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Understanding the "Blue Spot"

Sodium Chloride Hot Salt Stress-Corrosion Cracking in Titanium-6246 during fatigue testing at low pressure

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Abstract

During hot component fatigue tests there have been two cases of low life crack initiation of gas turbine rotating parts manufactured from the Titanium alloy Ti-6246. Both exhibited a small (~0,1mm) elliptical ,blue spot" at the origin. Through validated striation count work and fracture mechanics it was established that fatigue had propagated with a near-nil initiation life. Early investigation suggested that the ,blue spot" was possibly a region of stage 1 fatigue growth, and was therefore a material behaviour concern with potential implications for service. During an investigation of a later cracking incident in this alloy, subsequently shown to have resulted from Stress-corrosion cracking (SCC), near-identical fractographic characteristics to that seen in the "blue spot" were found that subtly differentiated it from stage 1 fatigue. Also, similar ,blue spots" have since been identified on Ti6246 Laboratory hot LCF test specimens and found to have been due to contamination by NaCl, through the application of focussed long-term EDX examination and other novel chemical analyses techniques. By the application of those techniques, fractography, and comparison against these specimens, Rolls-Royce and Imperial College London have collaborated to show that the original two component ,blue spots" were subtle examples of NaCl-related Hot Salt Stress-Corrosion Cracking (HSSCC). Such cracking has not been found to Laboratory and component tests at near-atmospheric pressure or below.

Keywords

Hot Salt Stress-Corrosion Cracking Titanium-6246 Fractography Pressure implication Novel technology application in failure analysis

1. Introduction

Titanium and its alloys spontaneously form stable and continuous surface TiO_2 oxide films on exposure to oxygen – the "passive layer" – the reason for very good protection against corrosive attack [1-3]. Even when the passive layer is broken it instantaneously heals, so long as oxygen is not prevented from reaching it [2].

In addition to this corrosion resistance, high fatigue strength to density ratios [1,3,4] have ensured titanium alloys have broad applications in aero-gas turbine engines [5, 6].

In the gas turbine, due to these properties, there is a desire to use titanium as far back in the engine and at as high a temperature as possible [5], promoting increased strength, higher temperatureresistant alloy development [5,7]. One such is the lamellar-microstructure beta (β)-forged and alpha (α)- β solution heat treated α / β titanium alloy Ti-6Al-2Sn-4Zr-6Mo (Ti-6246) [3,5,8,9], which is found in many components such as compressor discs.

Spin testing of such rotating parts is a fundamental requirement as part of the demonstration of component fatigue life [10].

Two such hot (350, 400°C) cyclic fatigue spin tests were carried out on Ti-6246 components, and found cracked in low cycle fatigue (LCF) at unexpectedly short lives. For this article only, the two tests have been labelled as ST1 and ST2.

Initial macroscopic fractographic examination at Rolls-Royce revealed tiny optically blue-coloured elliptical features of ~0,1mm dimension present at the origin of both component crack systems. These have come to be known as the "blue spot" (sometimes "blue/ grey") [11]; figure 1.

The "blue spots" were bounded by an abrupt colour change that is unconventional compared to normal ,growth-out" temper-colouration on hot cyclic fatigue fracture surfaces [12,13].

Quantitative fractography and fracture mechanics had together indicated that propagation from the "blue spot" periphery had occurred with near-nil initiation life, whilst the initial flaw size calculated via fracture mechanics [14] approximated to the "blue spot" dimension. Thus, it was considered that there was a Ti-6246 material behaviour concern with potential implications for service.

Initial investigation deemed that fractographic characteristics within the blue spot resembled microstructure ("structure-sensitive"; figure 2) [15,16]. A stress-corrosion mechanism was considered, but at the time no corrosive species were identified using the available techniques on either ST1 or ST2. It was generally commented that the crack was due to low cycle fatigue (LCF) development, but, although describing the fractographic characteristics within the "blue spot", no conclusion could be given as to its nature or cause at that time.

A collaborative PhD project was set-up between Rolls-Royce plc (Materials) and Imperial College London, which partly aimed to further understand the ,blue spot" crack initiation mechanism [11]. A number of the concepts presented herein have formerly been aired in [11], whilst this article explores other specimen and spinning rig results and related issues - as presented orally in the Sixth International Conference on Engineering Failure Analysis on 9th July 2014 (Lisbon, Portugal).

2. Fractography

Fractographic examination was carried out on a Leica DMLM Optical Microscope, and a Leo 1550 field emission gun scanning electron microscope (FEG-SEM) located in Rolls-Royce, Bristol.

2.1. Quantitative Fractography and "Near-nil Initiation Life"

Quantitative fractography via striation counting methodology [14, 17-19] carried out across the main LCF portion of both cracks established ,blue spot" formation to have occurred early in the test, and fatigue had developed from it soon after ("near-nil initiation life").

The validity of measured striation spacings with respect to macroscopic growth rate (da/dN) was confirmed by comparative counting on a corner-crack Ti-6246 LCF specimen with a known test parameters and macroscopic growth rate (via potential-difference monitoring). Striation counting is only valid above a certain value of stress-intensity range, (ΔK) [21], that being where an approximate 1:1 ratio of striation to applied load cycle is sufficiently accurate for counting to be useful within its usual bounds of error. That "valid" ΔK (above which striation counting matches actual cycles) is dependent on material and test parameters (stress range, R-ratio, temperature), and accordingly was established on the Ti-6246 corner crack specimen above. For both striation counts (on the ST1 and ST2 cracks), the corresponding ΔK values for all striation spacing measurements made above the "Engineering Crack Size" [22] of 0.76mm (0.030inch) surface length, were above that value of ΔK in the valid range. Striation counts then indicated very early development of the "blue spot" and transition to fatigue.

Supporting this, a good match of striation count data for ST1 and ST2 was found on comparison with a crack depth (a) versus accumulated cycles (N) curve ("aN-curve") separately generated via fracture mechanics [23]. Back calculation on the aN-curves from the total number of applied cycles

indicated initial flaw sizes (EIFS) of ~ 0.1 mm, which approximately corresponded to the "blue spot" dimensions, thus further supporting the conclusion of near-nil initiation life in both tests.

A Laboratory hot LCF specimen in Ti6246 "LF014" (Table 1) exhibited "blue spots" that transitioned in the same way from HSSCC to fatigue propagation. Striation counting and fracture mechanics applied in a similar way again found that propagation had occurred with a near-nil initiation life from the periphery of the ,,blue spot".

2.2. "Blue Spot" Fractography

Aside from ST1 and ST2, "blue spot" fractography was examined on numerous hot LCF test specimens – some known salt-contaminated, others not. Three of these specimens are referred to in this article (including one datum); Table 1. The ST1 and ST2 test parameters have not been related due to confidentiality reasons, though they were tested at 350°C and 400°C at low pressure (2mbar).

The "blue spots" exhibited a strongly "structure-sensitive" fractographic appearance, with primary α laths displaying a brittle/ cleaved appearance; figures 3, 4a (in some cases, separation at primary α lath boundaries to transformed β might have occurred). Secondary α also appeared cleaved, whilst fracture through transformed β had a more ductile nature. This gave rise to a "brittle structure-sensitive" descriptive, though the cleaved nature of the primary α laths may be considered as "translamellar cleavage" alluded to previously [24-26]. For further examples and description refer to [11].

This brittle fractographic appearance has formerly been linked to hot-salt stress corrosion cracking in titanium alloys [11, 24-26]. Very similar-appearing fractography had been observed by the authors on a known case of stress-corrosion cracking that had occurred later to the ST1 and ST2 tests, which provided recognition through comparison; figure 4b.

On occasion, a nodular oxidation/ corrosion product was visible on the surface, obscuring underlying fractography - indicative of an environmentally-assisted crack nucleation system [11].

The appearance of the "trans-lamellar cleavage" fracture mode only *subtly differs* from that of "structure-sensitive" stage 1 fatigue propagation, so recognition of the fracture type was enhanced by viewing transitions from "trans-lamellar cleavage" to fatigue within the same field of view; figure 5.

There was variation in the clarity of the "trans-lamellar cleavage", which is proposed to be in part related to the microstructure at the location of fracture (the scale of the primary α lath dimensions and the quantity of transformed β), and also in part related to the level of corrodant initially present and the extent of its reaction (being temperature-dependent). This makes recognition more difficult in some cases – as was found within the ST2 blue spot; figure 6.

Optical (microscopic) multi-focus fractographic imagery on the blue spot origins (200x, 500x), established a link between the blue colouration and the "brittle structure-sensitive" characteristics observed with electron optics; figure 7. The demarcation between the two fractographic types ("translamellar cleavage" to fatigue) was also visible as the blue colouration periphery seen optically.

Certain test specimens exhibited macroscopically visible ,patches" of deposit/ residue on the sideface immediately adjacent to the blue spot fracture surface; figure 8. These patches were often semielliptical in appearance (possibly ,splash" or ,droplet" related), not necessarily positioned centrally to the "blue spot". Corrosive-reaction product or sometimes pitting could be observed within the patches; figure 8(b).

Such patches were not optically visible adjacent to either the ST1 or ST2 "blue spots", but as these components had been cleaned in preparation for prior non-destructive examination, they might have been removed. This is an aspect that made original "blue spot" diagnosis more difficult.

"Blue spot" fractography sometimes appears within more conventional hot LCF growth-out temper colouration. This was clear on specimen LCF133, where brittle "trans-lamellar cleavage" was seen optically to a depth of 0.23mm, whilst blue to straw colouration was exhibited beyond the transition into conventional fatigue; figure 7(c). This is a potential cause for future confusion in identifying HSSCC against conventional fatigue growth-out cracking.

The non-salt-contaminated datum specimen (LCF127) showed only expected fatigue ,growth-out" temper colouration; brittle "trans-lamellar cleavage" characteristics were not observed.

3. Energy Dispersive X-ray Analysis (EDX)

SEM EDX was carried out on an Oxford Instruments INCA X-ACT system on the Leo 1550 SEG-SEM (in Rolls-Royce, Bristol), unless otherwise stated. Secondary electron images in figures 9-11 were taken on a Zeiss Auriga FEG-SEM at Imperial College.

EDX analysis on the side-face patches adjacent to the test specimen blue spots has revealed a chlorine presence [11].

Close examination of ST1 identified a tiny ,surface-negative" area (pit) of $12x21\mu m^2$ on the sideface immediately adjacent to the fracture surface blue spot; figure 9. Although no residue patch was observed, it is probable that the previous cleaning had removed it to expose a pit.

SEM-EDX analysis on the Zeiss Auriga FEG-SEM in Imperial College identified depleted titanium (Ti), and elevated oxygen (O), chlorine (Cl), sodium (Na) and trace calcium (Ca) within this surface negative area; figure 10 (x-ray dot maps) and figure 11 (semi-quantitative results).

The above instigated a more focussed search for chlorine on the blue spot fracture surfaces. This included (i) overnight (16 hours) x-ray mapping at low accelerating potentials (7.5KV, 10KV), and (ii) semi-quantitative line scans through and beyond the blue spot transition into fatigue.

The long-duration EDX maps identified an oxygen presence, and faintly chlorine, that matched blue spot dimensions optically; figure 12, and in [11]. The more commonly-applied, shorter duration, higher potential EDX dot mapping did not reveal these elements.

The semi-quantitative line scan paths as carried out on specimen ST2 are depicted in figure 13.

Figure 14 graphically depicts the results. A distinct change either side of the blue spot periphery was identified for each element studied (despite scatter): A notable drop in O concentration, and a near-matching converse increase for Ti, whilst Na, Cl, K, Ca, and Mg existed in trace levels within the blue spot - dropping to zero or near-zero after transition.

The ST1 ,blue spot" was analysed at Imperial, with very similar findings; figure 15.

Trace levels of Mg, Ca and K, in addition to Na and Cl, on the blue spot fracture surface suggested possible human contact in association with the original surface corrosive media. The 4 chief mineral elements in solutes derived from human perspiration are as in Table 3 [27].

As no corrosive media side-face ,patches" were found either on ST1 or ST2, bar the tiny surface pit on ST1, it is plausible that such had been cleaned off or been difficult to see prior to cleaning-circumstantially, this further suggests possible original human fingerprint contamination.

Similar analyses were performed on the known salt-contaminated LCF test specimen LCF133, with similar findings; figure 16. Mg, Ca and K were not identified in semi-quantitative EDX analysis of the blue spot fracture surface, for in that case NaCl had been applied in a purer form (not human perspiration derived).

A full repeat EDX study of the non-salt-contaminated datum specimen (LCF127) origin did not find evidence of Na, Cl, Mg, Ca or K.

4. Focussed Ion-Beam with Secondary Ion Mass Spectrometry (FIB-SIMS) of the Specimen Side-face Patches

FIB-SIMS dynamic depth profiling experiments were performed using a FEI FIB200-SIMS microscope at Imperial College as shown in figure 17 and as described in [11].

The methodology used for interpretation of the side-face patches adjacent to the fracture surface blue spots is described in [11], although brief salient features are re-produced here:

Ions were sputtered from the sample surface by bombardment with gallium ions (with 30keV energy) from a liquid metal source. Innovatively, the system was operated such that positive and negative sputtered ions could be detected simultaneously – the former by a FEI FIB200-SIMS detector, the latter by a Hiden EQS1000 system [11, 28].

All sites subject to FIB-SIMS compositional analysis were pre-sputter cleaned using the FIB-SIMS primary gallium ion beam at a current of 20nA (figure 17a). This cleans up the upper layers, so that initial data coming from the trenches can be judged uninfluenced by contamination. A series of trenches (depth profile craters), each of dimension 2 x 50 μ m (depth at least 1 μ m), were then FIB-milled with a 3nA gallium ion beam. The trenches were closely spaced (2 μ m) through the side-face patches (initial 40 μ m depth), then with increasing separation (10 μ m) beyond; figure 17b.

A second set of trenches were milled >1mm from the original set, to allow datum resultcomparison. Bulk mass spectrum analysis and baseline data was also obtained remote from the blue spot area [11]. The experimental methodology, including reason for the trench dimension selection, is described in detail in [11].

For ST1, LCF133 and other specimens [11], elevated ¹⁶O⁻, ³⁵Cl⁻, and ²³Na⁺ ions were identified in the profiles close to the fracture surface within the side-face patches (figure 18), although not found for specimen ST2. The same procedure on the control specimen LCF127 did not identify any significantly elevated ³⁵Cl⁻ or ²³Na⁺ compared to the datum trenches.

5. Energy Dispersive X-ray Analysis by Scanning Transmission Electron Microscopy (STEM-EDX) on Fracture Surface FIB "Lift-outs"

TEM foils were produced from the blue spot fractures of samples ST1, ST2, LCF133 and LCF127 (datum) using a focussed ion beam (FIB) lift-out technique at Imperial College using a dual beam FEI Helios NanoLab 600 with the primary Ga⁺ beam. The method is shown in figure 19, and described more fully in [11]. Foils were extracted from the ,blue spot" fracture surface, with results compared against foils lifted from the remote fatigue surface [31, 32].

The foils were then subject to STEM-EDX, focussing on the surface layer beneath the protective platinum layer – via mapping and semi-quantitative line scans. In [11] the surface layer was shown as an oxide film with an approximate 1:2 Ti:O atomic ratio (suggesting TiO₂), also containing chlorine less than 1% atomic weight.

The EDX maps demonstrated the oxide film to have variant thickness but typically \sim 200nm (figure 20), occasionally dropping to \sim 50-100nm. Chlorine was partly intermingled and lying immediately beneath the oxide layer (figure 20), suggesting the Cl presence to be a result of a reaction process, not post-contamination. Line scans through the oxide into the parent microstructure confirmed elevated O, Cl, with traces of Ca, K and Mg (figure 20).

Figure 20 (d) and (e) shows the elements O, Cl, Na, Mg, K and Ca present and confined to the oxide layer within the ST1 blue spot. Na and Cl rose to 1.3-1.4% with an additional peak toward the oxide layer base, dropping to ~0% in the parent material.

Similar findings were established on foils extracted from ST2 and LCF133. Furthermore, foils lifted from (1) fatigue remote from the blue spots, and (2) the fatigue origin of specimen LCF127 (datum), did not show evidence of elevated Cl, and had much lower oxide thickness (~20nm).

It is not the intention of this article to discuss the reason for the blue colour, though it is postulated that it may relate to the mix of Cl within the oxide layer, in addition to thin film interference effects.

6. Discussion – Mechanism and Chemistry

The proposed reaction chemistry behind the $HSSCC_{NaCl}$ mechanism is described within [11], as largely derived from interrogation of previous research [2,6,11,33-39]. It is considered that the HSSCC mechanism generates a level of hydrogen-embrittlement [6,11,33,34,37-39]. Very low levels of Ca, K (and trace Mg) in addition to Na/ Cl, combined with observational difficulty of corroded patches on specimens ST1 and ST2, suggest human contact (perspiration, fingerprints) might have initially caused contamination with ultimate fatigue initiation-life reduction.

For the purpose of this article, a much-shortened version of the chemistry explanation follows:

At temperatures >~550F (~290°C) for similar disc alloys to Ti6246 [1,2,34,40], a patch of salt (NaCl) can react with the protective surface oxide to form sodium titanates (eg Na₂TiO₃) and hydrochloric acid (HCl) [11,35,39, 41]. On breaking this passive layer, un-oxidised titanium beneath the patch may react with the HCl, producing titanium-alloy chlorides and atomic hydrogen that can ,charge" the parent [2,11,34,35,39,42]. Thermodynamic analyses indicate that HCl preferentially attacks aluminium and tin in the alloy [39,43,44], generating more hydrogen than from attack of the titanium alone [39].

Ti-alloy chlorides then react with moisture (H_2O) to produce Ti, Al and Sn oxides over the reaction site, and further HCl [33,34,39]. This is a looping pyrohydrolysis reaction where HCl generated can continue to react with exposed titanium, producing more hydrogen [11,39].

In this situation, the balance of hydrogen-charging versus the diffusion into the bulk material (dilution) favours charging and the material becomes locally embrittled. If applied tensile stress overcomes the resulting reduced fracture toughness, then cracking takes place [2,11,33]. This is the initiation of the hot salt stress corrosion crack.

Continuation of the looping reaction embrittles the crack tip with further hydrogen, and cracking advances as long as the applied stress-intensity exceeds locally reduced fracture toughness at the crack tip [11,33], leaving a brittle fractographic appearance [2,11,24-26,33,34] and a layering of corrosion by-products away from the reaction surfaces (titanium-alloy chlorides, sodium titanate, then oxides such as TiO₂) [11,34,35,39]. It follows that if the pyrohydrolysis reactions are going to produce HSSCC then it should occur early in a test when the reactions are likely to be at their most vigorous, or not all, consistent with striation evidence and Fracture Mechanics analysis.

In a simple experiment to assess thermodynamic favourability of these reactions, Ti-230 alloy plates were immersed overnight in a mixture of NaCl and TiO₂ at temperatures of 450°C and 500°C. On removal, a yellow-tinged deposit at localised sites indicated reaction (figure 21), similar to that seen in [35]. Although Na₂TiO₃ was not directly identified in the deposit by EDX analysis, it consisted of a mix of Ti, O, Na, Cl and other alloy elements (Cu, Fe). Of particular note is that subsequently scraping off the sample deposit areas initiated a reaction with airborne moisture consisting of gaseous bubbling and a black deposit, as per [40] (EDX: richer in Cl), with subsequent pit formation (figure 21). The level of reaction was more vigorous following 500°C exposure than at 450° C.

HSSCC cracks usually have a finite area, indicating exhaustion of original corrodant supply and of the consequent reaction chemistry with H-production tailing off. A potential explanation is as follows: At 450°C, there are five Ti6246-alloy chlorides [11,39,45], which react with water to form

oxides over the reaction site. Three of these chlorides are vapour and can progressively escape, especially as the corrosion crack growth exceeds the reaction site that initiated it: Combined with an increasing crack area (dilution), this reduces HCl concentration, reaction rate and consequential H-charging at any given point on the crack tip. Local fracture toughness in the embrittled zone rises and, when it exceeds the stress intensity at the HSSCC crack tip, the mechanism halts. Transition to LCF then occurs if the crack tip stress-intensity amplitude ΔK is large enough for fatigue to progress. This is thought to explain the often-observed abrupt transition from HSSCC to LCF (eg. figure 5).

There is an alternate hot reaction – that of Ti-alloy chlorides with oxygen (O_2) to form Ti-alloy oxides, predominantly TiO₂, and Cl₂ - neither HCl nor hydrogen [11,39]. At typically elevated engine operation pressures (higher oxygen partial pressures), that reaction is favoured over the pyrohydrolysis one such that HCl-formation diminishes. Consequently, the balance of hydrogen-charging versus diffusion away favours the latter, and the material does not attain a sufficient level of embrittlement to crack under prevailing tensile stress and HSSCC does not occur.

The above is supported by Cranfield University data from 1994 [39], which showed notable improvements in the life of salt-coated Laboratory LCF specimens with increasing pressure [39], depending on applied stress; eg. figure 22.

A hydrolysis reaction of remnant Ti-alloy chlorides, from the high temperature reactions, can also occur at room temperature [35,41], but the H-charging rate is likely to be relatively slow [35]. Although diffusion away from the local concentration is also likely to be slower, the material does not achieve a sufficient level of embrittlement to lead to cracking when next loaded, and the stress-corrosion cracking process is suppressed.

The above explains why $HSSCC_{NaCl}$ is not observed in engine service, but is confined to Laboratory specimen and component spin rig tests at atmospheric pressure and below [1].

7. Conclusions

Small (~0,1mm across) optically blue or blue/ grey features ("blue spots") at LCF origins of two Ti-6246 alloy hot cyclic fatigue spin tests, not formerly explained, have now been understood via the collaboration of Rolls-Royce (Industry) with Imperial College (Academia) by combining elements of classical failure analysis with developed existing and novel technologies. Repeatability, despite some variability, of results from "blue spot" LCF laboratory test specimens and negativity in datum (non-contaminated) samples, has lent confidence to the conclusion:

- The "blue spots" were due to a hot salt stress-corrosion cracking mechanism that stemmed from small surface sodium chloride (NaCl) contaminant deposits - HSSCC_{NaCl}. Transition to conventional low cycle fatigue (LCF) occurred at ~0,1mm depth, relating to exhaustion of the original contaminant reaction chemistry.
- 2. Propagation from the "blue spot" had occurred with a near-nil initiation life, as demonstrated by validated striation counting combined with fracture mechanics logic.
- Advocated by focussed EDX work, STEM-EDX measurements on TEM foils FIB lifted from blue spot fracture surfaces found a relatively thick ~200nm TiO₂ surface layer, with trace Cl mixed within and underneath the layer (confirming a process of corrosive-reaction chemistry, not post-contamination).
- 4. Evidence supported probable original contamination by ,human touch" (eg fingerprint).
- 5. Previous research interrogation shows hot reaction chemistry of NaCl with titanium alloys that generates hydrogen as a consequence of a looping pyrohydrolysis reaction at high temperature and "low" pressure. Fracture toughness is locally reduced by hydrogen-charging, and if

sufficiently low, cracking occurs under applied tensile stress - resulting in brittle trans-lamellar cleavage fractography (HSSCC).

6. Proposed lack of implication for the HSSCC_{NaCl} mechanism in operation under the high pressures of the gas turbine environment is based on an alternate hot reaction chemistry with O₂ occurring at increased oxygen partial-pressures that does not generate hydrogen (competing with the pyrohydrolysis reaction). In this way the hydrogen charging rate slows, insufficient to allow HSSCC.

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8. Tables

Table 1. LCF test parameters of samples referred to in this article; test temperature (T), maximum stress amplitude (σ_{max}), number of cycles to failure (N_f) and R ratio ($\sigma_{min}/\sigma_{max}$). All were tested at atmospheric pressure. Specimen "LCF133" was supplied by Rolls-Royce Derby (Elton Road), and "LF014" by Rolls-Royce Deutschland.

Label	Т	σ_{max}	N_{f}	R	Form	Environment
"LCF133"	450°C	560 MPa	4474 cycles	0	LCF (Cylindrical	Deliberately NaCl-
			broken		form)	contaminated.
"LF014"	450°C	600 MPa	9757 cycles	0.1	LCF (Bowtie	Intended as clean. Pressure
			broken		form)	atmospheric
"LCF127"	450°C	640 MPa	50882 cycles	0	LCF (Cylindrical	Datum – Not salt-
			broken		form)	contaminated.

{*Note for editor – Table 2 is embedded within figure 11*}

Table 3. Average levels of the 4 chief elements identified in human perspiration [27].

Element	g/l		
Na	0.9		
K	0.2		
Ca	0.015		
Mg	0.013		

9. Figure Captions

Figure 1 - (a) A "blue spot" may be seen in this optical image of the ST1 crack origin on the fracture surface, located where an aligned alpha lath colony met the surface shown by the fern-shaped region of growth. Such microstructural features are not uncommon in this material (others may be seen in the image, without "blue spots"). (b) Schematic of the area highlighted in (a). "Blue spots" in other specimens (including ST2) were not located at aligned alpha lath colonies or other particular microstructural feature.

Figure 2 - (a) Optical micrograph of typical microstructure of Ti-6246 (in this case an aligned α colony at a prior β grain boundary can be seen), and (b) a secondary electron image of "structure-sensitive" growth.

Figure.3 - Secondary electron image showing the "brittle structure-sensitive/ trans-lamellar cleavage" fracture appearance of the ST1 origin "blue spot" region.

Figure 4 - Secondary electron images of the "brittle structure-sensitive" or "trans-lamellar cleavage" appearance in (a) the ST1 origin "blue spot" region, and (b) a known stress-corrosion crack in Ti-6246 at the same magnification (on that occasion associated with silver chloride, and occurred after the initial investigation work on ST1 and ST2).

Figure 5 - Transition between "trans-lamellar cleavage" and stage 1 fatigue seen in the same field of view-highlighting the difference in fractography type: (a) From the other ,known SCC in Ti-6246" in figure 4 – "trans-lamellar cleavage" lower left, and fatigue upper right. (b) From specimen LCF133 – the more brittle "trans-lamellar cleavage" over the majority of the image transitions to a ,softer"-appearing structure-sensitive fatigue in the upper left corner.

Figure 6 - Secondary electron image of fracture appearance within the test ST2 "blue spot". The "trans-lamellar cleavage" appearance in this case has less clarity than was observed in ST1 (refer to figure 4).

Figure 7 - (a), (b) ST1 and (c), (d) ST2 fractography with optical images and superposed secondary electron images. In ST1, the blue spot was co-located at an aligned alpha-colony aspect, but this was not an aspect of the others shown here. (e), (f) Specimen LCF133. The actual "blue spot" occurs within a region of normal hot LCF growth-out temper colouration, with "trans-lamellar cleavage" visible both optically and in electron optics.

Figure 8 - (a) Example of a specimen side-face ,patch" adjacent to a fracture surface "blue spot" – specimen LF014 tilted to show both the fracture surface (including the blue spot) and side-face. (b) Optical view of the LF014 ,,blue spot" on the fracture surface, which appears blue-grey centrally with a pit.

Figure 9 - (a) Secondary electron image of the ST1 specimen side-face surface (lower image half) with the blue spot on the fracture surface at high incline (upper image half). A surface negative area (pit) can be seen in darker contrast to the surrounding normal etched surface. (b) Imperial College false colour topographic image via light interferometry mapping of the ST1 specimen side-face showing surface negativity (-2 μ m) of this area in blue.

Figure 10 - EDX x-ray dot maps on specimen ST1 side-face pit. (a) Secondary electron image of the area mapped, with maps for (b) Ti K α (depleted), (c) O K α (elevated), (d) Na K α (elevated), (e) Cl K α (elevated), and (f) Ca K α (trace).

Figure 11 and Table 2 - Semi-quantitative EDX spot analyses within and outside the ST1 pit. Enrichment of O and depletion of Ti with low levels of sodium and chlorine confirmed (with some Na outside the pit at a lower level).

Figure 12 - (a) and (b) Blue spot fractographs compared against low potential long term duration SEM-EDX dot maps for ST2: (c) Ti K α , (d) O K α and (e) Cl K α . Although faint, the oxygen ,marks out" the blue spot shape, with tentative Cl visual evidence.

Figure 13 - Depiction of the semi-quantitative EDX line scan directions across the specimen ST2 , blue spot". The blue line depicts the optically blue periphery, and the brown line the periphery of a surrounding narrow dark straw-coloured band. Compare with optical image; figure 7b.

Figure 14 - 20KV EDX semi-quantitative analysis line scans through the ST2 blue spot –in weight %. Percentages given are based on numbers of x-rays emitted from the electron beam penetration volume (not a precise interpretation of surface layer composition). Either side of the blue spot periphery, (a) O drops from 15-25% to 12-20%, Ti from 50-60% to 60-70%, (b) Cl and Na drop ,,dramatically" from 0.05-0.25% to near 0%, and (c) trace K, Ca and Mg drop to near 0%.

Figure 15 - 20KV semi-quantitative EDX line scans through the ST1 ,blue spot" (marked in grey) in atomic %, for (a) Na and Cl, (b) Na, Mg, K and Ca, all existing at low levels in the blue spot, dropping to near-zero after its periphery.

Figure 16 - Graphical display of 20KV semi-quantitative EDX line scans through a LCF133specimen blue spot fracture surface - for Na and Cl only: Both were detected to percent fractions within the blue spot, but dropped to near-zero beyond.

Figure 17 - FIB-SIMS dynamic depth profiling for chemistry-interpretation, applied here to the specimen ST1 side-face surface feature (patch) adjacent to the fracture surface blue spot. (a) Shows the pre-sputter cleaned area. (b) Shows the trenches (depth profile craters). The location of the TEM ,,lift-out" foil (as described in section 5) on the fracture surface can be seen in both images.

Figure 18 - Sputtered secondary ion profile FIB-SIMS data from specimen ST1 plotted against distance from the ,blue spot" fracture surface (in μ m), with each measurement point taken from the base of individual trenches. The profiles are: (a) ¹⁶O⁻ and ³⁵Cl⁻, (b) ²³Na^{+/16}O⁻ and ³⁵Cl⁻, with elevation for each over the initial 10µm from the fracture surface. Ambient oxygen can enhance positive secondary ion yield [11, 29, 30], so the ²³Na^{+/16}O⁻ ratio has been used to account for increased oxygen content in the initial 10µm from the fracture surface - elevated ²³Na⁺ remains apparent.

Figure 19 - Producing a "lift-out" foil from the blue spot fracture surface: (a) A platinum-containing layer is initially deposited with the FEI Helios NanoLab 600 gas injection system - this protects the area of interest underneath from the FIB beam. (b) Material is FIB-milled around the protected area to a depth of several microns. (c) An omniprobe needle is platinum-welded to the potential foil following FIB milling around the periphery bar a small ligament – which is then cut to allow foil removal. (d) The foil is welded to a TEM omniprobe grid, and then further thinned by FIB milling to allow electron passage (three stages of thinning may be seen - with microstructure visible in the thinnest area (~150nm).

Figure 20 - (a) TEM electron image of an example area from a specimen ST1 blue spot fracture surface ,lift-out" foil – with ~200nm oxide film. The spots indicate the semi-quantitative EDX line scan path. (b) O K α EDX map displaying the oxide layer. (c) Cl K α EDX map showing ,intermingling of low level Cl through and underneath the oxide layer. The Pt layer is also visible (green) because there is a Pt M_{III} line of similar excitation energy (2.65keV) and intensity to the Cl K α

peak (2.62keV) [11]. Semi-quantitative line scan results in atomic % are shown for (d) O and Cl, and (e) Na, Mg, K and Ca. The grey area indicates the oxide film.

Figure 21 - Optical images of yellow-tinged reaction product on Ti-230 alloy plate by NaCl following overnight exposure at 450°C - beneath individual NaCl crystals ((a) and (b)). (c) Also shows a darkened pit in the upper half of the image that formed where the reaction product came away – this was richer in Cl (with very little Na) than the yellow material. Compare ref 35 figure 1.

Figure 22 - Demonstrating significant improvements in life with pressure for salt-coated LCF specimens (on alloy IMI834 at 500° C) – from work at Cranfield University in 1994 [39]. Two lines for two different applied stress conditions (560 and 580 MPa) are shown.



Figure 1b Click here to download high resolution image











Figure 4b











30µm

Understanding the "blue spot": sodium chloride hot salt stress-corrosion cracking in titanium-6246 during fatigue testing at low pressure



EHT 15.00 kV WD = 17mm Signal A = SE2









30 µm

EHT 20.00 kV WD = 9mm Signal A = SE2

Figure 8a Click here to download high resolution image





Figure 9a Click here to download high resolution image









	Composition – Atomic %											
	Ti	Al	Sn	Zr	Mo	0	Cl	Na				
1	24	4.5	0.2	1.0	0.5	67	0.7	1.8				
2	15	3.2	0.1	1.0	1.0	76	0.7	3.2				
3	24	4.9	0.3	0.9	0.4	67	0.9	1.7				
4	41	5.7	0.4	1.5	0.3	50		0.9				
5	44	4.7	0.5	1.9	2.2	46	-	0.6				
6	45	7.0	0.5	1.5	0.4	45	-	0.5				

Figure 12a Click here to download high resolution image

Understanding the "blue spot": sodium chloride hot salt stress-corrosion cracking in titanium-6246 during fatigue testing at low pressure



Optical



















Figure 15a Click here to download high resolution image



Figure 15b Click here to download high resolution image





Figure 17a and b Click here to download high resolution image



Figure 18a Click here to download high resolution image



Figure 18b Click here to download high resolution image



















Figure 20d Click here to download high resolution image











Figure 22 Click here to download high resolution image

