Environmentally assisted fatigue crack nucleation in Ti-6Al-2Sn-4Zr-6Mo

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Abstract

An unexplained feature was observed at the fatigue crack origin of a number of α/β titanium specimens tested at 450 °C in the low cycle fatigue regime. The origin was discoloured blue but this was not a result of temper colouration; this feature sometimes resulted in large reductions in fatigue lives. A number of specimens were examined to determine the cause and formation mechanism of these “blue spots.” This feature was associated with elevated oxygen and chloride levels and the presence of sodium. A mechanism based on hot-salt stress-corrosion cracking is proposed and the implications for service components are discussed.

Keywords: A. titanium, B. STEM, B. SIMS, C. hot corrosion, C. stress corrosion, C. oxidation

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1. Introduction

Titanium alloys are widely used in the fan and compressor of aerospace gas turbines, owing to their good specific fatigue strength and low occurrence of intrinsic defects, such as the ceramic inclusions or gas porosity present from melting that occur in many of the major industrial alloys [1, 2]. Titanium alloys typically possess very good corrosion resistance in most circumstances, which makes them attractive in a variety of static applications in the aerospace and chemical process industries [3].

The prototypical titanium alloy, Ti-6Al-4V, has historically seen very wide utilisation in the cooler sections of gas turbines. Of the other two main classes of alloys, near-alpha alloys such as Ti-6Al-2Sn-4Zr-2Mo-0.1Si and IMI834¹ are used in high temperature applications such as high pressure compressor discs, whilst

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¹IMI834: Ti-5.8Al-4.0Sn-3.5Zr-0.7Nb-0.5Mo-0.35Si-0.06C (wt.%)

heavily beta stabilised alloys such as Ti-5Al-5Mo-5V-3Cr are used for their very high strengths in applications such as landing gear [4]. However, recently
15 stronger and more heavily beta stabilised alloys such as Ti-6Al-2Sn-4Zr-6Mo (Ti-6246) have started to be used in elevated temperature applications such as high temperature compressor discs, by all of the major jet engine manufacturers.

The present work concerns the appearance of an initially unknown blue-coloured fatigue crack initiation feature, that has been observed in the elevated
20 temperature low cycle fatigue (LCF) testing of Ti-6246. These “blue spots” were observed on the fracture surface at the fatigue crack origin, and were found to be around 100 μm in size. Blue is a so-called temper colour of titanium that can be associated with a TiO_2 oxide film of similar thickness to the wavelength of visible light. However, the unusual feature did not possess a temper colour gradient,
25 but instead demonstrated a sharp colour boundary between the initiation site and succeeding fatigue crack. It was initially unclear whether the fatigue crack origins were sub-surface or surface breaking, but all of the blue spots intersected the surface. Some hypotheses held that an initially sub-surface crack oxidised to the blue colour on becoming surface breaking, for example. The areas around
30 the origin locations were also oxidised slightly during testing, to the extent typical for air exposures of the alloys concerned - at 450 °C for ~ 20 -80 h.

One of the original attractions of titanium alloys was that they were thought to be immune to corrosion-enhanced fatigue, but this was soon found to be an erroneous assumption [5, 6, 7]. Properly processed, titanium alloys’ superior
35 fatigue performance are mostly due to a lack of intrinsic defects such as oxide inclusions, and hence a high fatigue crack initiation resistance [3]. Like many metals, Ti is also found to suffer enhanced plasticity in the presence of hydrogen [8], especially around crack tips, and can also suffer from hydride embrittlement [9, 10]. Hydrogen has also been found to affect fatigue crack growth
40 rates [11, 12]. Therefore, in certain circumstances where the protective TiO_2 scale is broken down, Ti alloys can suffer from stress corrosion cracking, which has been the subject of study through to the present day [13, 14].

The crack origin was investigated using scanning electron microscopy and energy dispersive spectroscopy (SEM-EDX), transmission electron microscopy
45 (TEM) foils lifted out from the fatigue fracture surfaces and initiation points, and focussed ion beam milling – secondary ion mass spectrometry (FIB-SIMS). This led to a diagnosis of the root cause of the blue spot features, and therefore to an explanation as to why these features are not observed in ex-service titanium components.

50 2. Material and Experimental Procedures

The Ti-6Al-2Sn-4Zr-6Mo samples investigated in this work were supplied by Rolls-Royce Deutschland. A number of samples have been studied and all samples produced consistent results. Thus for clarity, only one such sample is discussed, which had the specimen ID U7-086. Bow-tie samples were electro
55 discharge machined (EDM) in distilled water from Ti-6246 plate before low cycle fatigue testing at 450 °C in laboratory air at the Mechanical Testing Operations

Centre (MTOC), Rolls-Royce Deutschland. A maximum stress of 600 MPa and minimum stress of 60 MPa were used, and the sample endurance was 17,992 cycles. The gauge section of the samples was 6×6 mm, the gauge length was 30 mm, and a trapezoidal (1 s loading, 1 s hold, 1 s unloading, 1 s hold; 1-1-1-1) waveform was used. The sides of the samples cut by EDM were polished whilst the others (including the crack initiation location) retained a surface ground finish from the parent plate. After testing, the fracture surfaces were cleaned in ethanol and distilled water.

The microstructure of the plate material consisted of coarse, elongated primary alpha laths (α_p) as well as much finer secondary alpha laths (α_s) residing within a retained beta phase matrix (Figure 1). The microstructure is optimised to provide good fracture toughness (α_p) and high strength (α_s) that can be maintained up to $\sim 500^\circ\text{C}$. After β and $\alpha + \beta$ forging, this microstructure can be produced by fan air cooling from just below the β transus, followed by ageing at $\sim 600^\circ\text{C}$ to develop the fine scale secondary α structure, and air cooling.

[Figure 1 about here.]

The microstructure of the alloy was examined using a Zeiss Auriga field emission gun scanning electron microscope (FEG-SEM) using a 10 kV accelerating voltage. Backscatter electron imaging (BSEI) mode and secondary electron imaging (SEI) mode was used for metallography and fractography, respectively. Compositions of the blue spot and the underlying surface defect were measured using energy dispersive X-ray spectroscopy (EDX) in the same SEM. The aperture was increased from 30 to 120 μm during chemical mapping to enhance the count rate but the accelerating voltage was maintained at 10 kV to achieve a good compromise between high count rate and low interaction volume.

Transmission electron microscopy (TEM) samples were produced using the focussed ion beam (FIB) lift-out technique inside a dual beam FEI Helios NanoLab 600 using a 30 kV primary Ga^+ beam. To protect the area of interest, the gas injection system was used to deposit a platinum-containing² protective layer. Samples were thinned to ~ 180 nm. TEM-based EDX on the blue spot layer and underlying microstructure was carried out using a JEOL 2000FX TEM with an accelerating voltage of 200 kV. Scanning transmission electron microscopy (STEM) - based EDX was conducted using a JEOL JEM-2100F TEM/ STEM, again with a 200 kV accelerating voltage. The microscope was equipped with an Oxford Instruments X-Max 80 mm^2 silicon drift detector for chemical analysis.

Focussed ion beam-secondary ion mass spectrometry (FIB-SIMS) dynamic depth profiling experiments were performed using the FEI FIB200-SIMS ion microscope. The FIB-SIMS instrument used was an FEI FIB200 workstation with two electric quadrupole-based, charged particle filters that can be polarised to select and analyse either positive or negative secondary ions on a mass-to-charge ratio basis. Sputtered ions were produced by a gallium liquid metal ion

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²($\text{C}_9\text{H}_{16}\text{Pt}$)

source with gallium ion energy chosen to be 30 keV. The working distance for the
 100 gallium beam was 17 mm. Of the two SIMS detectors, one was an FEI SIMS
 detector and the second, newer detector was a Hiden EQS1000 system. The
 FIB-SIMS system was operated so that positive ions were detected by the FEI
 SIMS detector and simultaneously the negative ions generated were detected by
 the Hiden SIMS detector in concentration depth profiling mode [15].

105 Prior to any recorded FIB-SIMS compositional analyses, all the sites selected
 were sputter cleaned *in situ* using the FIB-SIMS primary gallium ion beam at
 a high current of 20 nA. Following this, analysis was undertaken by sputtering
 within rectangular craters $2 \times 50 \mu\text{m}^2$ in size, within the sputter cleaned area.
 The depth of each of the craters was at least $1 \mu\text{m}$, achieved after sputtering for
 110 a few minutes with a 3 nA gallium ion beam. Craters of this size were chosen
 in order to sample bulk material from a representative portion of the two phase
 material. Two sets of rectangular craters were milled into the specimen gauge
 length. The craters were positioned down the specimen gauge length with the
 long side of the rectangular crater parallel to the fracture edge. The first set of
 115 craters were placed directly beneath the blue spot with the second set at least
 1 mm away from it. Each set of measurements included test analyses on a single
 crystal silicon wafer so as to consider the residual gases in the vacuum system.
 A schematic illustration of the experiment set-up is given in Figure 2.

[Figure 2 about here.]

120 3. Results

3.1. Fracture surface examination

The light optical micrograph (LOM) in Figure 3 demonstrates discolouration
 at the fatigue crack origin corresponding to the blue spot. The blue colour
 appeared quite uniform across the feature and did not show a gradual colour
 125 change with crack length. Furthermore, the boundary or outline of the blue
 spot was observed to be very distinct and sharp. High temperature exposure of
 titanium in air often results in blue/purple discolouration of the alloy surface
 by temper colouration. The perceived colour is a product of the thickness of
 the resulting TiO_2 oxide film and its optical interaction with visible light *via*
 130 thin film interference. In the case of a growing fatigue crack and consequent
 discolouration of the fracture surface, thickness of the TiO_2 layer will be at a
 maximum at the origin and will gradually decrease with crack length. Therefore
 colour shows a progressive change across the fracture surface before final failure.
 Considering this, it is not believed that the blue spot has formed as a result of
 135 temper colouration.

[Figure 3 about here.]

By comparing the LOM to the secondary electron image (SEI) in Figure
 3, an apparent change in fractographic topography was seen to coincide with
 the edge of the blue discolouration. Again, the fractographic boundary of the

140 blue spot was very well defined. This is clearly illustrated in Figure 4(a). The
blue spot boundary is demonstrated by the black outline in (a), with a higher
magnification representation of this region given in (b). It is postulated that an
embrittling species had provided a preferential crack pathway along or across
primary alpha laths or lath boundaries, of particular orientations. Further sec-
145 ondary electron images from within the blue spot region revealed evidence of
the underlying microstructure as primary alpha lath structures on the fracture
surface; Figures 4(c) and (d). Figures 4(e) and (f) show nodular corrosion prod-
uct on the fracture surface close to the initiating edge. This partially obscured
the exposed microstructure and indicated an environmentally assisted crack nu-
150 cleation mechanism.

[Figure 4 about here.]

As the crack extends beyond the blue spot, characteristic stage I fatigue
features were observed on the fracture surface. Stage I fatigue is defined as the
portion of crack growth at very low stress intensities when the plastic zone at the
155 crack tip is confined within the microstructural unit size. A zig-zag crack path is
produced via shear along the single operative slip system [16]. Figure 5a(i) was
taken from a region $\sim 375 \mu\text{m}$ from the origin and illustrates facet formation. It
also demonstrates features with dimensions comparable to primary alpha laths
in the underlying microstructure. It should be noted that although evidence of
160 microstructural features has been observed outside the blue discoloured region,
they did not possess the same cleaved appearance as the primary alpha lath
structures observed within the blue spot. It is inferred that any embrittling
species is likely to have been confined to the blue spot region and had not
diffused far beyond it. With increasing stress intensity, a transition into stage II
165 fatigue crack growth is seen. When the microstructural unit size is comparable
to the crack tip plastic zone size, a mixture of stage I and stage II type growth
occurs. Figure 5b(i) illustrates a combination of facets (stage I) and cracking
associated with striated growth shown in b(ii), $\sim 400 \mu\text{m}$ from the origin.

[Figure 5 about here.]

170 Approaching $900 \mu\text{m}$ from the origin, extensive secondary cracking was ob-
served; Figure 5c(i). At higher magnification, fine striations parallel to these
secondary cracks can be resolved 5c(ii). At these higher stress intensities, the
plastic zone will extend over many grains and crack growth will occur *via* the
action of two slip systems [16]. A local deviation in crack growth direction was
175 observed at the arrows shown in Figure 5c(ii); this may be accounted for by the
operation of duplex slip, consistent with stage II fatigue cracking. Finally, at
very large ΔK when the crack was $> 5 \text{ mm}$ in length, the remaining ligament of
metal was no longer able to support the effective load experienced at the crack
tip, and thus final failure occurred by ductile microvoid coalescence.

180 To determine the presence of a possible compositional variance at the ori-
gin, SEM-based EDX maps were acquired. Qualitative chemical maps of the
crack origin are given in Figure 6 where bright pixels correspond to higher

counts/intensity. After comparing the oxygen ($K\alpha$) map with the optical micrograph adjacent, it became clear that the blue spot was associated with elevated oxygen levels. This is mirrored by a corresponding reduction in the titanium ($K\alpha$) map. The blue spot geometry exposed in the oxygen and titanium maps closely matched that of the optical micrograph. The boundaries were sharp (not blurred), thus indicating that the observed change in oxygen concentration was sudden. An apparent local Cl enhancement was also observed at the origin, however the elevation was much less extreme and the boundary more diffuse.

[Figure 6 about here.]

A limiting feature of SEM based-EDX is the poor spatial resolution, resulting from a large interaction volume. This is dependent on atomic number, Z , but is often quoted as being up to $5\text{ }\mu\text{m}$ [17]. Improved spatial resolution can be achieved by preparing very thin specimens ($\sim 150\text{ nm}$) for analysis inside a transmission electron microscope (TEM). With such thin samples, scattering within the depth of the specimen cannot occur, however the electron beam can still generate X-rays from beyond the probe focus spot and so spatial resolution is a function of foil thickness. Thus, to quantify composition near the surface, two TEM foils were lifted from the fracture surface using the FIB lift-out technique; (1) inside the blue spot, Figure 7(a), and (2) from an area of stage I fatigue growth. Initially, quantitative chemical data was extracted using TEM-based point EDX analysis. Even at low magnifications a surface layer was seen to reside along the fracture surface, directly beneath the platinum layer, Figure 7(b). Chemical analysis measurements were taken at a number of positions within this layer (1-4) and compared to measurements taken from primary alpha laths (5-6). Locations of the point spectra are shown in Figure 7(b) with data given in Table 1. The average atomic composition of the layer, as taken from spectra 1-4, was calculated as 29% titanium to 65% oxygen, plus trace elements. This approximate 1:2 atomic ratio suggested that the composition of the layer was TiO_2 . By contrast, chemical data measured from the primary alpha laths provided evidence for only trace amounts of oxygen. The presence of chloride had previously been implied by the faint halo of increased Cl intensity seen at the blue spot origin in Figure 6(d). Although very low, concentrations of Cl were again consistently detected within the four locations along the oxide layer, but not from elsewhere in the foil.

[Figure 7 about here.]

[Table 1 about here.]

High magnification STEM-EDX mapping clearly illustrates these findings (Figure 8). Dark field STEM images showed the varying contrasts generated by the protective platinum layer, the titanium alloy matrix and the oxide layer (DF-STEM). The white-dashed square demonstrates the mapping area, enlarged in the adjacent image. The oxygen map confirmed a 200 nm thick oxide scale with elevated oxygen counts throughout this region. As with the SEM-EDX

maps, this region of elevated oxygen counts was accompanied by a corresponding reduction in titanium intensity (Ti $K\alpha$), supporting the hypothesis that the composition of the blue spot is TiO_2 . Additionally, Cl was identified once more. On initial observation, it appeared as though Cl was also present in the platinum layer. However, although Cl concentrations are low and on the limit of instrument sensitivity, this unusual result is likely to be an artefact attributed to an insufficient energy resolution and mis-indexing of the platinum M_{III} edge energy (2.65 keV) in place of the measured chlorine $K\alpha$ peak (2.62 keV); see plot in Figure 8. Otherwise, the Cl $K\alpha$ map clearly demonstrates chloride residing near the base of the oxide layer and thus provides convincing data to suggest that both oxygen and chloride are associated with blue spot formation. A second foil was also taken from a region beyond the blue spot to act as a comparison. In this instance, the oxide layer measured only 30 nm in thickness and there was no evidence to suggest chloride was present elsewhere on the fracture surface. A number of positions along the fracture surface were analysed in this way and all the results were consistent with those given here. STEM-EDX mapping has shown that the oxide thickness within the blue spot is larger by approximately one order of magnitude, compared to elsewhere on the fracture surface. This sudden step change in thickness gives further confidence in the hypothesis that the blue spot is not formed simply by the high temperature oxidation of titanium.

[Figure 8 about here.]

3.2. Specimen gauge surface examination

Thorough examination of the fracture surface was followed by inspection of the specimen gauge surface. Figure 9 shows a semi-elliptical feature on the gauge surface directly beneath the blue spot, appearing to link the fracture surface to the gauge surface. This adjacent feature was not observed centrally beneath the blue spot but was positioned toward the blue spot boundary (Figure 9(a)). Both the blue spot and connected gauge surface feature were observed as a pair on both halves of the fracture surface. A similar feature was not observed at any other location along the fracture/gauge surface edge.

[Figure 9 about here.]

When viewed at higher magnification in SEI mode, Figure 9(b), the different surface appearance of the defect became clear. Non-contact interferometry was used to further characterise the surface of the defect. Initial results from surface maps and profilometry showed the defect to be surface negative, with a maximum depth of $\sim 3 \mu m$. Considering the concave form of the defect, and the association of oxygen and chloride on the fracture surface, a hypothesis involving corrosion attack may be inferred. General corrosion and pitting are often accompanied by surface roughening, so, to highlight the roughness component, a high pass fast Fourier transform (FFT) algorithm was applied to the data. The combination of the surface map and profile given in Figure 10 (right column) demonstrated the locally enhanced surface roughness, presumably from corrosion product build-up.

[Figure 10 about here.]

270 Further EDX analysis was then conducted on the gauge surface. As with
the blue spot, qualitative chemical mapping (Figure 11) demonstrated highly
elevated oxygen counts within the surface feature, accompanied by a corre-
sponding titanium reduction. Again, a more diffuse chloride enhancement was
also observed. Semi-quantitative point analyses were also acquired, which are
275 presented in Table 2. Spectra 1-3 were measured from within the feature and
suggested the composition of the adjacent surface layer was TiO_2 . Up to a sin-
gle atomic percent of Cl was also detected from the same positions, along with
low levels of sodium. Unlike the subsurface material analysed in the TEM, the
exterior surface of the specimen was uniformly exposed to the high temperature
280 environment for the duration of the test. Therefore the gauge length will have
undergone high temperature oxidation, which is demonstrated by the values
given from spectra 4-6. However, it could be significant that although exposed
for the same length of time, much higher concentrations of oxygen are detected
within the surface feature compared to surrounding regions (along with some
285 chloride). This is illustrated in Figure 11 and Table 2.

[Figure 11 about here.]

[Table 2 about here.]

FIB-SIMS dynamic depth profiling was employed in order to analyse bulk,
near surface material, as well as to confirm that the chemical species measured
290 were not from post test contamination. The sputter cleaning method described
in Section 2 applied a primary ion dose density (PIDDD) of $\sim 5 \times 10^{17} \text{ Ga}^+$ ions per
 cm^2 to the selected region. Each surface titanium atom was bombarded >100
times, ensuring none of the surface material remained in the original, uncleaned,
condition. Figure 12(a) shows the surface feature beneath (and adjacent to) the
295 blue spot on the gauge surface. Referring back to Figure 9(b) the concave profile
of this adjacent feature was measured to extend $\sim 20 \mu\text{m}$ down from the fracture
edge. The trenches used to produce the plots given in Figure 12(c) and (d) are
illustrated in Figure 12(b). Each data point in the graphs correspond to data
extracted from a single $2 \times 50 \times 1 \mu\text{m}^3$ volume. In this case, each data point is an
300 average of the final 5 measurements at a depth approaching $1 \mu\text{m}$.

[Figure 12 about here.]

Figure 12(c) and (d) show the chemical profiles for $^{16}\text{O}^-$, $^{35}\text{Cl}^-$ and $^{23}\text{Na}^+$ ions
directly beneath the blue spot (set 1) compared to a datum region (set 2); refer
to Figure 2 for a schematic representation of the experimental procedure. It was
295 observed for data set 1 that both $^{16}\text{O}^-$ and $^{35}\text{Cl}^-$ species demonstrated elevated
counts within the $20 \mu\text{m}$ corresponding to the surface feature pit, and returned
to baseline levels thereafter. The profiles of the oxygen and chloride appeared
synchronised. Considering the results from both STEM-EDX and SIMS, it is
clear that the presence of chloride is not a result of post test contamination. To

310 summarise, the STEM-EDX data provided evidence for chloride residing near the base of the blue spot oxide layer and chloride was again measured *via* SIMS depth profiling, after undertaking the initial *in situ* sputter clean procedure.

In the SIMS community, it is widely acknowledged that ambient oxygen can enhance positive secondary ion yield [18, 19]. Considering the data from Figure 12(c) it was important to account for the increased oxygen levels within the 315 initial 20 μm before analysing $^{23}\text{Na}^+$ data. The sodium profile illustrated in Figure 12(d) is therefore normalised to the equivalent oxygen data to provide a $^{23}\text{Na}^+ / ^{16}\text{O}^-$ ratio. Evaluating the sodium profile as a ratio to oxygen ensures that the trend observed is independent of the local oxygen concentration. After 320 studying Figure 12(d) there was also a clear elevation in the $^{23}\text{Na}^+ / ^{16}\text{O}^-$ profile within the same 20 μm , as shown in Figure 12(d); this was not synchronised with the chloride (and oxygen) but has been consistently demonstrated in this way across a number of samples. Again, upon exiting the first 20 μm sodium counts returned to baseline. When this was compared to the second data set it was 325 apparent that the set 2 profiles did not deviate from the baseline measurement, even in the first 20 μm . This therefore demonstrated that the elevation in counts seen in the set 1 data was likely to be an effect of its proximity to the blue spot on the fracture surface and/or the linking feature on the gauge surface, perpendicular to the fracture plane.

330 4. Discussion

4.1. Summary of main observations in context

The uniformity of colour and well-defined outline of the blue spot led to the conclusion that formation of this feature was not a result of temper colouration. A study from the 1950s previously examined the cracking mechanism of gas 335 turbine fan blades manufactured from Ti-8Al-1Mo-1V [20]. In one case, the subcritical crack growth area was described to be flat and containing a number of blue discoloured semi-elliptical zones. These observations are consistent with the appearance of the blue spot described in the present study. The same authors were able to reproduce the discoloured features by deposition of salt 340 slurry on to a four-point bend loaded specimen. They concluded the initial subcritical crack growth region in one of the fan blades to have initiated from salt in a fingerprint, but later to transition to a mechanism of fatigue crack growth [20]. Other studies discuss similar findings of blue discoloured fracture surfaces. These have been detected during post failure fractographic inspection 345 of salt coated specimens under load [21, 22].

As part of initial analysis of the specimens in the present study, both halves of the fracture surface were examined in detail. It was found that the fractographic details on opposing sides matched closely. This was seen particularly clearly within the blue spot region where evidence of underlying microstructure was seen as primary alpha laths on both sides of the fracture surface. 350 Similar findings are quoted in papers discussing hydrogen embrittlement mechanisms. Some authors attribute the apparent symmetry to decohesion along

α - β interfaces, based on arguments suggesting hydrogen to segregate at these regions [23, 24, 25]. Other authors discuss possible combinations of mechanisms for crack propagation, including that of cleavage [26, 27]. It is suggested that transgranular cleavage through the α -phase platelets could result in the mirror-like appearance of these features on opposing sides of the fracture surface.

An embrittlement mechanism, possibly involving hydrogen, was inferred from the appearance of the cleaved primary lath structures on the fracture surface. In Figures 4(e) and (f) evidence of corrosion product on the fracture surface was demonstrated within the blue spot, and along with the pit-like profile on the adjacent surface (Figure 10), gave further evidence toward corrosive attack. Additionally, chloride has been observed within both the blue spot and the adjacent feature, with sodium detected within the pit-like feature *via* SIMS analysis. Rideout et al described a series of tests involving various polished titanium alloy specimens in 4-point bend, with NaCl deposited and loaded to 85% of yield in a 350 °C air atmosphere [28]. Cracks forming from NaCl exposure displayed evidence of corrosive attack on the fractured surfaces and were found to contain chloride down the length of the crack, whereas sodium was only detected at the crack mouth. This is consistent with the present study. They proposed that pyrohydrolysis of the salt produced a halogen acid, which was able to penetrate the oxide film and promote hydrogen embrittlement [28]. Other authors provide evidence of chloride detection [22, 29] and support the theory of HCl formation [5].

4.2. Mechanism

Considering the data obtained from postmortem examination of the test specimen, a hot-salt stress corrosion cracking (HSSCC) mechanism is proposed as the method by which blue spot formation occurred. It is suggested that sodium chloride was deposited onto the specimen prior to testing, due to inadequate handling /cleaning controls. HSSCC requires a number of pre-cursors for the mechanism to initiate; (1) a salt deposit, (2) the availability of water molecules, (3) temperatures exceeding ~ 300 °C, and (4) a surface tensile stress (residual or applied) [6]. All the aforementioned conditions were met during LCF testing of this group of specimens, thus the following reactions are suggested. Reference is made to Figure 13, that schematically illustrates the mechanism.

[Figure 13 about here.]

At ambient temperature (prior to starting the test), a thin passive oxide layer will exist across the surface of the specimen. The $\text{NaCl}_{(s)}$ is deposited onto this surface film. During low cycle fatigue testing, specimens were exposed to temperatures in the range of 400-500 °C. Under such temperatures, titanium will react with oxygen in the static air environment. Titanium oxide is known to be an anion deficient scale, with oxygen ions acting as the mobile species which can diffuse inward through the oxide layer and react with the base alloy at the metal/oxide interface [3, 30]. Growth of the oxide scale is into the base alloy [31]. The surface of the specimen will now be coated with a uniform oxide layer

<100 nm thick. It is then proposed that the sodium chloride salt deposit reacts with the surface titanium oxide scale (in the presence of moisture) to produce sodium titanate and gaseous hydrogen chloride. Most studies do not explicitly state where the water comes from, though it is commonly considered either to be from moisture in the atmosphere, or fluid inclusions in the salt [6], or adsorbed onto the titanium surface [32]. Only small quantities are required [33]. Although no direct evidence was found from our results, traces of sodium titanate have been determined from X-ray diffraction experiments in previous studies [5] and production of Na_2TiO_3 (*via* reaction 1) has been found to be thermodynamically favourable [34].

Reaction 1 is thought to occur at specific sites beneath the salt deposit. It is not fully understood but is considered to be dependent upon local concentration/chemistry of the contaminant, defects in the oxide scale and possibly underlying slip systems and/or orientations of surface primary α . In any case, reaction 1 consumes TiO_2 , disrupts the thin oxide scale and exposes the underlying titanium base alloy. Titanium is a very reactive metal and is normally considered to be resistant to stress corrosion cracking. In oxygen or water containing environments titanium forms a passive and self-healing surface oxide film [35]. However, in the HCl-rich environment under the salt deposit, re-passivation by regeneration of the oxide is inhibited. In effect, the metal is shielded from oxygen by a stronger oxidiser - Cl. Under fatigue loading conditions such as those experienced here ($\sigma_{max}=600$ MPa), surface tensile stresses promote slip activity that expose bare metal at the crack tip. This bare metal is then not re-passivated, leaving it susceptible to corrosive attack. It is suggested that the highly reactive bare metal reacts with the gaseous hydrogen chloride, dissolving the base alloy and allowing a narrow channel to advance into the metal. Such channels have been observed in the earliest stages of hot salt attack [36].

The result of reaction 2 is the generation of monatomic hydrogen and titanium chlorides. One of the titanium chlorides - TiCl_2 - is solid in the 400-500 °C range, whereas TiCl_4 is gaseous and volatile. TiCl_3 is a solid at 400 °C and is unstable above 425 °C, decomposing into the other two chlorides [37]. The volatile TiCl_4 then meets water molecules under or at the deposit, generating TiO_2 and fresh HCl *via* reaction 3.

This continues the supply of HCl to the reaction site and thus of hydrogen into the titanium. During cyclic loading, shear along preferential crystallographic planes will occur on the positive tensile loading portion of the cycle, promoting formation of a slip step and access to newly generated bare metal [38]. Blackburn and Williams agree with the theory of formation of a large slip step for

crack nucleation [27]. Gaseous hydrogen chloride continues to react with newly
 435 exposed metal, extending channels deeper into the base alloy until the supply of
 HCl is exhausted. The deduction is that nascent hydrogen is adsorbed onto the
 exposed titanium at the base of the channel from where it diffuses into the bulk
 metal. It is widely accepted that the hydrogen concentrates just ahead of the
 channel, in a region of high hydrostatic stress when under load [39, 40, 33, 41].
 440 Hydrogen would be expected, for instance, to concentrate at dislocation cores
 and other plasticity related defects that increase the volume of interstitial sites.
 This theory is consistent with findings from previous work that show evidence
 of microporosity at the tip of an advancing crack, at stress intensities well below
 the critical value for the bulk alloy [42]. Furthermore, the porosity is said to
 445 reside at the α/β interface which has been proposed as the region of highest
 hydrogen concentration [24, 43]. The result of localised hydrogen segregation is
 embrittlement of a narrow region around the tip of the reaction channel where
 there is now likely to be a stress concentration. At some point after load is
 applied, the fracture toughness of the locally embrittled zone falls below the
 450 stress intensity at tip of the channel and promotes corrosion crack initiation.
 The previously created channels therefore act as precursors to crack initiation
 as they are sites providing transport of hydrogen into the metal and a stress
 concentration to localise it, leading to embrittlement.

Two different explanations for the embrittlement mechanism have been in-
 455 dicated. These are based on either a decohesion type model, or one involving
 hydrogen enhanced plasticity [8]. Many authors have previously hypothesised
 about intergranular separation of α/β interfaces as a result of weakened lat-
 tice bonds due to hydrogen interstitials [30, 25, 23]. However, considering the
 transgranular appearance of the fracture surface in the blue spot region, it is
 460 speculated that hydrogen enhanced localised plasticity (HELP) is the mecha-
 nism of embrittlement in this case [8]. In either instance, embrittlement enables
 crack advance from the channel root at stress intensities below that required for
 cracking bulk, uncharged material. It is proposed that crack advance occurs by
 transgranular cleavage of the alpha phase [27] along preferred slip planes [8].

The damaged oxide scale allows contact between chemical species formed in
 465 the crack and the external environment, leading to the continued loop of reac-
 tions 2 and 3. It is hypothesised that gaseous titanium chlorides move up toward
 the crack mouth to be hydrolysed. Hydrolysis of the gaseous titanium chlorides
 produces reaction products of solid titanium dioxide and a self-sustaining cycle
 470 of gaseous hydrogen chloride. This is consistent with previous findings that
 claim a regenerating cycle of chloride [5, 22]. Reaction 3 occurs at the crack
 mouth, thus it is proposed that TiO_2 is deposited at the crack mouth and blocks
 contact between species within the cracked channel and the hygroscopic salt de-
 posit. Previous authors have concluded that formation of TiO_2 during HSSCC
 475 can act as “a plug” and “inhibit further generation of titanium chlorides” [22].
 The present authors consider that shear at the crack tip and consequent slip dis-
 solution promotes formation of a slip step and provides access to bare titanium
 for hydrogen charging, resulting in embrittlement and crack extension. Rupture
 of the titanium alloy substrate will certainly cause rupture of the brittle reaction

480 product at the mouth of crack. The deposited TiO_2 splits and condenses onto
the crack walls near the mouth, allowing further hydrolysis of titanium chlorides
and a looping process between reactions 2 and 3 to proceed.

The proposed mechanism considers water, *via* gaseous HCl , to be the source
of hydrogen in this HSSCC mechanism, a hypothesis which is supported by
485 many from the 1960s and 70s [6, 33]. Chloride is therefore the means by which
hydrogen from water molecules is transported into the crack tip. Once the
looping reactions are initiated, gaseous HCl is supposed to move down the crack
towards the exposed titanium at the crack tip where it dissociates. A simultane-
ous reaction between exposed titanium and chloride ions produces the titanium
490 chlorides and provides free electrons to reduce H^+ ions and allow diffusion of
atomic hydrogen ahead of the crack tip.

Concentration of hydrogen at the reaction site is dependent on the balance
between the competing reactions of hydrogen charging vs hydrogen diffusion.
The rate of charging needs to be high enough to sufficiently embrittle the area
495 before the hydrogen diffuses away from the highly stressed material and into
the bulk. Assuming temperature, reaction rate and stress are maintained, local
increases in hydrogen content will cause the fracture toughness of the hydrogen
loaded region to reduce. Meyn showed that only small concentrations of hy-
drogen are required to cause cracking below the fracture toughness of the bulk
500 alloy [44]. Upon reaching a critical value, the stress intensity at the base of the
crack will exceed the fracture toughness of the hydrogen concentrated region,
allowing an increment of crack growth. Cracking stops upon contacting an area,
sufficiently low in hydrogen, that no longer exceeds the fracture toughness [32].
Further hydrogen is generated ahead of the crack and upon reaching a critical
505 value, the cycle repeats.

To the knowledge of the authors, blue spot features are not commonly ob-
served. $\text{Ti-6Al-2Sn-4Zr-6Mo}$ could be particularly susceptible to the HSSCC
mechanism. Referring back to Figure 1, it can be seen that the microstructure
consists of acicular primary alpha platelets in a continuous beta phase matrix.
510 The beta phase is known to have higher solubility for hydrogen and demon-
strates a much faster rate of hydrogen diffusion than the alpha phase [9, 10].
Materials with a continuous beta phase matrix (lamellar Ti-6246) are said to
provide a “short circuit transport path” for hydrogen [25, 45]. Equiaxed Ti-6Al-4V
is often used at lower temperatures than lamellar Ti-6246 , but to date,
515 blue spots have not been observed. The continuous beta phase in fully lamellar
 Ti-6246 could increase susceptibility to HSSCC by promoting efficient diffusion
of hydrogen.

It must be reiterated that the blue spot observed at the fatigue crack origin
is not thought to have formed as a result of temper colouration. Titanium
520 specimens subjected to high temperature fatigue are sometimes found to have
progressively changing bands of colour originating at their fatigue crack origins.
Such temper colour banding results from high temperature exposure of bare
titanium during crack extension and formation of a thin oxide layer during
growth. The precise colour observed is dependent upon time at temperature
525 and the consequent thickness of the oxide layer. Therefore, oxide thickness is

at a maximum at the origin where exposure has been greatest, and gradually decreases to the point on the fracture surface coinciding with the transition to fast fracture. In this case however, it has been shown that the blue spot is associated with a sudden step change in oxide thickness, measuring in excess of 250 nm within the blue spot and less than 50 nm immediately adjacent to it. Furthermore, evidence from STEM-EDX mapping in Figure 8 demonstrates the presence of Cl within the blue spot layer.

It is postulated that upon formation of titanium chlorides in reaction 2, the solid species and some of the gaseous species are trapped during formation and deposition of TiO_2 in reaction 3. This would account for the chlorine identification in the blue spot layer and is consistent with previous studies that state chloride ions would be expected to extend down the crack [33]. It is hence believed that the blue spot layer is formed via reaction 3 and is associated with the deposition and consequent rupture of the TiO_2 reaction product near the mouth of the crack. Therefore, we differentiate between a temper colour and a blue spot by considering the former to result as a consequence of direct high temperature exposure of titanium over time, compared to the latter resulting as a product of the hydrolysis of titanium chlorides, produced as a by-product of the HSSCC mechanism.

4.3. Alloying effects

Commercially pure (unalloyed titanium) is considered to be immune to SCC, providing the oxygen content remains below a critical value [46, 47]. However, a large number of titanium-base alloys are found to be susceptible to SCC in varying degrees [28, 48]. Consequently, alloy composition is seen to have a significant effect on SCC sensitivity. Rideout et al conducted a study comparing the susceptibility of several aluminium containing alloys. They found the susceptibility of alloys to SCC increased with increasing aluminium content [28]. In other studies, workers found that Al was preferentially attacked by NaCl salts [6, 49]. Ordering of aluminium in slowly cooled Ti-Al alloys can give rise to planar slip, which provides an additional rationale for the enhanced vulnerability of aluminium containing alloys to HSSCC compared to commercially pure titanium [27].

Tin is another alloying element in Ti-6246 and, considering its alpha-stabilising nature, has been suggested to have a similar effect to aluminium [27]. In section 4.2, a very streamlined version of the reactions were suggested. In fact, many other reactions are possible and several different metal-chlorides have been detected in the past [28, 49]. Additional reactions at 450°C could therefore be as follows:

Of course, all these reactions produce atomic hydrogen and assuming all happen simultaneously may increase the rate of hydrogen charging into the metal. Additionally, considering the metal-chlorides produced in reactions 4-8, variations to reaction 3 are also introduced:

We therefore propose that the volatile gaseous metal chlorides are involved in the hydrolysis reaction, emphasising the regeneration cycle of gaseous HCl, whereas the solid titanium dichloride is likely to be the Cl species found in the blue spot layer. TiCl_2 has been detected either along the crack or on the fracture surface in several different HSSCC studies [50, 5, 22]. It is therefore proposed that attack of alloying elements is an important aspect of the HSSCC mechanism, without which it is unlikely that sufficient hydrogen charging would occur to promote hydrogen embrittlement of the base alloy and consequently lead to hot-salt assisted crack nucleation. This hypothesis is supported by Rideout et al [28], and by Chevrot [36], who laid out the thermodynamic basis.

4.4. Transition from HSSCC to LCF crack propagation

With infinite salt available and sufficient stress, the corrosion-assisted cracking mechanism described in section 4.2 will prevail for the duration of crack propagation. It will only cease when the crack length becomes so large that the remaining ligament of metal can no longer support the applied load, and fails by fast fracture. However, in the present case there was a transition from HSSCC to low cycle fatigue crack growth. The transition was sudden and accounts for the clear optical boundary associated with the blue spot, the change in fracture mode, and the step change in oxide thickness, relating to the TiO_2 reaction product in reaction 3. This mechanism change could result from several factors, however each refers back to insufficient embrittlement.

We consider the NaCl deposit to have resulted from finger prints or perspiration due to inadequate cleaning of the specimen immediately prior to testing. There is therefore a finite supply of the contaminant. Gaseous HCl is first formed in reaction 1. With a finite amount of NaCl available, the supply will soon be exhausted. Of course, the self sustaining generation of HCl through the looping of reactions 2 and 3 is still anticipated, however some of the titanium alloy chlorides are considered to be gaseous and therefore losses can be expected. A related effect that may decrease the rate of hydrogen charging is the declining concentration of HCl at any given point on the hot-salt crack front as the crack area increases. This may be compounded by the notable crack branching seen in the HSSCC of titanium. In either case, production of HCl, and therefore monatomic hydrogen, is adversely affected. As the rate of hydrogen charging slows (relative to the rate of diffusion away from the reaction site), there will

be a lower concentration of hydrogen after a given reaction time, reducing the extent of embrittlement ahead of the crack tip. At the point where the local concentration of hydrogen is insufficient to cause further cracking, it is proposed
610 that the lack of crack advance will mean the TiO_2 reaction product does not rupture and hence the looping reaction is stifled. No further HCl or hydrogen charging will occur and any hydrogen at the tip of the crack will diffuse into the bulk. Providing that applied stress is sufficient, it is expected that upon
615 reaching the stage of insufficient embrittlement to cause stress corrosion cracking, there is a transition to fatigue crack growth, which will continue to be the mechanism of crack growth until reaching fast fracture at the end of the fatigue life. The transition will be sudden. As the crack grows in fatigue, the oxide at the mouth of the crack should rupture due to increased crack opening, but for the aforementioned reasons, the embrittlement is too low to activate the HSSCC
620 mechanism. There is no evidence of a return to the HSSCC mechanism after the transition into fatigue crack growth.

4.5. Effect on gas turbine components

Salt deposits of up to 0.03 mg/cm^2 have been measured from unfailed ex-service gas turbine compressor aerofoils whilst concentrations of only 0.005 mg/cm^2
625 have been found to cause HSSCC in lab specimens [51, 52]. Therefore it is accepted that enough salt to trigger HSSCC exists during flight cycles, but despite this no service failures have been determined to have occurred as a direct result of HSSCC [51]. Many authors attribute this to one of the many inconsistencies between laboratory tests and real flights. Laboratory tests are frequently
630 undertaken in stagnant air environments whilst engine components operate at high rotational speeds in moving air. It is commonly proposed that the fast air streams present during real flights act to remove corrosion products thus preventing reactions leading to embrittlement [53, 34]. Other authors disagree with this conclusion suggesting the reaction products are not gaseous, and hence
635 do not believe high velocity gases would remove liquid/solid contaminants to prevent cracking in service [54].

Previous work undertaken on IMI 834 studied the effect of environmental pressure on the life of specimens subjected to HSSCC conditions. It was found that higher pressures significantly increased lives of specimens tested at two
640 stress levels [36]. The theory proposed by Chevrot uses a concept of insufficient hydrogen charging as a consequence of pressure dependent reactions to explain engine experience. It was proposed that at the lower pressures experienced during laboratory (atmospheric) and spinning rig tests (partial vacuum), the reactions operating are those stated in section 4.2, involving pyrohydrolysis of
645 titanium alloy chlorides. However, at the higher pressures within the core of an operating gas turbine engine, reaction 3 moves away from hydrolysis and towards a reaction with oxygen:

650 In this case the gaseous product is diatomic chlorine, rather than hydrogen chloride, and thus the self sustaining looping reaction to produce HCl, and therefore production of atomic hydrogen, is thought to be stifled. The consequence is an insufficient concentration of hydrogen to promote cracking at the applied stress levels. Therefore service components appear to be unaffected by
655 finger prints and are not susceptible to HSSCC. This theory implies there is a balance between pyrohydrolysis and oxidation, that is sensitive to the relative availability of oxygen.

5. Conclusions

A previously unexplained “blue spot” phenomenon found at the origin of fatigue cracks in elevated temperature test specimens has been determined to be the consequence of hot salt stress corrosion cracking in the presence of small deposits of NaCl contamination. The following observations are made:

1. The blue coloured fatigue crack origin is associated with trace Cl and a TiO₂ oxide scale on the order of 200 nm thick. In this region, the alpha plates have a cleaved appearance. These measurements were confirmed using STEM-EDX TEM foils removed by FIB milling.
2. On the adjacent surface, a shallow, rough Na and Cl-containing eroded region is observed by FIB-SIMS.
3. The crack origin is therefore consistent with a hypothesis of hot salt stress corrosion cracking. The mechanisms of HSSCC have been discussed in light of the results in order to clarify the extensive literature on the subject.
4. During the early stages of reaction, HCl formed from the NaCl deposit, and reacted with the titanium alloy. Hydrogen was adsorbed, embrittling the alloy and leading to cracking, e.g. via the hydrogen enhanced localised plasticity (HELP) mechanism. Titanium chloride(s) also formed, allowing the regeneration of HCl at the crack mouth. As the crack grew, the decreasing rate of reaction reduced the level of embrittlement, and thus the corrosion crack growth rate, until HSSCC could no longer occur at the prevailing stress, giving rise to a transition to conventional fatigue crack growth, and hence the observation of the “blue spot”.
5. It is proposed that at high pressures such as are present in operational gas turbines, the titanium alloy chloride reactions proceed more readily with oxygen than with water vapour due to its greater availability, thus reducing the regeneration of HCl. This provides a rationale for the non-observation of HSSCC in service components.

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Composition (at.%)							
	Ti	Al	Sn	Zr	Mo	O	Cl
1	26	2.8	0.1	0.5	0.1	70	0.6
2	24	4.2	0.7	0.9	3.0	66	1.2
3	32	5.2	0.4	1.0	0.1	61	0.7
4	32	2.4	0.1	1.0	0.4	63	0.8
5	81	14	0.9	2.2	0.4	1.8	0
6	82	13	0.9	2.4	0.4	1.2	0
	± 2	± 0.4	± 0.1	± 0.2	± 0.2	± 3	± 0.1

Table 1: TEM-EDX composition data for the blue spot (1-4) as compared to the metallic substrate (5-6). Average uncertainty (at.%) given to one significant figure.

Composition (at.%)									
	Ti	Al	Sn	Zr	Mo	O	Cl	Na	
1	26	3.8	0.3	0.7	0.9	67	0.6	0.4	
2	25	3.6	0.2	0.6	0.5	69	0.5	0.3	
3	26	3.4	0.3	0.7	1.3	66	1.1	0.4	
4	48	6.0	0.5	1.6	3.0	41	0	0.1	
5	47	5.4	0.6	1.5	3.9	42	0	0	
6	48	6.6	0.6	1.4	0.7	43	0	0.1	
$\pm$	0.4	0.07	0.03	0.04	0.05	0.7	0.03	0.04	

Table 2: SEM-EDX composition data from the machined specimen gauge surface beneath the blue spot. The positions of the acquired data are illustrated in Figure 11, with the average uncertainty (at. %) given to one significant figure. Acquired using a 10 keV electron-beam energy.

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Figure 1: Micrographs demonstrating the microstructure of the material studied. (LOM) Light optical microscopy overview; (BC) Band contrast formed image from electron backscatter diffraction; (α/β IPF). Alpha and beta phase inverse pole figure (IPF) colour images, coloured parallel to the loading direction-indexed at 76%; (BSEI) Backscatter electron images demonstrating the fine secondary alpha laths residing within the beta matrix.

Figure 2: Schematic illustration of FIB-SIMS set-up: (1) Blue spot; (2) adjacent surface feature; (3) set 2 data; (4) set 1 data; (5) mass spectrum 0-200 AMU; (6) depth profile trenches, similar to trenches in sets 1 and 2.

Figure 3: Light optical micrograph (LOM) and secondary electron image (SEI) demonstrating the semi-elliptical morphology and the uneven boundary of the blue spot on the fracture surface.

Figure 4: Secondary electron images taken from areas within the discoloured fatigue crack origin: (a) and (b) distinctive fractographic boundary coinciding with the blue discolouration, (c) and (d) evidence of underlying microstructure on the fracture surface, (e) and (f) build up of corrosion product on the fracture surface.

Figure 5: Secondary electron images exhibiting features observed across the fatigue fracture surface (outside the blue spot); a corresponds to crack length. Top row - x5k magnification, bottom row - x20k magnification; from left to right increasing ΔK , (a) structure sensitive growth accompanied by facetting, (b) adjacent facets and (torn) striations, c(i) distribution of secondary cracks and fine striations parallel to the secondary cracks c(ii), (d) ductile microvoids. Crack growth directions are shown by the arrows.

Figure 6: Qualitative long-exposure SEM-EDX maps from the fatigue crack origin. (LOM) Demonstrating the semi-elliptical morphology of the “blue spot”; (O) Significant oxygen enhancement and (Ti) Titanium reduction within the blue spot region; (Cl) Tentative visual evidence of the local presence of Cl in the blue spot region.

Figure 7: (a) Overview of TEM foil showing the microstructure underlying the blue spot; (b) The blue spot layer observed at higher magnification (dotted lines). EDX spectra data from the blue spot (1-4) and subsurface primary alpha laths (5-6) are given in Table 1.

Figure 8: (Top) High magnification STEM-EDX chemical maps taken from a region encompassing the platinum protected fracture surface, the supposed blue spot and base metal matrix. An overview of the sample is shown in Figure 7(a). Top right micrograph illustrates the area from which the maps were measured. Camera length 15cm, spot size 1.5 nm. (Bottom) X-ray spectra from locations within the platinum layer (circle) compared to within the oxide layer (square), demonstrates overlapping peaks for Pt and Cl.

Figure 9: Secondary electron images of the blue spot and underlying surface feature: (a) 30 ° stage tilt with the fracture surface $\sim 60^\circ$ to the electron beam; (b) specimen gauge surface normal to the electron beam.

Figure 10: Light interferometry on the surface defect shown on the gauge section in Figure 9: False colour surface maps (upper) and surface profiles (lower) of the defect on the machined gauge surface of the specimen. (Left) data as measured; (Right) measured after application of high pass fixed FFT filter selecting frequency information $>50 \text{ mm}^{-1}$ to emphasise roughness data.

Figure 11: Qualitative SEM-EDX mapping of the defect on the machined gauge surface of the specimen: (SEI) includes the positions of spectra as given in Table 2 - spectra 1-3 defect, spectra 4-6 machined surface.

Figure 12: FIB-SIMS data: (a) SEI at 0° tilt before FIB sputter clean; (b) SEI at 30° tilt after 20 nA sputter clean and depth profiling at 3 nA; (c) $^{16}\text{O}^-$ and $^{35}\text{Cl}^-$ profiles; (d) $^{23}\text{Na}^+ / ^{16}\text{O}^-$ and $^{35}\text{Cl}^-$ profiles.

Figure 13: Proposed HSSCC mechanism: (a) NaCl deposition; (b) HSSCC crack nucleation; (c) volatile TiCl_4 reacts with water molecules or oxygen to form TiO_2 at the crack mouth; (d) blue spot formation - TiO_2 overlaid on and mixed with titanium chlorides.