



(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
01.01.2014 Bulletin 2014/01

(51) Int Cl.:
C25F 1/02 (2006.01) C25F 5/00 (2006.01)

(21) Application number: **12174048.4**

(22) Date of filing: **28.06.2012**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME

(72) Inventors:
• **Power, Billy**
County Waterford (IE)
• **Diaz, Fernando Pedraza**
17000 La Rochelle (FR)
• **Bouchaud, Baptiste**
17000 La Rochelle (FR)

(71) Applicants:
• **SR Technics Airfoil Services Limited**
Cork (IE)
• **Universite De La Rochelle**
17000 La Rochelle (FR)

(74) Representative: **Litton, Rory Francis et al**
Cruickschank & Co.
8a Sandyford Business Centre
Sandyford
Dublin 18 (IE)

(54) **Electrolytic stripping**

(57) 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. The process involves connecting the test sample to a lead of a power supply and submerging a portion of the test sample into a bath of electrolytic stripping solution with a pH less than 1. The test sample is then subjected to combined cycles of anodic and cathodic polarisation steps for a period of time which is effective to strip the corrosion and the oxide products and oxidation resistant metallic coatings from the test

sample. The open circuit potential is measured before and after at least one step of the combined cycle of polarisation in order to monitor the progress of the coating removal, and, the test sample is removed from the electrolytic stripping solution when the corrosion and oxide products and oxidation resistant metallic coatings are removed and the open circuit potential 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). The test sample lastly undergoes a final cleaning and rinsing step.

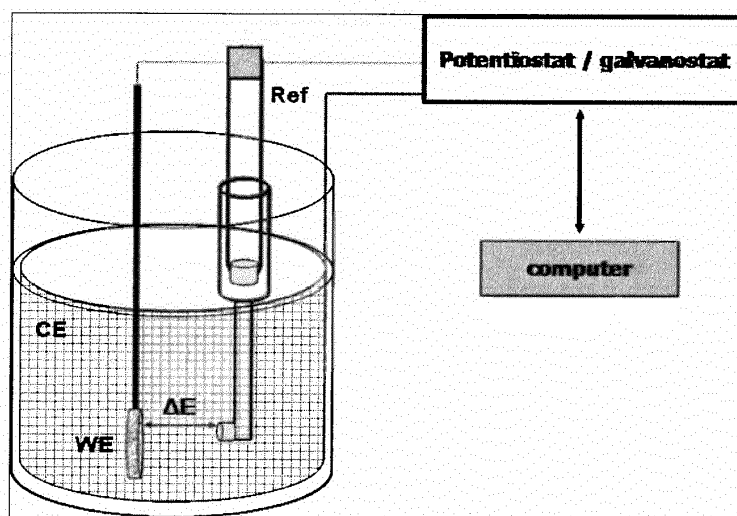


Fig. 1

Description**Introduction**

5 **[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.

15 **[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 (HNO₃), Sulphamic Acid (H₃NSO₃), Phosphoric Acid (H₃PO₄) and alkaline solutions mainly based on Sodium Hydroxide (NaOH).

20 **[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).

25 **[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.

30 **[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.

35 **[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 H₂SO₄. Water mixtures of fluoroboric acid (HBF₄) and phosphoric acid (H₃PO₄) 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).

40 **[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.

45 **[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.

50 **[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

55 **[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 ($\text{C}_3\text{H}_8\text{O}$) 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 $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}]$ 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 (C₃H₈O) with Copper Chloride salt (CuCl₂) 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 (HNO₃) and sulfamic acid (H₃NSO₃), 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 (SNEC-MA 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 $E = + 0.242 \text{ V/HSE}$. The three-electrode set-up is connected to a Potentiostat / Galvanostat PARSTAT2273A and fully monitored through the software PowerCorr.

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.

The bath operates at ambient temperature under soft magnetic stirring.

iii) Test Sample: as defined above

Method:

Step 1:

[0059] 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:

[0060] The o.c.p. (open circuit potential) value of the test sample was measured according for 1 to 10 min.

Step 3: Electrolytic stripping.

[0061] 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.

[0062] 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.

[0063] 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

[0064] 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.

[0065] 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

[0066] 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:

[0067] 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.

[0068] 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**

[0069] 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.

[0070] 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.

[0071] 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

[0072] 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)

[0073] 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.

[0074] 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.

[0075] 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:

[0076] 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

[0077] 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.

[0078] 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

[0079] 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

[0080] 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)

[0081] 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.

[0082] 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

[0083] 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:

[0084] 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

[0085] 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.

[0086] 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

[0087] 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:

[0088] Fig. 10 shows cross-sections of the aluminide coating before and after stripping using the present invention.

General Conclusion:

[0089] 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.

[0090] 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.

[0091] 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 maintained. Another advantage of this method, is that the base material/test sample passivates itself when becoming in contact with the stripping solution.

[0092] 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.

[0093] 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 ($\text{C}_3\text{H}_8\text{O}$) 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.

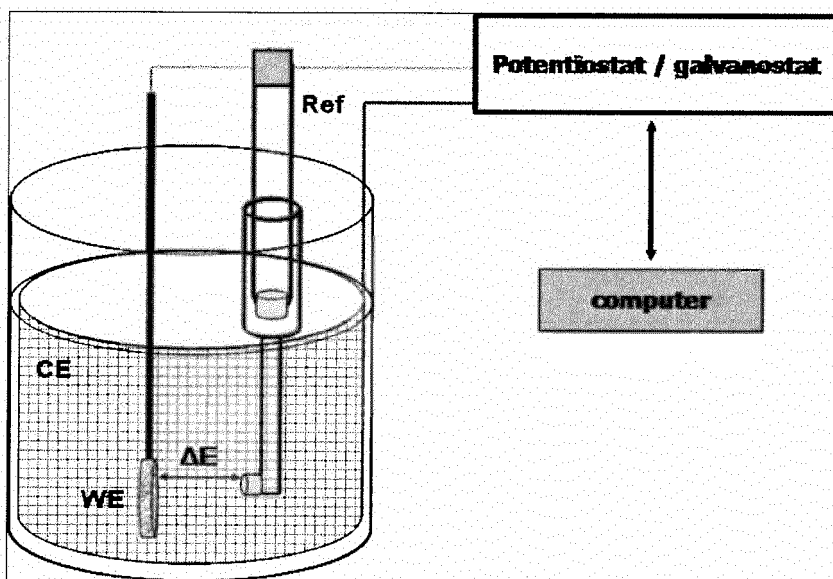


Fig. 1

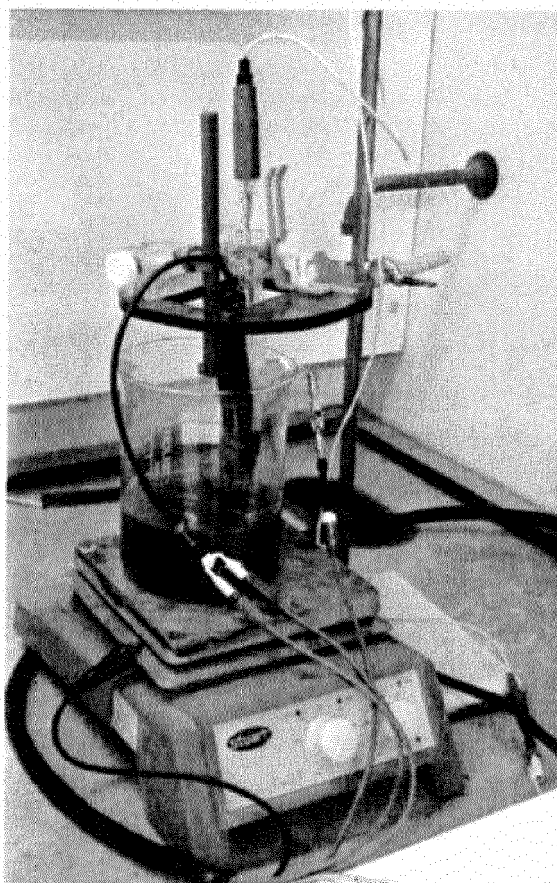


Fig. 2

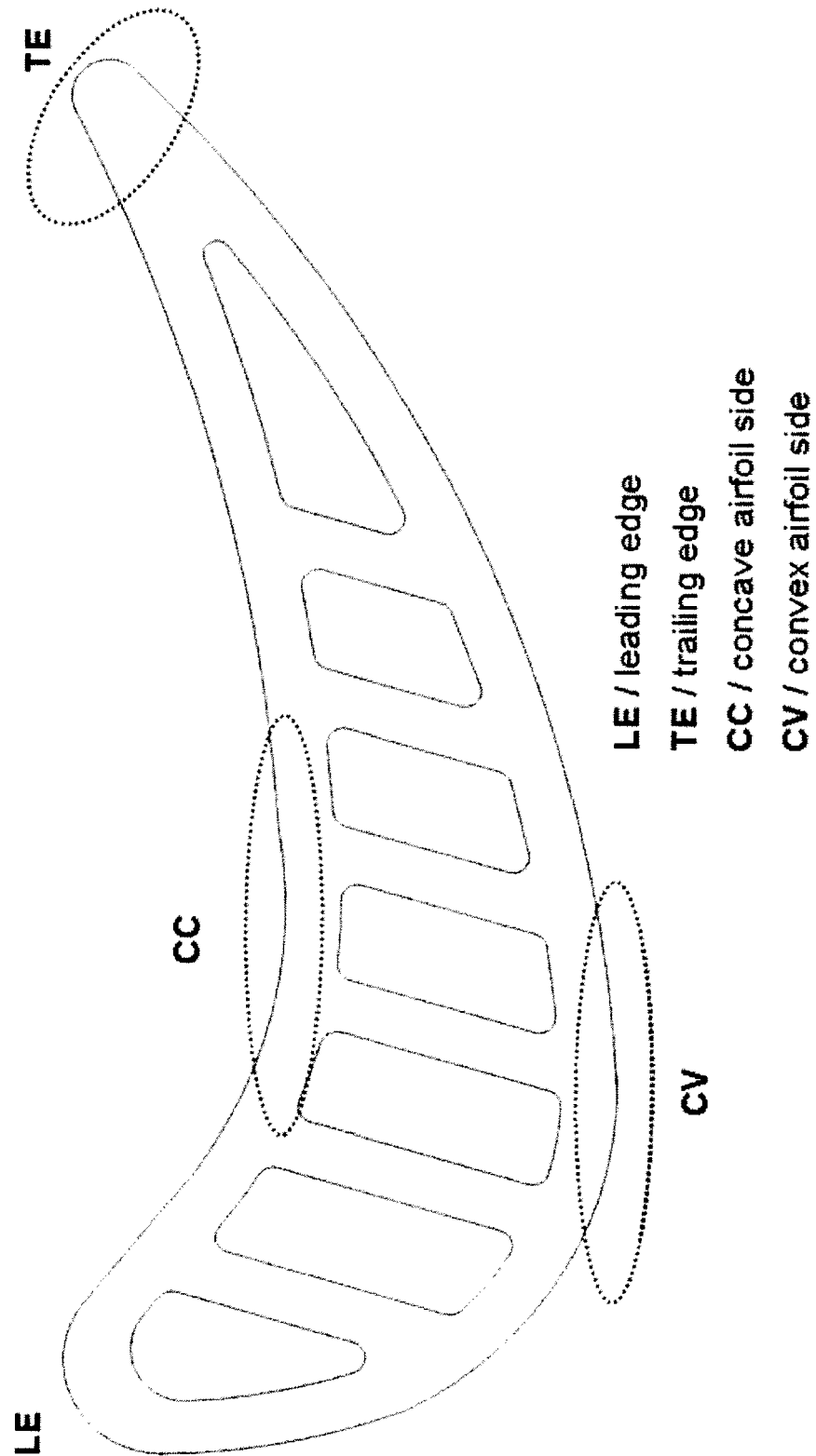


Fig. 3

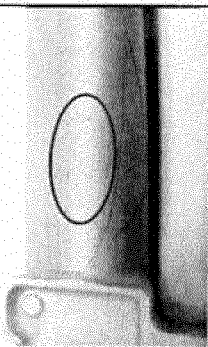
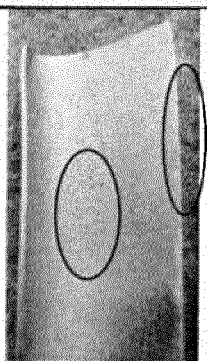
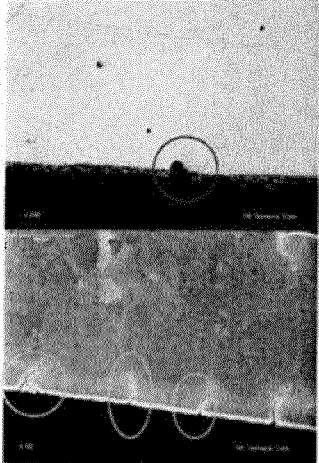
	Convex side	Concave side
Top surface macrographs		
Remarks	Evidence of macroscopic pitting	Remnants of coating on the concave side of the airfoil and on the trailing edge after stripping
Cross-section micrographs		
Remarks	Pitting & IGA attacks due to the lack of control	Inhomogeneous stripping due to 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

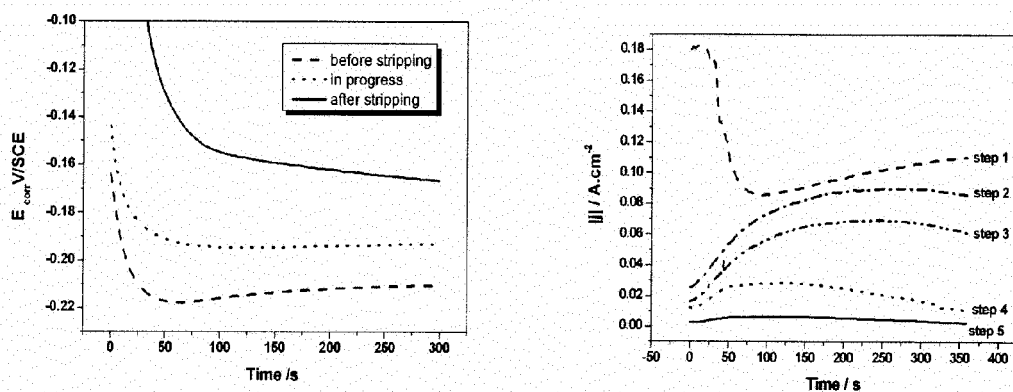


Fig. 5

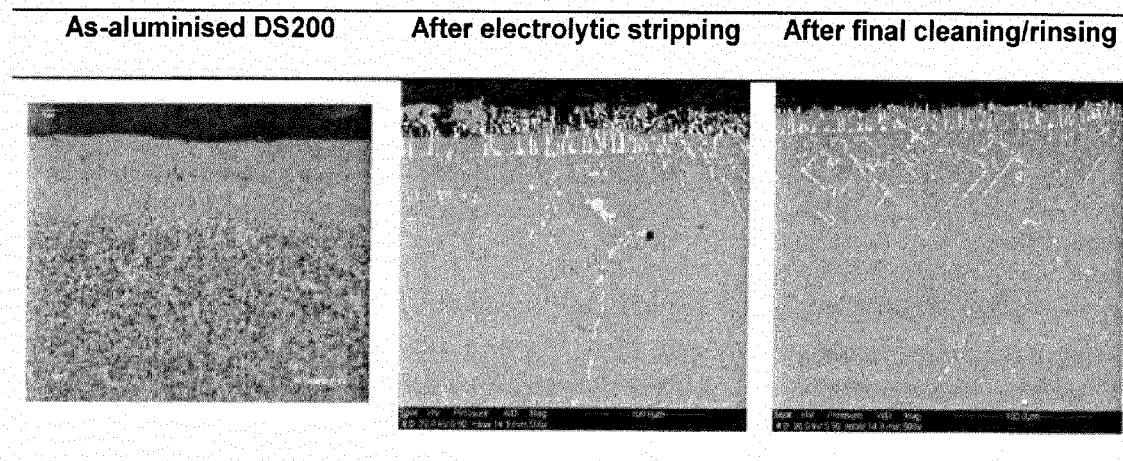


Fig. 6

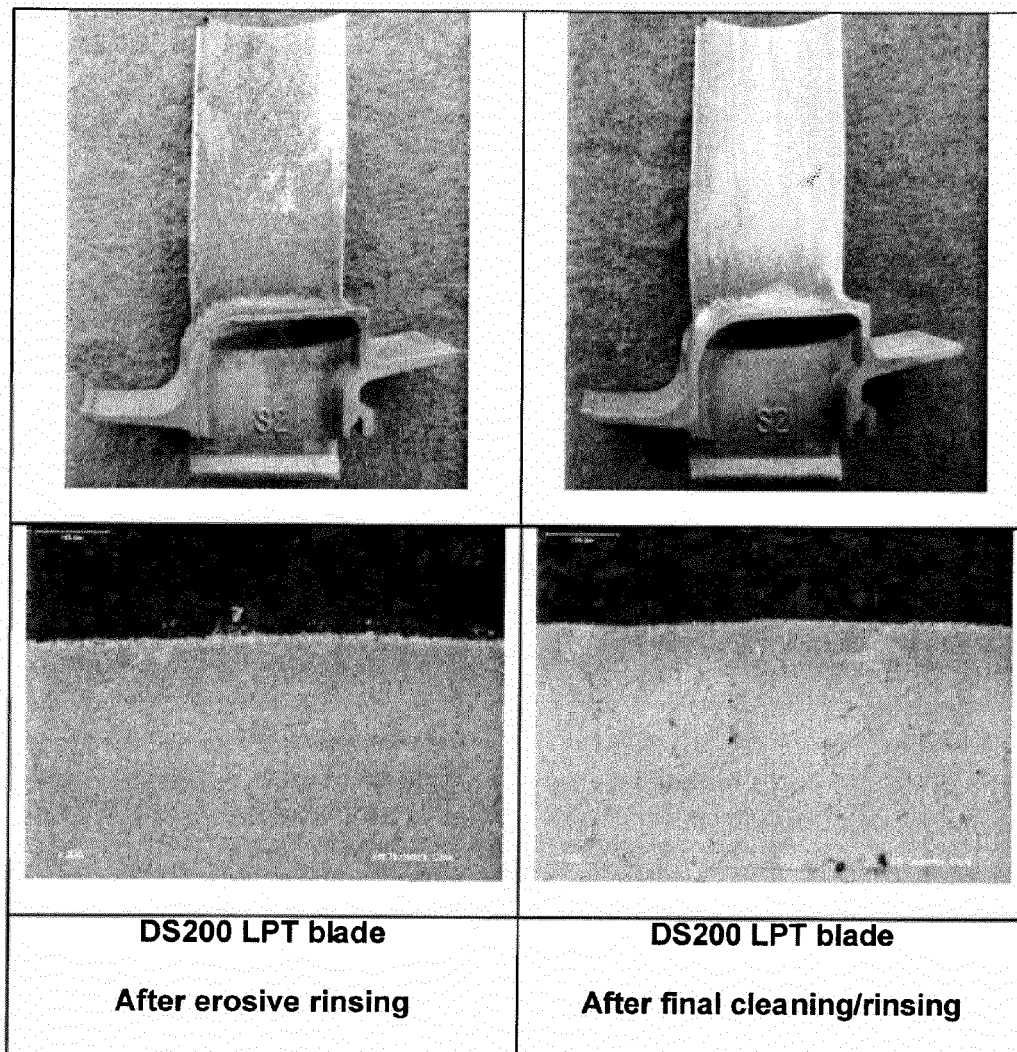


Fig. 7

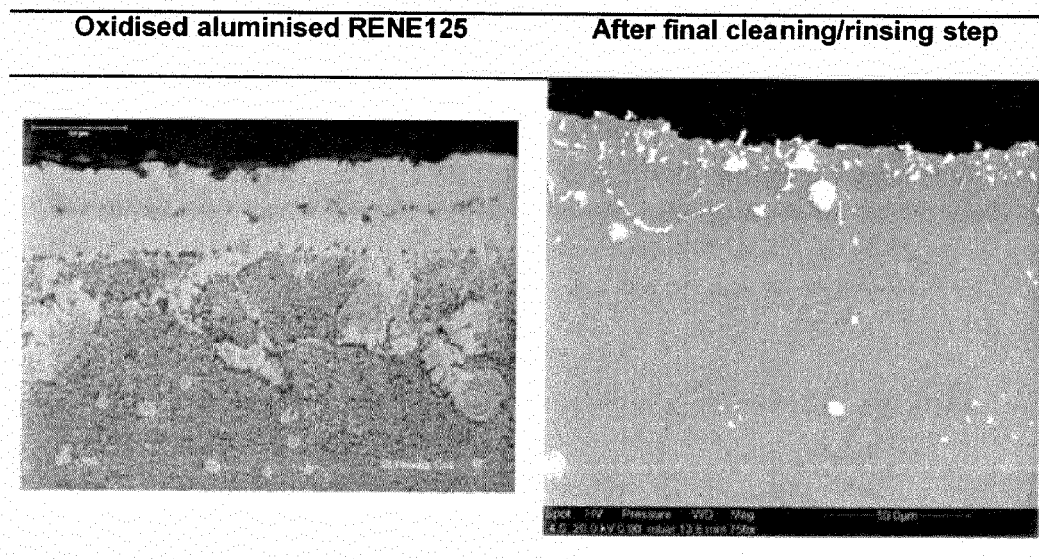


Fig. 8

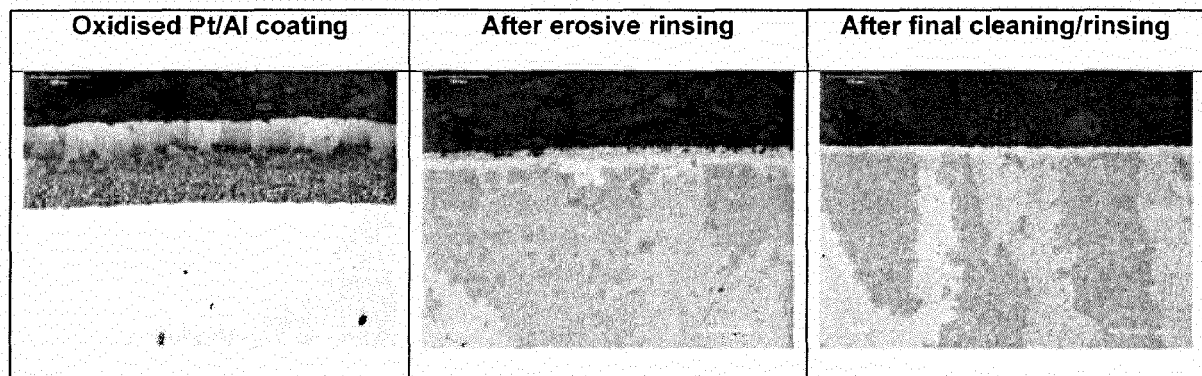


Fig. 9

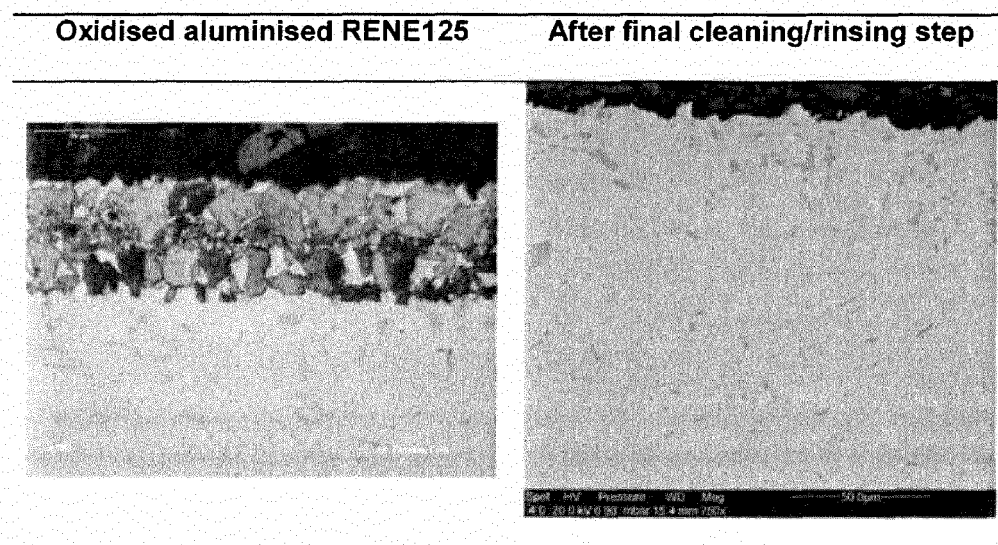


Fig. 10



EUROPEAN SEARCH REPORT

Application Number
EP 12 17 4048

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	US 6 176 999 B1 (JAWOROWSKI MARK [US] ET AL) 23 January 2001 (2001-01-23) * abstract; claims 1-5 *	1-6	INV. C25F1/02 C25F5/00
A	US 5 202 002 A (TSUCHINAGA MASAMITSU [US] ET AL) 13 April 1993 (1993-04-13) * claims 6,7 *	1-6	
A	US 3 409 487 A (FRY JOHN S ET AL) 5 November 1968 (1968-11-05) * column 7, line 18 - column 8, line 34; claim 1 *	1-6	
			TECHNICAL FIELDS SEARCHED (IPC)
			C25F
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 28 November 2012	Examiner Hammerstein, G
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

1
EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 12 17 4048

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

28-11-2012

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
US 6176999	B1	23-01-2001	DE	69932024 T2		11-01-2007
			EP	1010782 A1		21-06-2000
			JP	2000178800 A		27-06-2000
			SG	81336 A1		19-06-2001
			US	6176999 B1		23-01-2001

US 5202002	A	13-04-1993	DE	69206478 D1		18-01-1996
			DE	69206478 T2		22-08-1996
			EP	0513753 A1		19-11-1992
			ES	2080372 T3		01-02-1996
			JP	2588646 B2		05-03-1997
			JP	4337094 A		25-11-1992
			US	5202002 A		13-04-1993

US 3409487	A	05-11-1968	NONE			

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

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]