, a novel and simple approach has been developed to produce a single phase of either γ or γ' Pt-diffused bond coat, in comparison of the standard procedure, as shown in Figure 1. The novel bond coats are fabricated firstly by selective etching from CMSX-4 superalloy for a certain thickness to form a porous single phase (γ' or γ) coating, where voids are left in the etched region. Then such voids are filled by Pt by electroplating. Finally, Pt diffuses into the γ' or γ phase at the etched region after vacuum heat treatment to form a single phase layer. The study of such bond coats can effectively explain the different diffusion behaviors of Pt in the single γ -phase and γ' -phase, and the experimental results have shown that the inwards diffusion of Pt towards the CMSX-4 substrate can be avoided by the fabrication of the γ' -phase bond coat.

Experiments

Sample preparation

[0064] CMSX-4 single crystal superalloy (nominal composition Ni 9.6Co 6.4Cr 6.4W 6.6Ta 5.6Al 2.9Re 1.03Ti 0.1Hf in wt.%) was cut into a size of 10mm*10mm*2mm as substrate. Substrate surface was grinded by 600 grit SiC paper and degreased by ethanol in an ultrasonic bath, and then washed by deionized water. A solution which contains 150~170ml/L HCl(37%) and 250~330g/L $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was used as γ' -etchant. The substrate was immersed in the γ' -etchant solution at ambient temperature for 1~10 min. For γ -etchant, electrolytic etching was applied with a solution containing 10% H_3PO_4 and 90% H_2O . Platinum foil was used as the cathode and the substrate was etched for 1~10min under constant current density of 100~200mA/cm² with a slow magnetic stirring. Next, the etched substrate was rinsed in boiling sodium hydroxide solution (NaOH, 5%) for 10min to remove the residual acid and then washed by deionized water. After the substrate was well-prepared, platinum was electroplated on the substrate surface by using P salt (diammine-dinitrito-platinum(II) solution, Sigma-Aldrich, UK) under a constant current density of 10~20mA/cm² for 30~60min. The electroplated substrate was then washed by deionized water and dried at ambient temperature overnight, followed by a diffusion treatment at a temperature of 1100~1200 °C for 1~2 hours in a vacuum tube furnace at a pressure of 10⁻⁵ mbar [13]. The sample was then defined as the as-received Pt-diffused bond coat.

Thermal treatment and characterization

[0065] Long-term diffusion was carried out at 1150°C for 50 hours in vacuum. Oxidation was then carried out at 1150°C for 50 hours in air. Scanning electron microscopy (SEM, Philip XL30) was used to examine the microstructure. Energy-dispersive X-ray (EDX)

mapping was obtained from SEM (FEI Quanta 650). Electron Microprobe (EPMA, Cameca SX 100) was used to do the quantitative element mapping and measure the concentration profiles of platinum parallel to the diffusion direction. The electron beam was accelerated at 20kV, with a beam of 1 μ m, a beam current of 100nA, and a dwell time per pixel of 20mS.

Results

Diffusion of Pt in the standard Pt-diffused bond coat

[0066] Figure 2 shows the cross-sectional BSE images of standard Pt-diffused bond coat with top coat deposited by electron beam physical vapor deposition (EBPVD), before and after diffusion and oxidation experiments. It is worth noting that, under the Backscattered Electrons (BSE) mode, heavy elements, especially Pt, can strongly backscatter electrons, hence those areas appear brighter; while lighter elements tend to absorb electrons, and thus appear darker. It is observed that Pt is not evenly distributed but enriched in a certain phase with highly segregated microstructure, which is known as γ' -(Ni, Pt)₃Al phase (where Pt replaced Ni). A significant inwards diffusion of Pt towards substrate is observed after diffusion experiment, which results in a significant increased thickness of the Pt-diffused layer which is in bright color from 37 μ m to 50 μ m, and finally 62 μ m. Moreover, a depletion layer of γ -Ni (Pt) phase is found underneath the TGO layer.

[0067] Figure 3 shows the corresponding concentration profile of Pt on the cross-section of standard Pt-diffused bond coat at each stage. The concentration profile of Pt initially shows a high peak and then significantly dropped and broadened after the long-term diffusion and oxidation treatment. These results confirm that significant inwards diffusion of Pt towards substrate did occur during the heat treatment.

Selective etching and electroplating of Pt

[0068] Figure 4 shows the surface and cross-sectional SEM images of the etched substrate with different etching time. It is observed that γ' -etchant penetrates into the substrate and continuously etches away γ' -Ni₃Al cubes which leaves γ -Ni matrix with cubic holes. Similarly, by using γ -etchant, γ -Ni matrix is etched away; and γ' -Ni₃Al cubes remain in the original microstructure. Even though γ' -Ni₃Al cubes are isolated with no supporting matrix, they still remain intact on the substrate surface perhaps due to the electrostatic force between the cubes. Thus, a layer of either γ' -Ni₃Al phase or γ -Ni phase is obtained on the substrate surface by selective etching. Besides, in Figure 4(C) and 3(D), the etched thickness increases almost linearly with the etching time and the maximum thickness can reach 15~20 μ m on the γ' -etched substrate and 80~100 μ m on the γ -etched substrate.

[0069] Figure 5 (A) shows the cross-sectional image of the as-electroplated γ' -etched substrate. After the porous γ -Ni matrix was completely filled with Pt, an additional layer of Pt was electroplated on the surface for the consideration of a sufficient Pt supply since chemical γ' -etching can only remove a limited amount of γ' -phase. Figure 5 (B) shows the cross-sectional image of the as-electroplated γ -etched substrate with the enlarged inset image at the substrate/coating interface. It is observed that the interspace between γ' -cubes is perfectly filled with Pt, so that a composite layer, which is consisted of Pt and γ' -cubes, is then obtained on the CMSX-4 substrate with a clear and straight interface. In this composite layer, γ' -cubes are periodically embedded in the Pt-matrix and remain the same microstructure, distribution and orientation with those in the CMSX-4 substrate. In other words, Pt has completely replaced the γ -Ni matrix without breaking its periodic microstructure.

Diffusion of Pt in the γ and γ' -phase Pt-bond coat

[0070] Figure 6 shows the cross-sectional BSE images of γ -phase Pt-diffused bond coat (A) as-received; (B) after long-term diffusion; (C) after oxidation. An outer depletion layer of γ -phase is observed in the as-received γ -phase Pt-diffused bond coat and the thickness of the Pt-diffused layer increased 73% (from 26 to 45 μ m) after diffusion, and 100% (from 26 to 52 μ m) after oxidation, which shows an even more severe inwards diffusion of Pt in comparison with that in the standard Pt-diffused bond coat.

[0071] Figure 7 shows the cross-sectional BSE images of γ' -phase Pt-diffused bond coat (A) the as-electroplated; (B) as-received after vacuum heat treatment; (C) after long-term diffusion; (D) after long-term oxidation. After the vacuum heat treatment, Pt is uniformly dissolved in the γ' -phase, and a coherent layer of Pt-enriched γ' -phase then forms on the CMSX-4 substrate. Surprisingly, the diffusion of Pt occurred only along the in-plane direction, rather than vertical direction towards the substrate. The thickness of the Pt-enriched γ' -layer still remains 14 μ m after the long-term diffusion treatment; but increases to 18 μ m after long-term oxidation. Figure 7 (E~H) shows the coating/substrate interface which remains clear and straight. The γ' -cubes, which were originally embedded in the Pt-matrix of the as-electroplated substrate, maintain the same microstructure and positions without any coarsening or rafting. However, a coherent layer of Pt-enriched γ' -phase is observed to thicken after long-term diffusion and oxidation, which indicates a minor inwards diffusion of Pt and outwards diffusion of Al from the substrate to form γ' -phase.

Element distribution associated with Pt diffusion

[0072] Figure 8 shows the cross-sectional BSE images of (A) the standard Pt-diffused bond coat and (B) the γ' -phase Pt-diffused bond coat after oxidation at 1150°C for 50 hours

In the standard Pt-diffused bond coat, the distribution of γ' -phase is highly scattered and closely surrounded by γ -phase. While in the γ' -phase Pt-bond coat, the distribution of γ' -phase is uniform as a coherent layer above the substrate with $\gamma+\gamma'$ phase.

[0073] Figure 9 shows the cross-sectional images of the TGO layer after oxidation on the (A) standard Pt-diffused bond coat; (B) γ -phase Pt-bond coat; (C) γ' -phase Pt-bond coat; (D~F) corresponding EDX mapping of Pt beneath the TGO/bond coat interface. The TGO layers on the three kinds of bond coat are all intact and adhesive after oxidation, which is consisted of pure Al_2O_3 (no other oxide has been detected under EDX analysis, such as NiO and NiAl_2O_4). A Pt depleted layer of γ -phase underneath the TGO layer is observed in both the standard Pt-diffused bond coat and γ -phase Pt-bond coat, as confirmed by the EDX mapping in Figure 9 (D) and (E). Meanwhile, in the γ' -phase Pt-bond coat in Figure 9 (F), Pt is evenly distributed underneath the TGO layer in the γ' -phase, which can maintain the strong adhesion at TGO/bond coat interface as mentioned before.[10] On the other hand, the TGO thickness on the γ' -phase Pt-bond coat and γ -phase Pt-bond coat is similar, which is around $2\mu\text{m}$. This is thinner than that of the standard Pt-diffused bond coat which is around $3\mu\text{m}$. Even though, it indicates a slower TGO growth rate on the γ' -phase Pt-bond coat, however, it should be noted that the presence of top coat may affect the the oxidation rate of Pt-diffused bond coat. As Zhao et al. [12] reported, the TGO thickness on the standard Pt-diffused bond coat with EBPVD top coat is nearly 50% higher than the uncoated sample, due to a retarded phase transformation from $\theta\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$ which leads to a higher oxidation rate. Therefore, the oxidation rate of the γ' -phase Pt-bond coat and γ -phase Pt-bond coat should be similar with that of the standard Pt-diffused bond coat.

Conclusion

[0074] The diffusion behaviour of Pt in the Pt-diffused bond coat has been investigated. The results show that the diffusion of Pt towards the substrate is more severe in the γ -phase Pt-bond coat than that in the standard Pt-diffused bond coat with $\gamma+\gamma'$ phase. Furthermore, almost no such diffusion of Pt is detected in the γ' -phase Pt-bond coat after 50 hours' diffusion and 50 hours' oxidation at 1150°C . It shows that Pt has a higher diffusion coefficient in the γ' -phase than that in the γ -phase at 1150°C . Pt is observed to be more enriched in the γ' -phase with an inhibited activity, which is believed to be caused by the negative chemical interactions with Al and Ta. A considerable cost saving can therefore be realised by applying γ' -phase Pt-diffused bond coat as the inwards diffusion of Pt towards the substrate at high temperature will be avoided.

Example 2**Experimental procedure**

[0075] CMSX-4 single crystal superalloy (nominal composition Ni 9.6Co 6.4Cr 6.4W 6.6Ta 5.6Al 2.9Re 1.03Ti 0.1Hf in wt.%) was cut into a size of 10mm*10mm*2mm as substrate. Substrate surface was grinded by 600 grit SiC paper and degreased by ethanol in an ultrasonic bath, and then washed by deionized water.

[0076] The alloy was subject to γ -etching with a solution containing 10% H_3PO_4 and 90% H_2O . Platinum foil was used as the cathode and the substrate was etched for 1~10min under constant current density of 100~200mA/cm² with a slow magnetic stirring. Next, the etched substrate was rinsed in boiling sodium hydroxide solution (NaOH, 5%) for 10min to remove the residual acid and then washed by deionized water. After the substrate was well-prepared, platinum was electroplated on the substrate surface by using P salt (diammine-dinitrito-platinum(II) solution, Sigma-Aldrich, UK) under a constant current density of 10~20mA/cm² for 10~30min at 70°C. The electroplated substrate was then washed by deionized water and dried at ambient temperature overnight.

Results

[0077] Figure 10 shows the surface of a poorly-electroplated sample and the well-electroplated sample. One possible explanation for the difference in electroplating is the different surface geometry of the etched substrate during electroplating (see Table below). The etched substrate may have an extended surface area which will result in an insufficient current density for the deposition of Pt in some areas.

Table 2 Current density analysis on the non-etched and γ -etched substrate

	Non-etched	Etched	
Geometry			
Length a	a_0	$\sqrt{2}a_0$	$2a_0$
Area $A = A_0$	$a_0^2 = A_0$	$2a_0^2 = 2A_0$	$4a_0^2 = 4A_0$
Current density $J = \lim_{A \rightarrow 0} \frac{I}{A}$	$\frac{I}{A_0} = J_0$	$\frac{I}{2A_0} = \frac{1}{2}J_0$	$\frac{I}{4A_0} = \frac{1}{4}J_0$

[0078] Figure 11 shows that, if the current is too high, the deposition of Pt may result in a thin porous micro-structure with massive stress (see Figure 11 (A)) rather than thick dense layer (see Figure 11 (B)). Insufficient current density will result in non-uniform distribution of the deposition as shown in Figure 11 (C).

[0079] This is even though, according to Faraday's law, the electroplating rate is proportional to the current density. However, there is an optimum range of current density in which it can produce both uniform and thick coatings as shown in Figure 12.

[0080] This is proven in Figure 13, whereby the deposition within the γ -matrix is completed and then Pt atoms started to be deposited on the surface substrate under an excessive current density. This would easily result in a crack with a thin porous layer of Pt on the surface (see Figure 14). The thickness of the thin layer is less than $1\mu\text{m}$ and there also is a gap between this layer and the substrate which indicates the high stress within the coating so that it has a tendency to shrink and crack.

[0081] In Figure 15, the cross-sectional image of the as-electroplated composite coating was edited by using the software of Image-Pro plus 6.0 in order to calculate the volume fraction of Pt. The results showed that the red area% which represents the γ' - Ni_3Al phase was 73%, while the green area% which represents Pt was 27%. However, since the depth of focus for SEM is large, it may cause an over-estimation of volume fraction due to the sub-surface effect. Therefore, the real volume fraction of platinum should be smaller than 27%. At the same time, another method was also employed to estimate the volume fraction of Pt by measuring the weight gain of Pt after electroplating which has been shown as follows:

h	Pt + γ' coating thickness
A	Electroplating area
ρ	Density of platinum
m_1	Estimated weight gain of Pt
m_2	Measured weight gain of Pt
$M\%$	Mass fraction of Pt
$V\%$	Volume fraction of Pt

$$M\% = \frac{m_2}{m_1} \times 100\% = \frac{m_2}{\rho Ah} \times 100\% \approx 18\%$$

Since Pt coating contains some porosity,

$$\underline{V\% > M\% = 18\%}$$

Table 3 The volume fraction of Pt analysed by different methods

Methods	$V\%$ of γ'	$V\%$ of Pt
Image-Pro Plus analysis	>73%	<27%
Weight gain analysis	<82%	>18%
Literature: CMSX-4*	77%	23% (γ)

Conclusion

[0082] According to this result, it can be concluded that Pt has completely replace the γ -matrix and the volume fraction of Pt in the composite layer of Pt+ γ' is around 23%. Figure 16 shows the cross-sectional images of a layer of 100% Pt and a composite layer of 23% Pt+ 77% γ' . It indicates that by applying this new method the amount of Pt required can be reduced by at least 77%.

Example 3 – self-bonding gamma-prime layer

[0083] In this example, single crystal γ' -coating without platinum was prepared on the CMSX-4 single crystal turbine blade after selectively removing γ -Ni matrix and then subjecting the coating material to a vacuum heat treatment. This methodology is named as 'self-bonding' and the oxidation behaviour of the self-bonded γ' -coating was also investigated. With these results, the beneficial effect of platinum on the oxidation resistance of γ' -coating can be then revealed.

Experiments

Sample preparation

[0084] The substrates used in this study are CMSX-4 single crystal superalloy (nominal composition Ni 9.6Co 6.4Cr 6.4W 6.6Ta 5.6Al 2.9Re 1.03Ti 0.1Hf in wt. %) cut into a size of 10mm*10mm*2mm for each sample aligned to the [110] axis considering the etching effect. Surface grinding with the SiC papers of 320, 600, 1200 grit was then performed on both sides and all edges. It was treated with a solution containing 10% H₃PO₄ and 90% H₂O to dissolve the matrix phase of γ -Ni. A platinum foil was used as the cathode with the substrate as the anode which was then electrolytic etched for 1~10min under constant current density of 100~200mA/cm² with a slow magnetic stirring. Finally, the etched substrate was rinsed in boiling sodium hydroxide solution (NaOH, 5%) for 10min to remove the residual acid and then ultrasonic washed by deionized water. In addition, with a longer electrolytic etching time for more than 1 hour, γ' precipitates can be extracted from CMSX-4 substrate and collected by washing, centrifuging, and drying. The γ' -precipitates were then carefully placed on a silicon disc with silicone grease for X-ray diffraction analysis.

Thermal treatment

[0085] The etched substrate was then dried at ambient temperature for overnight, followed by a diffusion treatment at a temperature of 1100~1200°C for 2 hours in a vacuum tube furnace at a pressure of 1.0×10^{-5} mbar. In order to investigate the oxidation behavior of the γ' -coating, CMSX-4 substrate was selected as a comparison due to the same crystal orientation, similar chemical and phase composition ($\gamma + \gamma'$). Isothermal oxidation was performed at 1150°C in laboratory air for 100 hours within a Thermo-gravimetric platform (TG, SETARAM, K/SETEVO16-1A). Early oxidation test was carried out at 1150°C for 30min, 60min and 120min in a rapid cycle furnace (CM Furnaces Inc.) with a moving stage. Heating and cooling (to room temperature) were both finished within 10min.

Characterization methods

Scanning Electron Microscopy (SEM, Philip XL30) was used to examine the morphology and microstructure of the samples. EDX mapping was measured by SEM (FEI Quanta 650). Grain size of Al₂O₃ was measured and analysed by Image Pro-Plus (6.0, Media Cybernetics). Electron Microprobe (EPMA, Cameca SX 100) was used to do the element concentration mapping, with a 20kV electron beam of size 1 μ m, a beam current of 100nA, and a dwell time per pixel of 20mS. The phase compositions were analyzed by X-ray diffraction (XRD, Philips X'Pert) with Cu K α radiation ($\lambda = 0.15405$ nm) using a 40 kV accelerating voltage and a 40 mA current. The element compositions were determined by X-

ray fluorescence analysis using energy dispersive spectrometer (XRF, MiniPal 4 PANalytical).

Results

Characterisation of γ' -coating

[0086] Figure 17 shows the microstructure on the surface and the internal part of the γ -etched CMSX-4 substrate. Well-arranged γ' -precipitates with a shape of cubes and a size of 0.5~1.0 μm were observed underneath the etched surface. Figure 17 (C) and (D) show the cross-sectional images of the etched substrate and a layer which is consisted of γ' -cubes was obtained on the substrate. The isolated γ' -cubes had remained attached even with no support from the γ -matrix rather than fell off. This is perhaps due to the electrostatic force, which is essential to the formation of self-bonded γ' -coating on the CMSX-4 substrate.

[0087] Figure 18 shows the cross-sectional images of the self-bonded γ' -coating after vacuum heat treatment for 2 hours at different temperatures. During vacuum heat treatment, the γ' -precipitates cubes on the substrate undergo coarsening and densification which involves a diffusive process. The driving force for such process is the reduction in the total interfacial energy of the system. In Figure 18 (A), the cuboidal shape of the γ' -precipitate can still be seen after being treated at 1100°C but disappeared in the ones that treated at 1150°C and higher.

Table 4 Chemical composition of CMSX-4 substrate and the γ' -coating (weight%)

	Ni	Cr	Co	Al	Mo	W	Ti	Re	Ta	Hf
CMSX-4[#]	Bal.	6.5	9	5.6	0.6	6	1.0	3	6.5	0.1
CMSX-4	63.4	5.8	9.3	5.6	0.52	5.5	0.94	1.3	7.4	0
γ'-coating (Before treatment)	66.3	2.2	6.3	9.0	0.40	4.3	1.1	0.22	10.1	0
γ'-coating (After treatment)	63.9	2.2	6.1	12.0	0.33	4.8	1.1	0.19	9.3	0

([#]Appendix A in Chapter 12 in the book written by David Young)

[0088] The chemical composition of the γ' -coating is shown in Table 4. After the removal of γ -Ni matrix, the concentration of Al increased to 9.0wt% from 5.6wt% and then to 12.0 wt% after vacuum heat treatment. An increase is also observed in the concentration of Ta and Ti; meanwhile, elements, such as Cr, Co and W, still exist in the γ' -coating but all of them are at a decreased concentration.

[0089] Figure 19 shows the X-ray diffraction pattern of the self-bonded γ' -coating, the CMSX-4 substrate and the γ' -cubes (powder) extracted from the CMSX-4 substrate. The lattice parameter a and the full width at half maximum (FWHM) at the peaks of (100), (200) and (300) are listed in Table 5. A sharp peak at (200) is observed in both the patterns of the γ' -coating and the CMSX-4 substrate, which submerges other peaks, especially the peak at (111) which is supposed to be the strongest in the pattern of the γ' -cubes (powder) with isotropic properties, as shown in Figure 19 (B). The super-lattice peaks at (100) and (300) from the γ' -phase due to its ordered $L1_2$ crystal structure can be also observed in the both patterns of the γ' -coating and the CMSX-4 substrate as shown in the inset figures of Figure 19 (A). The two super-lattice peaks became more sharpen and stronger in the self-bond γ' -coating after the removal of γ -phase. Therefore, it can be concluded that the self-bond γ' -coating still remains the same single crystal structure with strong texture as that of the CMSX-substrate. A decrease of 0.3% is observed in the lattice parameter a of the γ' -coating, in comparison with that of the CMSX-4 substrate; while the lattice parameter a of the γ' -cubes is almost the same with that of the CMSX-4 substrate. Therefore, shrinkage must have occurred in the γ' -coating during vacuum heat treatment.

Table 5 Lattice parameters a and FWHM at the peaks of (200) and (300)

	(100)		(200)		(300)	
	$a(\text{\AA})$	FWHM($^\circ$)	$a(\text{\AA})$	FWHM($^\circ$)	$a(\text{\AA})$	FWHM($^\circ$)
CMSX-4	3.5981	0.1230	3.5966	0.3198	3.5936	0.3600
γ' -coating	3.5859	0.1476	3.5856	0.2460	3.5856	0.2400
γ' -cubes	—————		3.5933	0.2460	—————	

Table 6 The parabolic rate constant and duration time

	k_{p1} (g ² /cm ⁴ /s)	t_1 (h)	k_{p2} (g ² /cm ⁴ /s)	t_2 (h)
CMSX-4	1.1×10^{-11}	36	2.6×10^{-12}	64
γ'-coating	6.3×10^{-11}	2.5	1.7×10^{-12}	97.5
CMSX-4*			1.4×10^{-12}	100

* CMSX-4 substrate pre-treated at 1150°C for 2 hours in vacuum

Oxidation behavior of γ' -coating

[0090] Figure 20 shows the square of the weight gain of the self-bonded γ' -coating oxidation at 1150°C as a function of time, in comparison with that of the non-treated CMSX-4 substrate, as well as the pre-treated CMSX-4 substrate (vacuum heat treated at 1150°C for 2 hours). A rapid weight gain is observed at the beginning of the oxidation on the γ' -coating and after 2.5 hours, the curve abruptly levelled off at a constant increasing rate. This turning point can divide the curve into two oxidation stages, denominated as the initial stage and the constant stage. The oxidation rate at each oxidation stage can be estimated by the parabolic law, $k_p = (\frac{\Delta W}{A})^2 / t$ as listed in Table 9. The oxidation rate at the initial stage (k_{p1}) of the γ' -coating is much higher than that of the pre-treated CMSX-4 substrate, but the duration time at the initial oxidation stage (t_1) has shortened to 2.5 hours. The k_p of the pre-treated CMSX-4 substrate is observed to be constant at a very low value so that the whole curve can be considered as at the constant stage. The k_{p2} of the γ' -coating is slightly higher than that of the pre-treated CMSX-4 substrate but much lower than that of the non-treated CMSX-4 substrate.

[0091] In Figure 21, the fracture TGO cross-sectional images of the non-treated CMSX-4 substrate, the γ' -coating and the pre-treated CMSX-4 substrate were taken after the sample stage was tilted at 70°. In Figure 21 (A) and (D), voids are detected within the spinel oxide layer right above the inner columnar layer of Al₂O₃ grains. In Figure 21 (B) and (E), the equiaxed grains can be observed on the surface of the γ' -coating, as well as more white particles, which contain (Ti, Ta)-rich oxide. In Figure 21 (C) and (F), a coherent layer of Al₂O₃ with columnar grains is observed on the pre-treated CMSX-4 substrate.

[0092] Figure 22 shows the amount of the stable oxide as a function of oxygen partial pressure in the γ' -Ni₃Al system after long-term oxidation at 1150°C with the addition of Pt and it is calculated by Thermo-Calc 3.1 software with TCNi6 database. It can be observed that, with the increase in the addition of Pt, the formation of Al₂O₃ is much easier at a higher oxygen partial pressure and at the same time the formation of NiO as well as spinel oxide is

inhibited. With the addition of over 10at% Pt, the formation of NiO is excluded; and with the addition of over 30at% Pt, the formation of spinel can be excluded as well.

[0093] Figure 23 shows the activity of Ti or Ta (left Y) and the amount of phase (right Y) in the system of Ni₃(Ti, Ta) with the addition of Pt (0~1.0at%) at 1150°C and it is calculated by Thermo-Calc 3.1 software with TCNi6 database. It can be easily observed that with the addition of only 0.1at% Pt, the activity of Ta significantly dropped from 6.46×10^{-5} to 2.64×10^{-6} and the activity of Ta dropped from 6.23×10^{-5} to 1.82×10^{-5} . Besides, from the curve of the amount of phase, it shows that the addition of Pt simply replaces Ni and remains the ordered L1₂ crystal structure as γ' -phase. Since the formation of (Ta, Ti)-rich oxide is due to the outwards diffusion of Ta and Ti through the grain boundaries in the pre-formed Al₂O₃ layer, therefore, the decrease of the activity of Ti and Ta with the addition of 1.0at% Pt can effectively avoid the formation of (Ti, Ta)-rich oxide.

Conclusions

[0094] A single crystal γ' -coating without platinum was prepared on the CMSX-4 substrate with great compatibility and adhesion due to the same crystal orientation and similar composition. The oxidation behaviour of the self-bonded γ' -coating was also studied, in comparison with that of the CMSX-4 substrate. A rapid TGO growth is observed at the initial oxidation stage of the γ' -coating, and then the oxidation rate abruptly levelled off and remained constant. After oxidation, more α -Al₂O₃ with smaller equiaxed grains were observed both on the surface and in the internal part of the γ' -coating, than the larger columnar α -Al₂O₃ grains formed on the pre-treated CMSX-4 substrate. The possible mechanisms have been concluded as follows.

- The extended surface area in the porous γ' -coating promoted nucleation sites for α -Al₂O₃ which then induced a massive initial growth of α -Al₂O₃ grains;
- A rapid growth of (Ti, Ta)-rich oxide is also observed as a metastable oxide layer which could also promote the formation of α -Al₂O₃ grains;
- The pre-formed α -Al₂O₃ nucleus within the γ' -coating would inhibit the longitudinal growth of α -Al₂O₃ grains, which could also relieve the scale growth stress;

[0095] In the end, by using thermal calculation, it is found that the addition of Pt can effectively promote the formation of Al₂O₃ and inhibit the growth of other metastable oxides, which include NiO, spinel oxide and (Ti, Ta)-rich oxide. The beneficial effect of Pt was proven to be significant, in terms of the formation of protective TGO layer.

CLAIMS

1. A bond coat layer suitable for use in a thermal barrier coating, wherein said bond coat layer:
 - (i) is a gamma-prime phase of a nickel-based single crystal superalloy;
 - (ii) has a thickness of 10 to 100 micrometres; and
 - (iii) further comprises a platinum group metal.
2. A bond coat layer according to claim 1, wherein the layer has a thickness of 10 to 50 micrometres.
3. A bond coat layer according to claim 2, wherein the bond coat layer has a thickness of 10 to 20 micrometres.
4. A bond coat layer according to any one of the preceding claims, wherein the amount of platinum group metal present is 5 to 30 vol.%.
5. A bond coat layer according to any one of the preceding claims, wherein the platinum group metal is selected from platinum (Pt), ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os) and iridium (Ir).
6. A bond coat layer according to any one of the preceding claims, wherein the platinum group metal is platinum (Pt).
7. A nickel-based single crystal superalloy substrate comprising a bond coat layer according to any one of claims 1 to 6 on a surface thereof.
8. A nickel-based single crystal superalloy substrate according to claim 7, wherein the superalloy substrate comprises both gamma (γ) and gamma prime (γ') phases and the bond coat layer only comprises the gamma prime (γ') phase of the same superalloy.

9. A nickel-based single crystal superalloy according to claim 7 or claim 8, wherein the superalloy substrate comprises 50 to 70 weight% nickel and 1 to 7 weight% aluminium.
10. A nickel-based single crystal superalloy according to claim 9, wherein the superalloy further comprises (in weight%): chromium 0–10%, cobalt 0–15%, rhenium 0–7%, tantalum 0–12%, tungsten 0–10%, titanium 0–5%, molybdenum 0–4%, hafnium 0–2%.
11. A nickel-based single crystal superalloy according to any one of claims 7 to 10, wherein the nickel-based single crystal superalloy is CSMX-4.
12. A thermal barrier coating comprising:
- (i) a nickel-based single crystal superalloy substrate as defined in any one of claims 7 to 11;
 - (ii) a bond coat layer according to any one of claims 1 to 6 present on a surface of the nickel-based single crystal superalloy layer; and
 - (iii) a ceramic top-coat layer contacting the opposing surface of the bond coat layer.
13. A thermal barrier coating comprising:
- (i) a nickel-based single crystal superalloy substrate as defined in any one of claims 7 to 11;
 - (ii) a bond coat layer according to any one of claims 1 to 6 present on a surface of the nickel-based single crystal superalloy layer;
 - (iii) a thermally grown oxide layer contacting the opposing surface of the bond coat layer; and
 - (iv) a ceramic top-coat layer contacting the opposing surface of the a thermally grown oxide layer.
14. A thermal barrier coating according to claim 12 and claim 13, wherein the ceramic top coat layers if formed from yttria-stabilised zirconia.
15. A process for forming a bond coat layer according to claim 1 or nickel-based single crystal superalloy substrate according to claim 7, the process comprising:

- (i) providing a nickel-based single crystal superalloy substrate onto which the bond coat is to be formed;
- (ii) forming a layer of gamma-prime nickel-based single crystal superalloy having a thickness of 10 to 100 micrometres on a surface of the nickel-based single crystal superalloy substrate to form a bond coat layer; and
- (iii) infusing the layer of gamma-prime nickel-based single crystal superalloy with a platinum group metal.

16. A process for forming a thermal barrier coating as defined in claim 12, the process comprising:

- (i) providing a nickel-based single crystal superalloy substrate;
- (ii) forming a layer of gamma-prime nickel-based single crystal superalloy having a thickness of 10 to 100 micrometres on a surface of the nickel-based single crystal superalloy substrate;
- (iii) infusing the layer of gamma-prime nickel-based single crystal superalloy with a platinum group metal to form a bond coat layer; and
- (iv) applying a ceramic top-coat layer to the surface of the gamma-prime layer.

17. A process according to claim 15 or claim 16, wherein in step (ii) the layer of gamma-prime nickel-based single crystal superalloy is formed by gamma etching a surface of the nickel-based single crystal superalloy substrate to selectively remove all, or substantially all, of the gamma phase present in a 10-100 micrometre layer of the substrate material.

18. A process according to any one of claims 15 to 17, wherein in step (iii) the layer of gamma-prime nickel-based single crystal superalloy is infused with a platinum group metal by electroplating the platinum group metal into the gamma-prime nickel-based single crystal superalloy to form the bond coat layer, followed by certain vacuum diffusion heat treatment.

19. A process according to any one of claims 16 to 18, wherein in step (iv) the ceramic topcoat is applied by electron beam physical vapour deposition (EBPVD).

20. A component for use in a gas turbine engine, said component comprising a thermal barrier coating as defined in claims 12 to 14.

21. A component according to claim 20, wherein the component is selected from the group consisting of turbine components (e.g. turbine blades), combustion chamber components and exhaust system components.

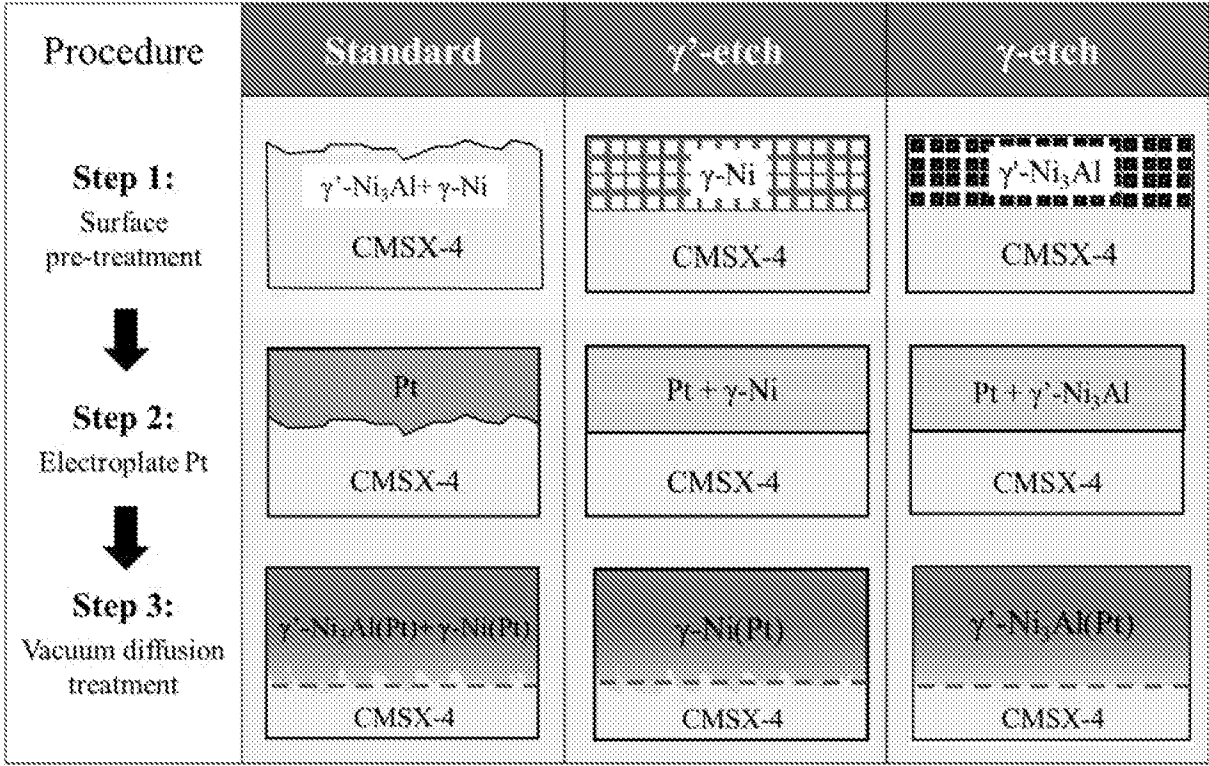


Figure 1

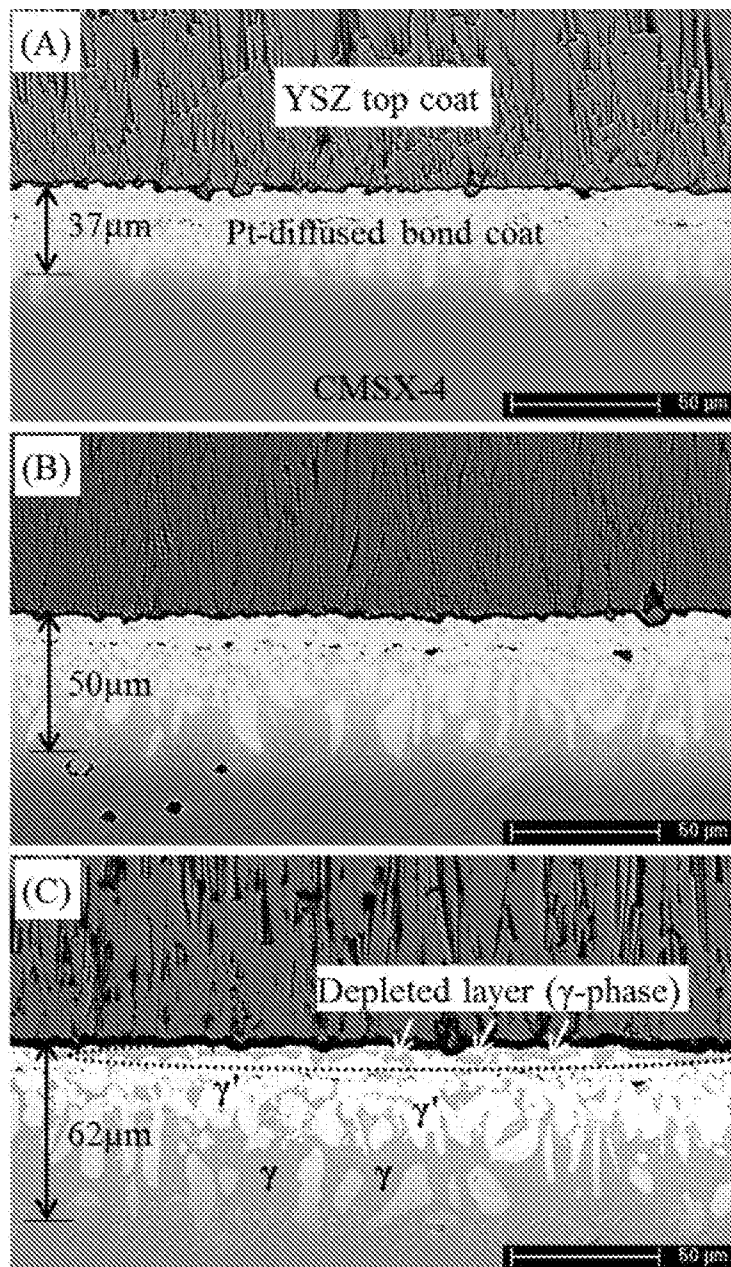


Figure 2

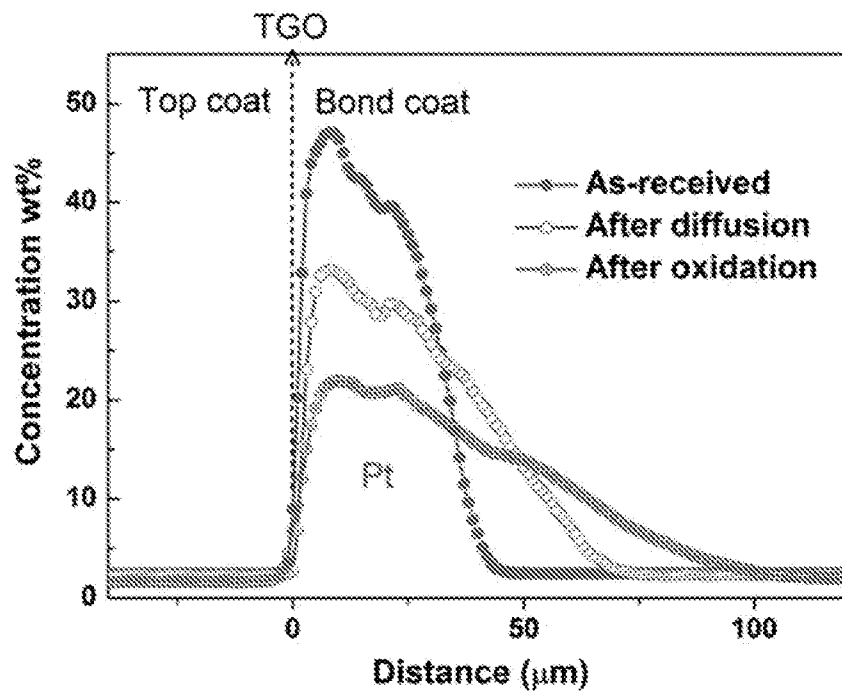


Figure 3

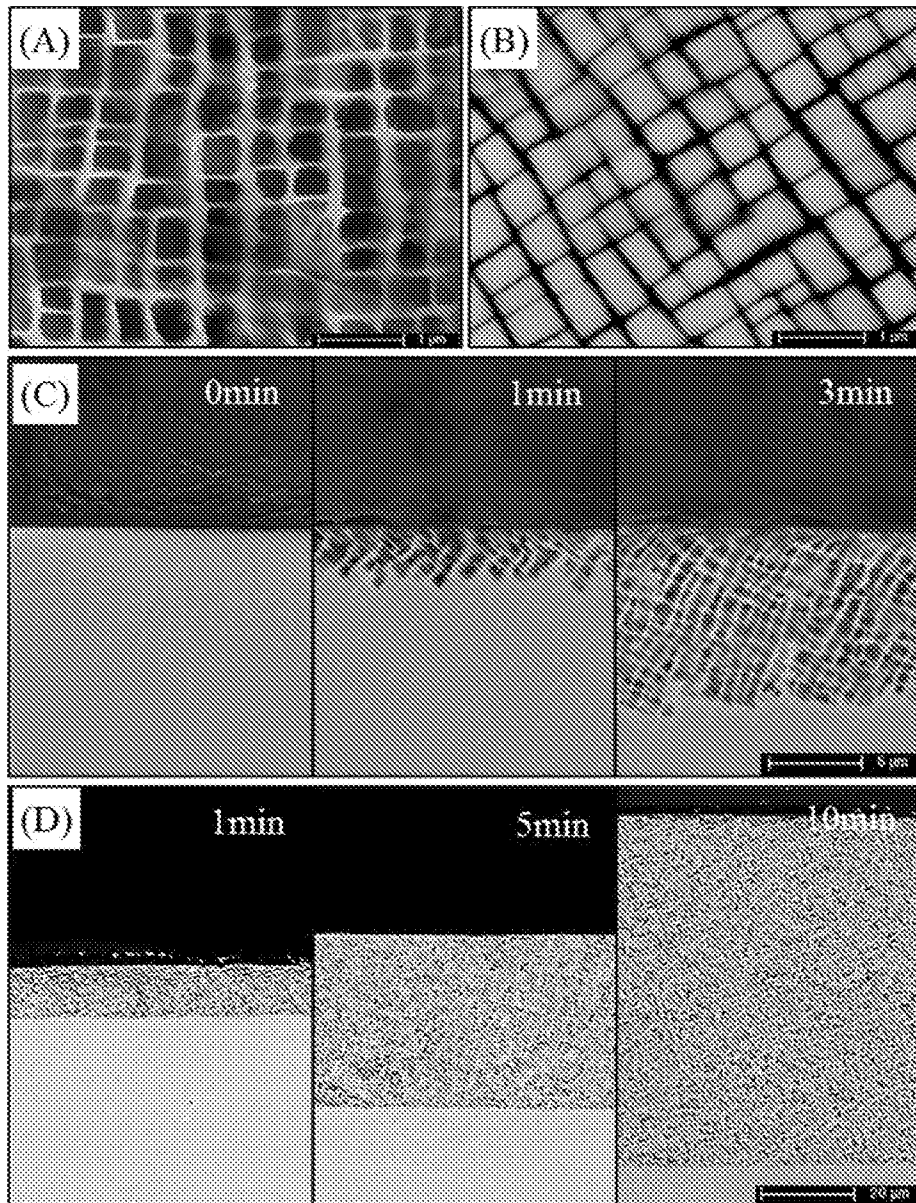


Figure 4

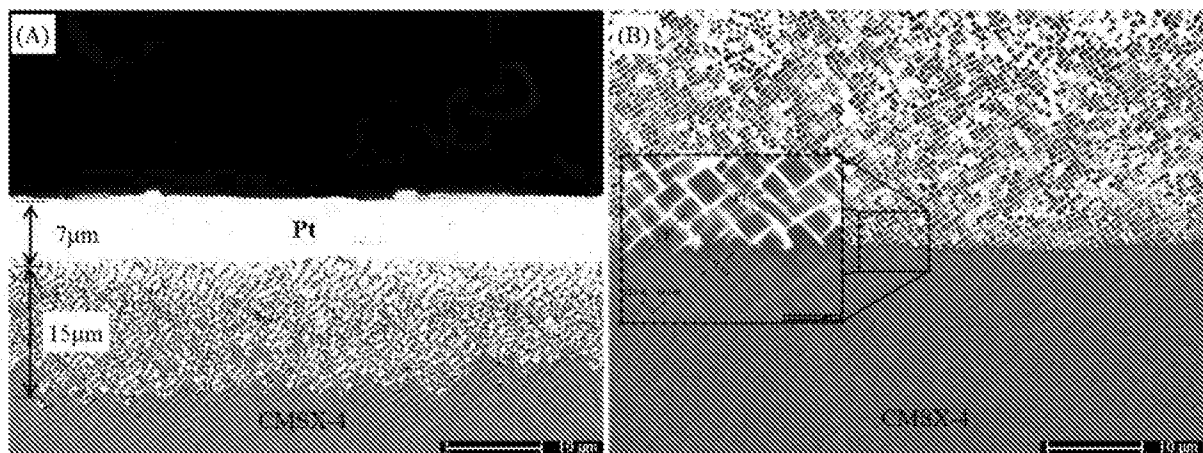


Figure 5

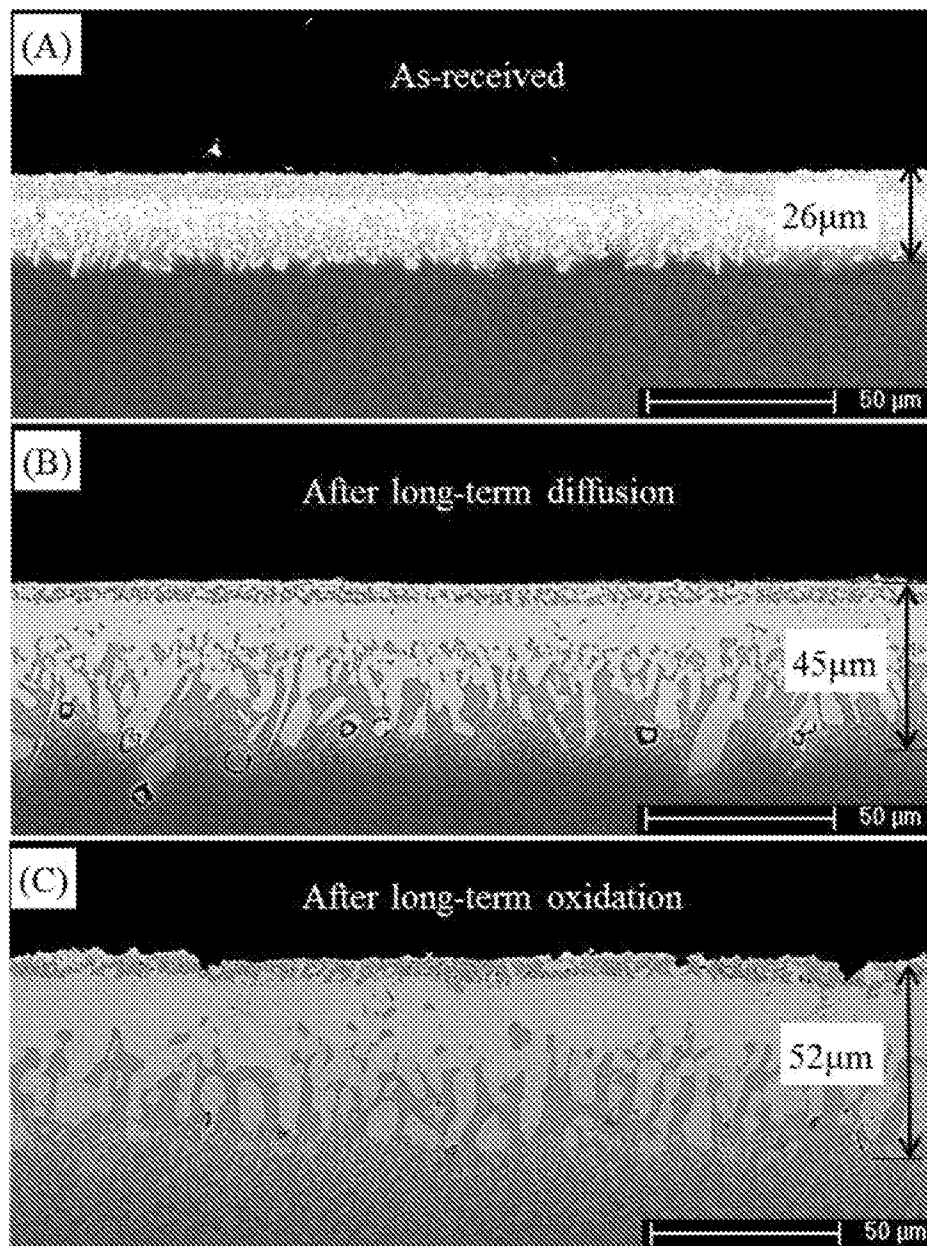


Figure 6

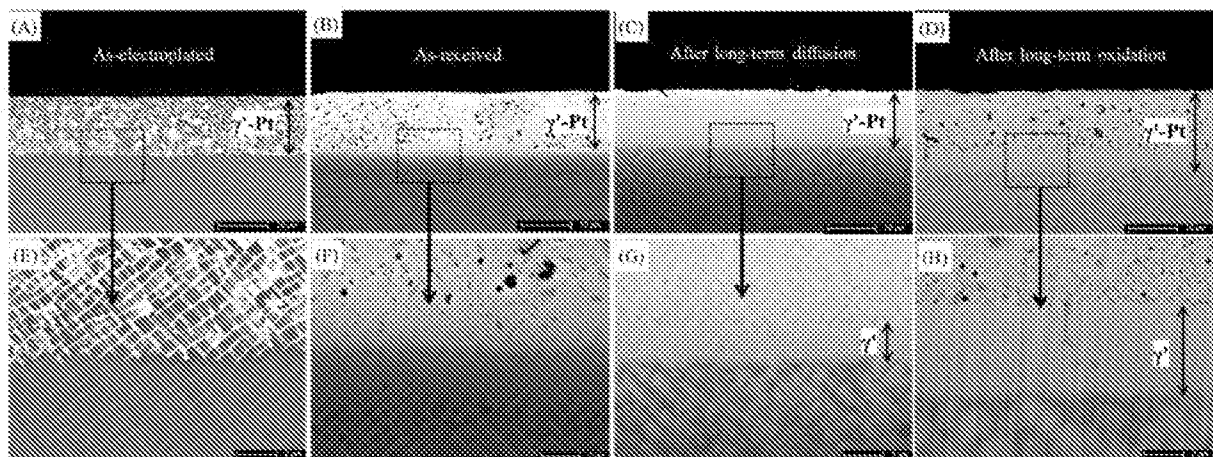


Figure 7

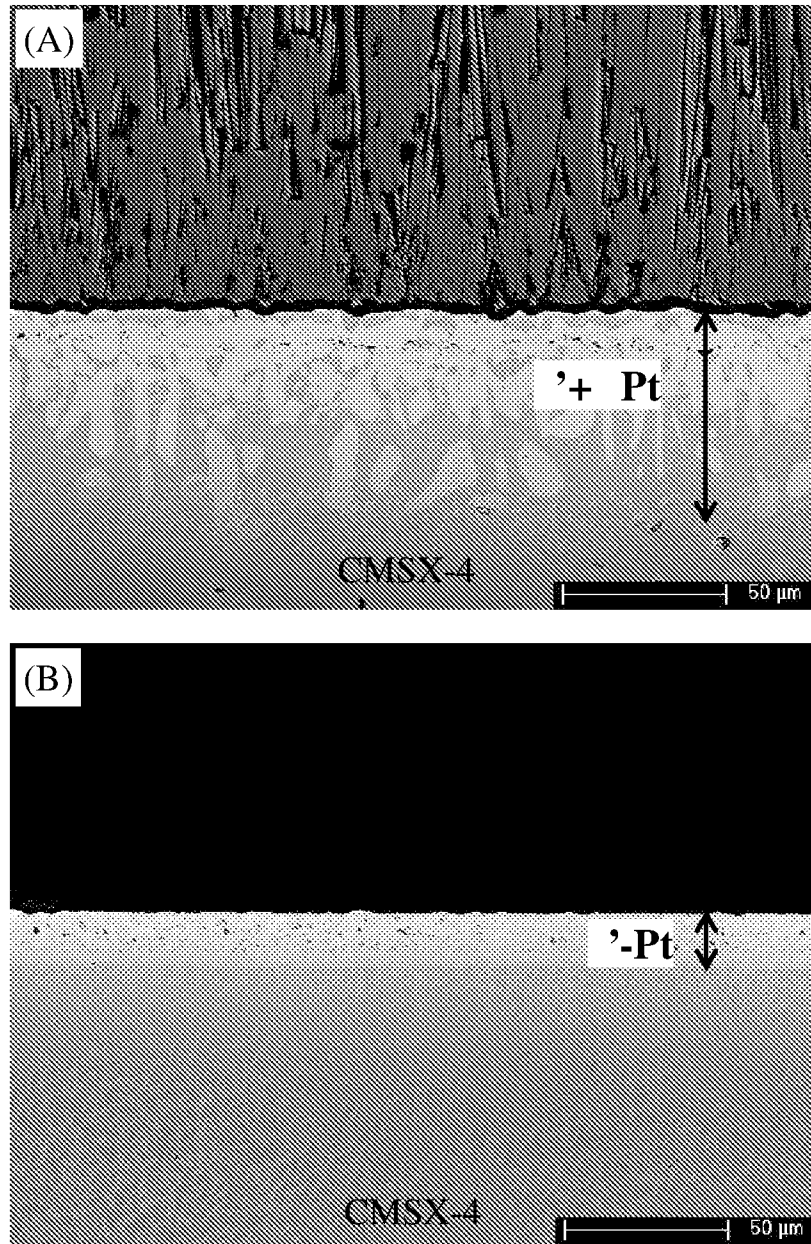


Figure 8

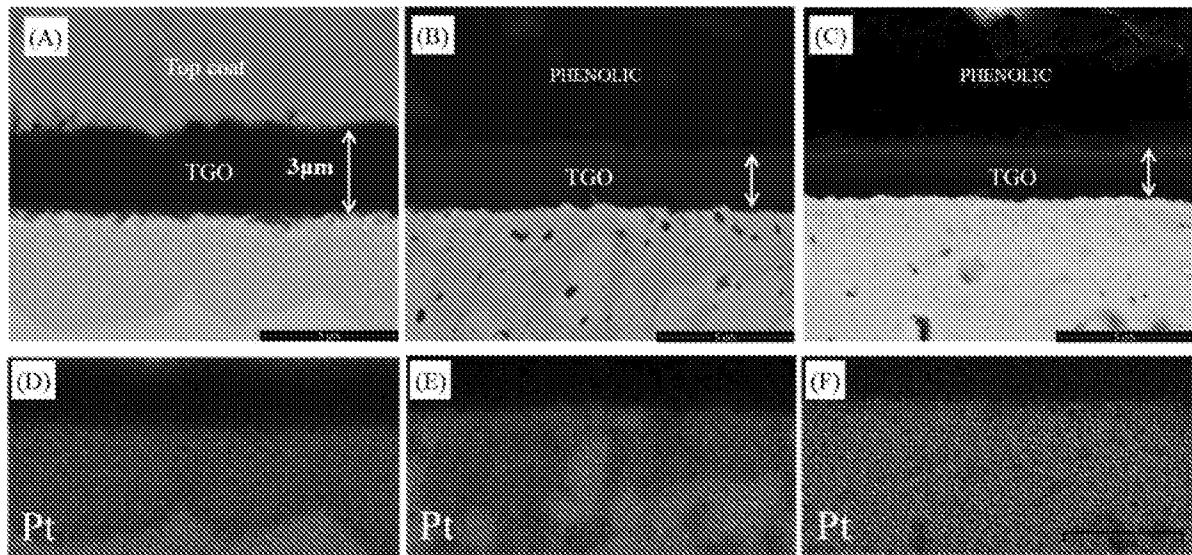


Figure 9

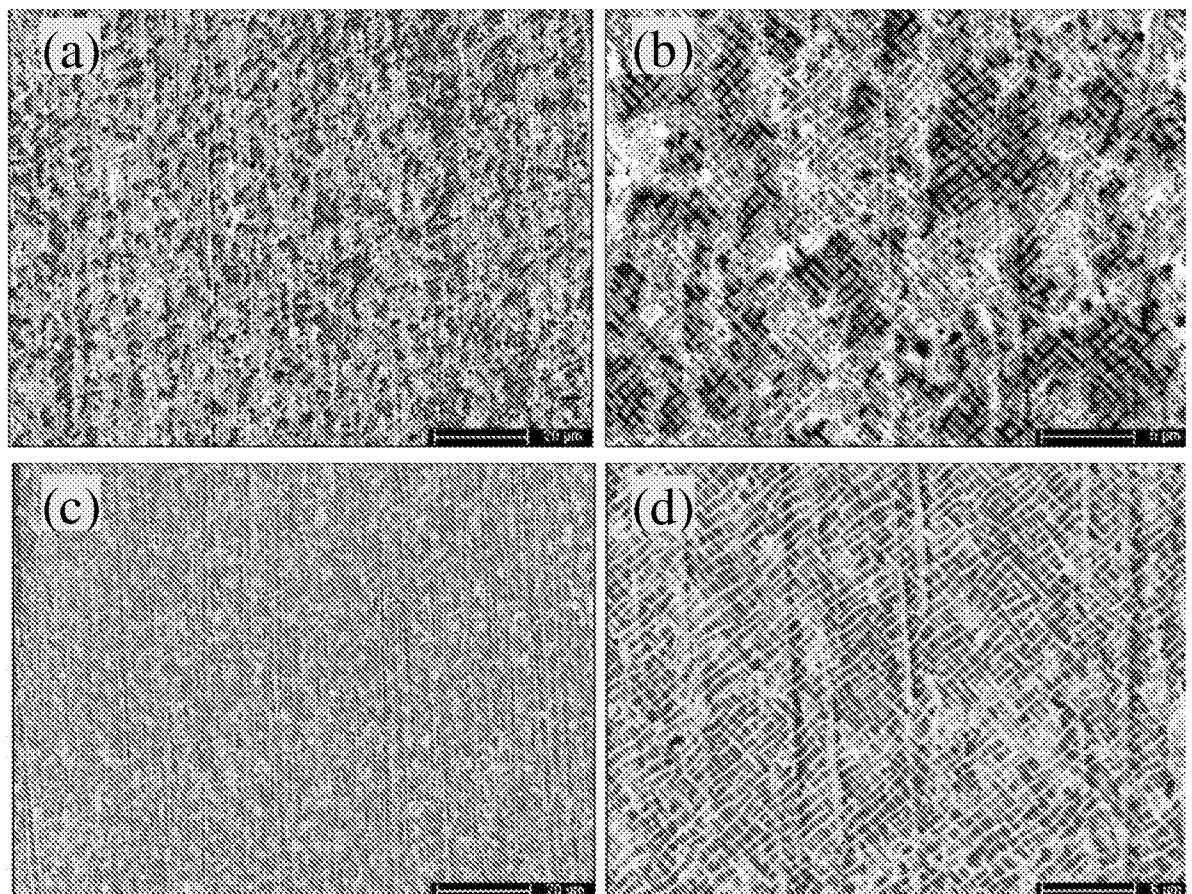


Figure 10

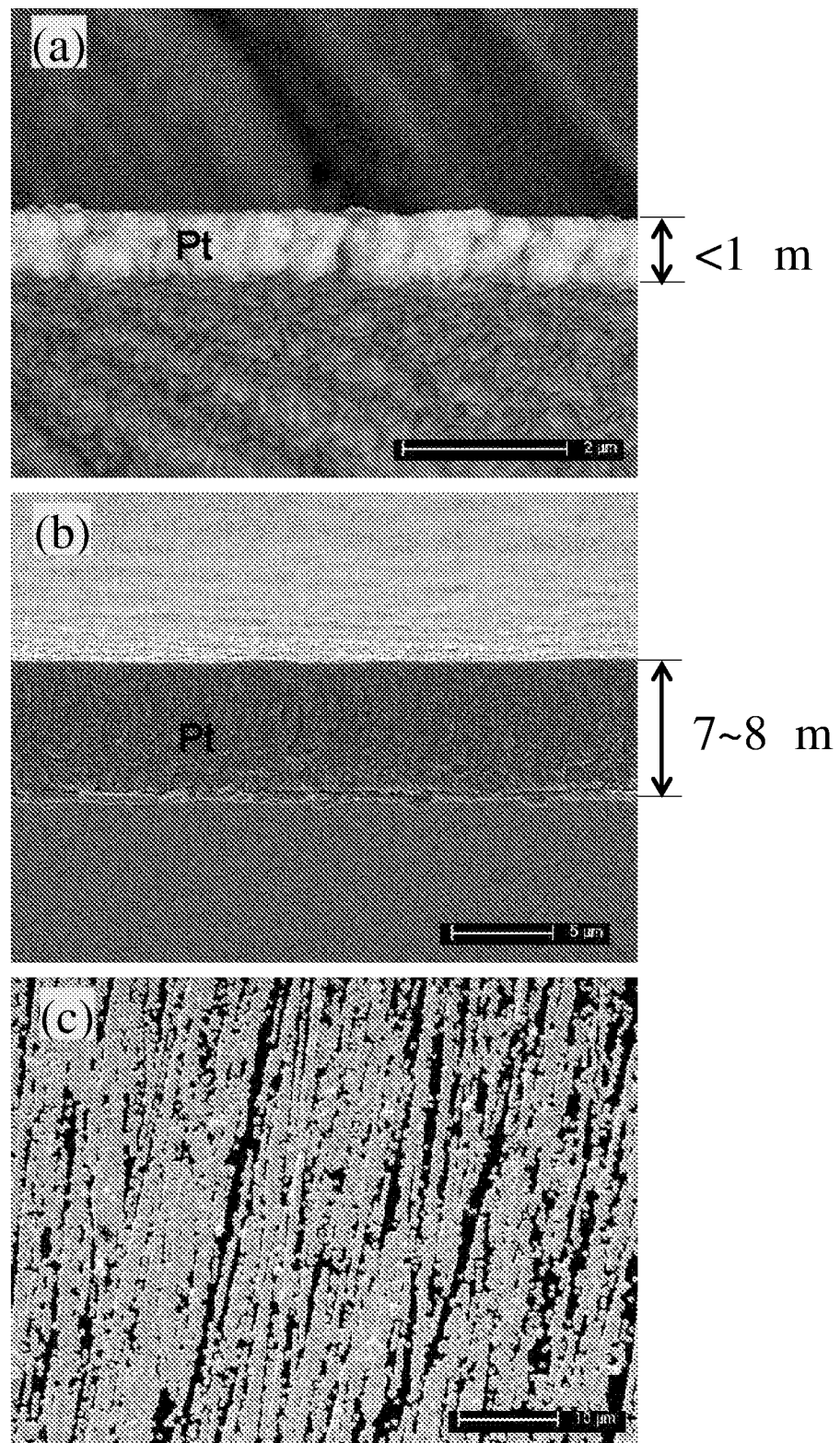


Figure 11

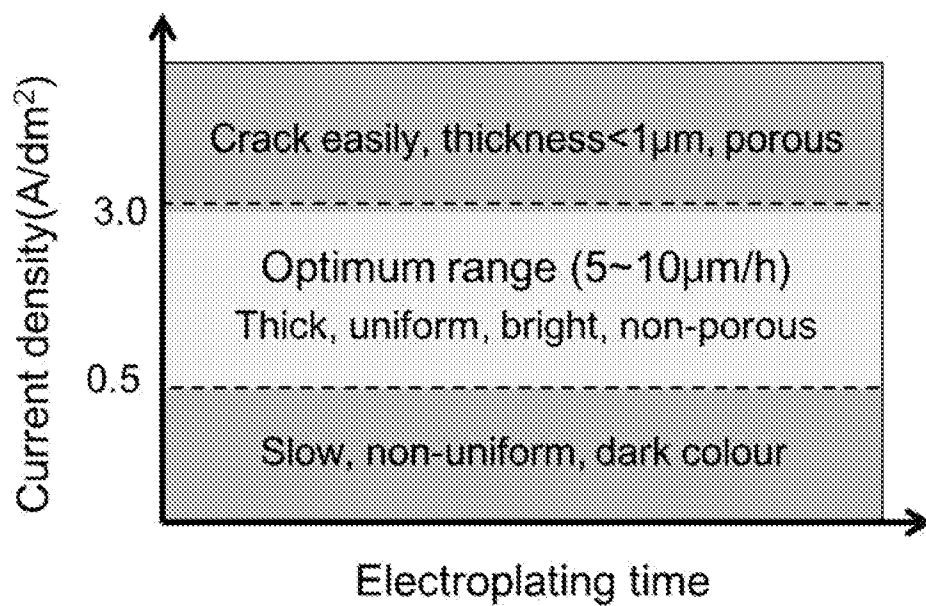


Figure 12

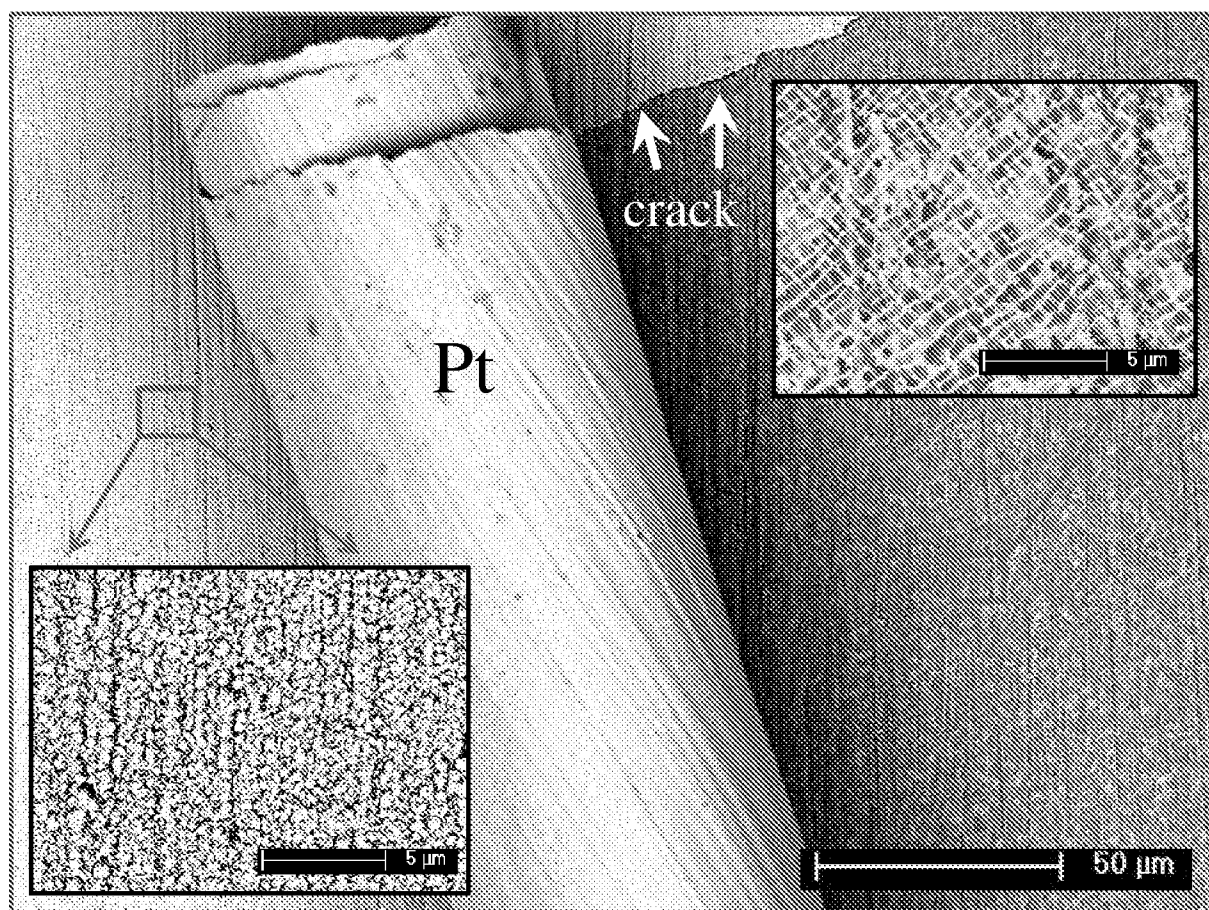


Figure 13

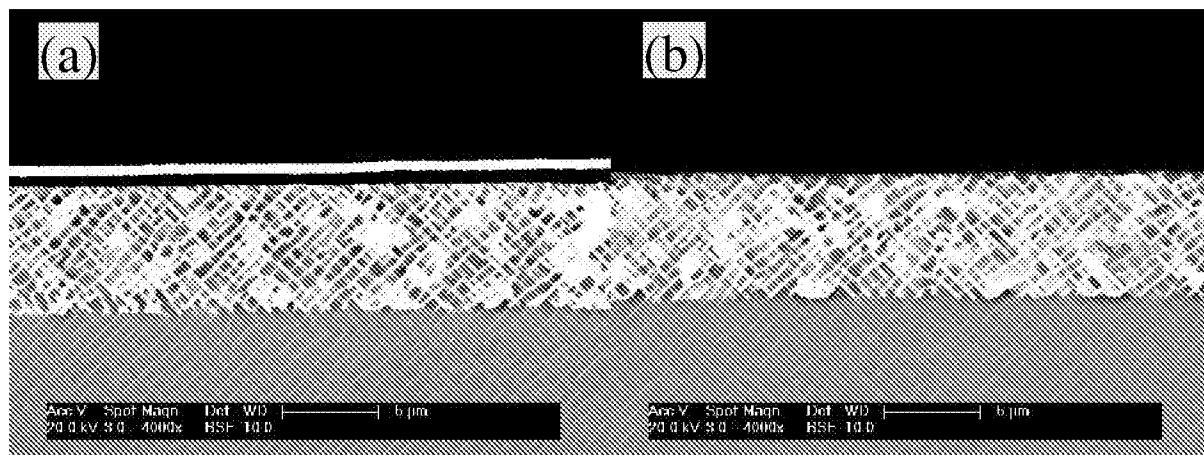


Figure 14

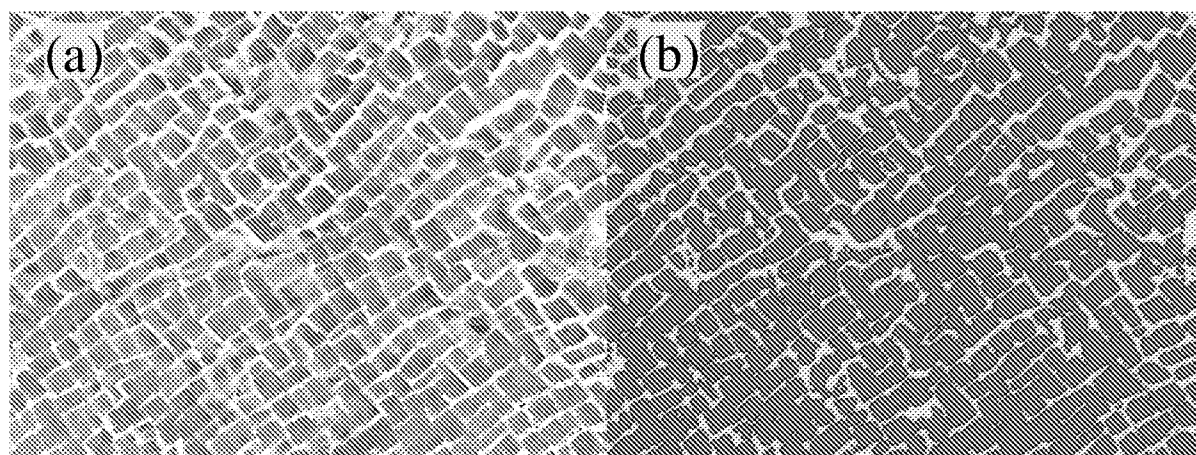


Figure 15

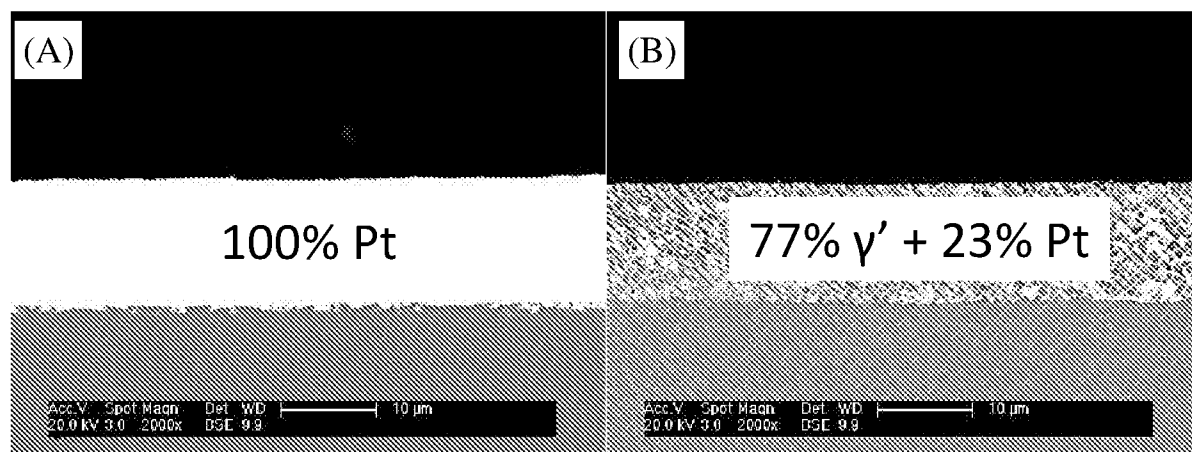


Figure 16

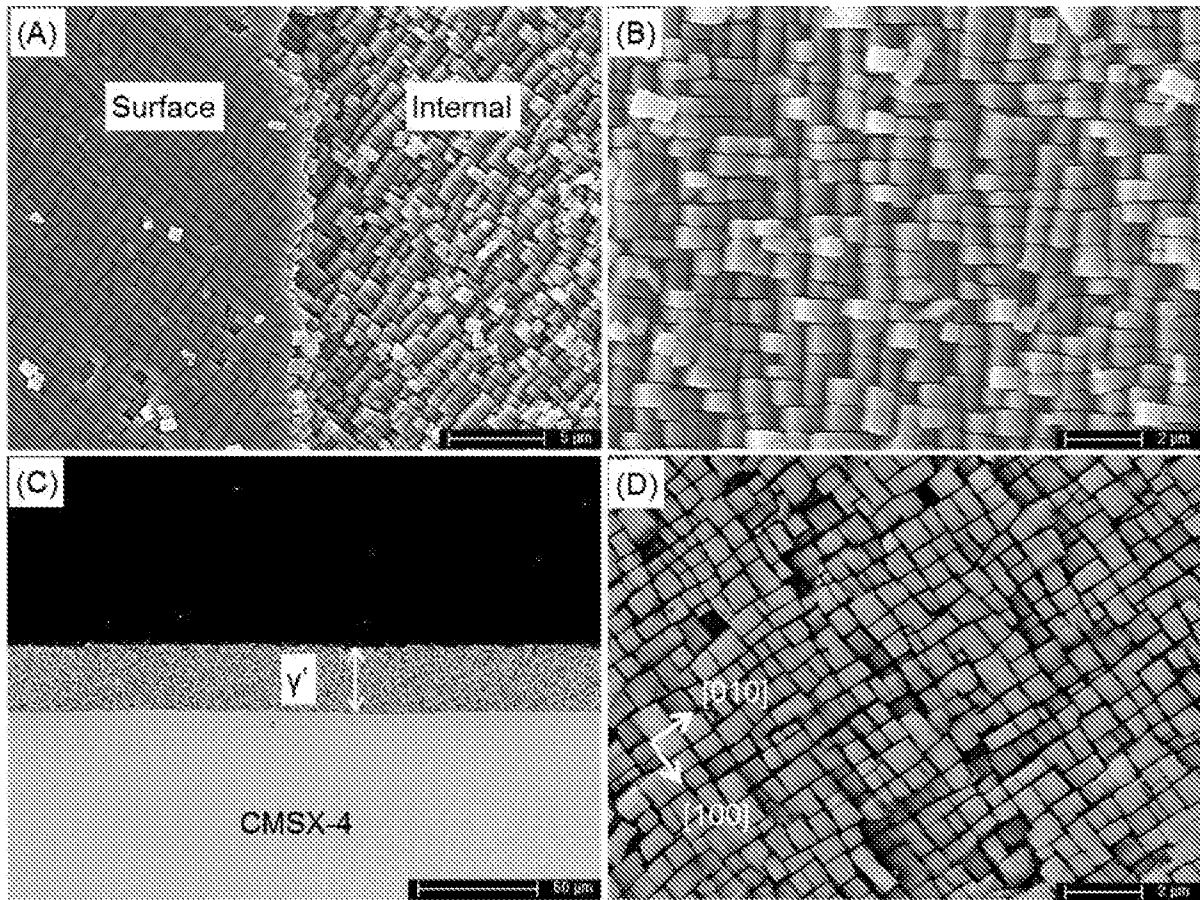


Figure 17

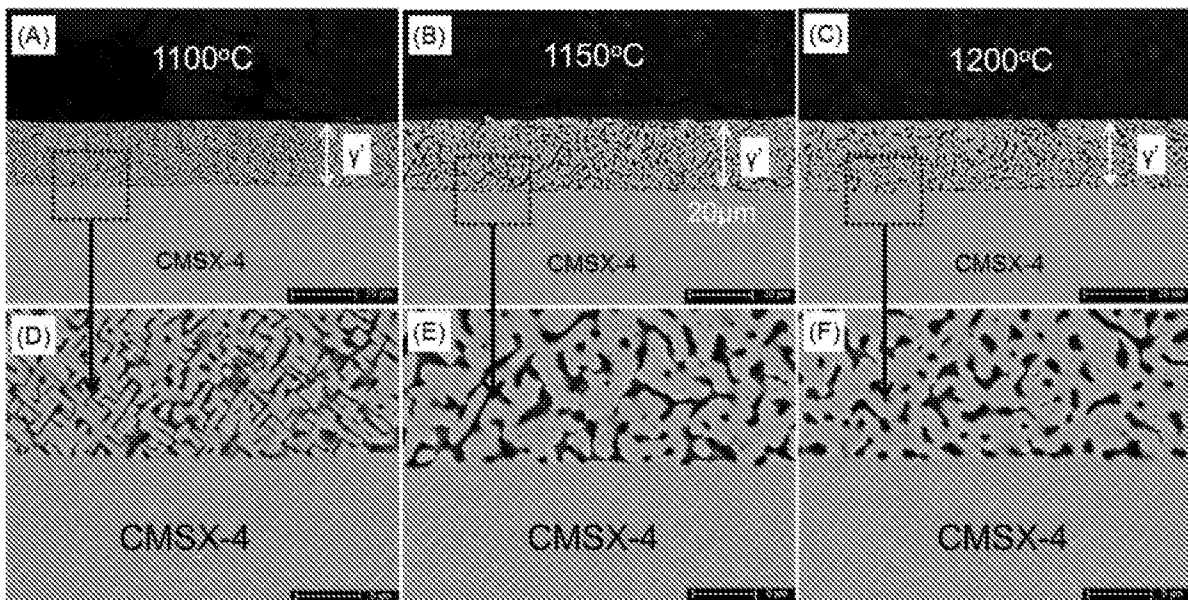


Figure 18

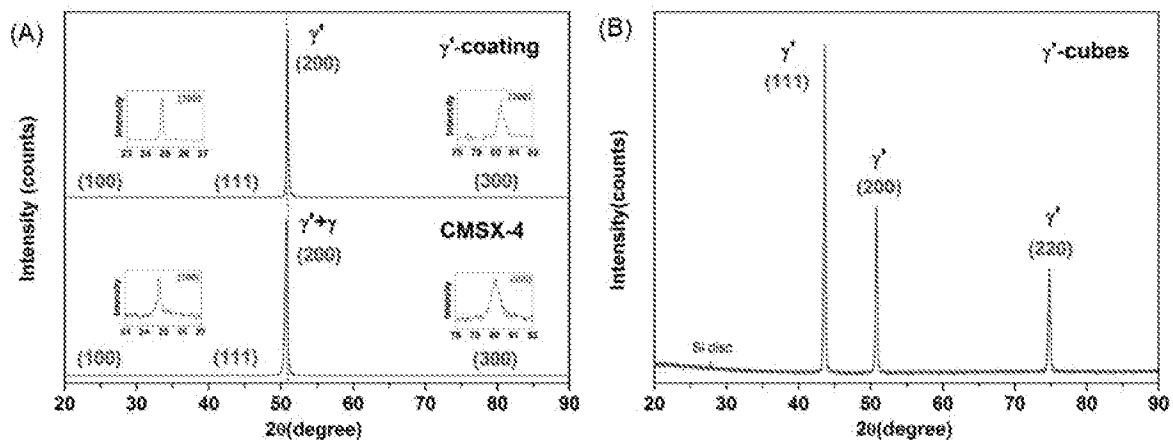


Figure 19

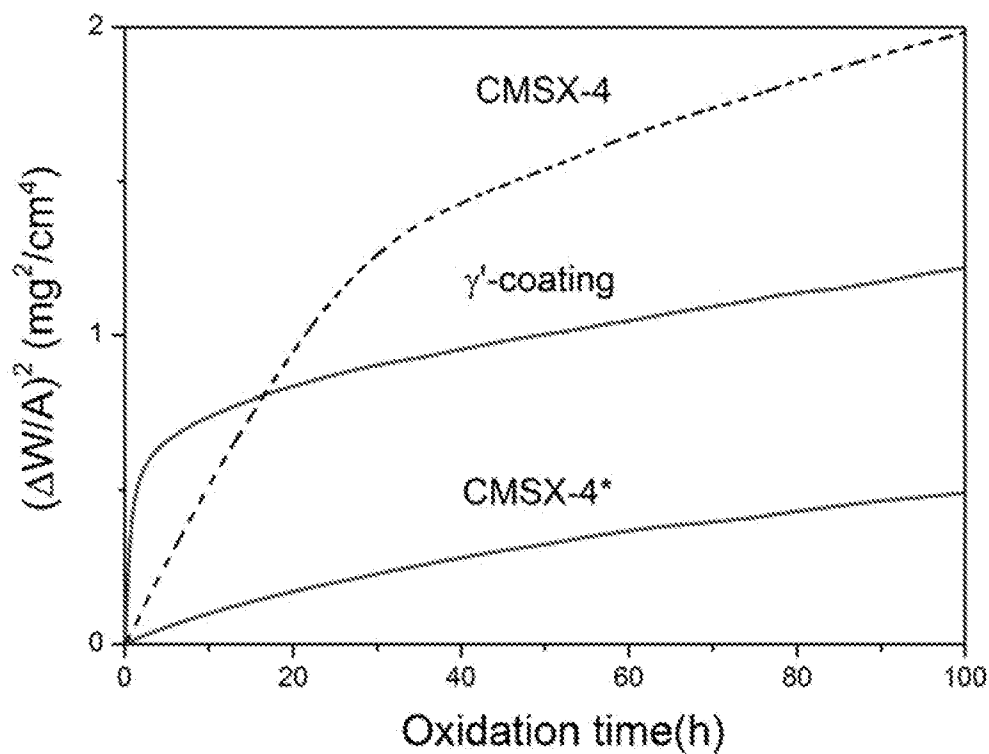


Figure 20

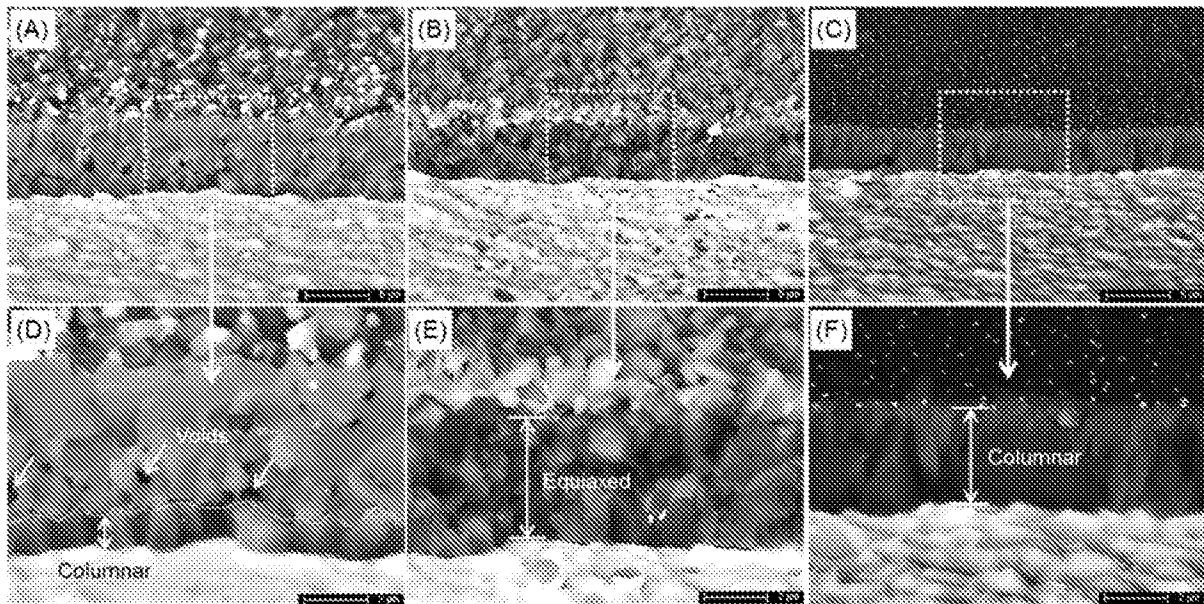


Figure 21

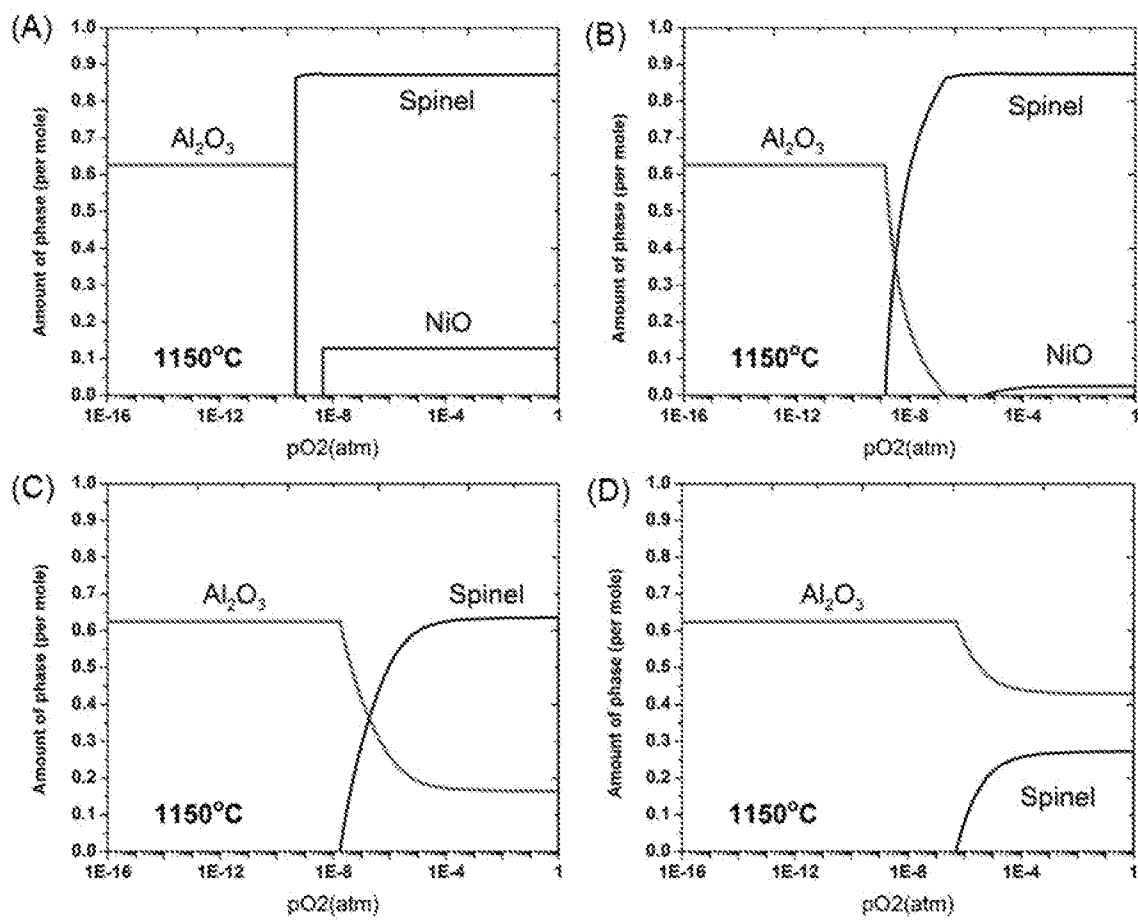


Figure 22

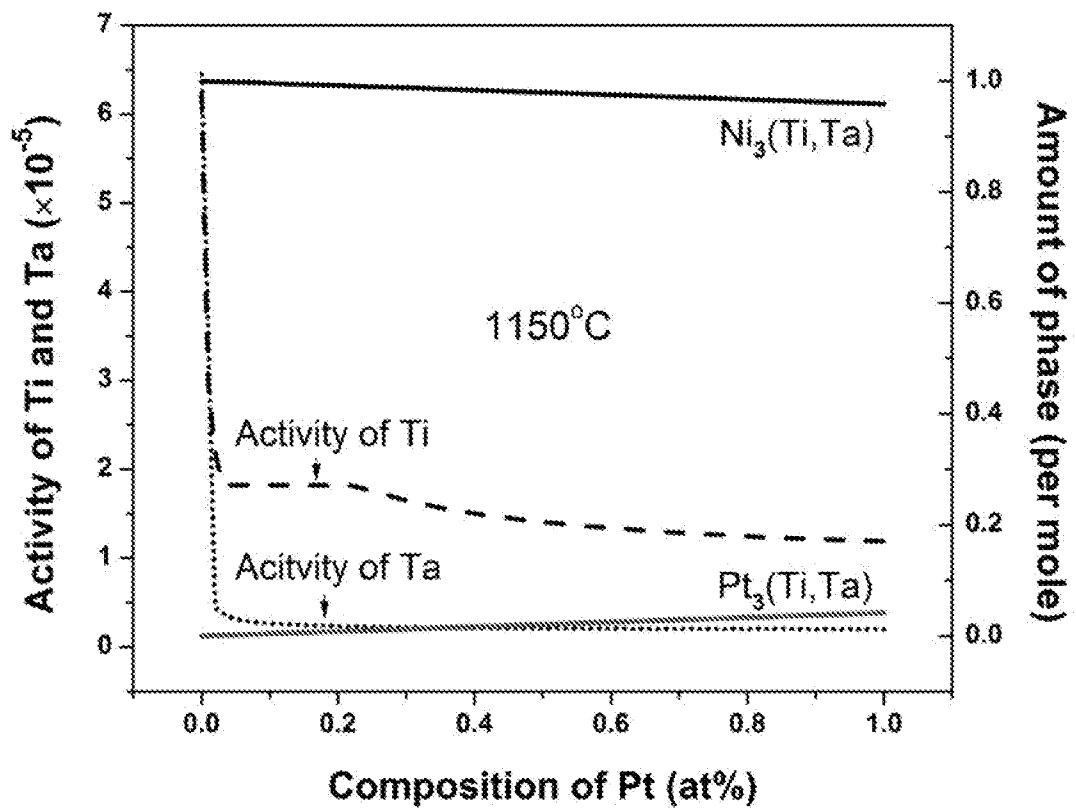


Figure 23

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2015/051549

A. CLASSIFICATION OF SUBJECT MATTER
INV. C23C28/02 C23C28/00 F01D5/28
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C23C F01D

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X A	US 2010/330295 A1 (HAZEL BRIAN THOMAS [US] ET AL) 30 December 2010 (2010-12-30) paragraphs [0010], [0014], [0016], [0017], [0021], [0024] - [0030], [0027], [0034] - [0042] -----	1-16, 18-21 17
X A	US 2006/210825 A1 (GLEESON BRIAN [US] ET AL) 21 September 2006 (2006-09-21) paragraphs [0008] - [0010], [0014], [0033] - [0035], [0039] - [0045], [0059]; figure 16; example 7 ----- -/-	1-16, 18-21 17



Further documents are listed in the continuation of Box C.



See patent family annex.

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"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

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"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

"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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"&" document member of the same patent family

Date of the actual completion of the international search

26 August 2015

Date of mailing of the international search report

02/09/2015

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Tsipouridis, P

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2015/051549

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X A	US 2006/127695 A1 (GLEESON BRIAN [US] ET AL) 15 June 2006 (2006-06-15) paragraphs [0007], [0014] - [0017], [0036] - [0040], [0049] - [0052], [0054], [0057], [0058], [0063], [0065], [0068], [0072], [0073]; claims 1-7 -----	1-16, 18-21 17

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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