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(54) **Title:** PRE-WELD HEAT TREATMENT OF Y' PRECIPITATION STRENGTHENED NICKEL-BASED SUPERALLOYS

(57) **Abstract:** A method for improving the weldability of nickel-based superalloys involving pre-weld heat treating a nickel-based superalloy at a temperature sufficient to minimize boron segregation at grain boundaries and maintaining this heating temperature for a period of time sufficient to dissolve any borides that might have formed during casting and prior processing of the nickel-based superalloy. The heated nickel-based superalloy is then slowly cooled at a rate that is slow enough to minimize further boron segregation. By minimizing boron segregation at grain boundaries and eliminating boride formation in the treated pre-weld nickel-based superalloy, resistance to intergranular HAZ liquation cracking is improved and a pre-weld microstructure that exhibits the desirable hardness and ductility properties suitable for welding are achieved.



PRE-WELD HEAT TREATMENT OF γ' PRECIPITATION STRENGTHENED NICKEL-BASED SUPERALLOYS

FIELD OF THE INVENTION

[0001] The present invention relates to the field of materials technology and, in particular, to a pre-weld method for heat treating γ' precipitation strengthened nickel-based superalloys to improve weldability.

BACKGROUND OF THE INVENTION

[0002] Significant advancement has been made in the development of nickel-based
5 superalloys for applications involving stringent operating conditions such as those
experienced by components of gas-turbine in aero and land-based engines. About 60%
by weight of most modern gas-turbine engine structural components are made of
nickel-based superalloys. As the performance requirements of gas turbines are being
increased continually, their operating conditions become more stringent. Therefore,
10 cost effective heat resistant alloys with improved elevated temperature properties have
been of great interest. In particular, precipitation strengthened nickel-based superalloys,
especially the advanced grades containing relatively high contents of strengthening
gamma prime (γ') precipitates, are becoming of increasing interest.

[0003] The overall economy of operation of turbine engines is, however, dependent
15 upon the ability to maintain, repair and overhaul the cost intensive engine parts.
However, known weld repair techniques for superalloy materials have met with only
limited success, due primarily to the propensity of superalloy materials to develop
cracks during such welding operations. In this respect, precipitation strengthened
nickel-based superalloys are known to be very difficult to weld due to their high
20 susceptibility to heat-affected zone (HAZ) intergranular liquation cracking.

[0004] Pre-weld microstructure has been found to be critical in determining the
susceptibility of precipitation strengthened nickel-based superalloys to HAZ
intergranular cracking. Several techniques have been proposed to improve the

weldability of superalloy materials by modifying the materials' microstructural characteristics through thermal treatment. The pre-weld thermal treatment that is currently applied to most γ' precipitation strengthened nickel-based superalloys is the widely known standard solution heat treatment (SHT) which involves heating the material to the solutionizing temperature to dissolve the strengthening γ' particles, usually followed by rapid cooling. While SHT has been found to be effective in improving the weldability of certain nickel-based superalloys, it has not proven effective in the more difficult to weld advanced materials, such as some γ' precipitation strengthened nickel-based superalloys.

[0005] Pre-weld thermal treatments for such advanced materials have been investigated and described in the earlier work of the present inventors (A.T. Egbewande, H.R. Zhang, R.K. Sidhu, and O.A. Ojo, Metallurgical and Materials Transactions A, 2009, Vol. 40A, p. 2695; A Thakur, N.L. Richards and M.C. Chaturvedi, International Journal for the Joining of Materials, 2003, Vol. 15, p.21, herein incorporated by reference). In such thermal treatment methods, SHT was followed by further pre-weld heat treatments. These combination pre-weld thermal treatments, designated as UMT and NUMT were found to significantly reduce HAZ intergranular liquation cracking in the precipitation strengthened nickel-based superalloy, IN 738, during fusion welding. The UMT treatment requires water quenching as a process step during heat treatment and, as a result, is difficult to implement in the aerospace industry where most of the thermal processing is performed under vacuum conditions, while the NUMT, in addition to multiple heating cycles, requires significantly longer processing time.

[0006] Other pre-weld techniques for heat treating advanced nickel-based superalloys, where water quenching is not required, are described. United States Patent No. 7,653,995 describes a process for pre-conditioning the nickel-based superalloy CM-247LC through defined heating, soaking, and multiple cooling steps in order to grow γ' particles to a desired volume percent, thereby providing a degree of ductility to the material that allows it to undergo a fusion welding process at ambient conditions with little or no cracking of the base material.

[0007] United States Patent No. 5,509,980 describes a pre-weld overageing heat treatment process that involves heating, soaking, cooling, and intermittently heating the cooling material to obtain uniformity in the coarse equiaxed γ' precipitates in the microstructure.

- 5 [0008] This background information is provided for the purpose of making known information believed by the applicant to be of possible relevance to the present invention. No admission is necessarily intended, nor should be construed, that any of the preceding information constitutes prior art against the present invention.

SUMMARY OF THE INVENTION

- [0009] Disclosed herein are exemplary embodiments pertaining to a pre-weld method
10 for heat treating nickel-based superalloys to improve weldability. An exemplary embodiment of the present disclosure relates to a pre-weld heat treatment method for nickel-based superalloys that comprises: (a) heating a nickel-based superalloy at a temperature sufficient to achieve a balance between equilibrium and non-equilibrium boron segregation in the nickel-based superalloy, wherein balancing equilibrium and
15 non-equilibrium boron segregation results in minimized boride formation; (b) maintaining the temperature of the nickel-based superalloy for a period of time sufficient to dissolve any borides formed in the heated nickel-based superalloy; and (c) cooling the heated nickel-based superalloy at a rate of cooling that is slow enough to minimize further non-equilibrium boron segregation; wherein the treated nickel-based
20 superalloy comprises γ' precipitates and MC carbides, with minimized observable boride particles.

- [0010] In accordance with another aspect of the disclosure, there is described a method for joining a nickel-based superalloy that comprises: (a) treating the nickel-based superalloy to the pre-weld heat treatment method described herein; and (b)
25 joining the treated nickel-based superalloy obtained in (a).

[0011] In accordance with another aspect of the disclosure, there is described a pre-weld heat treatment method for a nickel-based superalloy comprising the following nominal composition expressed as weight percentages: carbon 0.11%; chromium

- 15.84%; cobalt 8.5%; tungsten 2.48%; molybdenum 1.88%; niobium 0.92%; iron 0.07%; aluminum 3.46%; titanium 3.47%; tantalum 1.69%; zirconium 0.04%; boron 0.012%; and the balance nickel, the method comprising: (a) heating the nickel-based superalloy at a heating temperature of from about 1110°C to about 1130°C; (b) maintaining the temperature of the nickel-based superalloy for at least about 16 hours; and (c) furnace cooling the heated nickel-based superalloy.

[0012] In accordance with another aspect of the disclosure, there is described a nickel-based superalloy treated according to the pre-weld heat treatment methods described herein, wherein the nickel-based superalloy comprises γ' precipitates and MC carbides, with minimized observable boride particles.

[0013] In accordance with another aspect of the disclosure, there is described a nickel-based superalloy treated according to the pre-weld heat treatment methods described herein, wherein the nickel-based superalloy comprises γ' precipitates and MC carbides, free of observable boride particles.

[0014] In accordance with a further aspect of the disclosure, there is described a nickel-based superalloy treated according to the pre-weld heat treatment methods described herein, wherein the nickel-based superalloy comprises γ' precipitates and MC carbides, at the exclusion of boride particles.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] These and other features of the invention will become more apparent in the following detailed description in which reference is made to the appended drawings.

[0016] **Figure 1** is a graphical representation of the relative Vickers hardness of furnace-cooled IN 738 materials treated at 1025°C, 1120°C and 1180°C for 2 hours;

[0017] **Figure 2** is a temperature-time plot showing furnace-cooling of IN 738 material treated at 1120°C;

[0018] **Figure 3** is a graphical representation of the relative total crack lengths in 10 sections each of IN 738 materials subjected to heat treatments at 1025°C, 1120°C and 1180°C for 2 hours, furnace-cooled;

[0019] **Figures 4A** and **4B** are SEM micrographs showing the persistence of borides
5 in IN 738 materials subjected to heat treatment at 1120°C for 2 hours, furnace-cooled;

[0020] **Figure 5** is a schematic representation of the concentration profile for the dissolution of a second phase precipitate;

[0021] **Figures 6A** and **6B** are SEM micrographs showing the persistence of borides in IN 738 materials subjected to heat treatments at 1120°C for 4 hours and 8 hours
10 respectively, furnace-cooled;

[0022] **Figure 7** is a graphical representation of the effect of holding time at 1120°C on HAZ intergranular cracking susceptibility for materials held for times from 2 hours to 24 hours, followed by furnace cooling;

[0023] **Figure 8** is a graphical representation of the Vickers hardness variation for IN
15 738 samples treated at 1120°C for different holding times, followed by furnace cooling;

[0024] **Figure 9** is a graphical comparison of HAZ cracking susceptibility in laser-arc hybrid welded IN 738 materials treated using known standard solution heat treatment (SHT) and the pre-weld heat treatment method according to embodiments of the present disclosure; and

[0025] **Figure 10** is an SEM micrograph of the microstructure of the IN 738 superalloy showing γ' precipitate, γ - γ' eutectic and MC carbide in the material subjected to the pre-weld heat treatment method according to embodiments of the present disclosure.
20

DETAILED DESCRIPTION OF THE INVENTION

Definitions

[0026] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs.

- 5 [0027] As used herein, the term “about” refers to an approximately +/-10% variation from a given value. It is to be understood that such a variation is always included in any given value provided herein, whether or not it is specifically referred to.

- [0028] The terms “precipitation strengthened nickel-based superalloy”, “ γ' precipitation strengthened nickel-based superalloy”, “nickel-based superalloy”, and
10 “superalloy” may be used interchangeably herein to refer to a range of nickel-based superalloys strengthened by γ' precipitates that are known to be difficult to weld materials due to their high susceptibility to heat-affected zone (HAZ) intergranular liquation cracking. These alloys typically comprise high volume fractions of γ' particles (>40%) and, according to certain embodiments, have high aluminum or titanium
15 content. The nickel-based superalloys, according to certain embodiments, may comprise the following nominal composition expressed as weight percentages: carbon 0.11%; chromium 15.84%; cobalt 8.5%; tungsten 2.48%; molybdenum 1.88%; niobium 0.92%; iron 0.07%; aluminum 3.46%; titanium 3.47%; tantalum 1.69%; zirconium 0.04%; boron 0.012%; and the balance nickel. In preferred embodiments, the nickel-
20 based superalloy is IN 738.

- [0029] The terms “joining” and “welding” may be used interchangeably herein to refer to techniques known to those skilled in the art for joining materials, usually metals or thermoplastics, by causing coalescence. For example, such joining and/or welding techniques encompassed herein, include without limitation, arc welding, fusion
25 welding, and cladding/buildup processes.

[0030] The present disclosure is based on an innovative approach to treating nickel-based superalloys to improve the weldability of such materials. In particular, the

methods described herein are based on the observation that most of the existing thermal treatment procedures result in boron segregation to grain boundaries and other interfaces prior to welding which results in the formation of borides in nickel-based superalloys. The decomposition of the borides contributes, significantly, to extensive intergranular liquation in the superalloy resulting in a crack-susceptible microstructure. Accordingly, the present disclosure describes a pre-weld method for heat treating nickel-based superalloys that involves a combination of heating and cooling steps that is believed to achieve both minimization or elimination of boride phases present in the cast alloy and the minimization of boron segregation at grain boundaries prior to welding.

[0031] Modification of the pre-weld microstructure, according to the embodiments described in the present disclosure, improves resistance to HAZ cracking in the treated nickel-based superalloy which further offers improved weldability of the material. In this way, the pre-weld heat treatment method according to the present disclosure, may be used to condition typically difficult to weld superalloys in order to enhance the prospect of adopting a wider range of welding techniques. For example, nickel-based superalloys treated according to embodiments of the present disclosure may be more amenable to low heat input laser beam welding. In other embodiments, the treated nickel-based superalloys may be more amenable to hybrid welding techniques. In still further embodiments, the treated nickel-based superalloys may be more amenable to laser-arc hybrid welding.

[0032] Pre-weld heat treatment methods according to embodiments of the present disclosure require a minimal number of steps and practicable implementation. In particular, according to certain embodiments, the pre-weld heat treatment methods described herein do not involve water quenching techniques to achieve the necessary cooling of the heated nickel-based superalloy. Cooling of the heated nickel-based superalloy, according to embodiments of the present disclosure, involves a slow rate of cooling and, therefore, may be achieved by furnace cooling. In this way, the methods of the present disclosure are practicable for implementation in the aerospace industry where most of the thermal processing is performed under vacuum conditions.

[0033] The methods for improving the weldability of nickel-based superalloys, according to embodiments of the present disclosure, involve pre-weld heat treating the nickel-based superalloys in order to eliminate boride phases present in the cast alloy and to minimize boron segregation at grain boundaries prior to welding. The pre-weld heat treating method described herein involves heating the nickel-based superalloy at a temperature sufficient to minimize boron segregation at grain boundaries and maintaining this heating temperature for a period of time sufficient to dissolve any borides that may have formed during casting or other prior processing of the nickel-based superalloy. The heated nickel-based superalloy is then slowly cooled at a rate that is slow enough to minimize further boron segregation. It is believed that the presently described method, by minimizing boron segregation at grain boundaries and minimizing or eliminating boride formation in the treated pre-weld nickel-based superalloy, results in resistance to HAZ cracking in the treated nickel-based superalloy and a pre-weld microstructure that exhibits the desirable hardness and ductility properties that are suitable for welding.

Thermal Treatment Temperature - Establishing Balance between Equilibrium and Non-Equilibrium Boron Segregation

[0034] As is known by those skilled in the art, segregation of boron to grain boundaries and other interfaces in the interdendritic regions can occur during thermal treatment prior to welding. Boron segregation is also possible during cooling of cast alloy ingots. Increase in concentration of boron at grain boundaries and other interfaces as a result of boron segregation has been found to result in the formation of borides in nickel-based superalloys. As demonstrated by Gleeble simulation by the inventors, the decomposition of borides caused extensive intergranular liquation in IN 738 superalloy and resulted in a crack-susceptible microstructure. Therefore, an effective thermal treatment procedure, according to embodiments of the present disclosure, must consider the elimination of boride phases present in the cast alloy and the minimization of boron segregation at grain boundaries prior to welding.

[0035] Segregation of boron can occur by two mechanisms, namely, equilibrium segregation and non-equilibrium segregation, both of which are affected by the thermal

treatment temperature. In particular, equilibrium boron segregation has been confirmed to decrease with increasing thermal treatment temperature, while non-equilibrium boron segregation increases with increasing temperature. Therefore, an increase in heat treatment temperature in an attempt to reduce equilibrium boron segregation could
5 result in higher susceptibility to non-equilibrium boron segregation.

[0036] The pre-weld heat treatment method, according to embodiments described herein, attempt to minimize boron segregation by balancing the equilibrium segregation with the non-equilibrium segregation occurring during thermal treatment of the nickel-based superalloy. According to embodiments of the present disclosure, the nickel-based superalloy is heated at a temperature wherein equilibrium segregation and non-equilibrium segregation of boron is balanced. The heating temperature may vary
10 depending upon the particular nickel-based superalloy being treated, but generally according to embodiments of the present disclosure, the heating temperature may range from about 1025°C to about 1220°C. In other embodiments, the heating temperature may range from about 1037°C to about 1200°C. In further embodiments, the heating temperature may range from about 1075°C to about 1180°C. In other embodiments, the heating temperature may range from about 1110°C to about 1200°C. In particular
15 embodiments, the heating temperature may range from about 1110°C to about 1130°C. In further embodiments, the heating temperature may range from about 1115°C to about 1125°C. In preferred embodiments, the heating temperature is about 1120°C.
20

Duration of Thermal Treatment – Boride Dissolution

[0037] In addition to minimizing the extent of boron segregation that occurs during thermal treatment of the nickel-based superalloy, the formation of borides is also minimized or eliminated in accordance with the pre-weld heat treatment methods
25 described herein. Specifically, the heat treatment of the nickel-based superalloy is maintained for a period of time sufficient to dissolve any borides formed in the heated nickel-based superalloy. In one embodiment, the heat treatment is maintained for at least about 16 hours. In other embodiments, the heat treatment is maintained for about 16 hours to about 24 hours. In further embodiments, the heat treatment is maintained
30 for about 16 hours to about 18 hours. In other embodiments, the heat treatment is

maintained for about 16 hours to about 20 hours. In other embodiments, the heat treatment is maintained for about 16 hours to about 22 hours. In further embodiments, the heat treatment is maintained for about 18 hours to about 24 hours. In other embodiments, the heat treatment is maintained for about 20 hours to about 24 hours. In preferred embodiments, the heat treatment is maintained for about 16 hours.

Cooling Rate – Minimizing Non-Equilibrium Segregation of Boron

[0038] Non-equilibrium boron segregation can be further minimized by very slow cooling, which can cause de-segregation of already-segregated boron. Accordingly, the pre-weld heat treatment methods described herein further involve slowly cooling the heated nickel-based superalloy at a rate of cooling that is slow enough to further minimize non-equilibrium boron segregation.

[0039] According to embodiments of the present disclosure, slow cooling is achieved by furnace cooling. In certain embodiments, the heated nickel-based superalloy is cooled at a rate of from about 0.10°C/s to about 0.29°C/s. In other embodiments, the heated nickel-based superalloy is cooled at a rate of from about 0.10°C/s to about 0.25°C/s. In further embodiments, the heated nickel-based superalloy is cooled at a rate of from about 0.12°C/s to about 0.29°C/s. In other embodiments, the heated nickel-based superalloy is cooled at a rate of from about 0.10°C/s to about 0.20°C/s. In other embodiments, the heated nickel-based superalloy is cooled at a rate of from about 0.10°C/s to about 0.15°C/s. In preferred embodiments, the heated nickel-based superalloy is cooled at a rate of about 0.12°C/s.

[0040] The slow rate of cooling of the heated nickel-based superalloys, treated in accordance with embodiments of the present disclosure, can be achieved using a variety of known cooling techniques known to those skilled in the art. In particular, the slow cooling rate of the described pre-weld heat treatment method can be achieved by furnace cooling. In preferred embodiments, cooling of the heated nickel-based superalloy is achieved solely by furnace cooling. Such embodiments, would be both practicable with vacuum heating methods and effective in minimizing non-equilibrium boron segregation during cooling from the thermal treatment temperature.

Pre-Weld Heat Treatment Method For Nickel-Based Superalloys

[0041] According to embodiments of the present disclosure, nickel-based superalloys can be treated to result in nickel-based superalloys comprising γ' precipitates and MC carbides, with minimized observable boride particles. As described herein, observable
5 boride particles include boride particles that are visible by known SEM imaging techniques, according to embodiments of the present disclosure. According to other embodiments of the present disclosure, nickel-based superalloys can be treated to result in nickel-based superalloys comprising γ' precipitates and MC carbides, free of observable boride particles. According to further embodiments, nickel-based
10 superalloys can be treated using methods of the present disclosure to give nickel-based superalloys comprising γ' precipitates and MC carbides, at the exclusion of boride particles.

[0042] According to certain embodiments, nickel-based superalloys are treated with a pre-weld heat treatment comprising a heating temperature of between about 1110°C and about 1130°C, a heating duration of at least about 16 h, and furnace cooling (FC).
15 In other embodiments, the pre-weld heat treatment comprises a heating temperature of between about 1110°C and about 1130°C, a heating duration of between about 16 hours to about 24 hours, and furnace cooling (FC). According to further embodiments, the pre-weld heat treatment comprises a heating temperature of between about 1110°C and
20 about 1130°C, a heating duration of between about 16 hours to about 18 hours, and furnace cooling (FC). According to other embodiments, the pre-weld heat treatment comprises a heating temperature of between about 1110°C and about 1130°C, a heating duration of between about 18 hours to about 24 hours, and furnace cooling (FC). In other embodiments, the pre-weld heat treatment comprises a heating temperature of
25 between about 1110°C and about 1130°C, a heating duration of about 16 hours, and furnace cooling (FC). According to further embodiments, the pre-weld heat treatment comprises a heating temperature of between about 1110°C and about 1130°C, a heating duration of at least about 16 h, and a cooling rate of from about 0.10°C/s to about 0.29°C/s. In other embodiments, the pre-weld heat treatment comprises a heating
30 temperature of between about 1110°C and about 1130°C, a heating duration of at least about 16 h, and a cooling rate of from about 0.10°C/s to about 0.25°C/s. According to

a further embodiment, the pre-weld heat treatment comprises a heating temperature of between about 1110°C and about 1130°C, a heating duration of at least about 16 h, and a cooling rate of about 0.12°C/s. According to a further embodiment, the pre-weld heat treatment comprises a heating temperature of about 1120°C, a heating duration of about 16 h, and furnace cooling. In another embodiment, the pre-weld heat treatment comprises a heating temperature of about 1120°C, a heating duration of about 16 h, and a cooling rate of about 0.12°C/s.

[0043] The pre-weld heat treatment method described herein can be used with any fusion welding process, such as TIG, plasma arc, laser welding, etc., any of which are known to those skilled in this art. As well, the pre-weld heat treatment method of the present disclosure can be used with hybrid welding processes. In certain embodiments, the pre-weld heat treatment method of the present disclosure can be used with laser-arc hybrid welding.

[0044] To gain a better understanding of the invention described herein, the following examples are set forth. It will be understood that these examples are intended to describe illustrative embodiments of the invention and are not intended to limit the scope of the invention in any way.

EXAMPLES

Materials and Experimental Procedures

Materials Preparation

[0045] Cast IN 738 LC (low carbon) was received in the form of plates having dimensions of 150 mm × 50 mm × 10 mm from PCC Airfoils, Ohio, USA. The chemical composition of the as-received alloy in weight percent is listed in **Table 1**. Pairs of welding coupons of dimensions approximately 75 mm x 20 mm x 5 mm were machined from the cast plates by using a Hansvedt model DS-2 traveling wire electro-discharge machine (EDM). The coupons were given the heat treatments listed in **Table 2**. The heat treatment designated SHT is “solution heat treatment,” which is the generally used pre-weld heat treatment for IN 738 superalloy. UMT (University of

Manitoba heat treatment) and NUMT (New University of Manitoba heat treatments) are pre-weld heat treatments developed by the research group of Chaturvedi and Ojo (A.T. Egbewande, H.R. Zhang, R.K. Sidhu, and O.A. Ojo, Metallurgical and Materials Transactions A, 2009, Vol. 40A, p.2695; A Thakur, N.L. Richards and M.C. Chaturvedi, International Journal for the Joining of Materials, 2003, Vol. 15, p.21, incorporated herein by reference) to minimize cracking in IN 738 superalloy. Heat-treated coupons were surface ground by using 120 grit size SiC papers to remove surface oxides that formed on the coupons during heat treatment. The pairs of welding coupons were butt-welded by laser-arc hybrid welding technique, using IN 718 as the filler alloy. The compositions of the filler alloy, which was received in the form of 0.9 mm diameter spool, is also included alongside the composition of the cast IN 738 base alloy in **Table 1**.

Table 1: Chemical compositions of the base alloy and the filler alloy (weight percent)

Element	IN 738	IN 718
C	0.11	0.05
Cr	16.09	17.3
Co	8.5	0.03
W	2.6	-
Mo	1.77	2.97
Nb	0.91	5.08
Fe	0.087	20.13
Al	3.33	0.5
Ti	3.44	0.94
Ta	1.77	-
Zr	0.033	-
B	0.01	0.004
Mn	-	0.03
Si	-	0.05
Ni	Bal	Bal

Table 2: A list of heat treatments used

Heat Treatments	
1120 °C / 2 h / AC	(SHT)
1120 °C / 2 h / AC + 1025 °C / 16 h / WQ	(UMT)
1120 °C / 2 h / AC + 1120 °C / 24 h / FC	(NUMT)
1120 °C / 2 h / FC	
1120 °C / 4 h / FC	
1120 °C / 8 h / FC	
1120 °C / 12 h / FC	
1120 °C / 16 h / FC	(FUMT)
1120 °C / 24 h / FC	
1025 °C / 2 h / FC	
1180 °C / 2 h / FC	

AC = Air-cooled, WQ = Water-quenched and FC = Furnace-cooled

[0046] The laser-arc hybrid welds were sectioned transverse to the welding direction
 5 using the Hansvedt model DS-2 traveling wire electro-discharge machine (EDM). 10
 sections were made from each of the butt welds. These were then prepared by standard
 metallographic procedures for microstructural examination and etched electrolytically
 in 12 mL H₃PO₄ + 40 mL HNO₃ + 48 mL H₂SO₄ solution at 6 volts for 5 seconds.

[0047] Cylindrical rods, 15 mm in length by 6 mm in diameter, for Gleeble
 10 simulation, were machined from heat-treated plates using the wire EDM. The surfaces
 of these specimens were also ground in order to remove surface oxides. Thermocouples
 were spot-welded on each of these cylindrical specimens at the axial centre for
 temperature control and measurement during Gleeble simulation. All simulated
 materials were sectioned in the radial direction at the location of the thermocouples,
 15 using the wire EDM. These were then prepared using standard metallographic
 techniques and electrolytically etched in 12 mL H₃PO₄ + 40 mL HNO₃ + 48 mL H₂SO₄
 solution at 6 volts for 5 seconds.

Laser-Arc Hybrid Welding

[0048] Laser-Arc hybrid butt welding of the coupons was carried out by using a robotic fibre laser-GMAW hybrid welding system at the Centre for Aerospace Technology and Training (CATT), Standard Aero Limited, Winnipeg, Canada. The parameters used for welding are listed in **Table 3**.

Table 3: A list of the laser-arc hybrid welding process settings and parameters

Parameters	
Filler Alloy	IN 718
Wire Diameter	0.9 mm
Laser Power	4kW
Arc Voltage	21 V
Arc Current	52 A
Laser Focus	-2 mm
Process Ordering	Laser Leading
Relative Position of Laser and Arc	2 mm
Welding Speed	2 m/min
Wire Feed Speed	4 m/min
Trailing Gas / Flow Rate	Ar / 40 L per min
Torch Gas / Flow Rate	He / 25 L per min
Joint Gap	0.15 mm

Gleeble Simulation

[0049] Gleeble simulation of the thermal cycling experienced by the HAZ during welding was carried out by using a Gleeble 1500-D Thermo-Mechanical Simulation System. Simulations were performed by rapidly heating the specimens at a heating rate of 150°C/s to temperatures ranging from 1120°C to 1220°C and held for different times ranging from 0.5 to 10 s, followed by air cooling.

Microscopy and Spectrometry (SEM)

[0050] The microstructures of the pre-weld, welds and Gleeble-simulated specimens were examined and analyzed by a scanning electron microscope (SEM) equipped with an Oxford (Oxford Instruments, Oxford, United Kingdom) ultrathin window energy-dispersive spectrometer (EDS) and Inca analyzing software.

Hardness Measurement

[0051] The hardness of the fusion zone of weldments was measured with a Buehler microhardness tester using a load of 300 g. The materials were polished to 1 μ m surface finish before hardness testing.

10 **EXAMPLE 1: Establishing Balance Between Equilibrium and Non-Equilibrium Boron Segregation in IN 738 Superalloy**

[0052] A balance between equilibrium and non-equilibrium boron segregation was achieved around 1037°C for nickel-based IN 718 superalloy (*X. Huang, M.C. Chaturvedi, N.L. Richards and J. Jackman, Acta Mater., 1997, Vol. 45, p.3095, incorporated herein as reference*). In IN 738 superalloy, 1120°C was found suitable for minimizing equilibrium boron segregation and effectively preventing boride formation in the alloy (*A.T. Egbewande, H.R. Zhang, R.K. Sidhu, and O.A. Ojo, Metallurgical and Materials Transactions A, 2009, Vol. 40A, p.2695, incorporated herein by reference*).

[0053] In order to establish a possible balance between equilibrium and non-equilibrium boron segregation in IN 738 superalloy at 1120°C, a welding experiment was set up for materials treated at 1025°C, 1120°C and 1180°C for 2 hours (h), followed by furnace cooling. The choice of these three temperatures was considered reasonable for two major reasons. Firstly, under furnace cooling condition, the hardness values of the materials at the three temperatures were comparable (**Fig. 1**). This suggests that the ability of the base materials to accommodate welding stress can be safely assumed to be similar. Secondly, all other phases that usually contribute to HAZ intergranular liquation, including γ' precipitates, γ - γ' eutectic and carbides, were present in the materials after the heat treatment. The cooling curve for the material

treated at 1120°C and furnace-cooled is presented in **Fig. 2**. The initial cooling rate was estimated to be around 0.12°C/s. The results of the welding experiment showed that the extent of HAZ intergranular cracking was least in the material treated at 1120°C (**Fig. 3**). Thermal treatment of IN 738 superalloy at 1025°C is known to result in formation of significant amount of boride in the alloy, due to excessive equilibrium boron segregation. The decomposition of borides, as also found by the inventors, in the UMT material that was treated at 1025°C in this work, could significantly increase the extent of intergranular liquation. Also, at 1180°C where equilibrium segregation of boron is expected to be minimal, non-equilibrium segregation could be the controlling mechanism due to the higher thermal treatment temperature. Thermal treatment at 1120°C appeared to have provided a balance between the two competing solute segregation mechanisms. Therefore, 1120°C and furnace cooling were chosen as the candidate temperature and cooling method, respectively, for the new heat treatment.

[0054] The results of the welding experiment for the furnace-cooled materials showed that, although the least cracking was obtained in the material that was treated at 1120°C for 2 h, the extent of HAZ cracking in this material was still unacceptably high. SEM microstructural analysis of the material showed that some of the borides persisted in the alloy after the 2 h heat treatment time (**Figs. 4A and 4B**). The presence of borides in the alloy after heat treatment indicates that the alloy is still highly susceptible to HAZ intergranular liquation cracking. Ability to completely dissolve the borides at 1120°C, where equilibrium segregation of boron can be effectively minimized, is desirable for the development of an effective heat treatment procedure for IN 738 superalloy. This possibility was investigated and is discussed next.

EXAMPLE 2: Dissolution of Borides in IN 738 Superalloy

[0055] The concentration profile for the dissolution of a precipitate, for example, in a binary system, may be schematically represented as shown in **Fig. 5**. Earlier analysis of the phenomenon of second phase dissolution in alloy systems have shown that, for a stationary interface approximation, the dissolution rate dR/dt can be obtained as (*H.B. Aaron and G.R. Kotler, Metall. Trans., 1971, Vol. 2, p.393, M.J. Whelan, Metal Science Journal, 1969, Vol. 3, p.95*)

$$\frac{dR}{dt} = -k \left[\frac{D}{R} + \sqrt{\frac{D}{\pi}} \right] \quad \text{Equation 1}$$

[0056] R is the radius of the precipitate, t is time, D is the volume interdiffusion coefficient (assumed to be independent of composition) and k is the supersaturation parameter, given as

$$k = \frac{2(C_I - C_M)}{(C_P - C_I)} \quad \text{Equation 2}$$

[0057] C_P is the concentration of the precipitate. C_I and C_M are the concentrations at the precipitate/matrix interface and in the matrix, respectively. Aaron and Kotler (*H.B. Aaron and G.R. Kotler, Metall. Trans., 1971, Vol. 2, p.393*) pointed out that $|k|$ is usually very small (≈ 0.1) in most alloy systems and that in this small $|k|$ limit, R becomes a slowly varying function of time. It has been suggested that the dissolution rate depends on both shape and size of the precipitate (*H.B. Aaron and G.R. Kotler, Metall. Trans., 1971, Vol. 2, p.393; M.J. Whelan, Metal Science Journal, 1969, Vol. 3, p.95*). For a planar precipitate, where $R = \infty$, dissolution rate is mainly governed by the $t^{1/2}$ term in equation 1. If $R = \infty$, then the D/R term tends to zero and does not contribute to the dissolution rate. This planar precipitate analysis can also be applied to spherical precipitates at the initial stages of dissolution, as stated by Whelan and Aaron et. al. (*H.B. Aaron and G.R. Kotler, Metall. Trans., 1971, Vol. 2, p.393; M.J. Whelan, Metal Science Journal, 1969, Vol. 3, p.95*). If the spherical precipitate is sufficiently large (large R), the precipitate/matrix interface may be approximated as being planar at the initial stages of dissolution before the precipitate becomes small enough for D/R to be significant. In this case, the dissolution rate is expected to be slow at the beginning but rapid when R becomes very small. In a more physical sense, it was suggested that the dissolution rate of a precipitate increases as the precipitate/matrix interfacial area decreases due to decrease in the size of the solute source with respect to the area of the diffusion zone surrounding it. Therefore, the kinetics of larger size precipitates is expected to be slower than that of very small precipitates. A careful observation of the microstructure of the boride phases in IN 738 superalloy in the present work showed that the particles are mostly irregularly shaped. They vary greatly in size, from sub-

micrometer sizes up to about 8 micrometer. While the smaller particles could have dissolved earlier during thermal treatment, the larger blocky ones survived for longer periods.

[0058] It should be noted that, apart from the influence of precipitate shape and size, there are other important factors that contribute to the dissolution rate. For diffusion-controlled dissolution, the diffusion rate of the slowest diffusing element may be the rate-controlling factor. The boride-forming elements in IN 738 superalloy, especially Mo and W, are known to be very slowly diffusing components of most nickel-based superalloys. The slowness in the diffusion of these elements in IN 738 superalloy could limit the dissolution rate of borides and result in very sluggish dissolution behaviour. Apart from a possible diffusion-limited dissolution, it has also been suggested that the occurrence of interface reactions that proceed slower than diffusion-controlled dissolution may limit the extent of dissolution of second phases. This has been attributed to a possible reduction in the flux of atoms crossing the precipitate/matrix interface, which reduces the actual interface concentration C_I to a value below the equilibrium interface concentration. Sluggishness in the dissolution of borides in IN 738 superalloy would result in a requirement for longer holding times at the thermal treatment temperature if the borides were to be completely dissolved.

[0059] The possible effect of holding time on the dissolution of the boride phase in IN 738 superalloy at the selected thermal treatment temperature was studied by subjecting specimens of the alloy to treatments at 1120°C for different times ranging from 2 h to 24 h. This study showed that some of the boride particles persisted in the alloy up to 12 h, showing that the dissolution behaviour of borides was sluggish indeed. For example, the SEM micrographs in **Figs. 6A** and **6B** revealed the persistence of boride phases in the alloy at 4 h and 8 h, respectively. The borides were observed to have dissolved completely in the alloy at 16 h.

[0060] In order to confirm the influence of boride dissolution on HAZ cracking susceptibility during welding and to correlate the result of the observation described above with actual welding data, IN 738 welding coupons were laser-arc hybrid welded after being subjected to pre-weld heat treatments at 1120°C for times varying from 2 h

to 24 h, followed by furnace cooling. The results are presented in **Fig. 7**, showing the dependence of HAZ cracking susceptibility on holding time at 1120°C. The least amount of cracking was realized in the material that was held for times from 16 h and above. This finding is in good agreement with the observed complete dissolution of borides in the alloy after 16 h. In addition, it should be noted that the hardness of the material did not vary with holding time at 1120°C (**Fig. 8**). This shows that the presence of borides in the materials treated for shorter time at 1120°C is a major factor contributing to HAZ intergranular cracking susceptibility in these materials. Therefore, the thermal processing of 1120°C / 16 h / FC, is chosen as a practicable and effective heat treatment for improving the weldability of IN 738 superalloy during laser-arc hybrid welding of the alloy. A comparison of HAZ cracking susceptibility in the newly developed method and the standard heat treatment (SHT) is given in **Fig. 9**, showing about 80% reduction in cracking susceptibility when the new method is used.

EXAMPLE 3: Microstructural Analysis of IN 738 Superalloy in the New Method Condition

[0061] The microstructure of the new method-treated IN 738 superalloy consisted of irregularly shaped γ' precipitates, as shown in the SEM image of **Fig. 10**. High magnification SEM analysis (inset of **Fig. 10**) also revealed the presence of very fine γ' precipitates that formed during the heat treatment. MC carbides and γ - γ' eutectics survived the new method treatment. Most importantly, no boride particles were observed in the new method material. The newly developed method treatment procedure is effective in drastically reducing HAZ intergranular cracking in IN 738 Superalloy.

[0062] The disclosures of all patents, patent applications, publications and database entries referenced in this specification are hereby specifically incorporated by reference in their entirety to the same extent as if each such individual patent, patent application, publication and database entry were specifically and individually indicated to be incorporated by reference.

[0063] Although the invention has been described with reference to certain specific embodiments, various modifications thereof will be apparent to those skilled in the art without departing from the spirit and scope of the invention. All such modifications as would be apparent to one skilled in the art are intended to be included within the scope

5 of the following claims.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A pre-weld heat treatment method for nickel-based superalloys, comprising:
 - (a) heating a nickel-based superalloy at a temperature sufficient to achieve a balance between equilibrium and non-equilibrium boron segregation in the nickel-based superalloy, wherein balancing equilibrium and non-equilibrium boron segregation results in minimized boride formation;
 - (b) maintaining the temperature of the nickel-based superalloy for a period of time sufficient to dissolve any borides formed in the heated nickel-based superalloy; and
 - (c) cooling the heated nickel-based superalloy at a rate of cooling that is slow enough to minimize further non-equilibrium boron segregation;wherein the treated nickel-based superalloy comprises γ' precipitates and MC carbides, with minimized observable boride particles.
2. The pre-weld heat treatment method according to claim 1, wherein the treated nickel-based superalloy comprises γ' precipitates and MC carbides, free of observable boride particles.
3. The pre-weld heat treatment method according to claim 1, wherein the treated nickel-based superalloy comprises γ' precipitates and MC carbides, at the exclusion of boride particles.
4. The pre-weld heat treatment method according to any one of claims 1 to 3, wherein the heating temperature is from about 1110°C to about 1130°C.
5. The pre-weld heat treatment method according to any one of claims 1 to 3, wherein the heating temperature is about 1120°C.
6. The pre-weld heat treatment method according to any one of claims 1 to 5, wherein the heating is maintained for at least about 16 hours.

7. The pre-weld heat treatment method according to any one of claims 1 to 6, wherein the heating is maintained for about 16 hours to about 24 hours.
8. The pre-weld heat treatment method according to any one of claims 1 to 7, wherein the heating is maintained for about 16 hours.
9. The pre-weld heat treatment method according to any one of claims 1 to 8, wherein the cooling comprises furnace cooling.
10. The pre-weld heat treatment method according to any one of claims 1 to 9, wherein the cooling rate is about 0.12°C/s.
11. The pre-weld heat treatment method according to any one of claims 1 to 10, wherein the nickel-based superalloy contains high volume fractions of γ' particles.
12. The pre-weld heat treatment method according to claim 11, wherein the nickel-based superalloy is IN738.
13. A method for joining a nickel-based superalloy, comprising:
 - (a) treating the nickel-based superalloy with the pre-weld heat treatment method according to any one of claims 1 to 12; and
 - (b) joining the treated nickel-based superalloy obtained in (a).
14. The method of joining a nickel-based superalloy according to claim 13, wherein the joining is by fusion welding.
15. The method of joining a nickel-based superalloy according to claim 13, wherein the joining is a hybrid welding technique.
16. The method of joining a nickel-based superalloy according to claim 14, wherein the hybrid welding technique is laser-arc hybrid welding.
17. A pre-weld heat treatment method for a nickel-based superalloy comprising the following nominal composition expressed as weight percentages: carbon 0.11%; chrome 15.84%; cobalt 8.5%; tungsten 2.48%; molybdenum 1.88%; niobium 0.92%;

iron 0.07%; aluminum 3.46%; titanium 3.47%; tantalum 1.69%; zirconium 0.04%; boron 0.012%; and the balance nickel, the method comprising:

- (a) heating the nickel-based superalloy at a heating temperature of from about 1110°C to about 1130°C;
- (b) maintaining the temperature of the nickel-based superalloy for at least about 16 hours; and
- (c) furnace cooling the heated nickel-based superalloy.

18. The pre-weld heat treatment method according to claim 17, wherein the treated nickel-based superalloy comprises γ' precipitates and MC carbides, with minimized observable boride particles.

19. The pre-weld heat treatment method according to claim 17, wherein the treated nickel-based superalloy comprises γ' precipitates and MC carbides, free of observable boride particles.

20. The pre-weld heat treatment method according to claim 17, wherein the treated nickel-based superalloy comprises γ' precipitates and MC carbides, at the exclusion of boride particles.

21. The pre-weld heat treatment method according to any one of claims 17 to 20, wherein the heating temperature is about 1120°C.

22. The pre-weld heat treatment method according to any one of claims 17 to 21, wherein the heating is maintained for about 16 hours to about 24 hours.

23. The pre-weld heat treatment method according to any one of claims 17 to 22, wherein the heating is maintained for about 16 hours.

24. The pre-weld heat treatment method according to any one of claims 17 to 23, wherein the cooling rate is about 0.12°C/s.

25. A nickel-based superalloy treated according to the pre-weld heat treatment method according to any one of claims 1 to 24, wherein the nickel-based superalloy comprises γ' precipitates and MC carbides, with minimized observable boride particles.

26. A nickel-based superalloy treated according to the pre-weld heat treatment method according to any one of claims 1 to 24, wherein the nickel-based superalloy comprises γ' precipitates and MC carbides, free of observable boride particles.

27. A nickel-based superalloy treated according to the pre-weld heat treatment method according to any one of claims 1 to 24, wherein the nickel-based superalloy comprises γ' precipitates and MC carbides, at the exclusion of boride particles.

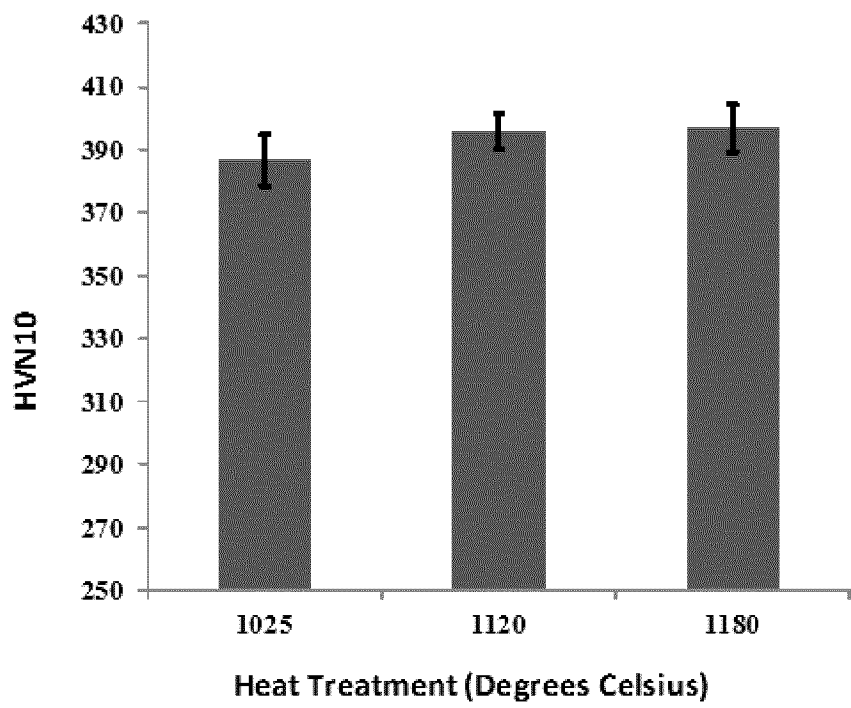
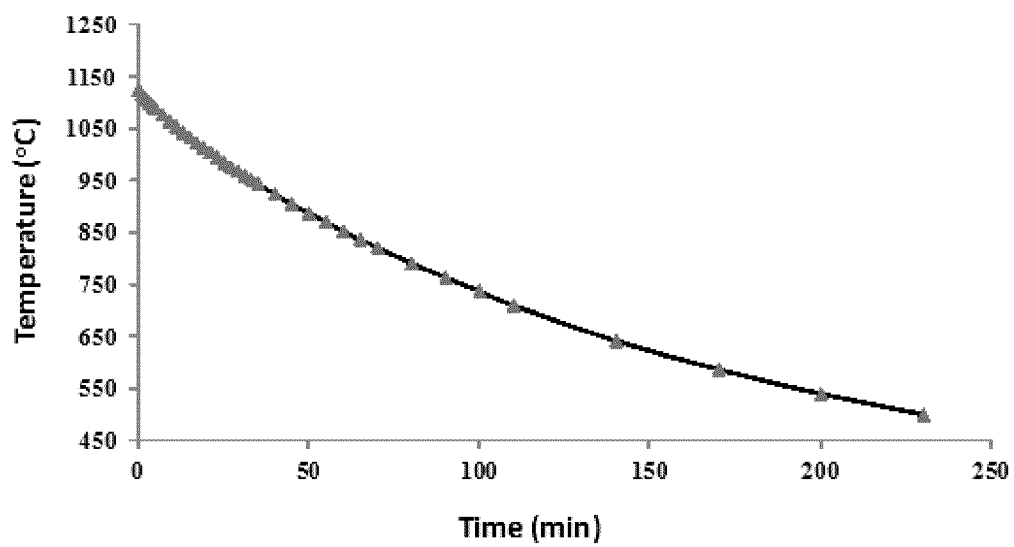


Fig. 1

**Fig. 2**

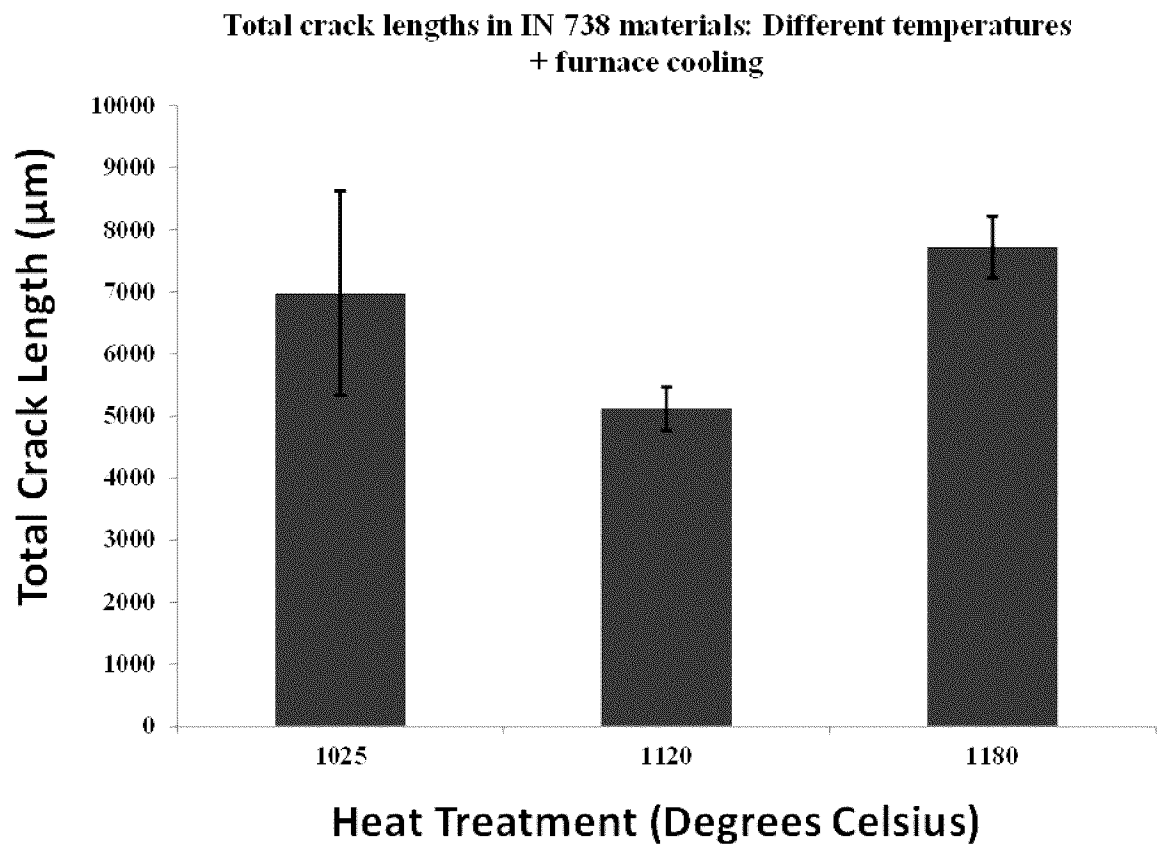
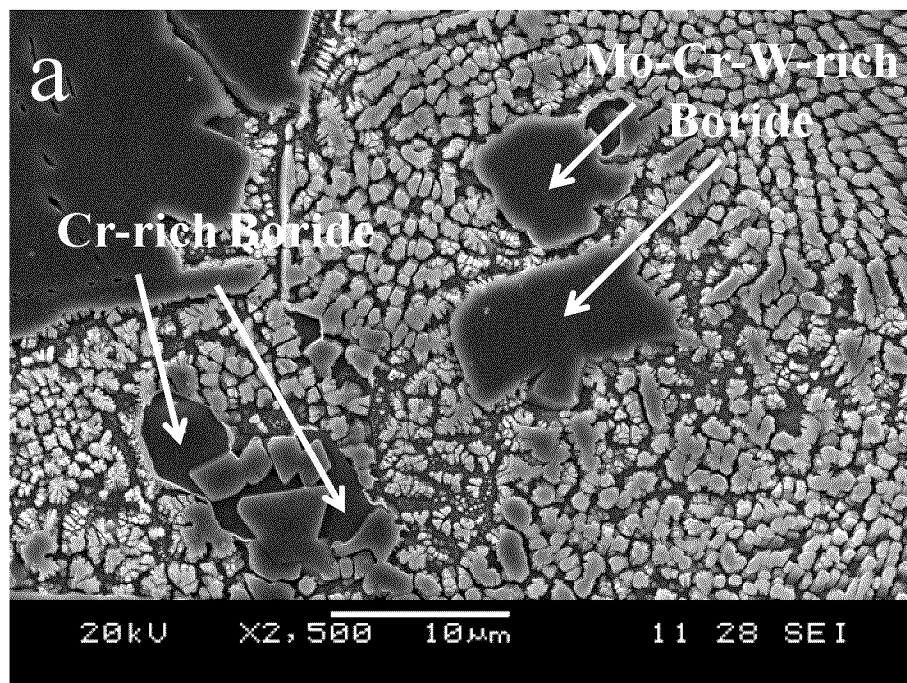
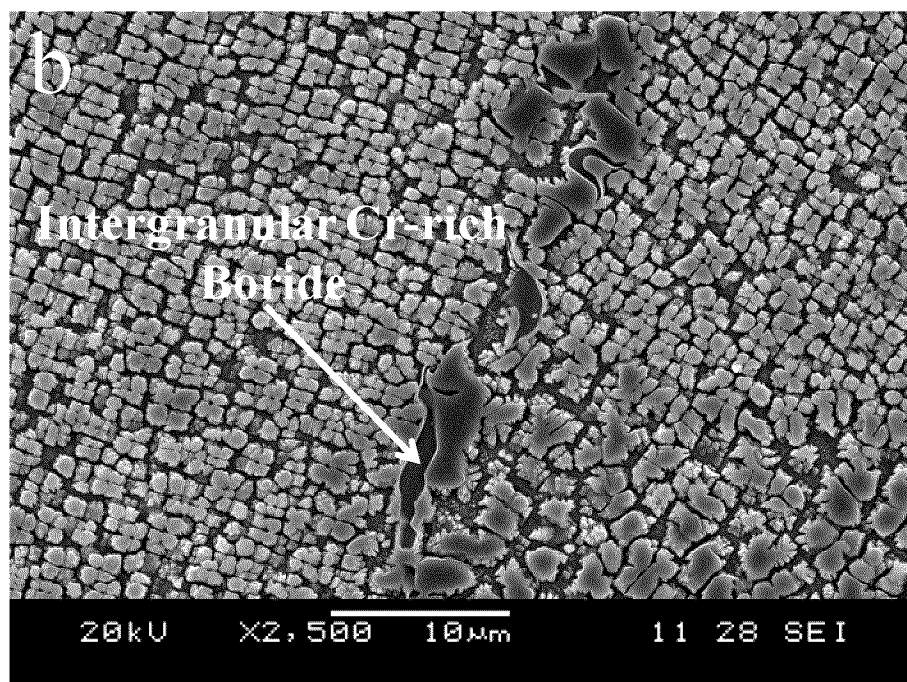


Fig. 3

**Fig. 4A****Fig. 4B**

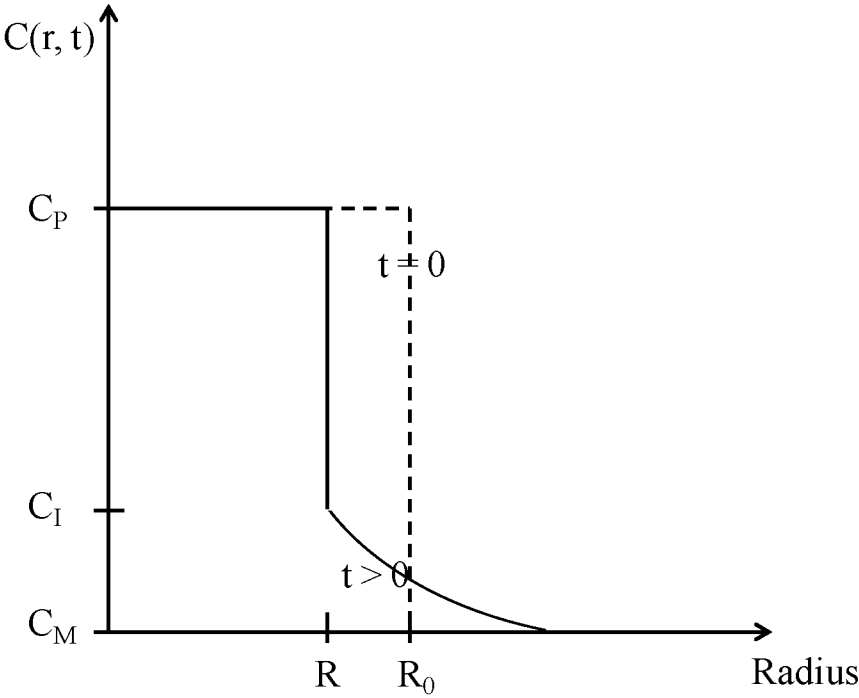


Fig. 5

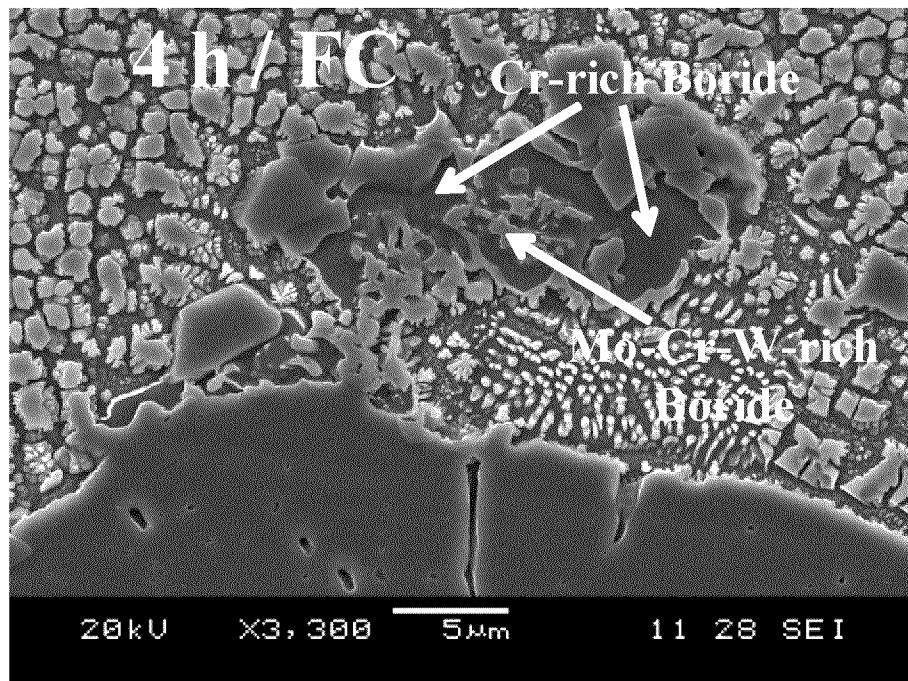


Fig. 6A

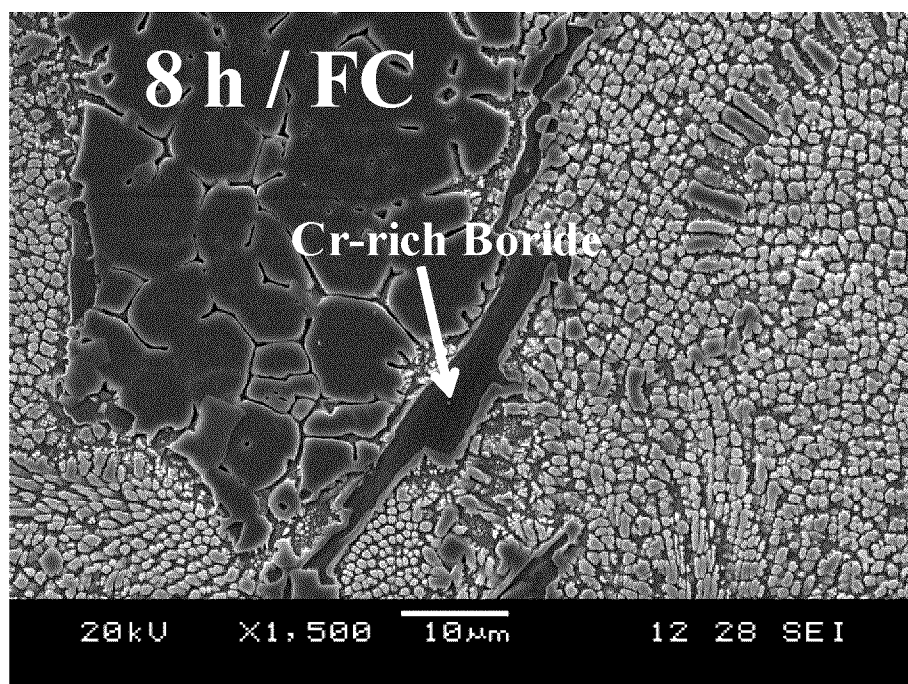


Fig. 6B

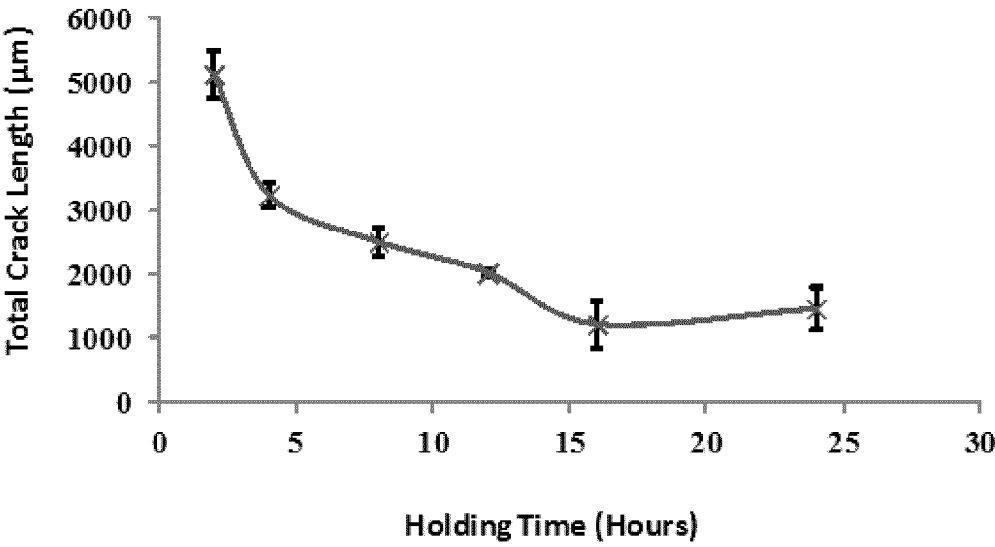


Fig. 7

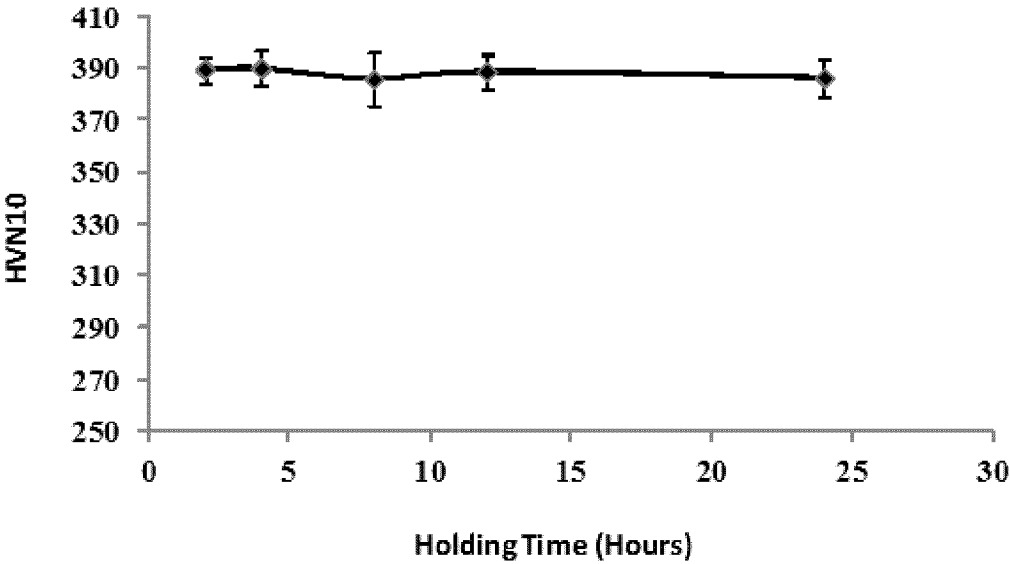
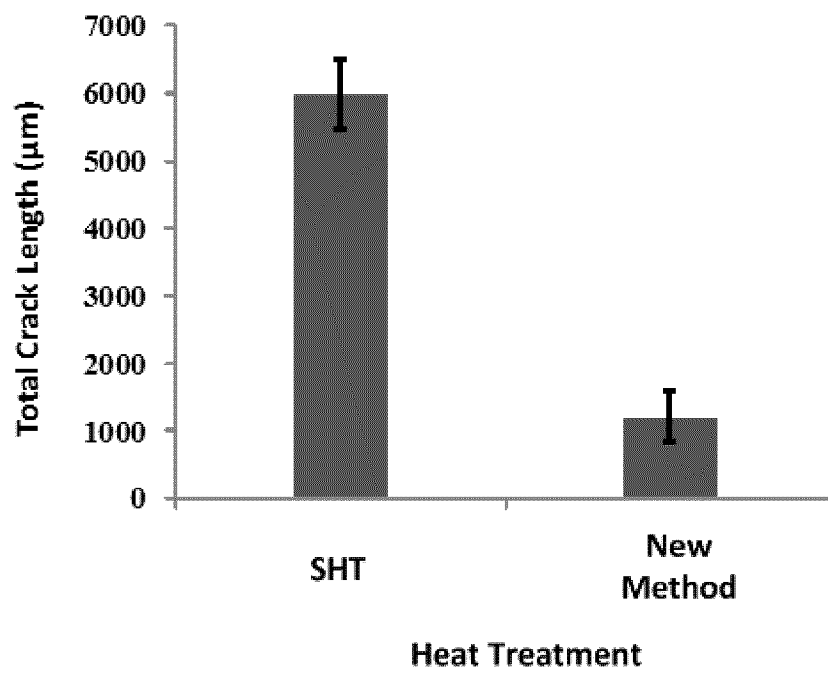
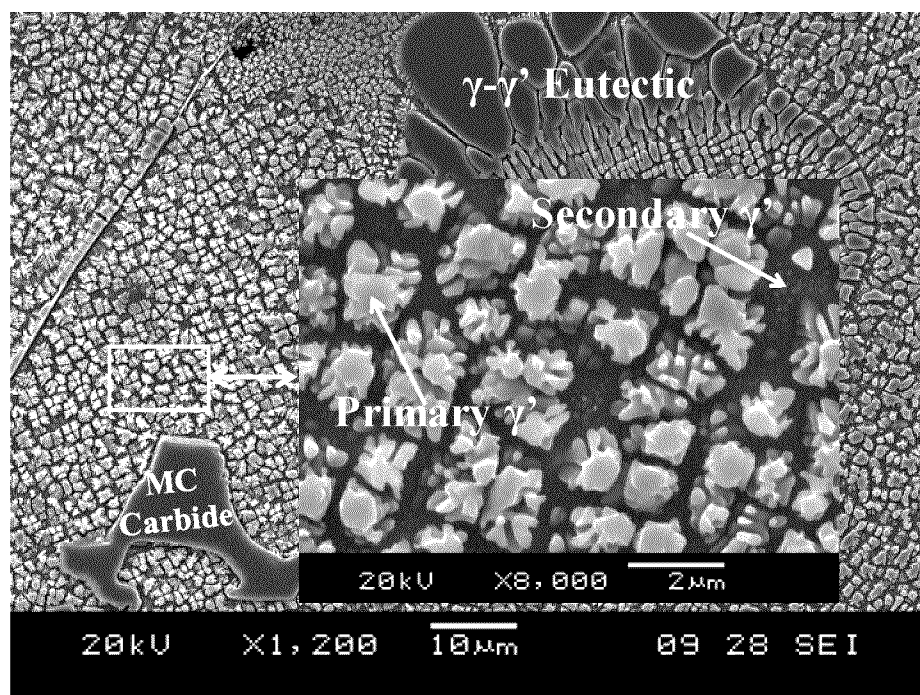


Fig. 8

**Fig. 9**

**Fig. 10**

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CA2014/050687A. CLASSIFICATION OF SUBJECT MATTER
IPC: **C22F 1/10** (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: **C22F 1/10** (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)

Databases: Totalpatent, Scopus, ScienceDirectKeywords: pre-weld, Y' precipitation, MC carbide, nickel-based superalloy, IN 738, heat treatment, boride, boron, segregation, crack, liquation, HAZ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X, P	A Study Of Laser-Arc Hybrid Weldability Of Nickel-Base Inconel 738 Lc Superalloy, OYEDELE TEMITOPE OLA, Department of Mechanical and Manufacturing Engineering University of Manitoba Winnipeg, August 2013	1-27
X	<i>Improvement in Laser Weldability of INCONEL 738 Superalloy through Microstructural Modification</i> , Metallurgical and Materials Transactions A, A.T. Egbewande, H.R. Zang, R.K. Sidhu, O.A. OjO, 2009, vol. 40A, p. 2695 *the entire document*	1-7 and 13-16
A	<i>The Effect Of B Segregation On Heat-Affected Zone Microfissuring in EB Welded Inconel 718</i> , M.C. Chaturvedi, W. Chen, A. Saranchuk, The Minerals, Metals & Materials Society, 1997	
A	US 7,653,995 B2 (Morin) 2 February 2010 (02-02-2010) *cited by the applicant*	
A	US 5,509,980 A (Lim) 23 April 1996 (23-04-1996)	

Further documents are listed in the continuation of Box C.

See patent family annex.

* "A" "E" "L" "O" "P"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance earlier application or patent but published on or after the international filing date 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) document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date claimed	"T" "X" "Y" "&"	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 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 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 document member of the same patent family
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Date of the actual completion of the international search
06 October 2014 (06-10-2014)Date of mailing of the international search report
22 October 2014 (22-10-2014)Name and mailing address of the ISA/CA
Canadian Intellectual Property Office
Place du Portage I, C114 - 1st Floor, Box PCT
50 Victoria Street
Gatineau, Quebec K1A 0C9
Facsimile No.: 001-819-953-2476Authorized officer: Patrick Mamputu
Tel.: 1-819-994-9537

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CA2014/050687**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of the first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claim Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claim Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claim Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Group A: 1-12, 17-24 and 25-27 are related to a pre-welded heat treatment method for nickel-based superalloys and a nickel-based superalloy treated according the said method; and

Group B: 13-16 are related to a hybrid welding technique for joining a nickel-based superalloy.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claim Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CA2014/050687

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
US5509980A	23 April 1996 (23-04-1996)	US5509980A SG32422A1	23 April 1996 (23-04-1996) 13 August 1996 (13-08-1996)
US7653995B2	02 February 2010 (02-02-2010)	US2009320966A1	31 December 2009 (31-12-2009)