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(54) Electrolytic stripping

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Procédé de décapage électrolytique

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Description

Introduction

[0001] The present invention is directed to an improved electrolytic stripping method.

[0002] The components of an aircraft engine operate at high pressure and temperature in an extreme corrosive environment and are thus subjected to both high thermal and mechanical stresses. To withstand these conditions, turbine components have to be made from specifically-designed materials such as superalloys. To improve their resistance to corrosion and/or oxidation, these turbine components must also be coated, hence increasing their lifetime in service by forming a protective oxide scale on the surface. For turbine components, the coatings are generally based on diffusion coatings (mostly aluminium diffusion coatings, including pure and modified aluminides) or overlays coatings (MCrAlY) as oxidation resistant coatings or as bondcoat layers for full Thermal Barrier Coatings (TBC) systems. However, despite this with the passage of time these turbine components still become damaged. Thus, when the turbine is eventually overhauled, refurbishment of these components is more cost effective than replacement.

[0003] The repair process involves various steps, including stripping of the old coating and deposition of a new one in the affected area. To date the stripping of old coatings from these components prior to the subsequent repair step is generally carried out using chemical baths to remove (a) the corrosion products, usually an oxide scale, and (b) the damaged coating layers. For example, presently the components are immersed in baths, containing mineral acid solutions comprising Hydrochloric Acid (HCl), Nitric Acid (HNO_3), Sulphamic Acid (H_3NSO_3), Phosphoric Acid (H_3PO_4) and alkaline solutions mainly based on Sodium Hydroxide (NaOH).

[0004] However, one limitation of this chemical stripping approach is that the solutions are not selective enough and are poorly reliable and therefore may damage the superalloy substrate by causing pitting and intergranular attack (IGA).

[0005] There is also the risk that components may have to be scrapped because of extensive attack inducing base material loss, including changes in critical dimensions (wall thickness and/or cooling holes diameter).

[0006] Furthermore from an environmental, health and safety viewpoint the stripping solutions are toxic and harmful and waste from these processes must be properly treated and/or disposed of. Additionally, many of the solutions require high temperatures to operate, thus, entailing evaporation issues and requiring additional exhausting systems and safety as well as handling precautions while also raising energy costs.

[0007] Additionally, these processes can require extensive masking of the components to shield selected and/or sensitive portions of the components, e.g. airfoil roots or internal cooling channels, due to the non-selective nature of chemical stripping baths.

[0008] Finally, intermittent grit blasting stages are often required (including before, during and/or after treatment) thus extending the overall processing time (up to 5-8 hours) to a critical level. Grit blasting which is a line-of-sight process, also reduces reproducibility, when it is either automated or by hand. It may also damage the substrate (causing roughness, excessive and/or non-homogeneous material removal), thereby limiting part life.

[0009] As an alternative to conventional chemical treatment processes, electrochemical approaches may also be adopted.

[0010] For example, US 2,840,521 (1958) is directed to the use of electrolytic stripping by applying current density (i.e. galvanostatic mode) to remove metal coatings from aluminium immersed in diluted sulphuric acid H_2SO_4. Water mixtures of fluoroboric acid (HBF_4) and phosphoric acid (H_3PO_4) also allowed to remove as-plated metal coatings from substrates of the group of titanium and of tungsten (US 3,793,172 (1972)). However, the majority of these electrochemical stripping approaches only remove the coatings (aluminide and MCrAlY) on the base metal or superalloy and do not address the removal of the corrosion or oxidation products grown from such coatings in the same electrolyte (bath).

[0011] J Appl Electrochem (2008) 38:817-825 "Controlled stripping of aluminide coatings on nickel superalloys through electrolytic techniques" discloses a generic process utilising either galvanostatic or potentiostatic polarisation and an electrolytic solution comprising a strong oxidising inorganic acid, a pitting inorganic acid and a number of complex inorganic molecules. No specific details are given on the electrolytic solution used.

[0012] As expanded above, conventional processes, whether chemical or electrochemical, for treating turbine components have many limitations and require many different steps which are both time-consuming and the processes themselves can damage the base metal itself.

[0013] Thus, the present invention is directed to an improved process for treating turbine components for use in the engine maintenance and repair industry.

Statements of Invention

[0014] The present invention is directed towards an electrochemical process for stripping corrosion and oxide products and oxidation resistant metallic coatings from a superalloy test sample comprising connecting the test sample to a lead of a power supply; submerging a portion of the test sample into a bath of electrolytic stripping solution with a pH less than 1, wherein the stripping solution comprises nitric acid (HNO_3) at a concentration from 2% to 20% by weight; hydrochloric acid (HCl) at a concentration from 1% to 10% by weight; and ammonium molybdate salt at a concentration from 0.2% to 3% by weight; and, water up to 100% by weight; subjecting the test sample to combined cycles of anodic and cathodic polarisation steps for a period of time effective to strip the corrosion and the oxide products and oxidation resistant metallic coatings from the test sample, wherein anodic polarisation involves making the test sample the anode at a potential lower than +2 volts for 1 min to 2 hours and cathodic polarisation involves making the test sample the cathode at a potential higher than -1.5 volts for 1 minutes to 20 minutes; measuring the open circuit potential (o.c.p.) before and after at least one step of the combined cycle of polarisation to monitor the progress of the coating removal; removing the test sample from the electrolytic stripping solution when the corrosion and oxide products and oxidation resistant metallic coatings are removed and the o.c.p. is close to that of the original superalloy test sample or the current value is getting closer to the passivation current value of the base material; subjecting the test sample to a final cleaning and final rinsing step wherein the final cleaning step comprises i) placing the test sample in a chemical etching solution comprising a mixture from 40/60 to 60/40 in volume ratio of Hydrochloric acid (HCl) and Isopropyl Alcohol (C_3H_8O) with Copper Chloride salt ($CuCl_2$) at a concentration from 2 g/l to 20 g/l, for 1 to 60 min; and the final rinsing step comprises ii) rinsing the test sample in water at room temperature for at least 1 min.

[0015] In a further embodiment, the test sample is a gas turbine hot section part made of Fe-, Ni-, Co- or Ti-based alloys.

[0016] In a further embodiment, the test sample is coated either with an aluminide or a modified aluminide coating.

[0017] In this manner, the base material is a gas turbine hot section part, having a distinct electrochemically composition feature from the coating, including any component made of Fe-, Ni-, Co- or Ti-based alloys.

[0018] In a further embodiment, cathodic polarisation is carried out at potentials ranging from -0.8 V/o.c.p. to -0.4 V/o.c.p. for steps between 2 to 10 minutes each and anodic polarisation is carried out at potentials ranging from +0.4 V/SCE to +0.75 V/SCE for steps between 5 to 10 minutes each.

[0019] In a further embodiment, the final cleaning step takes place for 5 to 15 minutes at a temperature below 75°C.

[0020] In a further embodiment, the final rinsing step additionally uses ultrasonic waves.

[0021] It will be understood that the process of the invention can be carried out for localized coating removal, for example, the tip area of the turbine blade. Alternatively, it can also be used to remove the complete coating by immersing the entire airfoil/turbine part in the stripping solution.

[0022] The present invention is directed to an improved electrochemical process which strips corrosion and oxides products and aluminide coatings from a test sample in the electrolytic stripping solution in an alternate manner by switching the polarity of the test sample.

[0023] The process of the present invention is highly selective and maintains the integrity of the base metal. This method preserves the desired structural and dimensional integrity of the underlying base metal, thus, reducing scrap parts and reducing reworking operations. The strong oxidizing substances in the bath allow the base material to develop a passive film.

[0024] Advantageously, the process of the invention minimizes or completely eliminates the need for masking. Only those parts which need to be stripped are allowed in contact with a bath where the afore-mentioned process is carried out. This greatly speeds up the process as no masking is required on critical parts of the test sample unless it is a requirement of process specifications.

[0025] The method of present invention is more environmentally friendly than conventional processes and produces less hazardous effluents and does not result in the formation of excessive hazardous fumes.

[0026] Furthermore, the method of the present invention operates at lower acid concentrations, lower temperatures than conventional techniques and under normal atmospheric conditions, without any special requirements of heating and stirring. Processing times are shorter than conventional techniques. Thus, the method of the present invention is simpler and more cost effective than conventional techniques.

[0027] It is an easily repeatable process which can be easily monitored.

Detailed Description of the Invention

[0028] The invention will be more clearly understood from the following description of some embodiments thereof, given by way of example only with reference to the accompanying figures and examples, in which:

Fig. 1 is a schematic diagram of the three-electrode electrolytic set-up for the method of the present invention for stripping alternatively corrosion and/or oxide products and worn aluminide coatings;

Fig. 2 is a photograph of apparatus of Figure 1 (Laboratory set-up);

Fig. 3 is a cross-section of an airfoil portion of turbine blade after removal of the coating by method of the present invention. Degradation modes that can be currently experienced using known stripping methods (chemical stripping) are shown by the dotted circles;

Fig. 4 is photographs of turbine blades highlighting the difficulties encountered using known stripping methods (chemical stripping);

Fig. 5 left hand side graph shows the evolution of the $E_{o.c.p.}$ (E_{corr}) and right hand side graph shows the evolution of the current density with the number of stripping steps using the method of the present invention;

Fig. 6 shows cross-sections of the oxidised aluminide coating before and after stripping using the method of the present invention;

Fig. 7 shows cross-sections of the oxidised aluminide coating after stripping using the method of the present invention;

Fig. 8 shows cross-sections of the oxidised aluminide coating before and after stripping using the method of the present invention;

Fig. 9 shows cross-sections of the oxidised Platinum/Aluminide coating before and after stripping using the method of the present invention; and,

Fig. 10 shows cross-sections of the oxidised aluminide coating before and after stripping using the method of the present invention.

[0029] The method of the present invention is based on a three-electrode cell, whose a schematic diagram of the set-up is shown in Fig. 1, whereby:

1. the working electrode (WE) is the part to be stripped;

2. the non-polarised reference electrode (Ref) ensures a safe live-monitoring of the stripping process and can be any commercially available electrode, but a saturated calomel electrode (SCE) is preferred for the purpose.

3. the counter-electrode (CE) is a conductive and inert material, preferably a fine platinum mesh or a platinum-coated Ti- or Ni- alloy or steel grid offering a high electro-active surface area and surrounding (1 and 2) with a geometry tailored to the part to be stripped.

[0030] Essentially, the test sample (or at least a portion of test sample) is immersed in contact with the highly conductive and acidic oxidizing electrolytic stripping solution up to the desired section of the blade and connected to a power supply. The test sample is polarized in such a manner that the test sample is alternatively the cathode and the anode. Therefore, the process allows to both dissolve the coating layers (stripping) as well as to remove the corrosion and oxide products through in situ gas bubbling that makes them brittle enough to detach from the surface. Simultaneously, the computerised system allows an in situ full feedback control of the electrical potential with respect to the reference electrode or of the electrical current at the surface of the part to be stripped.

[0031] In the present invention, the electrolytic stripping solution is a water-based stripping solution comprises a strong oxidizing inorganic acid in the form of nitric acid (HNO_3); a reducing and pitting inorganic acid in the form of hydrochloric acid (HCl); and a composition comprising both a corrosion inhibitor and an oxidizing agent in the form of an ammonium molybdate salt.

[0032] The chemical composition of the water-based electrolytic solution includes

- an oxidising acid (nitric acid, HNO_3) that allows to oxidise the species,

- a reducing and pitting acid (hydrochloric acid HCl) that allows to deepen the attack but limit the oxidising action of HNO_3 and

- a molecule comprising both a corrosion inhibitor and an oxidising agent, ammonium molybdate $[(NH_4)_6Mo_7O_{24}]$ that simultaneously allows to oxidise the species to be stripped and to avoid corrosion (like intergranular attack IGA) of the metal substrate.

[0033] Such a chemical composition ensures high electrical conductivity of the electrolyte and makes the pH to be lower than 1 over the entire stripping cycle and does not degrade the conventional waxes employed to protect the internal cooling holes and the roots of some of the components.

[0034] It will be understood that the exact chemistry of the bath must be adjusted depending upon the exact coating and base metal combination. A potential is preferably imposed to the part to remove all the coating from the localized region after an efficient period of time. The process parameters are related to coating thickness and composition as well as to the oxide scale features (cracking, composition, thickness) and part electro-active area and must be adjusted accordingly for each configuration.

[0035] Due to the high electrochemical selectivity and to the fully in situ monitored process, the base material is not affected as it passivates itself when it comes in contact with the electrolyte, thus preserving its structural and dimensional integrity and extending part life, while dissolution reactions still occurs on partially removed portions of the coating to complete the removal process.

[0036] Completion of the stripping process is achieved once the preset value of the current or of the potential is reached. This value is predetermined either by an extrapolation of the current/voltage polarisation curve, by a ratio of the initial potential or current, by intercalated open circuit potential measurements.

[0037] Ideally, the method of the invention involves the following general steps:

Step 1

[0038] This steps involves fixing the test sample to the insulated fixture that ensures the electrical contact to the test sample, putting in contact the desired portion of the test sample with the electrolyte (e.g. by immersion in a bath) operating at ambient temperature under soft magnetic stirring and connection of the fixture to one channel of the power source at least.

Step 2

[0039] This step involves measuring the electrochemical activity of the test sample to be stripped (open circuit potential - o.c.p.) for 1 to 10 min.

Step 3 - Electrolytic stripping

[0040] The test sample is alternatively made the cathode (connected to the negative lead of the power source) at a potential higher than -1.5 volts for 1 min to 20 min and the anode (connected to the positive lead of the power source) at a potential lower than +2 volts for 1 min to 2 hours.

[0041] Agitation of the solution is provided by any convenient means such as mechanical or magnetic stirring, air or ultrasonic agitation, or by constant circulation of the solution using a pump system, which can further allow the filtration of the electrolyte.

[0042] The required efficient stripping time to strip the test sample is subject to many parameters such as the applied voltage or current density, the concentration of the electrolyte, the coating thickness and/or composition and/or micro-structure, the basis material and the distance between the electrodes. Nevertheless, if portions of the test sample are removed more quickly than others, overrun will not lead to undesirable effects on structural and critical dimensions integrity of the part, owing to the above-mentioned selectivity of the process/solution and spontaneous passivation of the exposed base material.

Step 4

[0043] Erosive rinsing of the test sample (or any other erosive/abrasive means, e.g. scrubbing with a stiff brushing or gentle grit blasting) after complete stripping procedure and the removal from the electrolyte to tear off smut and/or sludge as well as coating porous layers, if any, using preferably deionised water at room temperature coupled to light erosive/abrasive particles/powder, e.g. pumice, grit particles or any other similar flaky particles/powder, for at least 1 min under ultrasonic agitation. For a larger production scale, this can be achieved through any known agitation way in order to maintain a turbulent flow and a homogeneous suspension of particles/powder. It will be understood that any other erosive, abrasive means may be employed, e.g. scrubbing with a stiff brush or gentle grit blasting.

Step 5

[0044] Final cleaning using a chemical etching solution at ambient temperature, optionally coupled to ultrasonic waves or any other commercially available agitation, comprising a mixture from 40/60 to 60/40 in volume ratio of Hydrochloric acid (HCl) and Isopropyl Alcohol (C_3H_8O) with Copper Chloride salt ($CuCl_2$) at a concentration from 2 g/l to 20 g/l, for 1 to 60 min, preferably 5 to 15 min. Further use of erosive/abrasive particles in combination with the cleaning solution is not excluded.

[0045] This step ensures even and smooth surfaces are obtained ready for subsequent repair steps without damaging the base material and avoiding grit blasting.

Step 6

[0046] Final rinsing of the part after likely final cleaning step, preferably using ultrasonic waves, in water at room temperature for at least 1 minute.

EXAMPLES

Preparation of test samples

[0047] The test samples used in the following examples (including the comparative examples) were derived from scrap metal parts from the airline industry, either complete scrap metal parts such as engine/turbine blade parts or gas turbine hot section parts or similar scrap metal samples cut into pieces to produce testing samples, or pieces made from a nickel-based superalloy, whose chemical composition is given in the table below:

	Substrate	Ni	Al	Cr	Co	Mo	W	Ta	Ti	C	B	Zr	other
wt. %	RENE™ 125	59	4.8	8.5	10	2	8	3.4	2.5	0.11	0.015	0.05	1.4Hf
	DS 200	59.6	5	9	10		12.5		2	0.15	0.015	0.05	1.8Hf
	INCONEL 100	60	5.5	10	15	3			4.7	0.18	0.014	0.06	1.0 V

[0048] Firstly, the test samples were extensively stripped, grit blasted and cleaned/degreased The stripping process consisted of a) aqueous cleaning, b) wet abrasive blasting, c) immersion in a stripping bath consisting of a mixture of nitric acid (HNO_3) and sulfamic acid (H_3NSO_3), d) aqueous rinsing, e) scrubbing and f) final coarse grit blasting] for each test sample.

[0049] The test samples were then aluminised using a conventional vapour phase process (the SVPA method (SNECMA vapour phase aluminising) is a commonly used and well-known aluminising treatment in the aircraft coatings technology) in which the aluminium-containing vapour species are generated from reaction between a donor (Cr-Al nuggets) and an activator (ammonium fluoride) at 1150°C/3 h for INCO-100 and RENE125 and at 1100°C/5h for DS200 material. The resulting thickness of coatings is of about 60 microns on average.

[0050] Some of the test samples were cyclically oxidised for cycles of 24h at 1100°C to promote interdiffusion with the substrate's elements and deplete the aluminium reservoir of the coating. This type of procedure also aimed at inducing cracking of the oxide scale to provide further easy penetration of the stripping solution to ensure that the following examples were performed on components as close as possible to real components after exposure to engine conditions (service).

[0051] The aluminised and oxidised test samples were then subjected to the following stripping methods.

Comparative Example

Conventional chemical stripping of test samples

Materials

[0052] Test samples used are described above.

Method

[0053] The test samples were firstly degreased, grit blasted and then immersed in a stripping bath consisting in a mixture of nitric acid at a concentration of approximately 14%wt and sulfamic acid at a concentration of approximately 5%wt. Water up to 100%wt is added to the mixture. After approximately 5 hours, samples were removed from the bath, rinsed with water and gently grit blasted.

Results and Conclusion

[0054] Fig. 3 is a cross-section of an airfoil portion of a turbine blade made of a superalloy. The dotted circles surround the degradation (i.e. general corrosion, pitting and/or intergranular attack) that can occur to the turbine blade using the chemical stripping method of this comparative example. These comparative methods reduce the wall section and induce crack formation, hence decreasing the mechanical properties for which the blade was designed for. For instance, the throat dimension between adjacent blades in an engine is defined by the distance between the trailing edge (TE) of one blade and the convex surface of the adjacent blade. Thus, the trailing edge (TE) of an airfoil is a very thin and critical section that must not be altered.

[0055] Using such a chemical stripping method, the risk is that the TE will get thinner or be dissolved (surrounded in Fig. 3). Such a loss of base material will result in a decrease of the engine efficiency due to the undesirable effect on the slowing down of gas flow through the throat or on the mechanical damage of parts.

[0056] In the case of chemical stripping methods, this is partly due to the non-selective nature of the chemical bath towards the substrate, if the latter is exposed, even if stripping is not completed on other portions of the part. This can lead to extensive pitting corrosion and/or inter-granular (IGA) attacks (see Fig. 4). These corrosion degradation modes (general corrosion, pitting and IGA) will be exacerbated in the electrochemical stripping mode when using a power source (or current source) in the particular case of the TE (relatively sharp edge), due to the high concentration of the electrical field (or current lines) at edges and corners of complex geometry parts such as turbine blades or vanes.

[0057] Fig. 4 shows the difficulties experienced using the stripping method of the comparative example. In a similar manner, the airfoil convex side (CV) mostly suffers from pitting and IGA due to the higher removal rate of the coating compared to the concave side (CC), which is less exposed to the solution, if not suspended or hung in the bath, due to the geometry and the difficulty to agitate and/or create a turbulent flow to regenerate the stripping solution close to this part. In this particular case, it will give rise to remnant portions of coatings on the CC most of the times.

Example 1

Materials

[0058] i) 3-electrode electrochemical cell: The electrochemical cell is a beaker containing the solution and a platinum grid of large area shaped to the part geometry and surrounding it perfectly. The reference electrode is a Saturated Calomel Electrode at a constant potential versus the Hydrogen Standard Electrode E = + 0.242 V/HSE. The three-electrode set-up is connected to a Potentiostat / Galvanostat PARSTAT2273A and fully monitored through the software PowerCorr.

[0059] ii) Electrolyte: The water-based stripping bath consisted of a mixture of

2 wt. % of hydrochloric acid,
5 wt. % of nitric acid and
0.7 wt. % of ammonium molybdate tetrahydrate.

[0060] The bath operates at ambient temperature under soft magnetic stirring.

iii) Test Sample: as defined above

Method:

Step 1:

[0061] The test sample was gently blasted with #220 mesh sieved alumina particles, immersed in the electrolyte operating at ambient temperature under soft magnetic stirring and connected to the power source.

Step 2:

[0062] The o.c.p. (open circuit potential) value of the test sample was measured according for 1 to 10 min.

Step 3: Electrolytic stripping.

[0063] The test sample is alternatively made the cathode (connected to the negative lead of the power source) at a potential of -0.8V/o.c.p. for 5 min and the anode (connected to the positive lead of the power source) at a potential of +

0.5V/SCE for 6 min. Simultaneously, the counter-electrode is connected to the other lead of the power source accordingly and the potential between the reference electrode and the working electrode is live monitored through the full computerised system connected to the three-electrode cell or by mean of any voltmeter/ammeter.

[0064] Agitation of the solution is provided by any convenient means such as mechanical or magnetic stirring, air or ultrasonic agitation, or by constant circulation of the solution using a pump system, which can further allow the filtration of the electrolyte. In this example, the stripping solution is magnetically agitated softly.

[0065] After the electrolytic stripping procedure, the test sample was removed from the bath, ultrasonically rinsed according to the following step 4.

Step 4: Erosive ultrasonic rinsing

[0066] After step 3 has been completed, the test strip is removed from the electrolyte. Smut and/or sludge as well as coating porous layers are removed using preferably deionised water at room temperature coupled to light erosive/abrasive particles/powder, e.g. pumice, grit particles or any other similar flaky particles/powder, for at least 1 min under ultrasonic agitation.

[0067] In these particular examples, the rinsing has been carried out in water under ultrasonic agitation and then scrubbing the samples with a stiff brush before being cleaned (step 5).

Step 5: Final cleaning

[0068] Final cleaning takes place using a chemical etching solution at ambient temperature, in a solution composed of a 50/50 (by volume) mixture of hydrochloric acid and isopropyl alcohol plus 1 wt. % of copper chloride $CuCl_2$ with ultrasonic waves before rinsing in water and drying with dry/hot air (step 6).

Results:

[0069] Fig. 5 shows the evolution of the $E_{o.c.p.}$ (E_{corr}) and of the current density with the number of stripping steps. The typical overall trends of $E_{o.c.p.}$ and of current density evolution during the stripping process are given in Fig. 5 (a) and (b) respectively. As a rule, after the step 1, the o.c.p. value stabilises at a value, which is close to the originally coated substrate. Subsequent cathodic bubbling/anodic dissolution steps bring about an increase of the o.c.p. value close to that of the raw substrate as a result of the effective removal of the coating layers. Simultaneously, the complete removal of the aluminide coating is strongly indicated by a slowdown of the dissolution kinetics associated with the passivation of the underlying substrate.

[0070] The following Examples relate to investigations of the cross-sections of the coating/base material systems using either optical or electron microscopy after different stages of processing according to the method of Example 1.

Example 2

Potentiostatic stripping of an oxidised aluminide coated DS200 sample cut from a Low Pressure Turbine (LPT) blade airfoil

[0071] The procedure of example 1 was followed and repeated several times until an o.c.p. value or a current density close to the one of the raw substrate was reached.

[0072] We found the following steps achieved the desired end results - Step 3 procedure was repeated 5 times in a row. Check-ups of the $E_{o.c.p.}$ (E_{corr}) are monitored after each anodic polarisation.

1. o.c.p. measurement for 5 min (Step 2);
2. cathodic polarisation at -0.8V/o.c.p. for 5 min; and
3. anodic polarisation at +0.5V/SCE for 5 min.

[0073] After stripping, the sample was ultrasonically rinsed in deionised water for 2 min then scrubbed with a stiff brush before being ultrasonically cleaned for 5 min and dried with air (Steps 4 to 6).

Results

[0074] Fig. 6 shows cross-sections of the coating before and after stripping.

Example 3

Full potentiostatic stripping of an oxidised aluminide coated DS200 LPT blade airfoil (for full repair purposes)

[0075] The procedure of example 1 was followed. The test sample was clamped by the root to a polymer fixture ensuring the electrical contact through inert platinum wires. The test sample was immersed tip downwards in the solution until the platform level so that the electrolyte was in contact with the areas requiring a coating removal but not the root section.

[0076] We found the following steps achieved the desired end results - Step 3 procedure repeated 6 times in a row. Check-ups of the $E_{o.c.p.}$ (E_{corr}) are monitored after each anodic polarisation.

1. o.c.p. measurement for 2 min (step 1);
2. cathodic polarisation at -0.8V/o.c.p. for 10 min;
3. anodic polarisation at +0.5V/SCE for 6 min.

[0077] The electrolytic stripping procedure was repeated several times until an o.c.p. value or a current density close to the one of the raw substrate was reached. After stripping, the sample was ultrasonically rinsed in deionised water for 2 min then scrubbed with a stiff brush before being ultrasonically cleaned for 10 min, and dried with air (steps 4 to 6).

Results:

[0078] **Fig. 7** shows cross-sections of the coating after stripping.

Example 4

Potentiostatic stripping of an oxidised aluminide coated RENE125 sample cut from a High Pressure Turbine (HPT) blade airfoil

[0079] The procedure of example 1 was followed and was repeated several times until an o.c.p. value or a current density close to the one of the raw substrate was reached.

[0080] We found the following steps achieved the desired end results - Step 3 procedure repeated 5 times in a row. Check-ups of the $E_{o.c.p.}$ (E_{corr}) are monitored after each anodic polarisation.

1. o.c.p. measurement for 5 min (step 1)
2. cathodic polarisation at -0.8V/o.c.p. for 5 min
3. anodic polarisation at +0.5V/SCE for 6 min

[0081] After stripping, the sample was ultrasonically rinsed in deionised water for 2 min then scrubbed with a stiff brush before being ultrasonically cleaned for 5 min and dried with air.

(steps 4 to 6)

Results

[0082] Fig. 8 shows cross-sections of the aluminide coating before and after stripping.

Example 5

Local stripping: potentiostatic stripping of an oxidised platinum aluminide coated RENE125 HPT blade airfoil (for tip repair purposes)

[0083] The procedure of example 1 was followed. The test sample was clamped by the root to a polymer fixture ensuring the electrical contact through inert platinum wires. The test sample was immersed tip downwards in the solution until the platform level so that the acid solution contacted the areas requiring a coating removal (only the tip of the airfoil) but not the entire part of the airfoil or the root.

[0084] We found the following steps achieved the desired end results - Step 3 procedure repeated 8 times in a row. Check-ups of the $E_{o.c.p.}$ (E_{corr}) are monitored after each anodic polarisation.

1. o.c.p. measurement for 2 min (step 1)
2. cathodic polarisation at -0.8V/o.c.p. for 5 min
3. anodic polarisation at +0.5V/SCE for 6 min

[0085] The electrolytic stripping procedure was repeated several times until an o.c.p. value or a current density close to the one of the raw substrate was reached. After stripping, the sample was ultrasonically rinsed in deionised water for 4 min then scrubbed with a stiff brush before being ultrasonically cleaned for 10 min and dried with air (steps 4 to 6)

Results:

[0086] **Fig. 9** shows cross-sections of the Pt/Al coating before and after stripping.

Example 6

Potentiostatic stripping of an oxidised aluminide coated INCO100 sample cut from a LPT blade airfoil

[0087] The procedure of example 1 was followed and was repeated several times until an o.c.p. value or a current density close to the one of the raw substrate was reached.

[0088] We found the following steps achieved the desired end results - Step 3 procedure repeated 6 times in a row. Check-ups of the $E_{o.c.p.}$ (E_{corr}) are monitored after each anodic polarisation.

1. o.c.p. measurement for 5 min (step 2)
2. cathodic polarisation at -0.6V/o.c.p. for 5 min
3. anodic polarisation at +0.5V/SCE for 6 min

[0089] After stripping, the sample was ultrasonically rinsed in deionised water for 4 min then scrubbed with a stiff brush before being ultrasonically cleaned for 10 min and dried with air.

Results:

[0090] **Fig. 10** shows cross-sections of the aluminide coating before and after stripping using the present invention.

General Conclusion:

[0091] As shown in the comparative example, conventional chemical stripping processes removed the aluminide coating, but also resulted in a significant amount of damage in the form of pitting and inter-granular attacks (IGA) of the base material. Moreover, the time required for efficient stripping often surpasses three (3) hours when considering the grit blasting, stripping per se and rinsing steps required.

[0092] In contrast, as shown in Examples 1 to 6, the method of this present invention required less time and operates at ambient temperature. These improvements can be attributed to the combined effect of using a new electrolytic process and a new electrolyte.

[0093] Additionally, we have also shown that the method of the invention using this improved electrolyte solution enables a highly selective coating removal while ensuring in every instance the structural and dimensional integrity of the base material/test sample is maintains. Another advantage of this method, is that the base material/test sample passivates itself when becoming in contact with the stripping solution.

[0094] In the specification the terms "comprise, comprises, comprised and comprising" and the terms "include, includes, included and including" are all deemed totally interchangeable and should be afforded the widest possible interpretation.

[0095] The invention is in no way limited to the embodiment hereinbefore described which may be varied in both construction and detail within the scope of the appended claims.

Claims

1. An electrochemical process for stripping corrosion and oxide products and oxidation resistant metallic coatings from a superalloy test sample comprising:

Connecting the test sample to a lead of a power supply;
Submerging a portion of the test sample into a bath of electrolytic stripping solution with a pH less than 1,

wherein the stripping solution comprises:

nitric acid (HNO_3) at a concentration from 2% to 20% by weight;
hydrochloric acid (HCl) at a concentration from 1% to 10% by weight; and
ammonium molybdate salt at a concentration from 0.2% to 3% by weight;
water up to 100% by weight,

Subjecting the test sample to combined cycles of anodic and cathodic polarisation steps for a period of time effective to strip the corrosion and the oxide products and oxidation resistant metallic coatings from the test sample, wherein anodic polarisation involves making the test sample the anode at a potential lower than +2 volts for 1 min to 2 hours and cathodic polarisation involves making the test sample the cathode at a potential higher than -1.5 volts for 1 minutes to 20 minutes;
Measuring the open circuit potential (o.c.p.) before and after each at least one step of the combined cycle of polarisation to monitor the progress of the coating removal;
Removing the test sample from the electrolytic stripping solution when the corrosion and oxide products and oxidation resistant metallic coatings are removed and the o.c.p. is close to that of the original superalloy test sample or the current value is getting closer to the passivation current value of the base material;
Subjecting the test sample to a final cleaning and final rinsing step wherein the final cleaning step comprises i) placing the test sample in a chemical etching solution comprising a mixture from 40/60 to 60/40 in volume ratio of Hydrochloric acid (HCl) and Isopropyl Alcohol (C_3H_8O) with Copper Chloride salt ($CuCl_2$) at a concentration from 2 g/l to 20 g/l, for 1 to 60 min; and the final rinsing step comprises ii) rinsing the test sample in water at room temperature for at least 1 min.

2. The method of claim 1 wherein the test sample is a gas turbine hot section part made of Fe-, Ni-, Co- or Ti-based alloys.

3. The method of claim 1 or claim 2 wherein the test sample is coated either with an aluminide or a modified aluminide coating.

4. The method of any of the preceding claims wherein cathodic polarisation is carried out at potentials ranging from -0.8 V/o.c.p. to -0.4 V/o.c.p. for steps between 2 to 10 minutes each and anodic polarisation is carried out at potentials ranging from +0.4 V/SCE to +0.75 V/SCE for steps between 5 to 10 minutes each.

5. The method according to any of the preceding claims wherein the final cleaning step takes place for 5 to 15 minutes at a temperature below 75°C.

6. The method according to any of the preceding claims wherein the final rinsing step additionally uses ultrasonic waves.

Patentansprüche

1. Elektrochemisches Verfahren zum Entschichten von Korrosions- und Oxidprodukten und oxidationsresistenten metallischen Beschichtungen von einer Untersuchungsprobe aus Superlegierung, das Folgendes umfasst:

Anschließen der Untersuchungsprobe an ein Stromversorgungskabel;
Eintauchen eines Teils der Untersuchungsprobe in ein Bad mit einer elektrolytischen Entschichtungslösung mit einem pH von kleiner als 1, worin die Entschichtungslösung Folgendes umfasst:

Salpetersäure (HNO_3) in einer Konzentration von 2 Gewichts-% bis 20 Gewichts-%;
Salzsäure (HCl) in einer Konzentration von 1 Gewichts-% bis 10 Gewichts-%; und
Ammoniummolybdat-Salz in einer Konzentration von 0,2 Gewichts-% bis 3 Gewichts-%;
Wasser bis zu 100 Gewichts-%,

Unterziehen der Untersuchungsprobe kombinierten Kreisläufen von anodischen und kathodischen Polarisationsschritten für eine wirksame Zeitdauer, um die Korrosions- und die Oxidprodukte und oxidationsresistenten metallischen Beschichtungen von der Untersuchungsprobe zu entschichten, worin die anodische Polarisation einschließt, dass die Untersuchungsprobe zur Anode bei einem Potential von niedriger als +2 Volt für 1 min bis 2 Stunden wird, und die kathodische Polarisation einschließt, dass die Untersuchungsprobe zur Kathode bei einem Potential von höher als -1,5 Volt für 1 Minute bis 20 Minuten wird;

Messen des Ruhepotentials (OCP = open circuit potential) vor und nach jedem mindestens einen Schritt des kombinierten Kreislaufs der Polarisation, um den Verlauf der Beschichtungsentfernung zu überwachen;
Entnehmen der Untersuchungsprobe aus der elektrolytischen Entschichtungslösung, wenn die Korrosions- und die Oxidprodukte und oxidationsresistenten metallischen Beschichtungen entfernt sind und das OCP nahezu dem der ursprünglichen Untersuchungsprobe aus Superlegierung entspricht oder sich der Stromwert dem Passivierungsstromwert des Grundmaterials nähert;
Unterziehen der Untersuchungsprobe einem letzten Reinigungs- und letzten Spülschritt, worin der letzte Reinigungsschritt Folgendes umfasst: i) Einbringen der Untersuchungsprobe in eine chemische Ätzlösung, die eine Mischung vom Volumenverhältnis von 40/60 bis 60/40 an Salzsäure (HCl) und Isopropylalkohol (C_3H_8O) mit Kupferchlorid-Salz ($CuCl_2$) in einer Konzentration von 2 g/l bis 20 g/l umfasst, für 1 bis 60 min; und der letzte Spülschritt Folgendes umfasst: ii) Spülen der Untersuchungsprobe in Wasser bei Raumtemperatur für mindestens 1 min.

2. Verfahren nach Anspruch 1, worin die Untersuchungsprobe ein Teil eines heißen Bereichs einer Gasturbine ist, das aus Fe-, Ni-, Co- oder Ti-basierten Legierungen hergestellt ist.

3. Verfahren nach Anspruch 1 oder Anspruch 2, worin die Untersuchungsprobe entweder mit einer Aluminid- oder einer modifizierten Aluminidbeschichtung beschichtet ist.

4. Verfahren nach einem der vorstehenden Ansprüche, worin die kathodische Polarisation bei Potentialen im Bereich von -0,8 V/OCP bis -0,4 V/OCP für Schritte jeweils zwischen 2 bis 10 Minuten durchgeführt wird und die anodische Polarisation bei Potentialen im Bereich von +0,4 V/SCE bis +0,75 V/SCE für Schritte jeweils zwischen 5 bis 10 Minuten durchgeführt wird.

5. Verfahren nach einem der vorstehenden Ansprüche, worin der letzte Reinigungsschritt für 5 bis 15 Minuten bei einer Temperatur unterhalb von 75°C stattfindet.

6. Verfahren nach einem der vorstehenden Ansprüche, worin in dem letzten Spülschritt zusätzlich Ultraschallwellen eingesetzt werden.

Revendications

1. Procédé électrochimique pour extraire des produits de corrosion et oxydés et des revêtements métalliques résistants à l’oxydation d’un échantillon d’essai en superalliage, comprenant les étapes consistant à :

relier l’échantillon d’essai à une ligne d’alimentation ;
submerger une portion de l’échantillon d’essai dans un bain de solution d’extraction électrolytique ayant un pH inférieur à 1, la solution d’extraction comprenant :

de l’acide nitrique (HNO_3) à une concentration allant de 2 % à 20 % en poids ;
de l’acide chlorhydrique (HCl) à une concentration allant de 1 % à 10 % en poids ; et
un sel de molybdate d’ammonium à une concentration allant de 0,2 % à 3 % en poids ;
de l’eau jusqu’à 100 % en poids,

soumettre l’échantillon d’essai à des cycles combinés d’étapes de polarisation anodique et cathodique pendant une période de temps efficace pour extraire les produits de corrosion et oxydés et des revêtements métalliques résistants à l’oxydation de l’échantillon d’essai, la polarisation anodique impliquant le fait de faire de l’échantillon d’essai l’anode à un potentiel inférieur à +2 volts pendant 1 min à 2 heures et la polarisation cathodique impliquant le fait de faire de l’échantillon d’essai la cathode à un potentiel supérieur à -1,5 volt pendant 1 minute à 20 minutes ;
mesurer le potentiel en circuit ouvert (o.c.p.) avant et après chaque au moins une étape du cycle combiné de polarisation pour suivre la progression de l’élimination du revêtement ;
retirer l’échantillon d’essai de la solution d’extraction électrolytique lorsque les produits de corrosion et oxydés et les revêtements métalliques résistants à l’oxydation sont éliminés et que l’o.c.p. est proche de celle de l’échantillon d’essai d’origine en superalliage ou que la valeur du courant se rapproche de la valeur du courant de passivation du matériau de base ;
soumettre l’échantillon d’essai à une étape de nettoyage final et de rinçage final, l’étape de nettoyage final comprenant le fait de i) placer l’échantillon d’essai dans une solution d’attaque chimique comprenant un mélange

de 40/60 à 60/40 en rapport volumique d'acide chlorhydrique (HCl) et d'alcool isopropylique (C_3H_8O) avec du sel de chlorure de cuivre ($CuCl_2$) à une concentration de 2 g/l à 20 g/l pendant 1 à 60 min ; et l'étape de rinçage final comprenant le fait de ii) rincer l'échantillon d'essai dans de l'eau à température ambiante pendant au moins 1 min.

2. Méthode selon la revendication 1, dans laquelle l'échantillon d'essai est une pièce de section chaude de turbine à gaz fabriquée en alliages de Fe-, Ni-, Co- ou Ti.

3. Méthode selon la revendication 1 ou la revendication 2, dans laquelle l'échantillon d'essai est revêtu soit par un revêtement d'aluminure, soit d'aluminure modifié.

4. Méthode selon l'une quelconque des revendications précédentes, dans laquelle la polarisation cathodique est effectuée à des potentiels s'échelonnant de -0,8 V/o.c.p. à -0,4 V/o.c.p. pour des étapes comprises entre 2 à 10 minutes chacune et la polarisation anodique est effectuée à des potentiels s'échelonnant de +0,4 V/SCE (électrode au calomel saturée) à +0,75V/SCE pour des étapes comprises entre 5 à 10 min chacune.

5. Méthode selon l'une quelconque des revendications précédentes, dans laquelle l'étape de nettoyage final se déroule pendant de 5 à 15 minutes à une température inférieure à 75°C.

6. Méthode selon l'une quelconque des revendications précédentes, dans laquelle l'étape de rinçage final utilise en outre des ondes ultrasoniques.

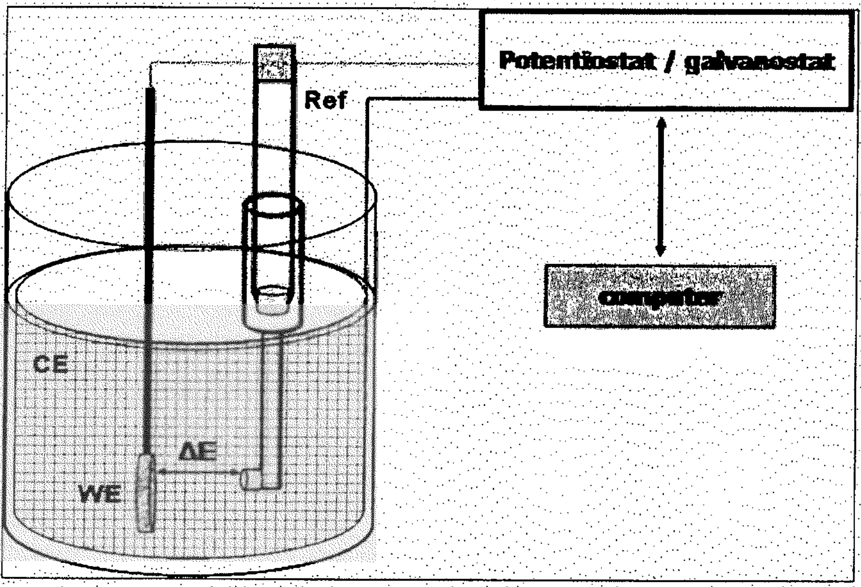


Fig. 1

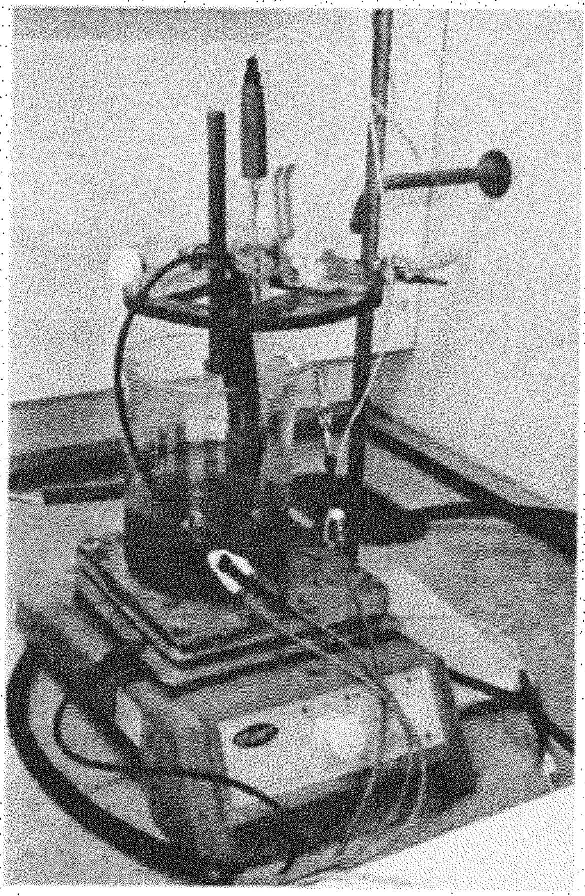


Fig. 2

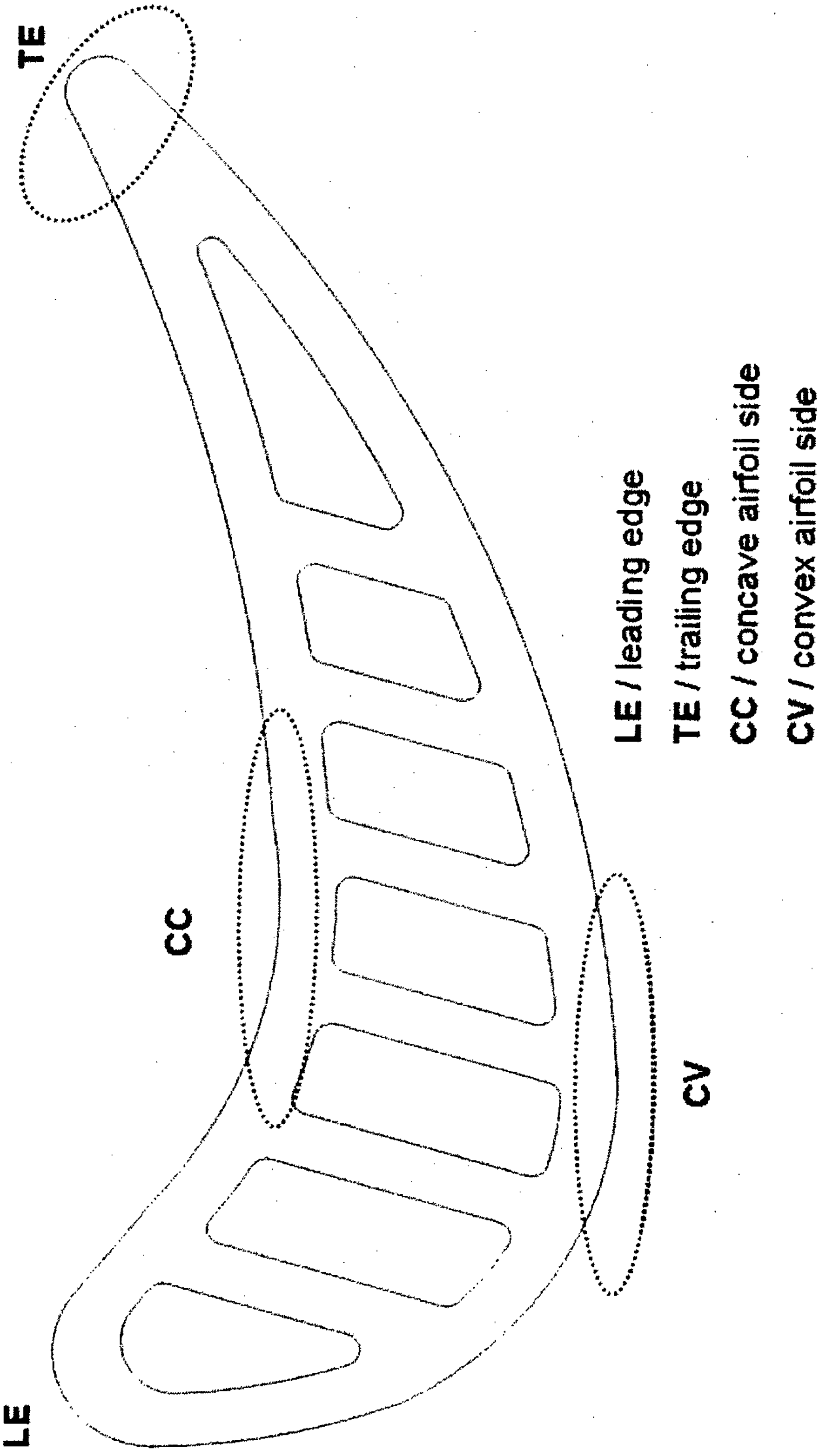

TE
CC
CV
LE
LE / leading edge
TE / trailing edge
CC / concave airfoil side
CV / convex airfoil side

Fig. 3

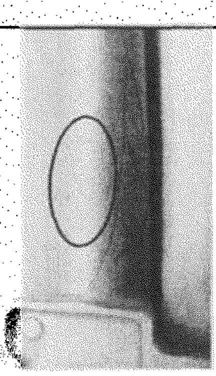
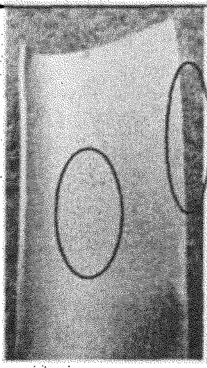
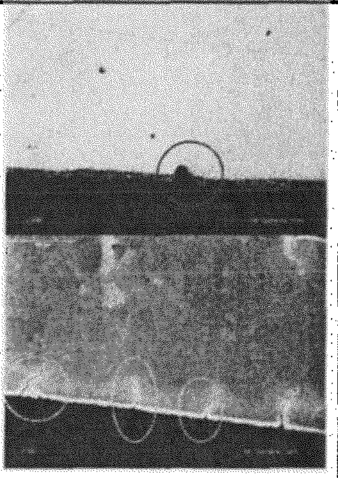
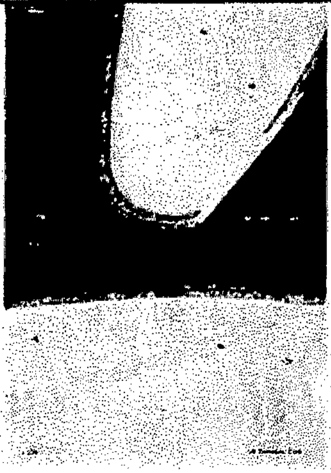
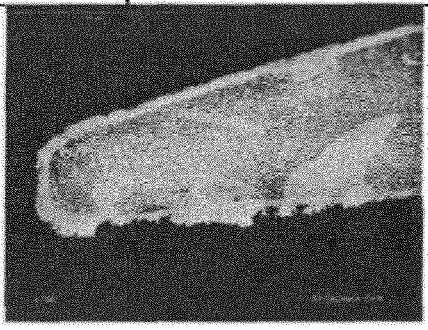
	Convex side	**Concave side**
Top surface macrographs		
Remarks	Evidence of macroscopic pitting	Remnants of coating on the concave side of the airfoil and on the trailing edge after stripping
Cross-section micrographs		
Remarks	Pitting & IGA attacks due to the lack of control	Inhomogeneous stripping due to the lack of selectivity
		
Remarks	Structural and dimensional damaged trailing edge of the airfoil due to the high agressivity of the solution towards the base material when it becomes exposed.	

Fig. 4

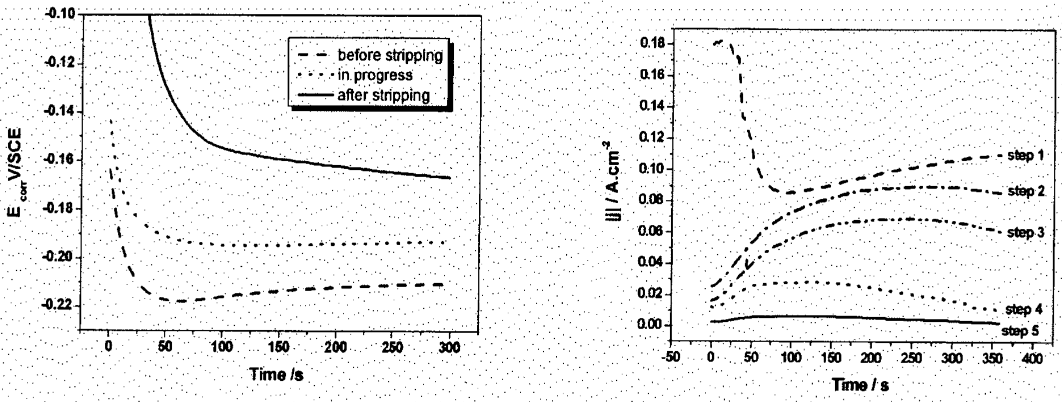


Fig. 5

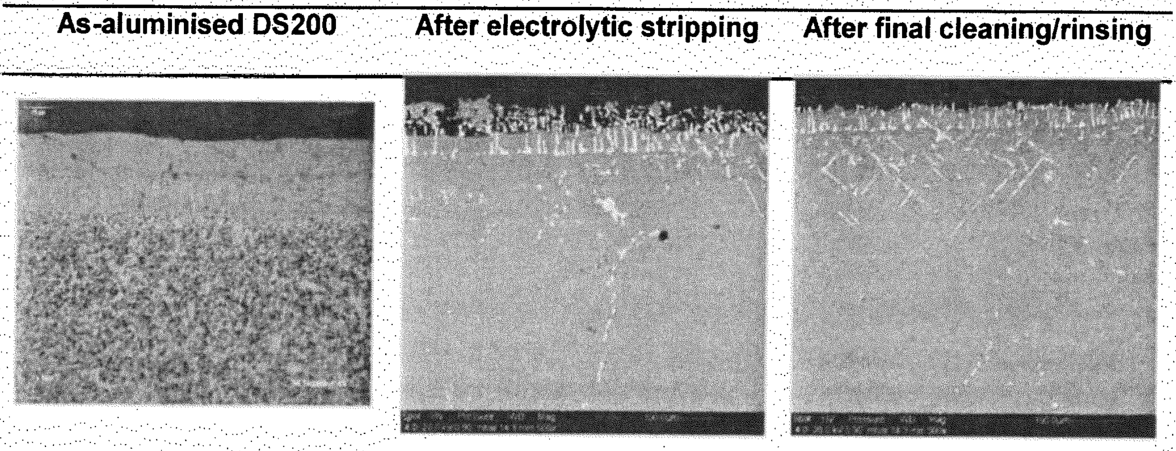
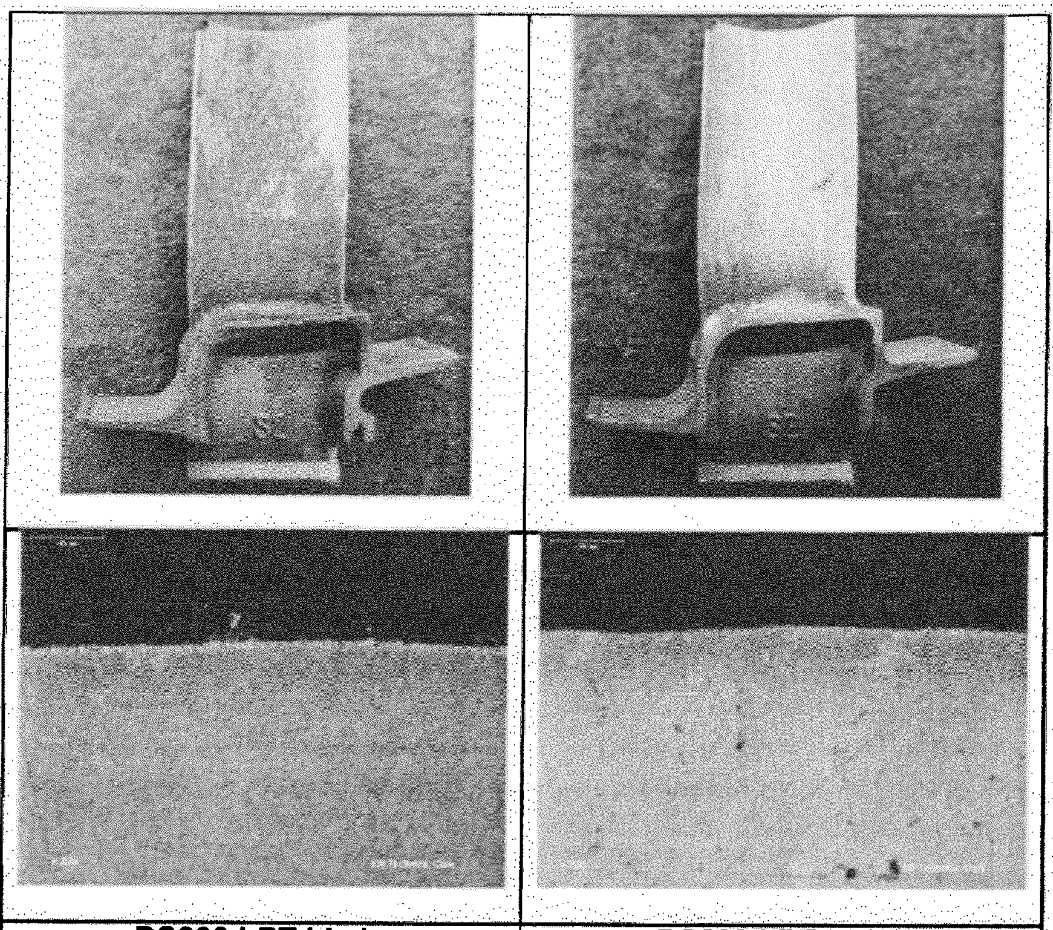

As-aluminised DS200
After electrolytic stripping
After final cleaning/rinsing

Fig. 6



DS200 LPT blade After erosive rinsing	DS200 LPT blade After final cleaning/rinsing

Fig. 7

Oxidised aluminised RENE125	After final cleaning/rinsing step

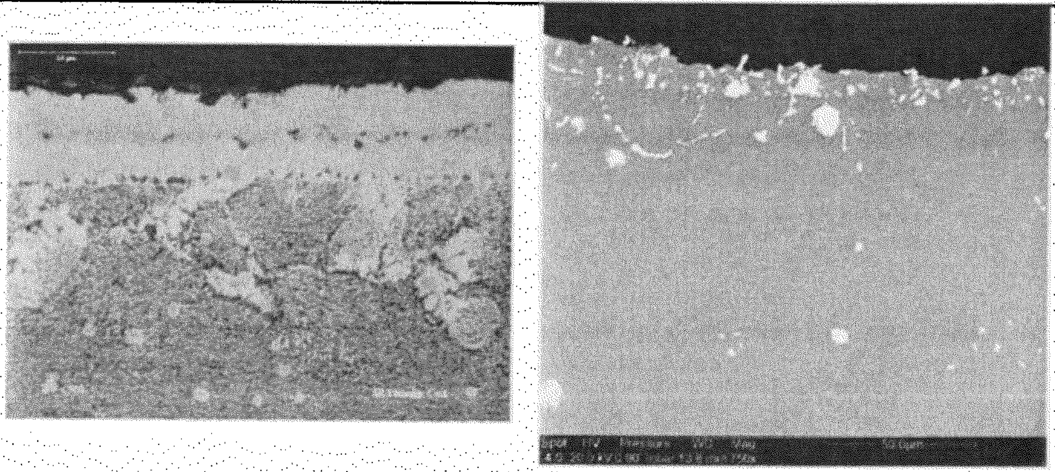


Fig. 8

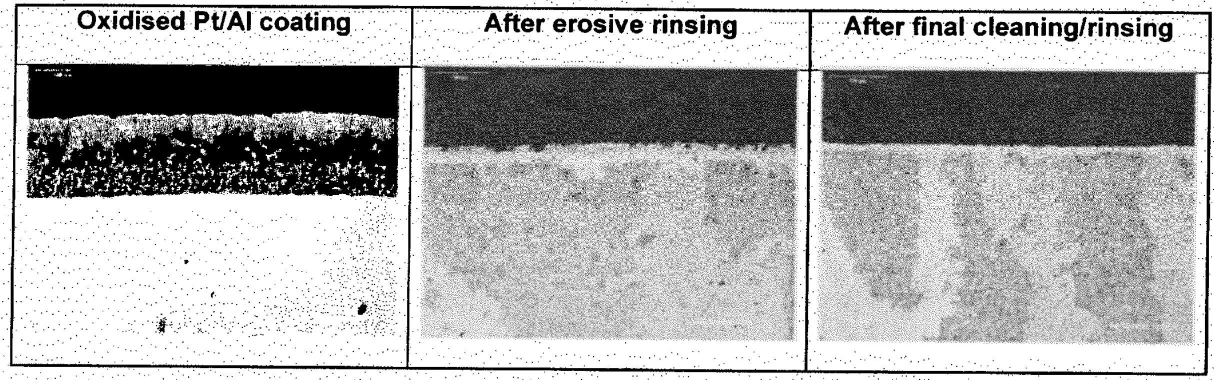

Oxidised Pt/Al coating
After erosive rinsing
After final cleaning/rinsing

Fig. 9

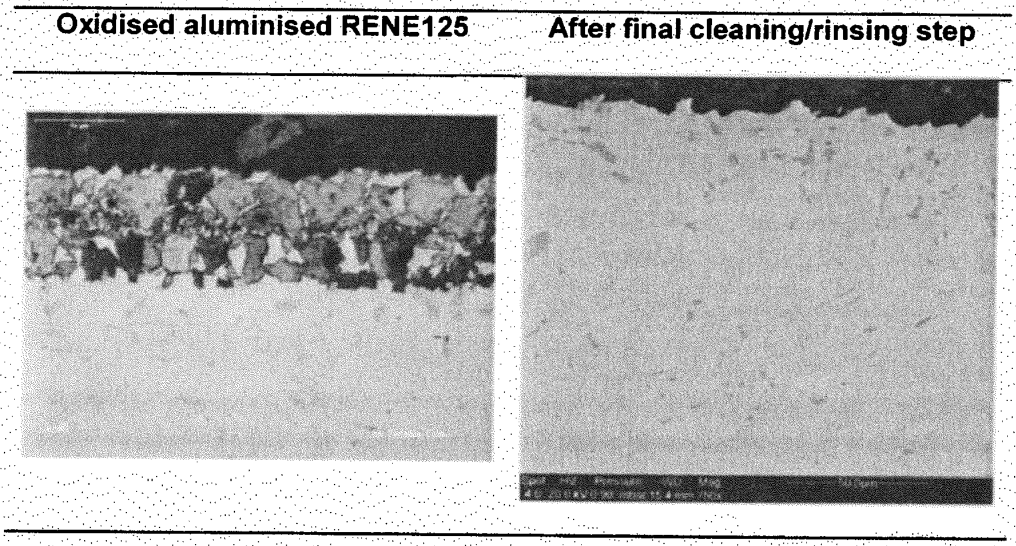

Oxidised aluminised RENE125
After final cleaning/rinsing step

Fig. 10

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- US 2840521 A **[0010]**
- US 3793172 A **[0010]**

Non-patent literature cited in the description

- Controlled stripping of aluminide coatings on nickel superalloys through electrolytic techniques. *J Appl Electrochem,* 2008, vol. 38, 817-825 **[0011]**