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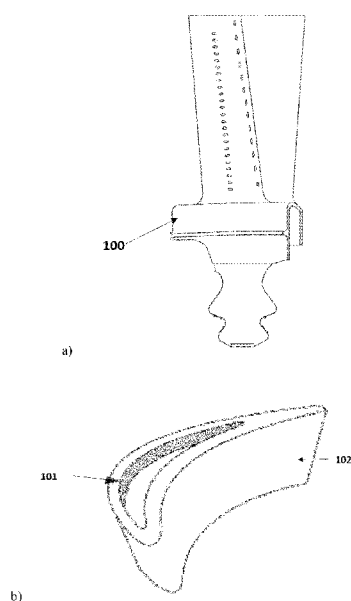


Figure 1

(57) Abstract: The high gamma prime nickel based superalloy, which comprises 10 - 13 wt. % Co, 3 - 10 wt. % Cr, 0.5 - 2 wt. % Mo, 3 - 7 wt. % W, 0.5 - 10 wt. % Re, 5 - 6 wt. % Al, 5 - 7 wt. % Ta, 0.5 - 2 wt. % Hf, 0.01 - 0.15 wt. % C, 0.005 - 0.05 wt. % B and 0.01 wt. % Zr, was first describe in the US Patent 4,169,742. Later on the optimized the optimized version of this alloy that comprises 12 wt. % Co, 6.8 wt. % Cr, 1.5 wt. % Mo, 4.9 wt. % W, 2.8 wt. % Re, 6.15 wt. % Al, 6.35 wt. % Ta, 1.5 wt. % Hf, 0.12 wt. % C, 0.015 wt. % B and 0.02 wt. % Zr became well-known as Rene 142 or R142 superalloy that has been widely used as welding material and structural material for a manufacturing of directionally solidified (DS) turbine blades due to unique combination of oxidation resistance and high mechanical properties that were achieved by the optimization of Ta+Al+Cr content coupled with no titanium addition and high aluminum content combined with the special multi step heat treatment, refer to per Earl W. Ross and Kevin S. O'Hara, "Rene 142: A high strength, oxidation resistant DS turbine airfoil alloy", Superalloys 1982, pp. 257 - 265. The optimization of rupture properties of Rene 142 DS as per Earl W. Ross and Kevin were achieve by a homogenization at 2335°F for 2 hours followed by annealing at 2050°F for four hours, primary aging at 1975°F for four hours and secondary aging at 1650°F for four hours (referred to as R142 HT).

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**HIGH GAMMA PRIME NICKEL BASED WELDABLE SUPERALLOY AND  
METHOD OF REPAIRING AND MANUFACTURING OF TURBINE ENGINE  
COMPONENTS USING THE SAME**

[0001] The high gamma prime nickel based superalloy, which comprises 10 – 13 wt. % Co, 3 – 10 wt. % Cr, 0.5 – 2 wt. % Mo, 3 – 7 wt. % W, 0.5 – 10 wt. % Re, 5 – 6 wt. % Al, 5 – 7 wt. % Ta, 0.5 – 2 wt. % Hf, 0.01 – 0.15 wt. % C, 0.005 – 0.05 wt. B and 0.01 wt. % Zr, was first describe in the US Patent 4,169,742. Later on the optimized the optimized version of this alloy that comprises 12 wt. % Co, 6.8 wt. % Cr, 1.5 wt. % Mo, 4.9 wt. % W, 2.8 wt. % Re, 6.15 wt. % Al, 6.35 wt. % Ta, 1.5 wt. % Hf, 0.12 wt. % C, 0.015 wt. % B and 0.02 wt. % Zr became well-known as Rene 142 or R142 superalloy that has been widely used as welding material and structural material for a manufacturing of directionally solidified (DS) turbine blades due to unique combination of oxidation resistance and high mechanical properties that were achieved by the optimization of Ta+Al+Cr content coupled with no titanium addition and high aluminum content combined with the special multi step heat treatment, refer to per Earl W. Ross and Kevin S. O'Hara, "Rene 142: A high strength, oxidation resistant DS turbine airfoil alloy", Superalloys 1982, pp. 257 – 265. The optimization of rupture properties of Rene 142 DS as per Earl W. Ross and Kevin were achieve by a homogenization at 2335°F for 2 hours followed by annealing at 2050°F for four hours, primary aging at 1975°F for four hours and secondary aging at 1650°F for four hours (referred to as R142 HT).

Table 1. Typical Chemical Composition of Rene 142 and Some Single Crystal Materials with Nickel to Balance, wt. %

| Alloy                                              | Cr   | Co   | Mo  | W   | Ta   | Re  | Al   | Zr   | Ti   | Hf   | C    | B     | Other | Si  |
|----------------------------------------------------|------|------|-----|-----|------|-----|------|------|------|------|------|-------|-------|-----|
| <b>Rene 142 Based Materials</b>                    |      |      |     |     |      |     |      |      |      |      |      |       |       |     |
| <b>R142</b>                                        | 6.8  | 12   | 1.5 | 4.9 | 6.35 | 2.8 | 6.15 | 0.02 | -    | 1.5  | 0.12 | 0.015 | -     | -   |
| <b>LW1</b>                                         | 6    | 11   | 1   | 4   | 6    | 2.5 | 5.5  | 0.01 | 0.15 | 1.2  | 0.01 | 0.01  |       | 0.4 |
|                                                    | -    | -    | -   | -   | -    | -   | -    | -    | -    | -    | -    | -     | -     | -   |
|                                                    | 8    | 13   | 2   | 6   | 7    | 3.5 | 6.5  | 0.02 | 0.25 | 1.8  | 0.15 | 0.02  |       | 0.5 |
| <b>1-st Generation of Single Crystal Materials</b> |      |      |     |     |      |     |      |      |      |      |      |       |       |     |
| <b>PWA1480</b>                                     | 10.0 | 5.0  | -   | 4.0 | 12.0 | -   | 5.0  | -    | 1.5  | -    | -    | -     | -     | -   |
| <b>Rene N4</b>                                     | 9.8  | 7.5  | 1.5 | 6.0 | 4.8  | -   | 4.2  | -    | 3.5  | 0.15 | 0.05 | -     | 0.5Nb | -   |
| <b>CMSX-3</b>                                      | 8.0  | 5.0  | 0.6 | 8.0 | 6.0  | -   | 5.6  | -    | 1.0  | 0.1  | -    | -     | -     | -   |
| <b>2-nd Generation of Single Crystal Materials</b> |      |      |     |     |      |     |      |      |      |      |      |       |       |     |
| <b>PWA1483</b>                                     | 12.2 | 9.0  | 1.9 | 3.8 | 5    | -   | 3.6  | -    | 4.1  | -    | 0.07 | -     | -     | -   |
| <b>PW14840</b>                                     | 5.0  | 10.0 | 2.0 | 6.0 | 9.0  | 3.0 | 5.6  | -    | -    | 0.1  | -    | -     | -     | -   |
| <b>Rene N5</b>                                     | 7.0  | 7.5  | 1.5 | 5.0 | 6.5  | 3.0 | 6.2  | -    | -    | 0.15 | 0.05 | 0.004 | 0.05Y | -   |
| <b>CMSX-4</b>                                      | 6.5  | 9.0  | 0.6 | 6.0 | 6.5  | 3.0 | 5.6  | -    | 1.0  | 0.1  | -    | -     | -     |     |
| <b>3-rd Generation of Single Crystal Materials</b> |      |      |     |     |      |     |      |      |      |      |      |       |       |     |
| <b>Rene N6</b>                                     | 4.2  | 12.5 | 1.4 | 6.0 | 7.2  | 5.4 | 5.8  | -    | -    | 0.15 | 0.05 | 0.004 | 0.01Y | -   |
| <b>CMSX-10</b>                                     | 2.0  | 3.0  | 0.4 | 5.0 | 8    | 6.0 | 5.7  | -    | 0.2  | 0.03 | -    | -     | 0.1Nb | -   |
| <b>MC-NC</b>                                       | 4.0  | 0.2  | 1.0 | 5.0 | 5.0  | 4.0 | 6    | -    | 0.5  | 0.1  | -    | -     | 4.0Ru | -   |
| <b>4-th Generation of Single Crystal Materials</b> |      |      |     |     |      |     |      |      |      |      |      |       |       |     |
| <b>TMS-</b>                                        | 2.9  | 6.2  | 1.9 | 1.9 | 2.0  | 2.0 | 13.4 | -    | -    | 0.04 | -    | -     | 2.3Ru | 1.0 |

|                                 |     |     |     |     |     |     |      |   |   |      |   |   |       |     |
|---------------------------------|-----|-----|-----|-----|-----|-----|------|---|---|------|---|---|-------|-----|
| <b>138-Cr +<br/>Si</b>          |     |     |     |     |     |     |      |   |   |      |   |   |       |     |
| <b>TMS-<br/>138-Mo +<br/>Si</b> | 3.9 | 6.2 | 0.9 | 1.9 | 2.0 | 2.0 | 13.4 | - | - | 0.04 | - | - | 2.3Ru | 1.0 |

[0002] Despite that silicon was used to improve oxidation resistance of some solution hardening alloys such as Haynes HR160, which comprises 29 wt. % Co, 28 wt. % Cr, 2 wt. % Fe, 2.75 wt. % Si, 0.5 wt. % Mn, 1 wt. % W, 1 wt. % Nb, 0.4 wt. % Al and nickel to balance, Si was not considered for a manufacturing of first, second and third generation of SX (single crystal) materials and high gamma prime superalloys due to its selective precipitation along grain boundaries that reduced mechanical properties of these material as shown in Table 1, refer to Tresa M. Pollock and Sammy Tin, “Nickel based superalloys for advanced turbine engines: Chemistry, Microstructure, and Properties”, Journal of Propulsion and Power”, Vol., 22, No. 2, March-April 2006, pp. 361 – 374.

[0003] The first attempt to improve oxidation resistance of 4<sup>th</sup> generation of SX materials was made by A.C. Yeh et al. “Development of Si-Bearing 4<sup>th</sup> Generation Ni-Base Single Crystal Superalloys”, TMS, Superalloys 2008, pp. 619 – 628. TMS-138A-Cr-Si and TMS-138A-Mo+Si alloy with chemical composition shown in Table 1 comprised of 1 wt. % Si. Both these alloys demonstrated superior oxidation resistance but as most single crystal materials have extremely poor weldability.

[0004] Later on Magnus Hasselqvist and Gordon McColvin created the silicon bearing titanium free nickel based superalloy that was disclosed in EP Patent 2 100 982 aiming to improve weldability. This alloy comprises up to 20 wt. % Co, 17 – 21 wt. % Cr, 2 – 5 wt. % Mo+W+Re, 4 – 4.7 wt. % Al, 3 – 7 wt. % Ta, 0.01 – 0.3 wt. % C+Zr+B, 0.05 – 1 wt. % Hf, 0.05 – 1 wt. % Si, 0.01 – 0.2 wt. % Sc+Y and micro alloying elements selected from among actinides and lanthanides. Inventors did not provide mechanical properties of this alloys. However, based on the lower content of gamma strengthening Al and elevated content of Cr, which alternated the ratio of Ta+Al+Cr from optimal, as it was established for Rene 142 superalloy, it is likely to assume that mechanical and oxidation properties of the superalloy described in EP Patent 2 100 982 were be below of properties of Rene 142 superalloy.

Therefore, despite poor weldability, Rene 142 the best compromise for welding material for repair of turbine engine components.

[0005] To improve weldability and avoid cracking, welding of equiaxed, DS and SX high gamma prime superalloys has been performed with a preheating of turbine engine components to 1800°F to 2100° F as per US Patent 5,897,801. The ‘Superalloy Welding at Elevated Temperature’ (SWET) partially resolved cracking problem. However, as it was found by experiments, Rene 142 SWET welds demonstrated low mechanical properties despite superior properties of the original Rene 142 DS superalloy.

[0006] Low tensile and stress rupture properties of extruded articles with the equiaxed structure is another disadvantage of Rene 142 superalloy.

[0007] Therefore, a significant improvement of Rene 142 superalloy is required to enhance weldability and mechanical properties of welds maintaining at the same time optimal ratio of Ta+Al+Cr.

## **BRIEF DESCRIPTION OF THE INVENTION**

[0008] We have found out that despite the common belief that titanium reduces oxidation resistance of superalloys and silicon reduces mechanical properties, the high gamma prime superalloy comprised of the 10 – 13 wt. % Co, 5 – 8 wt. % Cr, 1.0 – 2.5 wt. % Mo, 4 – 6 wt. % W, 6 – 7 wt. % Ta, 1.5 – 3.5 wt. % Re, 5.5 – 6.5 wt. % Al, 1.2 – 1.8 wt. % Hf, 0.01 – 0.02 wt. % B, 0.05 – 0.15 wt. % C with 0.15 – 0.25 wt. % Ti and 0.4 – 0.5 wt. % Si, where Si is preferably in the form of refractory Ti, Ta and W silicide and disilicide, and preferably titanium disilicide (TiSi<sub>2</sub>), further LW1 superalloy, has good mechanical and oxidation properties, and better weldability than known Rene 142 superalloy.

[0009] To enhance the preferential formation of Ti, Ta and W silicide and reduce formation of various nickel based silicide, the invented materials comprises the titanium and silicon with a ratio of 0.5 – 0.625 and preferably 0.5, when contents of titanium and silicon are in wt. % to allow preferential formation of Ti disilicide minimizing silicon content in a

nickel based solid solution matrix and achieve combination of high oxidation resistance and mechanical properties at temperature  $\geq 1800^{\circ}\text{F}$ .

Table 2. Titanium to Silicon Ratio

| Ti,<br>wt. % | Si,<br>wt. % | Ti/Si | Mechanical<br>Properties $\geq 1800^{\circ}\text{F}$ | Oxidation Resistance<br>at $2048^{\circ}\text{F}$ |
|--------------|--------------|-------|------------------------------------------------------|---------------------------------------------------|
| 0.15         | 0.4          | 0.375 | Poor                                                 | Good                                              |
| 0.15         | 0.5          | 0.30  | Poor                                                 | Good                                              |
| 0.25         | 0.4          | 0.625 | Good                                                 | Good                                              |
| 0.25         | 0.5          | 0.50  | Good                                                 | Good                                              |

[00010] In accordance with the another preferable embodiment the high gamma prime nickel based weldable material is selected from among welding wires and welding powder, equiaxed, directionally solidified and single crystal cast materials, extruded and cast articles, repair sections of turbine engine components and various materials and articles produced by 3D additive manufacturing process.

[00011] In accordance with the preferable embodiment the method of repairing and manufacturing of turbine engine components, preferably turbine blades, includes the steps of pre-weld heat treatment of engine component using process parameters selected from among prescribed for the base material of engine component or the engine component manufactured of the same; pre-weld preparation of a base material by removal of a damaged material and contaminants to reveal a defect and contamination free base material; weld repair of a blade tip using a fusion welding process selected from among welding at an ambient temperature and preheating with the speed preferably from 1 to 3 inch per minute to enhance a formation of Ti-Ta-W silicide and disilicide, and preferably titanium disilicide, during welding, solidification and cooling of a welding pool, and a welding material comprising of 11 - 13 wt. % Co, 5 - 8 wt. % Cr, 1.0 - 2.0 wt. % Mo, 4 - 6 wt. % W, 6 - 7 wt. % Ta, 1.5 - 3.5 wt. % Re, 5.5 - 6.5 wt. % Al, 1.2 - 1.8 wt. % Hf, 0.01 - 0.02 wt. % B, 0.05 - 0.15 wt. % C, 0.01 - 0.02 wt. % Zr, 0.15 - 0.25 wt. % Ti, 0.4 - 0.5 wt. % Si and Ni with impurities to balance; post weld heat treatment selected from among an annealing, primary and secondary aging and

stress relief or all above; restoration of the geometry of the repaired area and non-destructive testing.

[00012] In accordance with the preferable embodiment of repairing and manufacturing of turbine engine components manufactured of single crystal materials, the post weld heat treatment comprises following below steps:

- a) Primary aging at a temperature of 1975 - 2150°F for 2 - 4 hours
- b) Secondary aging at a temperature of 1300 – 1400 °F for 16 - 24 hours
- c) An additional heat treatment cycle at a temperature of 1550 - 1700°F for 4 - 24 hours, which exceed the temperature of the secondary aging aiming to allow further improvement mechanical properties of a weld metal after restoration of properties of the base material; further LW1 SXHT heat treatment.

[00013] In accordance with the preferable embodiment of the method of repairing and manufacturing of turbine engine components manufactured of equiaxed and directionally solidified materials, the post weld heat treatment comprises following below steps:

- d) Annealing at a temperature of 2190 - 2230°F for 2 - 4 hours
- e) Primary aging at a temperature of 1975 – 2040 °F for 2 - 4 hours
- f) Secondary aging at a temperature of 1550 - 1625°F for 16 - 24 hours aiming to maximize of properties of welds by optimizing precipitation of gamma prime phase and Ti-Ta-W based silicide; further LW1 DSHT heat treatment.

Table 3. Post-Weld Heat Treatments

| Post-Weld Heat Treatment                                     | Anneal                         | Primary Aging                  | Secondary Aging                 | Additional Heat Treatment      |
|--------------------------------------------------------------|--------------------------------|--------------------------------|---------------------------------|--------------------------------|
| Single Crystal Material<br>(LW1 SXHT)                        | -                              | 1975-2150° F<br>for 2-4 hours  | 1300-1400° F<br>for 16-24 hours | 1550-1700° F<br>for 4-24 hours |
| Equiaxed and Directionally Solidified Material<br>(LW1 DSHT) | 2190-2230 ° F<br>for 2-4 hours | 1975-2040 ° F<br>for 2-4 hours | 1550-1625 °F<br>for 16-24 hours | -                              |

[00014] To allow a preferential formation of Ti disilicide and minimize the silicon content in a nickel based solid solution, the preferable embodiment of the invented superalloy comprises the titanium and silicon with a ratio of 0.5 – 0.625 and preferably 0.50.

[00015] As per the another preferable embodiment, the tip of repaired blade is selected from among a squealer, tip cap or combination of above, wherein the squealer weld build up is performed after radial cracks repair.

[00016] As per the preferable embodiment of repairing of turbine blades with the tip cap, the tip cap is manufactured by preferably an extrusion or 3D additive manufactured (further 3D AM) or casting and has equiaxed or directionally solidified or single crystal structure followed by annealing and two steps aging.

**DESCRIPTION OF DRAWINGS**

[00017] **Figure 1** is a typical HPT blade with the squealer tip design comprises: 100 – HPT blade, 101 – squealer and 102 – airfoil.

[00018] **Figure 2** is a typical HPT blades that comprise 200 – airfoil, 201 – tip cap, 202 – squealer, 203 – weld of the tip cap to the airfoil depicting:

- a) The tip cap prior to installation to the blade tip;
- b) Blade tip with the combination of tip cap and squealer;
- c) Tip cap replacement.

[00019] **Figure 3** depicts test weld samples after tensile testing at 1800°F with the test report on the background

[00020] **Figure 4** is micrographs of LW1 weld metal made with different magnifications depicting:

- a) Precipitation of discrete silicide,
- b) Precipitation of the cuboidal gamma prime phase in the gamma matrix.

[00021] **Figure 5** is mapping of alloying elements in the LW1 weld metal wherein:

- a) Micrograph produced using ESM
- b) Distribution of Si in the weld metal shown in Figure 5a.

[00022] **Figure 6** is mapping of alloying elements in the LW1 weld metal wherein:

- a) Distribution of Ti in the weld metal shown in Figure 5a.
- b) Distribution of Ta in the weld metal shown in Figure 5a.

[00023] **Figure 7** is mapping of alloying elements in the LW1 weld metal wherein:

- a) Distribution of W in the weld metal shown in Figure 5a.

- b) Distribution of Ni in the weld metal shown in Figure 5a that depicts a depletion of silicide with Ni.

[00024] **Figure 8** is micrographs of Rene 142 welds that were additionally alloyed with Si depicting a formation of interdendritic silicide that reduced mechanical properties at high temperatures.

[00025] **Figure 9** is the HPT blade manufactured of PWA1484 SX material after welding and heat treatment, wherein:

- a) HPT blades after PWHT
- b) Micrograph of the LW1 – PWA1484 crack free interface

## ACROMYMS

**LW1** – Invented superalloy

**ASTM** - American Society for Testing and Materials (standards)

**AMS** – Aerospace Material Specification

**HAZ** – Heat Affected Zone

**NDT** – Non Destructive Testing

**PWHT** – Post Weld Heat Treatment

**UTS** – Ultimate Tensile Strength

**TMF** – Thermo-Mechanical Fatigue

**WGB** – Wide Gap Brazing

**IPM** – Inch Per Minute

**EDS** – Energy-dispersive X-ray spectroscopy

**FPI** – Fluorescent Penetrant Inspection

**SX** – Single Crystal Superalloy

**DS** – Directionally Solidified Superalloy

**HPT** – High Pressure Turbine

**OEM** – Original Equipment Manufacture

**EM** – Engine Manual

**SPM** – Standard Practice Manual

**GTAW** – Gas Tungsten Arc Welding

**SWET** – Superalloys Welding at Elevated Temperature

**LBW** – Laser Beam Welding

**PWA** – Plasma Arc Welding

**MPW** – Micro Plasma Welding

**3D AM** – Three Dimension Additive Manufacturing

**EDM** – Electrical Discharge Machining

**LPT** – Low Pressure Turbine

**SRT** – Stress-Rupture Test

**GTAW-MA** – Manual Gas Tungsten Arc Welding

**Equiaxed** – having approximately equal dimensions in all directions; used especially of a crystal grain in metals and superalloys.

## **DETAILED DESCRIPTION OF THE INVENTION**

[00026] The invented superalloy can be used in the form of weld wire and powders for welding and plasma spray, equiaxed, DS and SX casting, various cast and extruded articles and repaired sections of turbine engine components. However, welding materials in the form of welding wire and powder are major applications.

[00027] Welding wire is manufactured of ingots, which are also known as billets, produced in vacuum or argon by standard induction melting technologies or other melting processes followed by extrusion. Therefore, mechanical properties and ductility of billets in the ‘as cast’ and heat treat conditions are very important for a successful extrusion of welding wire and manufacturing of tip caps for a repair of turbine engine components. By experiments it was found that in the ‘as cast’ condition LW1 superalloy has sufficient for extrusion ductility within the temperature range from 70°F to 1800°F as shown in Table 2, while maximum mechanical properties of LW1 superalloy were achieved using LW1 DSHT heat treatment parameters developed for the heat treatment of DS and equiaxed materials.

**Table 2 Mechanical Properties of Equiaxed LW1 Cast Superalloy**

| <b>Condition and Heat Treatment of LW1 Superalloy</b> | <b>Test Temp. , °F</b> | <b>0.2% Offset Yield Strength, KSA</b> | <b>UTS, KSI</b> | <b>%, Elongation</b> | <b>%, Reduction</b> |
|-------------------------------------------------------|------------------------|----------------------------------------|-----------------|----------------------|---------------------|
| LW1 'As Cast'                                         | 70                     | 112.4                                  | 149.4           | 13.4                 | 20.8                |
| LW1 'As Cast'                                         | 1800                   | 40.3                                   | 52.4            | 13.4                 | 14.4                |
| As Extruded                                           | 1800                   | 39.4                                   | 49.9            | 19.5                 | 25.7                |
| LW1 Heat treated as per R142 HT                       | 1800                   | 44.7                                   | 48.7            | 4.9                  | 5.1                 |
| LW1 Heat Treated as per LW1 DSHT                      | 1800                   | 49.3                                   | 59.9            | 7.5                  | 13.7                |

[00028] It was found by experiments that extrusion resulted in a formation of elongated grains that reduced UTS but improved ductility as shown in Table 2, which is essential for the improvement of TMF. Therefore, extruded LW1 is most advanced material for a manufacturing of tip caps for a repair of HPT blades shown in FIG.2.

[00029] For a manufacturing of welding wire billets were produced in the form of rods with a diameter of approximately of 1 inch and reduced to a diameter of 0.045 inch by extrusion at a high temperature followed by standard surface finishing and rigorous cleaning procedure that ensured the welds will be free from contamination.

[00030] Welding powders about of 45 – 75  $\mu\text{m}$  in diameter were manufactured by standard gas atomization processes. During this process the melted superalloy with chemical composition as per the preferable embodiment is atomized by the inert gas jets into fine metal droplets that cool down during their fall in the atomizing tower or other standard processes. Metal powders obtained by gas-atomization had a perfectly spherical shape and high cleanliness level.

[00031] Powders are usually used for PAW, MPW, LBW and cladding also known as fusion welding and cladding processes, WGB and plasma spray. During fusion welding wire or powder is fed into the welding pool using standard wire and powder feeders. After solidification welding material is fused with the base material producing the weld metal. To reduce overheating and prevent HAZ cracking, welding and cladding are carried out with minimum dilution and heat input but at a low welding speed preferably of 1 – 3 inches per minute (ipm) aiming to increase the solidification time allowing a formation of complex refractory Ti-Ta-W based silicide and disilicide shown in Figures 5 -7 with melting temperatures from 2680 to 4000°F in the welding pool with the temperature of 2460 - 2500°F in lieu of a formation of various low temperature nickel silicide and disilicide (NiSi<sub>2</sub>) with melting temperature of 1819°F. Formation of refractory Ti-Ta-W silicide in the low temperature welding pool became possible metallurgically because enthalpies of formation of TaSi<sub>2</sub> of -120 kJ•mol<sup>-1</sup> and TiSi<sub>2</sub> of -171 kJ•mol<sup>-1</sup> were well below of enthalpy of formation of NiSi<sub>2</sub> of -88 kJ•mol<sup>-1</sup>, refer to M.S. Chandrasekharaom et al “The Disilicides of Tungsten, Molybdenum, Tantalum, Titanium, Cobalt, and Nickel, and Platinum Monosilicide: A Survey of Their Thermodynamic Properties”, Journal Phys. Chem. Ref. Data, Vol. 22, No. 6, 1993, pp. 1459 – 1468. Other publications provide the enthalpy of formation NiSi<sub>2</sub> of - (29 – 45) kJ•mol<sup>-1</sup>, which would explain also a formation of WSi<sub>2</sub> with the enthalpy of -79 kJ•mol<sup>-1</sup>. However, as it was found by experiment, to exclude a formation of NiSi<sub>2</sub> and minimize the silicon content in a Ni-Cr solid solution, the welding speed had to be within the range of 1 – 3 ipm. Also, it was found that further optimization of microstructure and properties of LW1 welds took place during PWHT annealing and primary aging heat treatment using developed for preferable embodiments parameters.

[00032] Further, the invented method is disclosed by way of the example of the repair of turbine blades with the different tip design shown in Figures 1 and 2 and examples of welding of samples manufactured of Mar M002 DS superalloy and repair of HPT turbine blade manufactured of PWA1484 SX superalloy using the invented LW1 welding wire. These materials were selected for a demonstration due to high sensitivity to overheating, susceptibility to cracking and wide usage of these superalloys for a manufacturing of HPT and LPT blades and vanes for industrial and aero turbine engines.

[00033] Prior to the weld repair, turbine blades are subjected to stripping of the protective coatings followed by a pre-weld heat treatment prescribed by relevant OEM EM and SPM. The type of a pre-weld heat treatment depends on the type of base materials. For example, only stress relief within the temperature range from 1800 to 2050°F can be used to prevent recrystallization of turbine blades manufactured of SX materials. Turbine blades manufactured of equiaxed and DS materials might be subjected to annealing heat treatment to improve weldability.

[00034] After cleaning, turbine blades are subjected to FPI as per AMS2647 and dimensional inspections followed by the tip grinding aiming to remove defective material and contaminants to reveal defects free base material.

[00035] The defective tip squealer of the HPT blade shown in Figure 1 is completely removed to reveal the defect free airfoil 101 or tip cap shown in Figure 2b followed by manual GTAW SWET or automatic LBW welding at an ambient temperature using LW1 welding wire or powder respectively.

[00036] HPT blades shown in Figure 1 in 'as welded' condition are subject to PWHT that depends of the type of the base material. For example, HPT blades manufactured of equiaxed and DS materials are subjected to annealing, for example for 2-4 hours at 2190-2230°F while HPT blades manufactured of SX material are subjected directly to a primary and secondary aging for 2-4 hours at 1975-2150 °F and for 16-24 hours at 1300-1400 °F respectively to exclude recrystallization of a base material.

[00037] The HPT blades with the tip cap 201 and tip squealer 204 shown in Figure 2b or just tip cap 201 shown in Figure 2c prior to heat treatment are subjected to machining to restore the original geometry and installation of the tip cap 201 by a fusion, preferably GTAW or LBW, welding 203 followed by the selected as above PWHT.

[00038] The tip cap can be manufactured by casting, 3D AM or extrusion and have equiaxed, DS or SX structure in a case of casting or equiaxed in case of using 3D AM and extrusion followed by PWHT. However, the extrusion is most technological process for a manufacturing of materials with high TMF properties.

[00039] After final welding, HPT blades are subjected to PWHT with parameters that depends on a type of a base material. It was found by experiments that to exclude recrystallization of SX materials and maximize mechanical properties of LW1 welds, HPT blades should be subjected to PWHT that includes:

- a) The primary aging at a temperature of 1975 - 2150°F for 2 - 4 hours
- b) The secondary aging at a temperature of 1300 – 1400 °F for 16 - 24 hours
- c) An additional heat treatment at a temperature 1550 - 1700°F for 4 - 24 hours, which exceed the temperature of the secondary aging.

[00040] However, to achieve maximum mechanical properties of LW1 welds as per the preferable embodiment, HPT blades manufactured of equiaxed and DS superalloys should be subjected to PWHT that includes:

- a) Annealing at a temperature of 2190 - 2230°F for 2 - 4 hours
- b) Primary aging at a temperature of 1975 – 2040 °F for 2 - 4 hours
- c) Secondary aging at a temperature of 1550 - 1625°F for 16 - 24 hours aiming to maximize mechanical properties of welds by optimizing a morphology and volume of gamma prime phase and Ti-Ta-W based silicide.

[00041] The PWHT of HPT blades manufactured of PWA1484 SX superalloy is described in more details in the Example 2.

[00042] After PWHT the tip of HPT blades are machined to the original dimensions using EDM or conventional milling process followed by polishing, macro etching, cleaning, dimensional inspection to the relevant EM standards, FPI in accordance with AMS2647 and radiographic inspection as per ASTM E192-04 or relevant OEM repair specifications to ensure that all repaired engine components have met specified requirements.

## **EXAMPLE 1**

[00043] Directionally solidified bars manufactured of Mar M002 superalloy were welded using GTAW-MA manual welding with LW1 welding wire of 0.045 inch in diameter, weld current of 70 - 90 A and arc voltage 9 - 11 V at a room temperature with argon protection. Welding speed was varied within the range of 1-3 ipm to ensure a formation of the optimal microstructure constituting of precipitation of discrete refractory titanium, tantalum and tungsten silicide and disilicide in the gamma matrix.

[00044] In addition to above, Mar M002 weld samples were produced using standard Rene 142 weld wire. Due to high sensitivity of Rene 142 welds to cracking SWET welding was conducted with the preheating of weld samples to a temperature 1600-1800°F.

[00045] After welding samples were subjected to PWHT using LW1 DSHT parameters as per the preferable embodiment:

- a) Annealing in vacuum at a temperature of 2210°F for two hours,
- b) Primary aging at a temperature of 2012°F for two hours, and
- c) Secondary aging at 1600°F for sixteen hours.

[00046] It was found by experiments that the developed PWHT parameters above produced better results than standard R142 HT PWHT.

[00047] Standard subsided samples were manufactured of welded bars as per ASTM E-8. Tensile tests were performed as per ASTM E-21 at a temperature of 1800°F. SRT was conducted as per ASTM E-139 at temperature of 1904°F and stresses of 18 KSI.

[00048] Cyclic oxidation testing of LW1 and Rene 142 weld samples was performed at the temperature of 600 - 2048°F. Samples were rapid heated from 600°F to 2048°F and held at 2048°F for 50 minutes to a total time of 800 hours. The oxidation rate was measured as mass loss ( $\Delta$ ) of test samples for 800 hours.

[00049] Transverse and longitudinal samples extracted from welds were used for a metallographic examination of a weld metal. After polishing, samples for light optical

microscopy were etched using the standard Marble's etchant. Samples for scanning electron microscopy (SEM) were etched electrolytically in 12 mL H<sub>3</sub>PO<sub>4</sub> + 40 mL HNO<sub>3</sub> + 48 mL H<sub>2</sub>SO<sub>4</sub> at 6V for 5 seconds. The SU-3500 Scanning Electron Microscope (SEM) with Energy Dispersive Spectroscopy (EDS) was used to study the distribution of alloying elements also known as mapping and particular silicon (Si), titanium (Ti), tantalum (Ta), tungsten (W) and nickel (Ni) in the weld metal as shown in Figures 5 - 7.

[00050] As shown in Figure 2, Mar M002 welded joints produced as per the preferable embodiment using LW1 welding wire demonstrated UTS approximately of 80 KSI. The yield strength and elongation (ductility) of these weld exceeded 60 KSI and 9 % respectively at the temperature of 1800°F.

[00051] SRT of LW1 weld samples at a temperature of 1904°F was 82.6 hours while samples produced using standard Rene 142 welding material failed in 6.4 hours.

[00052] Superior mechanical properties of LW1 welded joints were attributed to a high fraction of gamma prime phase shown in Figure 4b with the average size of around 276±82 nm that reached 41.4% and discrete precipitation of refractory Ti-Ta-W bases silicide shown in Figure 4a, 5-7 that was enhanced by titanium while in Rene 142 modified with silicon (Rene 142Si) continues formation of interdendritic and intergranular silicide shown in Figure 8 took place. Formation of nickel based interdendritic silicide weakened grain boundaries and reduced high temperature strength of welds as it was previously shown by Alex Gontcharov et al., "Self-Healing Fusion Welding Technology", Proceedings of ASME Turbo Expo 2014: Turbine Technical Conference and Exposition, GT2014, June 16 – 20, 2014, Düsseldorf, Germany, GT2014-26412.

[00053] As shown in Table 3, silicon significantly improved oxidation resistance of LW1 welds while addition of only Ti to Rene 142 reduced the oxidation resistance of test samples. However, the addition of both, Ti and Si improved oxidation resistance of LW1 test samples.

**Table 3. Oxidation of Samples at 1823°F**

| Test Sample | Rene 142 | Rene142Si | Rene142Ti | LW1 |
|-------------|----------|-----------|-----------|-----|
|-------------|----------|-----------|-----------|-----|

|                                      |         |         |         |         |
|--------------------------------------|---------|---------|---------|---------|
| $\Delta$ mass after<br>800 hours [g] | -0.0450 | -0.0023 | -0.0552 | -0.0019 |
|--------------------------------------|---------|---------|---------|---------|

## Example 2

[00054] To demonstrate a feasibility of using of LW1 welding material for a tip repair of HPT blade shown in Figure 9a manufactured of nickel based PWA1484 SX superalloy was carried out using GTAW-MA with LW1 welding wire of 0.045 inch in diameter. To protect back side of welds argon was continuously purged throughout the blade during welding. Welding current was limited to 30A. Welding speed was controlled within the range of 1 - 1.5 imp. The arc voltage varied from 8.5 to 10 V.

[00055] After welding the HPT blade was subjected to the primary aging at 1980°F for 4 hours in vacuum, followed by the secondary aging at 1300°F for 24 hours and additional heat treatment at 1625°F for 24 hours followed by machining to restore the original blade geometry, non-destructive testing (NDT) by radiographic inspection as per ASTM E1032-12, FPI as per ASTM E1209-10 “Standard Test Method for Radiographic Examination of Weldments” and dimensional inspection. No cracks and other linear indications and porosity exceeding 0.005” in diameter were permitted in welds and HAZ. All inspected blades had met acceptance standards. The typical microstructure of LW1 – PWA1484 interface and LW1 weld is shown in Figure 9b.

[00056] Therefore, as follows form the description of the invention and examples, superior mechanical and oxidation properties and weldability of the invented superalloy and method of repairing and manufacturing of turbine engine components were attributed to:

- a) Modification of Rene 142 simultaneously with Ti and Si within the established range and ratio that enhanced a formation of Ti-Ta-W discrete refractory silicide and disilicide that precipitated in the gamma matrix, which comprised silicon at the level of its solubility in the Ni based matrix;

- b) Performing welding of the invented superalloy at the low speed, preferably 1 – 3 ipm, that allowed a formation of refractory discrete Ti-Ta-W silicide and disilicide in the welding pool during welding and solidification in lieu of a formation of low temperature nickel based silicide that form low temperature nickel based interdendritic and intergranular silicide, which reduce mechanical properties of welded joints and nickel based superalloys at high temperatures.
- c) Using developed post weld heat treatment parameters for the invented superalloy that maximized mechanical properties of welds produced on single crystal materials and welds produced on directionally solidified and equiaxed materials and engine components manufactured of the same.

**Claims:**

1. A high gamma prime nickel based weldable superalloy comprises of the following alloying elements:

Cobalt from about 10 to 13 wt. %

Chromium from about 5 to 8 wt. %

Molybdenum from about 1.0 to 2.5 wt. %

Tungsten from about 4 to 6 wt. %

Tantalum from about 6 to 7 wt. %

Rhenium from about 1.5 to 3.5 wt. %

Aluminum from about 5.5 to 6.5 wt. %

Hafnium from about 1.2 to 1.8 wt. %

Boron from about 0.01 to 0.02 wt. %

Carbon from about 0.05 to 0.15 wt. %

Zirconium from about 0.01 to 0.02 wt. %

Titanium form about 0.15 to 0.25 wt. %

Silicon from about 0.4 to about 0.5 wt. %, and

Nickel with impurities to balance

2. The high gamma prime nickel based weldable superalloy as per claim 1 wherein the content of the following elements comprises:

Cobalt from about 11 to 13 wt. %

Chromium from about 6 to 8 wt. %

Molybdenum from about 1.0 to 2.0 wt. %

Rhenium from about 2.5-3.5 wt. %

3. The high gamma prime nickel based weldable superalloy as per claim 2 comprises the silicon in a form of selected from among a refractory Ti, Ta and W based silicide and disilicide and preferably titanium disilicide.
4. The high gamma prime nickel based weldable superalloy as per claim 2 comprises the titanium and silicon with a ratio of 0.5 – 0.625 and preferably 0.50 when contents of titanium and silicon are in wt.% adapted to provide preferential formation of Ti disilicide thereby minimizing the silicon content in a nickel based solid solution matrix.
5. The high gamma prime nickel based weldable superalloy as per claim 2 selected from among a welding wire, a welding powder, equiaxed cast material, directionally solidified cast material single crystal cast materials, extruded articles, cast articles, repair sections of a turbine engine components, and 3D additive manufactured materials and articles.
6. Method of repairing and manufacturing of the turbine engine components includes the steps of:
  - a) weld repair of the blade tip using a fusion welding process selected from among welding at an ambient temperature or welding with a preheating, and a welding material comprising:

Cobalt from about 10 to 13 wt. %

Chromium from about 5 to 8 wt. %

Molybdenum from about 1.0 to 2.5 wt. %

Tungsten from about 4 to 6 wt. %

Tantalum from about 6 to 7 wt. %

Rhenium from about 1.5 to 3.5 wt. %  
Aluminum from about 5.5 to 6.5 wt. %  
Hafnium from about 1.2 to 1.8 wt. %  
Boron from about 0.01 to 0.02 wt. %  
Carbon from about 0.05 to 0.15 wt. %  
Zirconium from about 0.01 to 0.02 wt. %  
Titanium from about 0.15 to 0.25 wt. %  
Silicon from about 0.4 to about 0.5 wt. %, and  
Nickel with impurities to balance

- b) Post weld heat treatment selected from among an annealing, primary and secondary aging and stress relief or all above.

7. The method of repairing and manufacturing of the turbine engine components as per claim 6 wherein the content of the following elements of the welding material comprises:

Cobalt from about 11 to 13 wt. %  
Chromium from about 6 to 8 wt. %  
Molybdenum from about 1.0 to 2.0 wt. %  
Rhenium from about 2.5-3.5 wt. %

8. Method of repairing and manufacturing of turbine engine components as per claim 6 where in the fusion welding is done with the speed of 1 – 3 inch per minute aiming to allow a formation of the refractory Ti-Ta-W based silicide and disilicide during welding and a solidification of a welding pool.

9. Method of repairing and manufacturing of turbine engine components as per claim 6 wherein the post weld heat treatment comprising the steps of:
  - a) The primary aging at a temperature of 1975 - 2150°F for 2 - 4 hours
  - b) The secondary aging at a temperature of 1300 – 1400 °F for 16 - 24 hours, and
  - c) An additional heat treatment at a temperature 1550 - 1700°F for 4 - 24 hours, which exceeds the temperature of the secondary aging aiming to allow further improvement of a mechanical properties of the weld metal after restoration of properties of the base material.
10. Method of repairing and manufacturing of turbine engine components as per claim 9 wherein the components are manufactured from single crystal material.
11. Method of repairing and manufacturing of turbine engine components as per claim 6 wherein the post weld heat treatment comprising the steps of:
  - a) Annealing at a temperature of 2190 - 2230°F for 2 - 4 hours
  - b) Primary aging at a temperature of 1975 – 2040 °F for 2 - 4 hours
  - c) Secondary aging at a temperature of 1550 - 1625°F for 16 - 24 hours aiming to maximize properties of welds by optimizing a morphology and volume of gamma prime phase and Ti-Ta-W based silicide and silicide.
12. Method of repairing and manufacturing of turbine engine components as per claim 11 wherein the components are manufactured from equiaxed and directionally solidified materials.
13. Method of repairing and manufacturing of turbine engine components as per claim 6 wherein the tip of the turbine blade is selected from among a squealer, tip cap or combination of above.

14. Method of repairing and manufacturing of turbine engine components as per claim 6 wherein the tip cap is selected from among of the equiaxed, directionally solidified, single crystal, 3D additive manufactured and preferably extruded materials.
15. Method of repairing and manufacturing of turbine engine components as per claim 6 wherein the pre-weld heat treatment of the tip cap comprises the steps of:
- a) Annealing at a temperature of 2190 - 2230°F for 2 - 4 hours,
  - b) Primary aging at a temperature of 1975 – 2040 °F for 2 - 4 hours,
  - c) Welding of the tip cap to the tip of the turbine blade, and
  - d) Secondary aging at the temperature of 1550 - 1625°F for 4 – 24 hours.

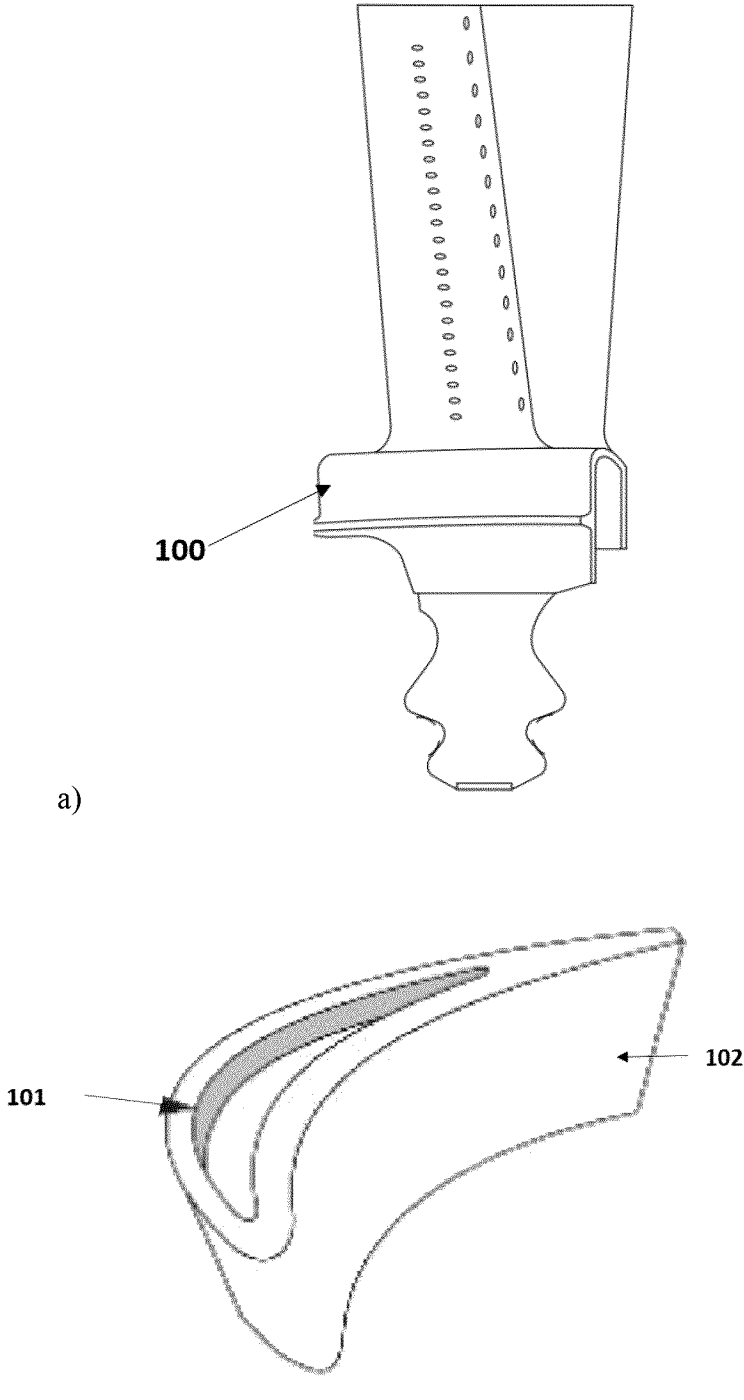


Figure 1

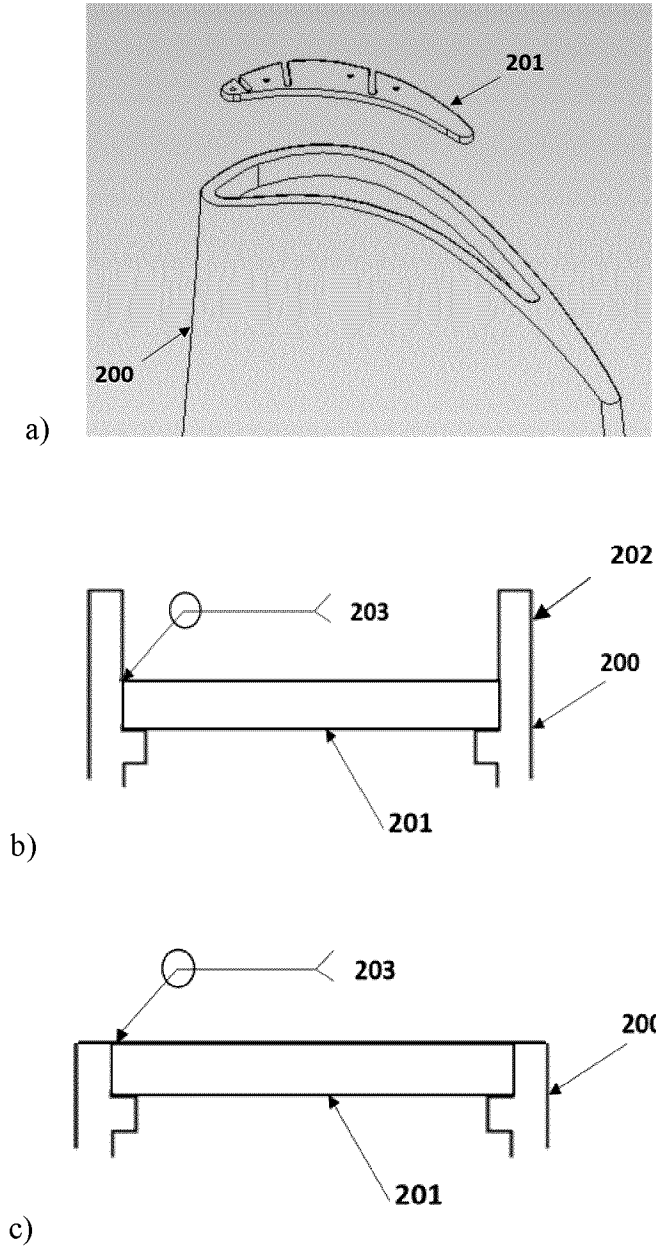


Figure 2

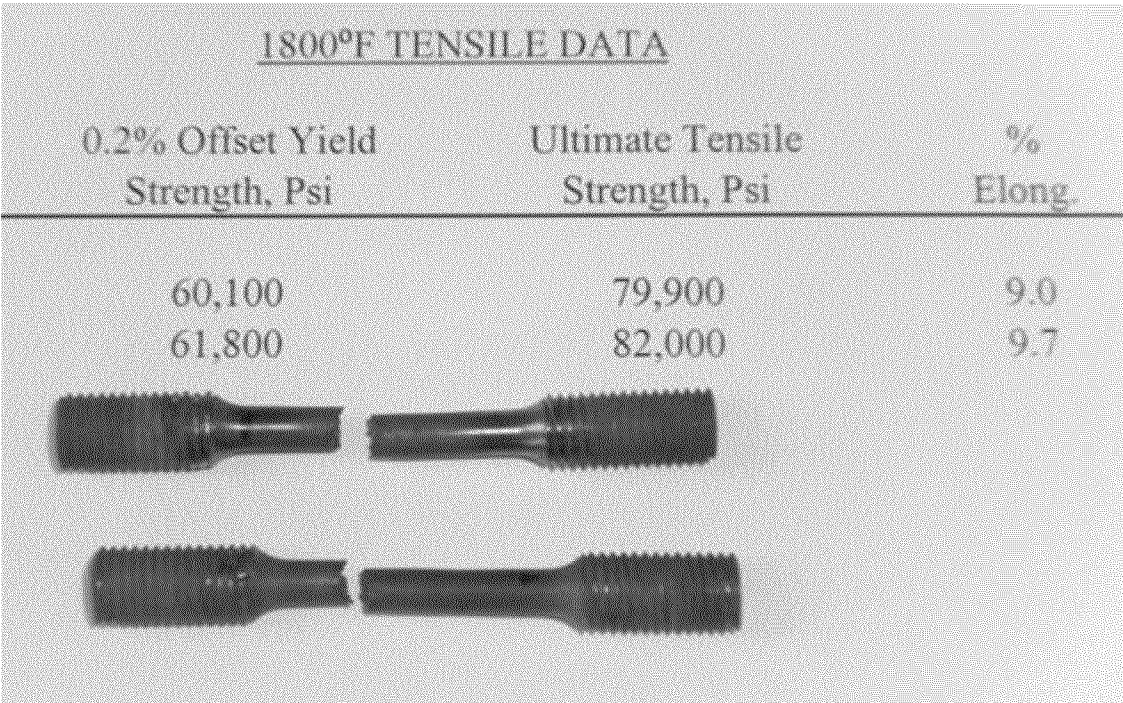


Figure 3

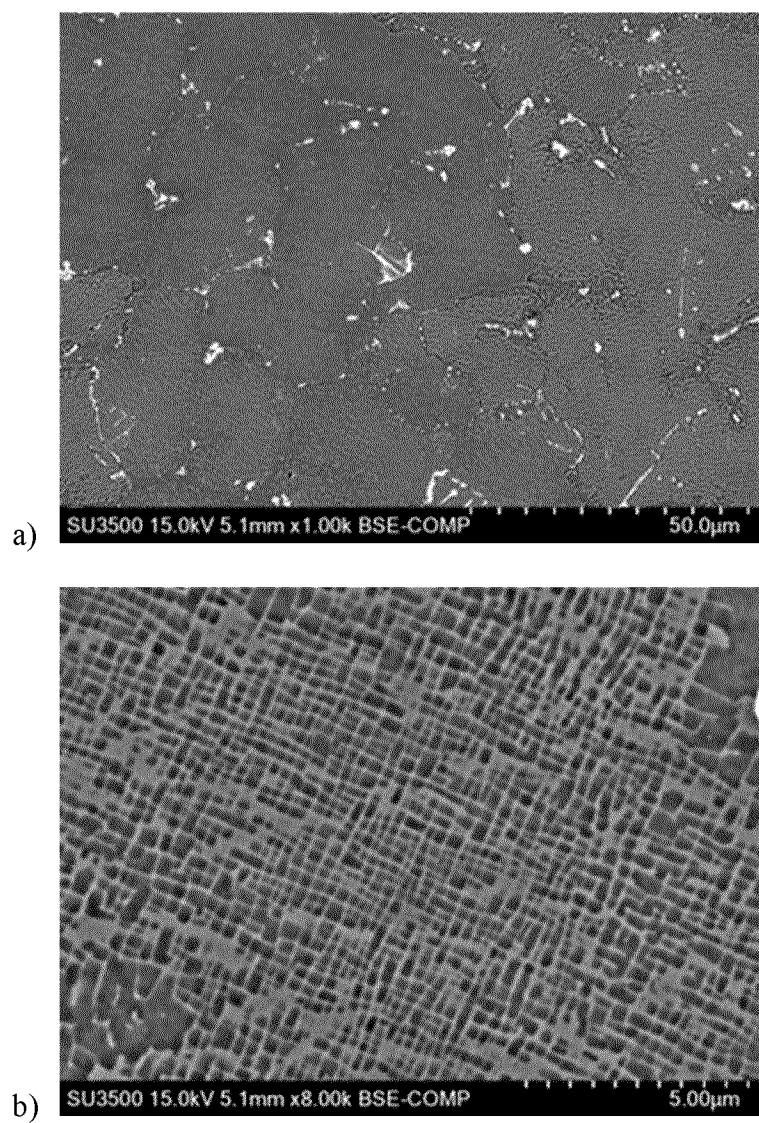


Figure 4

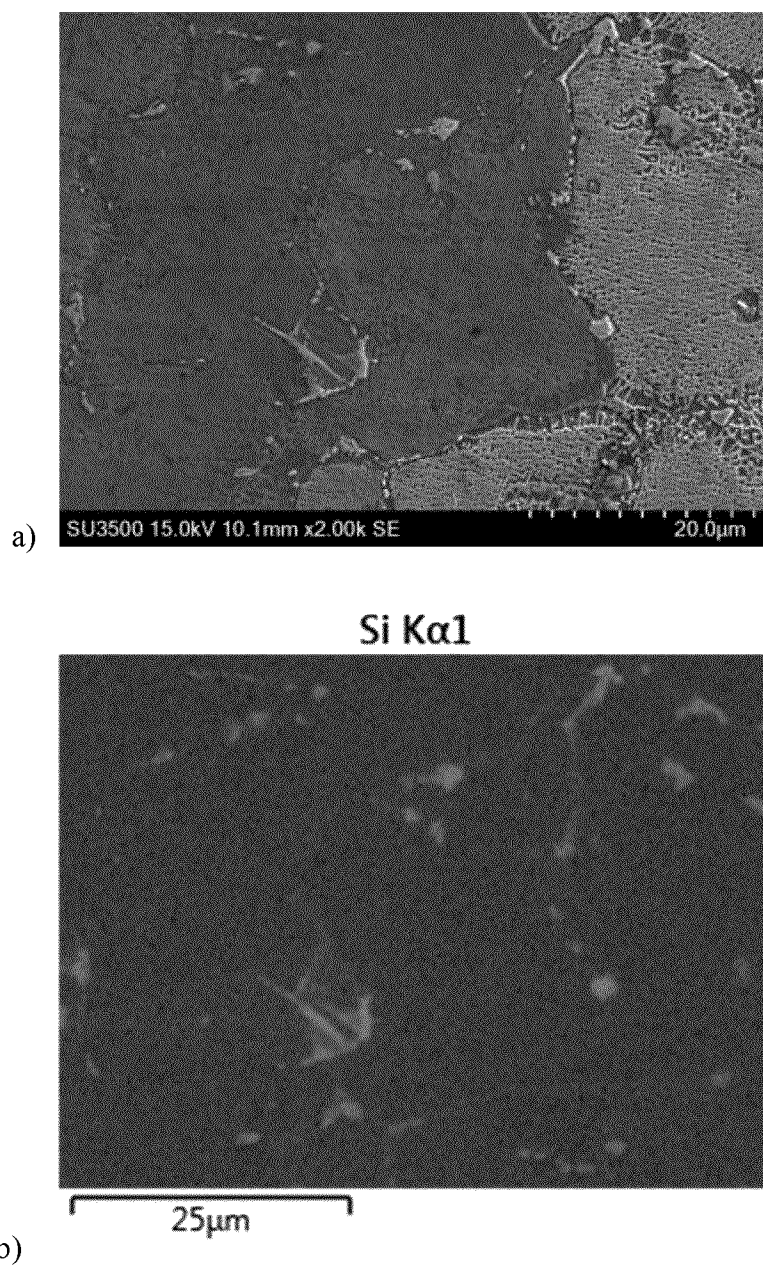


Figure 5

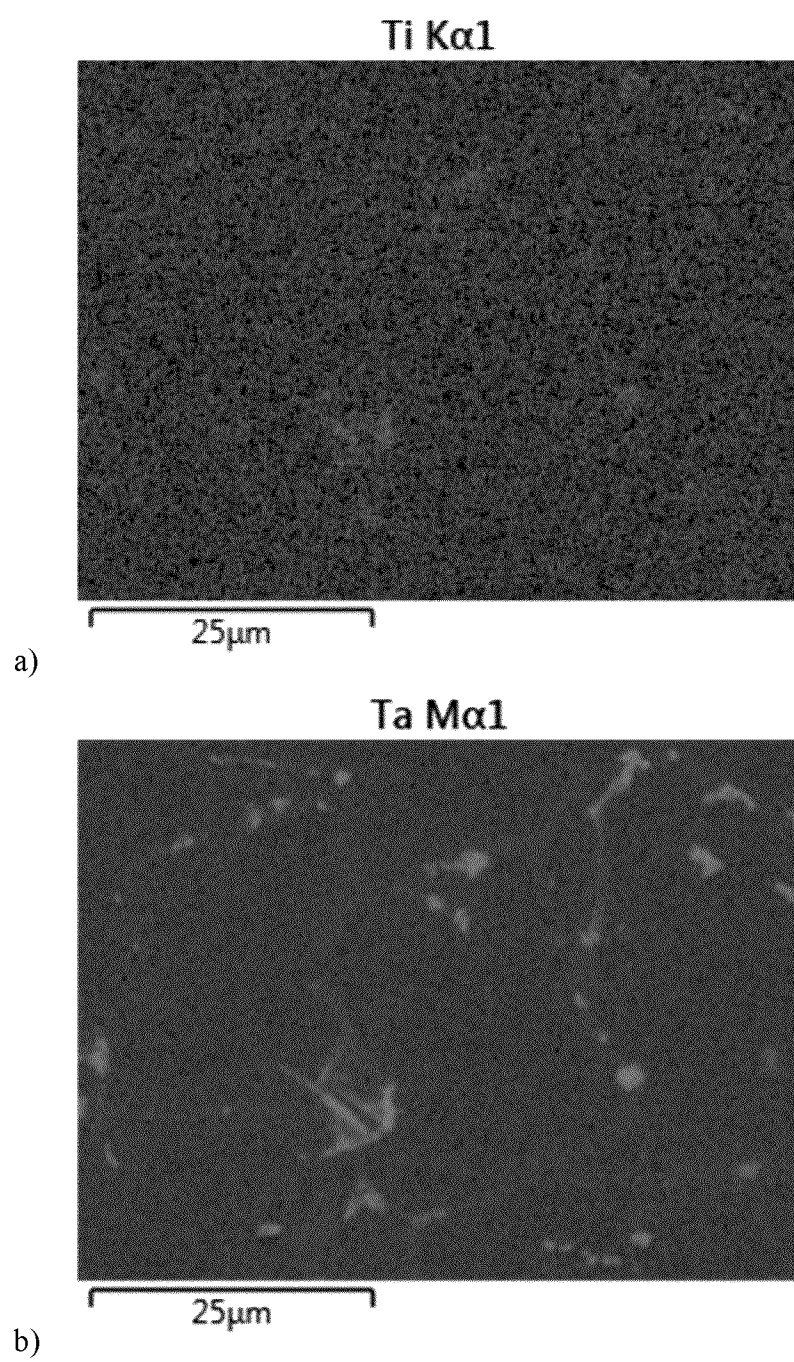


Figure 6

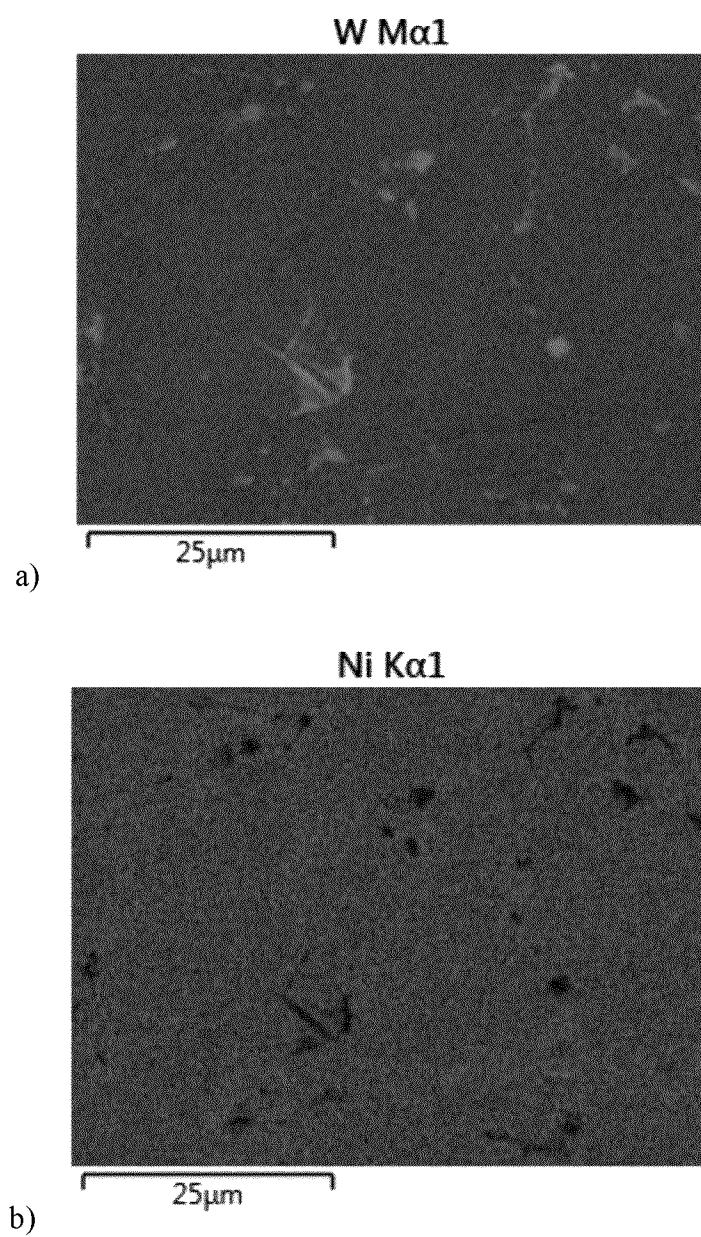


Figure 7

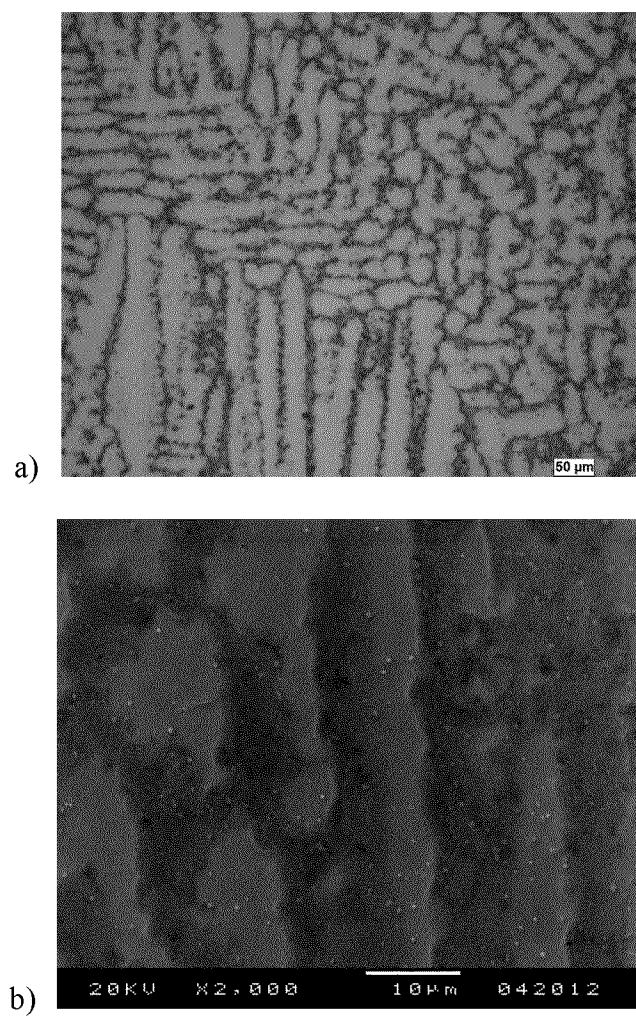


Figure 8

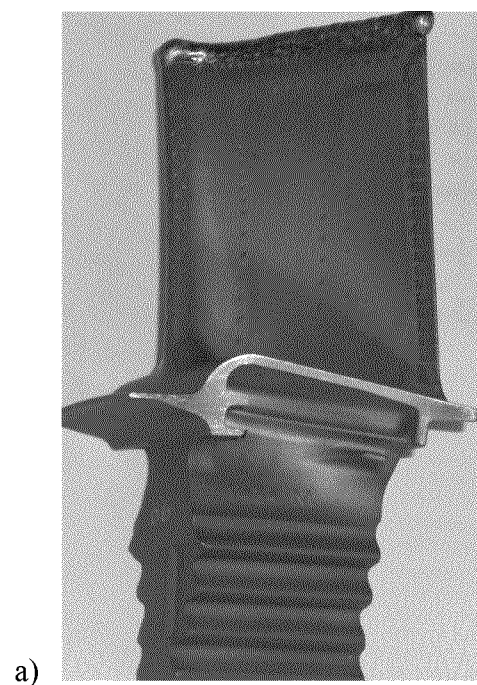


Figure 9

## INTERNATIONAL SEARCH REPORT

International application No.

**PCT/CA2017/050291**

## A. CLASSIFICATION OF SUBJECT MATTER

IPC: **C22C 19/05** (2006.01), **B23K 35/22** (2006.01), **B23P 6/00** (2006.01)

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

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: **C22C 19/05** (2006.01), **B23K 35/22** (2006.01), **B23P 6/00** (2006.01)

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

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

**Database:** Questel**Keywords:** CO, COBALT, CR, CHROMIUM, W, TUNGSTEN, TA, TANTALUM, AL, ALUMINUM, MO, MOLYBDENUM, RE, RHENIUM, HF, HAFNIUM, B, BORON, C, CARBON, ZR, ZIRCONIUM, TI, TITANIUM, SI, SILICON, NI, NICKEL

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                           | Relevant to claim No. |
|-----------|--------------------------------------------------------------------------------------------------------------|-----------------------|
| X<br>Y    | JP2006045654A, TAMAOKI, H., et al., 16 February 2006 (16-02-2006)<br>**machine translation, whole document** | 1-5<br>6-15           |
| X         | CA2865658A1, GONCHAROV, A., et al., 12 June 2014 (12-06-2014)<br>**whole document**                          | 1-3, 5-15             |
| X         | CA2898313A1, GONCHAROV, A., et al., 02 July 2015 (02-07-2015)<br>**whole document**                          | 1-15                  |
| Y         | CA2399210A1, FOSTER, M., et al., 22 November 2001 (22-11-2001)<br>**whole document**                         | 6-15                  |
| Y         | CA2343639A1, FOSTER, M., et al., 23 March 2000 (23-03-2000)<br>**whole document**                            | 6-15                  |

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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

Date of the actual completion of the international search  
30 November 2017 (30-11-2017)Date of mailing of the international search report  
30 November 2017 (30-11-2017)Name and mailing address of the ISA/CA  
Canadian Intellectual Property Office  
Place du Portage I, C114 - 1st Floor, Box PCT  
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Authorized officer

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## INTERNATIONAL SEARCH REPORT

International application No.

**PCT/CA2017/050291**

| C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT |                                                                                    |                       |
|-------------------------------------------------------|------------------------------------------------------------------------------------|-----------------------|
| Category*                                             | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| A                                                     | US5897801A, SMASHEY, R.W. et al., 27 April 1999 (27-04-1999)                       | 1-15                  |

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.  
**PCT/CA2017/050291**

| Patent Document<br>Cited in Search Report | Publication<br>Date           | Patent Family<br>Member(s)                                                                                                                                                                                                                                 | Publication<br>Date                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |
|-------------------------------------------|-------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| JP2006045654A                             | 16 February 2006 (16-02-2006) | JP2006045654A<br>JP4230970B2                                                                                                                                                                                                                               | 16 February 2006 (16-02-2006)<br>25 February 2009 (25-02-2009)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |
| CA2865658A1                               | 12 June 2014 (12-06-2014)     | CA2865658A1<br>CN104428101A<br>EP2822726A1<br>EP2822726A4<br>JP2016508070A<br>JP6086992B2<br>RU2014141779A<br>RU2610198C2<br>SG11201407192PA<br>US2014366996A1<br>WO2014085892A1                                                                           | 12 June 2014 (12-06-2014)<br>18 March 2015 (18-03-2015)<br>14 January 2015 (14-01-2015)<br>30 March 2016 (30-03-2016)<br>17 March 2016 (17-03-2016)<br>01 March 2017 (01-03-2017)<br>27 September 2016 (27-09-2016)<br>08 February 2017 (08-02-2017)<br>30 December 2014 (30-12-2014)<br>18 December 2014 (18-12-2014)<br>12 June 2014 (12-06-2014)                                                                                                                                                                                                      |
| CA2898313A1                               | 02 July 2015 (02-07-2015)     | CA2898313A1<br>CN105163898A<br>EP3086899A1<br>JP2017507033A<br>KR20160099467A<br>RU2015136378A<br>SG11201505425YA<br>US2015314399A1<br>WO2015095949A1                                                                                                      | 02 July 2015 (02-07-2015)<br>16 December 2015 (16-12-2015)<br>02 November 2016 (02-11-2016)<br>16 March 2017 (16-03-2017)<br>22 August 2016 (22-08-2016)<br>02 March 2017 (02-03-2017)<br>28 August 2015 (28-08-2015)<br>05 November 2015 (05-11-2015)<br>02 July 2015 (02-07-2015)                                                                                                                                                                                                                                                                      |
| CA2399210A1                               | 22 November 2001 (22-11-2001) | CA2399210A1<br>CA2399210C<br>AT511422T<br>AU8537801A<br>BR0108681A<br>CN1455714A<br>CN1187157C<br>EP1296796A2<br>EP1296796A4<br>EP1296796B1<br>JP2003533354A<br>JP4969756B2<br>MXPA02008147A<br>RU2265505C2<br>US6333484B1<br>WO0187528A2<br>WO0187528A3   | 22 November 2001 (22-11-2001)<br>05 August 2008 (05-08-2008)<br>15 June 2011 (15-06-2011)<br>26 November 2001 (26-11-2001)<br>12 November 2002 (12-11-2002)<br>12 November 2003 (12-11-2003)<br>02 February 2005 (02-02-2005)<br>02 April 2003 (02-04-2003)<br>11 July 2007 (11-07-2007)<br>01 June 2011 (01-06-2011)<br>11 November 2003 (11-11-2003)<br>04 July 2012 (04-07-2012)<br>29 November 2002 (29-11-2002)<br>10 December 2005 (10-12-2005)<br>25 December 2001 (25-12-2001)<br>22 November 2001 (22-11-2001)<br>28 February 2002 (28-02-2002) |
| CA2343639A1                               | 23 March 2000 (23-03-2000)    | CA2343639A1<br>CA2343639C<br>AT392290T<br>AU1439500A<br>BR9913669A<br>DE69938563D1<br>DE69938563T2<br>EP1148967A1<br>EP1148967A4<br>EP1148967B1<br>ES2306538T3<br>JP2002524268A<br>JP4889858B2<br>MXPA01002651A<br>PT1148967E<br>US6054672A<br>WO0015382A1 | 23 March 2000 (23-03-2000)<br>20 January 2009 (20-01-2009)<br>15 May 2008 (15-05-2008)<br>03 April 2000 (03-04-2000)<br>25 September 2001 (25-09-2001)<br>29 May 2008 (29-05-2008)<br>13 August 2009 (13-08-2009)<br>31 October 2001 (31-10-2001)<br>02 May 2007 (02-05-2007)<br>16 April 2008 (16-04-2008)<br>01 November 2008 (01-11-2008)<br>06 August 2002 (06-08-2002)<br>07 March 2012 (07-03-2012)<br>21 June 2002 (21-06-2002)<br>23 July 2008 (23-07-2008)<br>25 April 2000 (25-04-2000)<br>23 March 2000 (23-03-2000)                          |
| US5897801A                                | 27 April 1999 (27-04-1999)    | None                                                                                                                                                                                                                                                       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |