Effect of microstructure on oxygen rich layer evolution and its impact on fatigue life during high-temperature application of α/β titanium

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Abstract

The near alpha titanium alloy, Ti-6424S, is utilized in many critical high-temperature aerospace components due to its unique properties. However, oxygen ingress during elevated-temperature exposure induces formation of a subsurface brittle oxygen-rich layer (ORL), resulting in a deterioration of mechanical performance. This paper, for the first time, establishes the effect of the underlying microstructure on the formation and evolution of the ORL in α/β titanium alloys. In addition, models were developed to predict (i) the evolution of ORL as a function of the material *microstructure*, (ii) the effect of ORL on the critical strain for *in-service* crack initiation, and (iii) estimates of fatigue life of components made from a specific microstructure during in-service high temperature exposure and formation of ORL. In particular, five different microstructures were reproduced by tailored heat-treatments and thermally exposed at 650°C up to 420 hrs. The base metal and the ORL were quantified using microhardness indentations, optical microscopy, and scanning electron microscopy (electron backscatter diffraction (EBSD), backscattered electron (BSE), and secondary electron (SE) imaging). The effective diffusion coefficients (D_{eff}) for each microstructure were calculated and then integrated into a critical strain model to predict crack initiation strain as a function of exposure time. The predicted ORL thickness was used to estimate fatigue life using experimentally measured crack growth data. The largest D_{eff} coefficient was observed in a colony microstructure, while a basketweave microstructure showed the smallest D_{eff} . For several bimodal microstructures, D_{eff} was noted to increase with increasing area fraction of secondary alpha colonies.

Key Words

Oxygen-rich layer; alpha case; α/β titanium alloys; lifing; thermal protection systems

1 Introduction

A unique combination of excellent mechanical and physical properties, including high static and fatigue strengths, low density, corrosion resistance, weldability, and excellent high temperature strength, make titanium alloys ideal candidates for critical jet-engine components[1], with the potential weight benefit in hot structures of jet engines offered by the high specific properties of near-alpha titanium alloys causing increased interest in raising the temperature tolerance of the alloys. These properties also make titanium alloys good candidates for metallic thermal protection systems (TPS)[2,3]. However, rapid diffusion of oxygen into exposed surfaces at service temperatures above 600°C results in a brittle sub-surface oxygen rich layer (ORL) with detrimental effects on fatigue and fracture properties by affecting slip character under load[4]. Although the maximum oxygen solubility in the alpha and beta phase is ~33.9 at. % O and 3.8 at % O, respectively[5,6], an oxygen concentration of 0.51 wt% has been shown to increase the long crack growth rate by 5 to 10 times ($\Delta K < 12 \text{ MPa}\cdot\text{m}^{1/2}$ for $R=0.01$)[7]. Even small oxygen concentrations (0.06-0.18 wt%) have been observed to have deleterious impact on crack growth behavior[8]. Research simulating service-induced oxygen ingress and its effect on quasi-static and cyclic loading of Ti-6Al-2Sn-4Zr-2Mo by Pilchak et al.[4] showed that both tensile elongation to failure and fatigue life were severely deteriorated by the ingress of oxygen. It is worth noting that 3D atom probe tomography by Rugg et al[9] revealed that high temperature exposure introduced both oxygen and nitrogen into the subsurface layer. However, Gaddam et al.[10] found that the amount of nitrogen was below the detection limit of the electron probe micro-analyzer (EPMA). Although diffusivity data of nitrogen in Ti6242S is limited, the rate of diffusion in pure titanium is approximately two orders of magnitude slower than for oxygen[11,12], with alloys Ti6Al4V and Ti6242S showing additional retardation of diffusion compared to pure titanium[13,14]. As such, the brittle/hard subsurface layer at in-service

temperatures is considered rich in oxygen, and this layer is referred to hereafter as an oxygen rich layer (ORL).

Enhancing jet engine efficiency and avoiding failures during service requires accurate estimates of life expectancy under simulated loading conditions. Deriving such estimates from computer simulations may reduce the cost of experimental testing for component materials. Two types of families of models can be used: the first consisting of models predicting the evolution of the ORL under various environmental conditions of service temperatures and exposure time, and the second including models that capture the effect of the ORL thickness on the mechanical properties (including tensile ductility and fatigue life).

A number of efforts have been devoted to the first type of models that predict the evolution of the ORL by modeling oxygen diffusion in α/β titanium alloys[15–18]. In these models, the thickness of the ORL is assumed to be small compared to the thickness of the bulk, allowing the application of Fick's second law of diffusion to estimate the oxygen concentration profile and concomitant ORL thickness at various temperatures and exposure durations[19]. Many of these efforts utilize experimental data and/or simulations to calibrate Fick's second law diffusion coefficient[15–18,20]. An excellent summary of oxygen diffusivity in various titanium alloys has been provided by Liu and Welsch[21]. However, the absence of consistent accounting for the effect of microstructure (including both morphology and crystallography) reduces the practical implementation of the results across various microstructures for the same alloy. In addition, the emergence of jet-engine components with location-specific tailored microstructures for optimized performance (e.g. turbine disks with gradient microstructures, blisks, etc.) further highlights the need for microstructure-specific estimation of oxygen ingress. Recent work by

Tiley et al[22] confirmed the impact of morphological orientation of alpha laths on oxygen ingress in Ti-6424S with colony microstructure.

The large variability of microstructures in α/β titanium alloys[23] makes it difficult to extract unique trends in diffusion modeling parameters directly from published literature. In particular, analysis of the Arrhenius plots given by McReynolds et al.[18] gives an estimated diffusion coefficient of a Ti-6242S sample with a *bimodal* microstructure of $\sim 4 \times 10^{-3} \mu\text{m}^2/\text{s}$ at 649°C , based on optical measurements of ORL thickness. This is approximately 20 times higher than the value reported by Shamblen and Redden[17] at 639°C ($D_{(639^\circ\text{C})} \approx 2 \times 10^{-4} \mu\text{m}^2/\text{s}$), which is close to the diffusion coefficient reported for pure alpha titanium ($2.105 \times 10^{-4} \mu\text{m}^2/\text{s}$) by Brockman et al.[20], who used a representative volume element (RVE) approach and 2-dimensional FEM simulations based on electron backscatter diffraction data to simulate oxygen diffusion in microstructure constituents of Ti-6242S with a *globular* microstructure. In that work, separate diffusion coefficients were used for the alpha phase ($D_{\alpha(649^\circ\text{C})} = 2.105 \times 10^{-4} \mu\text{m}^2/\text{s}$), beta phase ($D_{\beta(649^\circ\text{C})} = 5.765 \times 10^{-4} \mu\text{m}^2/\text{s}$), and alpha/beta boundary ($D_{\alpha/\beta(649^\circ\text{C})} = 10^5 D_{\alpha(649^\circ\text{C})}$). The model calibration was conducted using electron probe microanalysis measurements of oxygen distribution after exposure at 650°C . Although the materials used in Refs.[18] and [20] were the same alloy (Ti-6242S), the calibrated model parameters were different, possibly due to the difference between bimodal and globular microstructures and/or the procedures used to experimentally measure the ORL thickness experimentally.

Estimation of the effect of ORL thickness on the mechanical behavior of titanium alloys has been the subject of many research projects[16,21,24,25]. In particular, Parthasarathy et al. proposed a life prediction model based on the work of Hutchinson and Suo[26] and Thouless et al.[27] accounting for crack formation in the brittle ORL on the surface of Ti-6242S samples

subjected to a time-temperature-environment cycle[16]. The model was linked to an oxygen-diffusion model to predict the depth of the ORL. The oxygen diffusion model was calibrated using the diffusivity of oxygen in beta titanium. However, at the temperature investigated in the paper (650°C), the alloy consisted of mainly alpha phase with less than 10% retained beta[21]. As such, a more accurate diffusivity value based on the underlying microstructure in the sample may have provided different results. Phase volume fraction variations with temperature and their effect on the mechanical properties of α/β titanium alloys were established by Liu and Welsch[21], who concluded that high bulk oxygen levels of 0.65 wt% embrittled the alpha phase with no embrittlement of the beta phase. Gurappa[25] postulated an equivalent life model based on variation of ORL thickness after exposure at temperatures from 600°C - 900°C for another high-temperature alloy, IMI834. However, since temperature transients are common during service, the lifing of the component based on oxygen ingress should be linked to the accumulative depth of the ORL at various temperatures.

Although most of the above mentioned efforts succeeded in fitting diffusion models to specific sets of experimental measurements of ORL, discrepancies were noted in the estimates of diffusion coefficients. These discrepancies directly impacted the fidelity of the mechanical-property predictions. Such discrepancies may arise from (i) a lack of consistency in accounting for the microstructure (morphological and crystallographic information) within the same alloy, (ii) the lack of reproducibility/repeatability between various techniques to quantify the depth of the ORL, (iii) the limited information available on the interplay between various diffusion coefficients for alpha-phase, beta-phase, and the interfaces between them, and (iv) the misuse of “alpha case” terminology to describe the ORL occurring in-service which, in the authors’ view, is important for differentiating between a high temperature phenomenon observed during casting

(above β transus) and thermomechanical processing close to or above the β transus (with a high volume fraction of beta phase which and controlled by oxygen diffusivity in β) leading to an obvious layer of hard globular α (different than the base metal microstructure) beneath the surface resulting in the known alpha-case and the phenomenon occurring during heating the material at moderate in-service temperatures below the β transus, resulting in a subsurface hard layer with an alpha phase volume fraction that is similar to the base metal and controlled by oxygen diffusion in α , β and α/β interfaces..

In order to overcome these shortcomings, the following workflow was designed and executed as follows: (i) Ti-6242S samples with various starting microstructures were used to capture the impact of microstructure on the depth of ORL after various exposure times; (ii) a protocol to measure the depth of the ORL based on microhardness measurements was employed; (iii) an effective diffusivity of each microstructure (instead of individual diffusivities for individual constituents) was determined based on modified Fick's second law, utilizing hardness measurements as an indicator of oxygen concentration; and (iv) the estimated effective diffusivity values were implemented into lifing models to demonstrate the integration of various material models accounting for microstructure spatial variability. Using the above, a protocol to account for the impact of oxygen ingress on the lifing of titanium alloys (with a location specific microstructure) during high temperature service was proposed. Finally, some discussion is also dedicated to providing a clarifying framework for the difference of terminology between ORL and alpha-case based on the differences in microstructure and phase composition during and after oxygen ingress, with an emphasis on the parameters to be used in each case.

2 Materials and Experimental Procedures

The overall strategy of this study involved production of differing microstructures using various heat treatments which were subsequently subjected to controlled oxidation testing. The resulting materials were characterized to investigate the ORL by etched optical measurements and microhardness profiling. The near alpha alloy Ti-6242S was chosen due to its widespread use in high temperature applications where property degradation due to oxygen ingress is a critical concern. Typical chemical composition of Ti6242S (in weight percent) is 6% Al, 2% Sn, 4% Zr, 2% Mo and about 0.1% Si with the balance being titanium[28]. The as-received material consisted of five 4.4 mm (0.18 inch) thick sheets with dimensions 147mm x 147mm (6 inch x 6 inch), in a mill-annealed condition with a microstructure consisting of mostly globular alpha with ~15% transformed beta and a beta transus of 988 °C (1810°F). In addition to the as-received (mill-annealed) microstructure, four heat treatments were conducted to produce other types of microstructures: (1) air cooling from above the beta transus, giving a colony microstructure with coarse lamellae; (2) quenching from above the beta transus, giving a basketweave microstructure with fine laths; (3, 4) duplex annealing giving two different bimodal microstructures with approximately 35% and 45% primary alpha. Heat treatments were conducted in a vacuum furnace from the mill-annealed condition, except for the quenched sample, which was heat-treated in air prior to quenching.

Characterization of the heat-treated samples was performed using backscattered electron (BSE) imaging and electron backscatter diffraction (EBSD) in a TESCAN VEGA3 scanning electron microscope equipped with a Bruker EBSD detector operating at 25kV. The beam current for EBSD data collection was set at 11nA. The morphology and spatial distributions of various constituents were revealed in BSE images for all five microstructures (Figure 1) while the

crystallographic texture was captured in inverse pole figure maps and pole figures (Figure 2). Large-area EBSD scans of 2.5mm x 2.5mm were conducted for the basketweave and colony microstructures in order to capture multiple prior beta grains. As each of the five microstructures studied was created from a common (i.e. mill-annealed) parent sample, similar texture components are present in each sample, minimizing any texture effect on oxygen ingress and subsequent characterization.

Figure 1- Backscattered electron images of Ti 6242S with various microstructures: (a) Basketweave, (b) Colony, (c) Bimodal (~35% α_p), (d) Bimodal (~45% α_p), and (e) Mill-annealed (~85% α_p).

Figure 2 - Inverse pole-figure maps and pole-figure data from EBSD for Ti 6242S with various microstructures: (a) Basketweave, (b) Colony, (c) Bimodal I (~35% α_p), (d) Bimodal II (~45% α_p), and (e) Mill-annealed (~85% α_p). Inverse pole figure maps are displayed along the indentation (rolling) direction. The length of the scale bar is 250 μ m.

2.1 Thermal Exposure

Prior to thermal exposure, test coupons from each microstructure were sectioned using abrasive waterjet cutting and then mechanically ground to 1200 grit to remove any ORL or alpha case created during previous thermomechanical processing steps. Isothermal oxidation experiments were then conducted in air at 650°C for 9, 25, 118, and 420 hours using a laboratory box furnace to enable quantification of the evolution of the depth of oxygen ingress for different microstructures. The rectangular samples were positioned on an insulating brick resting on one of the transverse faces, ensuring uniform exposure to the furnace atmosphere across the normal (plan) faces (corresponding to the original sheet top and bottom faces). The dimensions of each coupon were measured before oxidation and the weight was recorded before and after thermal exposure to calculate the weight gain due to oxygen ingress.

Figure 3 - Positioning of sample coupons during thermal exposure. The labels RD, TD, and ND denote the rolling, transverse, and normal directions of the sheet, respectively.

2.2 Measuring Depth of Oxygen-Rich Layer (ORL)

Two methods were used to quantify the depth of ORL and to establish protocols for repeatability and reproducibility; namely, optical microscopy of tint-etched surfaces and spatially distributed microhardness indentations.

2.2.1 Optical Microscopy

Samples were sectioned along the longitudinal plane to reveal a cross-section of the ORL (Figure 4), mounted in epoxy, and metallographically prepared by mechanical grinding and polishing followed by vibratory polishing to produce a deformation-free surface. A bright layer highlighting the ORL was produced by immersion for 9 seconds in an oxalic acid tint etchant consisting of 2 mL HF and 98 mL saturated aqueous $C_2H_2O_4$, which was measured optically to give an estimated ORL thickness [29]. While this data was not used for subsequent analysis of the rate of oxygen diffusion in each microstructure, it is often seen in the literature [10,29] and is useful for comparison between techniques. In order to quantify the oxygen ingress depth objectively, an image processing technique shown in Figure 5(a) was applied consisting of the following steps:

1. Contrast enhancement producing a thin line of saturated pixels at the sample surface
2. Creation of a depth-sensitive histogram by horizontal summation of gray-level over the image width (i.e., parallel to sample surface)
3. Extracting ingress depth as full width at half maximum (FWHM) of the peak in the brightness distribution corresponding to the bright tint-etched area (green dashed lines in Figure 5a). The height of this peak is referenced to the average intensity of the base metal in the image area. This is the vertical dashed line in Figure 5a

Figure 4 - Sectioning coupons for characterization of ORL depth

Figure 5 - Measuring Oxygen Ingress Depth: (a) Optical microscopy using FWHM of the Depth-Sensitive Histogram (b) Microhardness Indentation. Average oxygen counts as a function of depth from the surface across a 75 μ m width scan area are given for comparison.

2.2.2 Hardness measurements

To establish an automated procedure for measuring the depth of oxygen ingress using hardness as a proxy for oxygen concentration, Vickers microhardness profile measurements with a 25gf load were performed. The width of the resultant indents was approximately 10 microns. The profile was measured for each microstructure for a depth from the surface of 100 microns with additional indents performed at 100gf at greater depths to establish the base metal hardness. Due to the small diagonal length of the indentations, image processing of indentation captured by secondary electron images of the indented surface were used to provide an accurate measure of indent size. The hardness was calculated using[30]:

$$HV = \frac{2F \sin\left(\frac{136}{2}\right)}{d^2} \quad (1)$$

where F is applied force, and d is the average diagonal length of the indentation.

The hardness value decreased with depth (i.e. decreasing oxygen concentration), giving the ingress depth at the transition point between the ORL and the base metal hardness (see Figure 5b), which corresponds to the transition between ORL and base metal oxygen concentration.

Minimization of the texture effect on the value of hardness and depth of the ORL was an important consideration in experimental design, and was accomplished by maintaining a constant relationship between the allowed ingress direction, indentation direction, and the significant texture components (Figure 2). Additionally, multiple rows of indentations were spaced at wide intervals ($>50\mu\text{m}$ between neighboring indentations) to minimize the effect of local (i.e. $<20\mu\text{m}$) heterogeneity of microstructure[22].

In addition to the indentation depth traces performed on the transverse section, indentations were also performed on the plan (ingress) surface at 15gf, 25gf, and 100gf on samples exposed for 118hr and 430hr to evaluate the assumption of a fixed surface oxygen concentration required for Fick's second law analysis.

3 Modeling Approach

3.1 Analysis of oxygen diffusion

The thickness of the oxygen-rich layer is usually small compared to typical component dimensions leading to a reasonable assumption of a fixed bulk oxygen concentration[16,17,29,31]. Fick's second law is usually expressed as

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} \quad (2)$$

where z is the distance from the surface and C is concentration. The relation was applied here to describe the development of the oxygen-rich layer upon exposure to elevated temperature.

Under boundary conditions of fixed concentrations in the bulk and at the interface between the metal and thin adherent stoichiometric metal oxide (TiO_2) layer[17,32,33], a solution to Equation 2 is given by[19]:

$$\left[1 - \frac{C - C_o}{C_s - C_o} \right] = \text{erf} \left(\frac{z}{2\sqrt{(D_T t)}} \right) \quad (3)$$

giving the oxygen concentration, C , at any distance, z , from the metal-metal oxide interface after exposure for time, t , at temperature, T , where C_s and C_o are the surface and bulk material oxygen concentrations, respectively. Using an observed direct proportional relationship between oxygen content and hardness at low concentrations, Rosa[6]proposed the following modified solution using hardness to describe the gradient:

$$\frac{H(z) - H_0}{H_s - H_0} = 1 - \operatorname{erf}\left(\frac{z}{2\sqrt{D_T \cdot t}}\right) \quad (4)$$

Calibration of experimental measurements to Eq. (4) using nonlinear regression allows an estimation of the effective (homogenized) diffusion coefficient D_T for each exposure temperature, T .

As a thermally activated process, the variation of the diffusion coefficient with temperature can be further described by an Arrhenius rate equation as

$$D_T = D_o e^{-Q/RT} \quad (5)$$

where D_o is the pre-exponential constant, Q is the activation energy, and R is the universal gas constant. Evaluating D_T at various temperatures allows for an estimate of the value of Q [29].

In order to account for the inherent heterogeneity in the α - β microstructures, the calibrated values of the diffusion coefficient have been assumed to represent an effective (homogenized) value for individual microstructures, incorporating all of the mesoscale details of the microstructure (e.g., grain morphology and crystallography, grain and phase boundaries).

3.2 Prediction of Surface Crack Initiation in the ORL

Due to the formation of the brittle ORL on Ti-6424S surfaces, the material response of the samples to mechanical loading was compared to the behavior of a composite material for predicting elastic and plastic properties[34]. The degradation in the mechanical behavior of Ti-6424S[4,16] due to the brittle ORL is similar to other materials with hard surface layers including nitride steel and chromium-plated copper where surface cracks are formed across the brittle ORL under tensile loading[34]. Consequently, the following effects are assumed to occur based on the presence of the brittle ORL[4,34] :

- (a) Increasing the thickness of the ORL decreases the ductility.
- b) Formation of surface cracks in early stages of tensile testing is equivalent to introducing notches before testing.
- (c) The thickness of the brittle ORL affects the mechanical behavior in a manner similar to a notch of the same depth.

Figure 6 (a) Schematic of surface cracks in the brittle ORL under tensile loading; (b) Secondary electron image showing periodic cracking orthogonal to the loading direction

The critical tensile strain to initiate cracks on the surface of ORL of Ti-6424S was predicted using the thickness of the ORL[16]. In particular, the thickness of the ORL (w) (Figure 6), as measured using microhardness data, was used to estimate the critical stress for crack initiation in the ORL $\sigma_{ORL,crit}$ as:

$$\sigma_{ORL,crit} = \left[\frac{3\Gamma\tau E_{ORL}}{2w} \right] \quad (6)$$

where Γ is the fracture energy per unit area of the ORL (estimated as 300 J/m^2 [16]), $\tau = 448 \text{ MPa} = (0.47 * \sigma_Y)$ is the shear stress at the ORL/base metal interface, and $E_w = 110 \text{ GPa}$ is the Young's modulus of the embrittled ORL[16].

The critical applied strain to initiate a crack in the ORL was provided by

$$\varepsilon_{crit} = (\sigma_{ORL,crit} + \sigma_{ORL,resid})/E_w \quad (7)$$

where $\sigma_{ORL,resid}$ is the compressive residual stress due to the expansion of Ti lattice from oxygen ingress. Due to a lack of property data in the ORL, an upper bound on the residual stress is assumed setting it equal to $\sigma_Y = 950 \text{ MPa}$ [16]. Figure 7 shows model predictions which are consistent with Ref [16].

Figure 7 – Predicted critical strain to nucleate surface cracks in the ORL under tensile loading. The model parameters and data were obtained from Ref [16].

3.3 Lifing Using Crack Growth

Parthasarathy et al.[16] and Pilchak et al.[4] showed that cracking of the ORL can occur during elastic loading and that the cracks penetrate through the embrittled layer until encountering the underlying ductile base metal which is able to arrest the crack. Pilchak et al.[4] also noted a reduction in fatigue life scatter due to the presence of an oxygen-enriched, embrittled layer. This is because the depth of the oxygen ingress and thus the embrittling effects were well controlled by the exposure process; therefore a “precrack” the depth of the ORL was formed on the first cycle. Thus, one can assume that a crack having a depth equal to the ORL is formed on the first cycle and then rely on deterministic, linear elastic fracture mechanics predictions to calculate the remaining useful life time.

In this framework, the total lifetime depends primarily on the long-crack growth rates which are driven by the stress intensity range (ΔK) at the crack tip. This inherently assumes that the oxygen ingress depth is sufficiently deep that the crack formed produces a $\Delta K > \Delta K_{th}$ (the threshold stress intensity range for a long crack). If $\Delta K < \Delta K_{th}$ the crack may still grow, but probabilistic predictions which incorporate microstructural effects should be utilized.

Here, the modeled ORL thickness was used as a function of time for colony microstructure as initial crack sizes in crack growth lifetime predictions performed over a range of stresses relative to the yield stress. The model assumes a through-crack in a rectangular plate of dimensions 25 x 25 mm subjected to constant amplitude fatigue loading at $R = 0.1$. The number of cycles to failure, N_f , is calculated as:

$$N_f = \int_{a_i}^{a_f} \frac{da}{\left(\frac{da}{dN}\right)} \quad (8)$$

Where a_i and a_f are the initial and final crack sizes, respectively, with the latter being defined as the crack length at which $\Delta K > \Delta K_{IC}$ (the mode-I fracture toughness of the material). The crack growth rate, da/dN , was interpolated from a look-up table for a Ti-6242 alloy with similar microstructure[35]. The growth rate of cracks when $\Delta K < \Delta K_{th}$ utilized the small crack data of Jin and Mall[36]. The stress intensity range, ΔK , is the difference between $K_{max} - K_{min}$ where $K = F\sigma(\pi a)^{1/2}$ and F is a shape factor that depends on the crack geometry (a surface, through-crack here)[37].

4 Results and Discussion

4.1 Experimental Observations

The change in the mass of each sample after thermal exposure gives a qualitative estimate of the degree of oxygen uptake in the surface oxide scale and in the ORL. The mass change data are shown in Figure 8 normalized by the exposed surface area of each sample. A significant variation is noted, with the colony and basketweave microstructures exhibiting the highest and lowest weight gains, respectively. Optical measurements of ORL thickness after 420 hours show good correlation with the trends given by the weight gain measurements (Figure 8). Microhardness traverse data (Figure 8) also show good agreement with the trends noted in both the weight gain and optical measurements of ORL thickness with respect to sample microstructure, demonstrating the utility of using microhardness measurements to delineate the presence and extent of an ORL. Figure 9 shows the microhardness trace data for each of the five microstructures. The data is normalized according to Equation 4 to account for variation in base metal hardness for the different microstructures. In every case, there are significant differences between the colony, basketweave, and mill-annealed (globular) microstructures.

A key assumption made in using Fick's second law to model the oxygen ingress behavior is the existence of a constant oxygen concentration at the metal-metal oxide interface[32,33].

Indentations made on the exposed surface (Figure 10) indicate very little change in hardness and, by extension, oxygen concentration in the near-surface layer from 118hr to 430hr of exposure. It is worth noting that there was insignificant change in the hardness values between 15gf and 25gf. However there was a pronounced drop in the hardness at 100gf, which was noted to be greater at shorter exposure time (corresponding to shallower ORL) and decreased at longer exposure time (corresponding to deeper ORL). According to the expanding cavity model of Johnson for indentation in elastic-plastic materials[38,39], the size of the plastic zone beneath the indenter scales proportionally to the contact radius (i.e. core size) of the indentation ($\sim 7.5\mu\text{m}$ at 100gf vs. $\sim 2.5\mu\text{m}$ at 15gf). The observed drop in hardness with increased indentation load is likely attributable then to the increased volume of the plastic zone, which increases the contribution of the softer base metal beneath the ORL. The hardness drop was less pronounced after 420 hr because the ORL thickness is increased at longer exposure time, reducing the contribution from the softer base metal. It is also worth noting that the difference in observed surface hardness between the two microstructures is proportional to the base metal hardness (402HV25g vs. 358HV25g for the basketweave and bimodal, respectively). The normalized surface hardness values for the basketweave and bimodal microstructures are 2.43 and 2.42 at 118hr exposure and 2.33 and 2.45 at 430hr exposure, respectively, validating the constant C_s assumption.

Figure 8 - Comparison of optical and microhardness measurements of ORL thickness with weight-gain data after 420hr exposure.

Figure 9 – Measured hardness profile for various microstructures, normalized according to Equation 4 to account for variation in base metal hardness between microstructures.

Figure 10 - Indentation hardness measurements under loads of 15gf, 25gf, and 100gf on the exposed surface for the bimodal microstructure with 45% a_p and the basketweave microstructure. Error bars indicate the standard deviation of 5 duplicate indentations per sample and force.

4.1.1 Stability of Microstructure during Thermal Exposure

It is necessary to evaluate the stability of the different phases during thermal exposure in order to successfully implement models developed using the collected data and thereby populate a database suitable for microstructure/oxygen ingress linkages. To accomplish this, test samples were removed from the furnace after 4 hours and water quenched. The samples were sectioned and examined using BSE imaging for comparison with micrographs taken prior to thermal exposure to look for any changes in the bulk microstructure attributable to thermal effects other than oxygen ingress (Figure 11). Image segmentation using TiSegTM[40] showed no significant difference in volume fractions of alpha and beta phases, or primary and secondary alpha in the case of the duplex annealed samples (Table 1). Also lacking from the micrographs is the presence of fine Widmanstatten structure developed by the transformation of excess beta during quenching from the alpha+beta region of the phase diagram. This stability in microstructure is expected for the exposure temperature of 650°C due to the flatness of the beta approach curve at the exposure temperature[41].

Figure 11—BSE images of the microstructure of the bimodal microstructure with 35% primary alpha as-heat treated (left) and after 4hr at 650C/WQ (right) showing the stability of microstructure at the exposure temperature

Table 1 - Metrics for bimodal and mill-annealed microstructures as-heat treated, after 4hr at 650C followed by water quenching(WQ), and after 420hr thermal exposure at 650°C

Microstructure	As-heat treated			4 hours at 650°C/WQ			420 hours at 650°C		
	$\alpha_P(\%)$	$\alpha_S(\%)$	$\beta(\%)$	$\alpha_P(\%)$	$\alpha_S(\%)$	$\beta(\%)$	$\alpha_P(\%)$	$\alpha_S(\%)$	$\beta(\%)$
Bimodal I	37.8	46.3	16.2	39.5	49	10.5	45.8	44.5	10
Bimodal II	44.3	38	18	44	43	13	50.5	38.8	11.3
Mill-anneal	84.3	2	14	87.3	2.3	9.7	92.5	1.3	5.8

4.1.2 Stability of Microstructure in the ORL

The microstructure in the ORL is also noted to be little changed with respect to the as-heat treated condition in spite of the presence of increased oxygen concentration (as indicated by microhardness measurements), as shown by micrographs taken at the surface before and after thermal exposure (Figure 12) and the data given in Table 1. A 6-8% increase in volume fraction of α_p is noted after 420hr exposure. While oxygen is a powerful alpha stabilizer, the relatively low temperature of thermal exposure relative to the beta transus is expected to result in little excess globular alpha characteristic of an “alpha case”, as described in more detail later.

Figure 12–BSE images of the bimodal microstructure with 45% primary alpha as received (top) and in the ORL after 420hr at 650°C (bottom) showing the slight increase in primary alpha in the ORL.

4.2 Model application

An oxygen diffusion model was developed incorporating hardness measurements, temperature, exposure time, and microstructure to predict the depth of ORL. This required calibrating an effective diffusion coefficient (D_{eff}) for each microstructure. The predicted depth of ORL was then used to predict the critical strain for surface cracking under tension using Equation 7 described in section 3.2.

4.2.1 Oxygen Diffusion Model

Application of the effective diffusion model to the measured microhardness traces provided values for the effective diffusion coefficients for oxygen in each of the five microstructures considered (Table 2). The basketweave microstructure is found to have the lowest diffusion coefficient, with an effective diffusion coefficient only 18% higher than that for pure alpha phase[20]. The calculated diffusion coefficient for the colony microstructure is more than quadruple that of the basketweave, with the other microstructures in agreement with results given by other techniques (e.g., optical and weight gain). Compared to the as-received (mill-annealed)

condition, the diffusion coefficient was reduced by 32% upon heat treatment to the basketweave microstructure and increased significantly for all other heat treatments.

Table 2 - Effective Diffusion Coefficients Calculated from Hardness Profiles

Sheet ID	Microstructure	$D_{\text{eff}}(\mu\text{m}^2/\text{s})$	$D_{\text{eff}}/D_{\alpha}$	$D_{\text{eff}}/D_{\text{eff}} (\text{Mill-annealed})$
Sheet 1	Basketweave with fine laths	2.48E-04	1.18	0.68
Sheet 2	Bimodal I (~35% α_p)	6.89E-04	3.27	1.88
Sheet 3	Colony with Coarse alpha laths	1.13E-03	5.37	3.08
Sheet 4	Mill-annealed (~85% α_p)	3.67E-04	1.74	1.00
Sheet 5	Bimodal II (~45% α_p)	5.59E-04	2.66	1.52

Validation of the model was performed using a set of hardness measurements of Ti-6424S sheet with an equiaxed microstructure from Parthasarathy et al.[16]. Fitting these values to Equation 1 resulted in an effective diffusivity $D_{\text{eff}}=2.57\text{E-}04 \mu\text{m}^2/\text{s}$, approximately 1.22 times the diffusion coefficient of oxygen in pure alpha phase[20]. Application of the solution to the diffusion equation yielded the normalized ORL thickness as a function of the distance from the surface (Figure 13).

Table 3 – Predicted thickness of the oxygen-rich layer after 420hr at 650°C

	Basketweave	Mill-annealed	Bimodal (45%)	Bimodal (35%)	Colony
ORL Thickness (μm)	31.5	38.3	47.2	52.5	67.2

Figure 13–Normalized predictions of the thickness of the oxygen-rich layer using Fick’s second law.

It is well known that the diffusivity of interfaces (e.g. grain boundaries or interphase boundaries) is typically several orders of magnitude higher than diffusion through the grain interior[20].

Thus, it is expected that the variation in diffusivity for various microstructures will be dominated

by the density and alignment of interfaces relative to the exposed surface. Phase composition is expected to introduce a secondary effect, as diffusivity of the beta phase is approximately 2.7 times higher than the alpha phase[20]. This is reflected by the large increase in effective diffusivity of the colony microstructure as compared to the mill-annealed microstructure. The long, highly oriented interphase boundary network present in the colony microstructure provides a preferential pathway for oxygen ingress, leading to rapid buildup of the brittle layer. Conversely, the mill-annealed microstructure lacks both the density and alignment of interphase boundaries, leading to slower ingress of oxygen. The performance of bimodal microstructures is mixed, showing an increase in diffusivity with increasing volume fraction of secondary alpha colonies. Of the five microstructures examined, the quenched basketweave structure was found to exhibit the lowest effective diffusivity and least depth of ingress, despite having a high density of interphase boundaries. This is likely due to the short length of boundary segments and lack of alignment as compared with the colony microstructure.

These results, for the first time, quantitatively confirm the necessity to explicitly account for the dependence of diffusion properties on microstructure when modeling the behavior of complex structures during exposure to in-service temperatures.

4.2.2 Surface Crack Initiation/Lifing Model

Integrating the crack initiation model (Figure 7) with the results of the oxygen ingress model (Figure 13) provided predictions of the critical strains to nucleate cracks at different exposure times (Figure 14). The predictions in Figure 14 can be linked directly to numerical models (e.g., finite element models) as an upper limit for location specific strain to avoid cracking in high temperature service under various loading conditions, exposure times, and microstructures.

Figure 14 – Predicted critical strain for crack nucleation as a function of exposure time at 650°C for various microstructures of Ti-6424S.

4.2.3 Crack Growth Lifting Model

The results of the deterministic crack growth calculation for colony microstructure, performed at various fractions of the yield strength of the alloy and for different initial oxygen ingress depths (i.e. initial crack size), are summarized in Figure 15. The red circles are tied to the right y-axis and top x-axis showing the ingress of oxygen into the material as a function of time. Each ingress depth was used as the initial crack size to calculate the total cycles to failure. The life curves are not smooth; each exhibits a transition at a different initial crack size with lower applied stresses corresponding to larger transition points. This is because an initial crack size less than the transition point will produce cracks with $\Delta K < \Delta K_{th}$, which is still of microstructurally small dimensions and has not yet developed significant closure in its wake. This is also a consequence of the change to a low ductility fracture process as described by Pilchak et al.[4]. As a result, the crack behaves as a typical small crack where it grows at accelerated rates at low ΔK . As the applied stress is increased, cracks with physically-small dimensions still satisfy $\Delta K > \Delta K_{th}$ and thus the cracks may propagate directly without the need to invoke small crack effects.

Figure 15 – Results from deterministic fatigue crack growth predictions at various stress levels utilizing the oxygen-ingress depth as a function of time for Ti-6424S as the initial crack size. The transition in behavior at smaller crack lengths for each applied stress level is due to the fact that the depth of the crack formed in the ORL did not have sufficient driving force to grow as a long crack and thus small crack effects had to be considered.

4.3 Differences Between Oxygen-Rich Layer (ORL) and Alpha-Case

The rapid uptake and drastic effect of oxygen on the microstructure and mechanical properties of titanium alloys make it a critical interstitial solute for the alloy. The diffusion of oxygen in near-alpha and alpha/beta alloys is highly dependent on temperature, exposure time, and microstructure constituents (e.g., alpha and beta phases). As such, and due to the frequent confusion in terms present in the literature, it is prudent to provide some discussion and

definition as to the precise definition of the oxygen-rich layer (ORL) as compared to the more frequently seen “alpha-case”.

4.3.1 Alpha-Case

During cooling of cast, beta-worked, or beta-annealed titanium alloys, the material absorbs oxygen from the environment. Oxygen ingress starts above the beta transus with 100% beta volume fraction, resulting in a surface layer rich in oxygen. Due to the powerful alpha stabilizing effect of oxygen, the beta transus temperature of this localized surface region is increased. In alloy Ti-6Al4V, this effect is approximated by: $T_{TRANS,NEW}(^{\circ}C) = 937 + 242.7 * wt\% O$ [21]. Consequently, the oxygen-rich surface layer transforms into a continuous layer of alpha phase before the rest of the material, resulting in a characteristic brittle surface layer of continuous alpha grains that is called “alpha case” with a drastic increase in the volume fraction of alpha phase within this layer[10,42]. Efforts to model this process need only take into account the diffusivity of oxygen in the beta phase at the alloy composition due to the single-phase constitution of the material during ingress. In addition, mechanical or chemical methods are typically used to remove the hard alpha case from finished components, minimizing its contribution to the mechanical properties of components during service.

4.3.2 Oxygen-rich layer (ORL)

In contrast to oxygen diffusion during high temperature processes such as casting and forging, components in service are exposed to more moderate temperatures. For example, the volume fraction of beta phase in Ti-6Al4V is typically less than 10% at room temperature[43], increasing to about 20% at 650°C[43]. Ti-6242S typically contains a smaller amount of beta phase (about 10%) at 650°C[41]. Due to the relatively small amount of beta phase, the observed oxygen rich layer at 650°C does not exhibit a characteristic large enrichment of alpha phase near the surface (Figure 12). Furthermore, with increasing oxygen concentration (below beta transus) the

enrichment of alpha phase is increased[21]. As such, modeling of oxygen ingress during service should account for the various volume fractions of alpha phase, along with retained beta, and the interphase boundaries. To avoid confusion between in service oxygen ingress that leads to enrichment only, and ingress that results in alpha phase evolution, the oxygen rich layer during service at temperatures less than 650°C should not be called “alpha case”. Herein, the term oxygen-rich layer (ORL) has been used to emphasize the need to use different modeling parameters to simulate oxygen ingress during service.

A more physically meaningful estimate of the upper limit of exposure that may be rightly called an ORL is related to the volume fraction of beta phase in the subsurface region, taking into account the enrichment of alpha phase with oxygen concentration. The work of Liu and Welsch[21] documented the effect of oxygen concentration on the volume fraction of beta for Ti-6Al4V (Figure 16) by monitoring the change in the volume fraction of beta at different bulk oxygen concentrations. Visual inspection revealed a dramatic increase in the rate of change of beta volume fraction at temperatures higher than 850°C (Figure 16). Consequently, that temperature can be the threshold temperature to distinguish between potential alpha case formation and ORL. Similarly, the procedure using the beta approach curve measured using quantitative metallography by Semiatin et al. for Ti-6Al4V[43] and Ti-6424S[41](Figure 17a) can be used to plot the rate of change in the beta volume fraction as a function of temperature, showing a pronounced increase in the rate of change of beta volume fraction ($dV_{F\beta}/dT$) above 850-900°C for both alloys (Figure 17b). Consequently, temperatures in the range of 850-900°C can be chosen as the range to differentiate between alpha case and ORL for Ti-6Al4V and Ti-6424S.

Figure 16 – The effect of oxygen on the fraction of alpha and beta phases at different temperatures[21].

Figure 17(a) Beta-approach curve experimentally measured for Ti-6Al4V[43] and Ti-6424S[41];(b) the calculated rate of change in the volume fraction of beta as a function of temperature. The critical temperature region for differentiation between alpha case and ORL is indicated.

5 Conclusions

The effect of various microstructures of Ti-6Al-2Sn-4Zr-2Mo on oxygen ingress during 650°C exposure up to 420 hours was investigated. Texture effects on measurements of oxygen ingress were minimized by producing each microstructure from the same parent material, thus maintaining similarity in texture components between samples. A distinction between the oxygen-rich layer (ORL) formed during service and alpha-case formed during casting was established to aid researchers in distinguishing between a primarily high temperature β -phase phenomenon causing discontinuity in microstructure between the brittle layer and base material (alpha-case) and the intermediate temperature interaction of diffusion in both α and β phases, as well as along interphase boundaries (ORL) with no significant discontinuity in microstructure. A practical protocol to estimate oxygen effective diffusivity in various microstructures was proposed using microhardness measurements and optical microscopy. An oxygen-ingress model was developed to predict the thickness of the ORL. The thickness was used to predict the critical strain for initiating cracks under tensile loading of various microstructures as a function of exposure time. A model predicting the effect of the depth of ORL on fatigue life was established. The following conclusions were reached:

1. An effective diffusion coefficient for a particular microstructure was proven practical for mean-field modeling of the response of the whole microstructure to oxygen ingress instead of modeling each constituent individually.
2. The colony microstructure had the highest effective diffusion coefficient (i.e. thickest ORL) while the basketweave microstructure had the smallest (i.e. thinnest ORL).

3. In the bimodal microstructures, the effective diffusion coefficient increases with increasing volume fraction of secondary alpha.
4. Using the oxygen ingress model, the critical strain to initiate cracking in the ORL can be predicted as a function of exposure time. These data also enable the estimation of the exposure time necessary for initiation at a given strain for the various microstructures. For example, at a critical strain to initiate cracks of 1.2%, the basketweave microstructure was predicted to survive 4 times longer (400hr) than the colony microstructure (100hr) before developing a surface crack at the same temperatures.
5. The addition of crack growth data allows for complete lifing taking into account the initial crack length as a function of ORL thickness (exposure time). In Ti-6424S with colony microstructure, increasing the loading stress from $0.5\sigma_Y$ to $0.7\sigma_Y$ was predicted to decrease fatigue life by 50% (from 400 hrs to 100 hrs) during heating at 650°C in atmospheric conditions.

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Ti-6242S

(Ti-6Al-2Sn-4Zr-2Mo-0.1Si)

Decreasing critical strain

Decreasing thickness of ORL

*Oxygen
Rich Layer
(ORL)*

graphical abstract

Fig. 1

Figure 1- Backscattered electron images of Ti 6242S with various microstructures: (a) Basketweave, (b) Colony, (c) Bimodal (~35% α_p), (d) Bimodal (~45% α_p), and (e) Mill-annealed (~85% α_p).

Fig 2

Figure 2 - Inverse pole-figure maps and pole-figure data from EBSD for Ti 6242S with various microstructures: (a) Basketweave, (b) Colony, (c) Bimodal I (~35% α_p), (d) Bimodal II (~45% α_p), and (e) Mill-annealed (~85% α_p). Inverse pole figure maps are displayed along the indentation (rolling) direction. The length of the scale bar is 250 μm .

Fig 3

Figure 3 - Positioning of sample coupons during thermal exposure. The labels RD, TD, and ND denote the rolling, transverse, and normal directions of the sheet, respectively.

Fig 4

Figure 4 - Sectioning coupons for characterization of ORL depth

Fig 5

Figure 5 - Measuring Oxygen Ingress Depth: (a) Optical microscopy using FWHM of the Depth-Sensitive Histogram (b) Microhardness Indentation.

Fig 6

Figure 6 (a) Schematic of surface cracks in the brittle ORL under tensile loading; (b) Secondary electron image showing periodic cracking orthogonal to the loading direction

Fig 7

Figure 7. Predicted critical strain to nucleate surface cracks in the ORL under tensile loading. The model parameters and data were obtained from Ref [12].

Fig 8

Figure 8 - Comparison of optical and microhardness measurements of ORL thickness with weight-gain data after 420hr exposure.

Fig 9

Figure 9. Measured hardness profile for various microstructures, normalized according to Equation 4 to account for variation in base metal hardness between microstructures.

Fig 10

Figure 10 - Indentation hardness measurements under loads of 15gf, 25gf, and 100gf on the exposed surface for the bimodal microstructure with 45% α P and the basketweave microstructure. Error bars indicate the standard deviation of 5 duplicate indentations per sample and force.

Fig 11

Figure 11 – BSE images of the microstructure of the bimodal microstructure with 35% primary alpha as-heat treated (left) and after 4hr at 650C/WQ (right) showing the stability of microstructure at the exposure temperature

Fig 12

Figure 12 – BSE images of the bimodal microstructure with 45% primary alpha in the ORL (top) and in the base metal (bottom) after 420hr at 650°C showing the slight increase in primary alpha in the ORL.

Fig 13

Figure 13 – Normalized predictions of the thickness of the oxygen-rich layer using Fick's second law.

Fig 14

Figure 14. Predicted critical strain for crack nucleation as a function of exposure time at 650°C for various microstructures of Ti-6424S.

Fig 15

Figure 15. Results from deterministic fatigue crack growth predictions at various stress levels utilizing the oxygen-ingress depth as a function of time for Ti-6424S as the initial crack size. The transition in behavior at smaller crack lengths for each applied stress level is due to the fact that the depth of the crack formed in the oxygen-rich layer did not have sufficient driving force to grow as a long crack and thus small crack effects had to be considered.

Fig 16

Figure 16. The effect of oxygen on the fraction of alpha and beta phases at different temperatures[17].

Fig 17

Figure 17 (a) Beta-approach curve experimentally measured for Ti-6Al4V[37] and Ti-6242S[35]; (b) the calculated rate of change in the volume fraction of beta as a function of temperature. The critical temperature region for differentiation between alpha case and oxygen-rich layer is indicated.