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Thermal oxidation of Ti-6Al–4V alloy and pure titanium under external bending strain: Experiment and modelling

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ABSTRACT

The thermal oxidation behaviour of Ti-6Al–4V alloy as well as pure titanium under external bending strains was investigated through experimental and modelling approaches. Dislocation accumulation due to creep deformation was responsible for the acceleration of oxidation at initial stage. However, the promoted formation of alumina would retard the subsequent scale growth. Moreover, the bending strain had a multi-fold influence on the formation of oxygen diffusion zone. An analytical model was developed to predict the variation of growth stress within the oxide layer along with time. The prediction results agreed well with experimental data.

1. Introduction

Owing to its excellent mechanical properties and corrosion resistance, Ti-6Al–4V alloy has been widely used in different industrial fields, including marine structure components, turbine engine blades and pressure vessels [1–4]. However, the poor thermal-oxidation resistance limited its applications at elevated temperatures. Moreover, the application of external loads made this situation more complicated because the external loads could significantly affect the oxidation behaviour of Ti-6Al–4V alloy [5].

A variety of research has been conducted to investigate the thermal oxidation behaviour of Ti-6Al–4V alloy [6–15]. When the alloy was exposed to an aggressive oxidizing environment, rutile nuclei would preferentially form on the alloy surface and then gradually cover the surface [6,8]. Meanwhile, outward diffusion of titanium and inward diffusion of oxygen would take place simultaneously [6,8,9]. The addition of vanadium would decrease the solubility of aluminum, prevent the formation of alumina at the oxide/substrate interface and promote the aluminum to diffuse outwards [6]. In the later oxidation stage, the inadequacy of activated titanium allowed more aluminium to diffuse outwards through the oxide layer [6]. Finally, nodular alumina became the favoured oxidation product at the gas/oxide interface [6]. Meanwhile, part of the oxygen atoms would diffuse and dissolve into the alloy substrate as interstitial atoms [6,8,9]. The absorption of oxygen into the underneath substrate promoted the phase transformation from beta-phase titanium to alpha-phase [11,13]. As a result, the oxygen diffusion zone (ODZ) would be formed underneath the oxide layer.

The research on the interaction between stress and oxidation can be mainly divided into two categories. The first category was to examine the origin and the development of growth stress during scale growth process. Many experiments have been carried out to measure the growth stress [16–19], and various theories were proposed to explain the generation of growth stress. The Pilling-Bedworth ratio (PBR), which was defined as the volume ratio between formed oxide and consumed metal, was once widely used to predict the sign of growth stress. It was generally believed that the oxide with larger volume was constrained by the underlying substrate when the value of PBR was higher than 1. It would result in the lattice mismatch between oxide and substrate and the generation of compressive stress within the oxide layer [20,21]. The growth strain was a time-dependent variable [16,22]. The linear relationship between growth strain and scale thickness was determined by Clarke et al. through describing the dislocations climb process during the diffusion of ions [22]. Following Clark's idea, a variety of analytical models were proposed to predict the evolution of growth stress along with time [23–27]. Among these models, the

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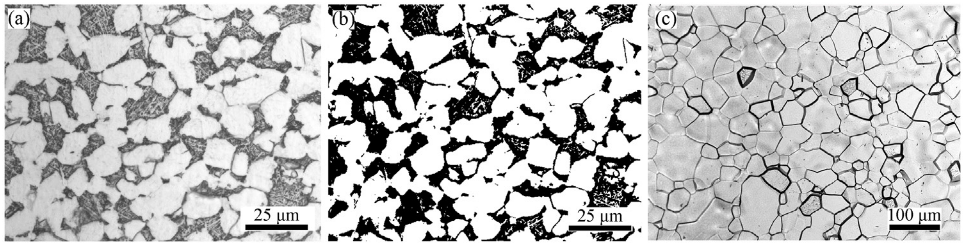

Fig. 1. (a) Cross-sectional microstructure of Ti-6Al-4V alloy, (b) binary image of Ti-6Al-4V microstructure, and (c) cross-sectional microstructure of pure titanium.

stress accumulation due to growth strain and its relaxation due to creep strain were considered by Maharjan et al. [24]. However, the additional component of growth strain due to ODZ has not been considered in the above analytical models. Meanwhile, if the oxidation kinetics is a piece-wise function of time, the constitutive equations should become much more complicated.

The second category was to investigate the effect of applied load on the oxidation behaviour. The main conclusions obtained from the available literature were controversial. It was generally believed that the tensile stress would accelerate the scale growth process. The formation of cracks in oxide layer due to tensile stress provided additional diffusion channels for the oxygen atoms [28,29]. However, the experimental results by Fargeix and Ghibaudo indicated that the formation of vacancies would promote the diffusion of elements through the oxide layer [30]. On the basis of Fick's law, Evans developed a model to describe the stress-dependent vacancy concentration [20], which was widely used in the subsequent research [31,32]. However, Irene et al. suggested that metals or alloys were always screened by previously formed oxide. Then the additionally compressive stress would increase the creep strain rate, leading to the removal of screening oxide and increment of reaction rate [33]. Moreover, the experimental results by Zhou et al. indicated that both externally tensile and compressive stresses would promote the nickel oxidation, and the compressive stress was more pronounced [34]. Hence, it can be concluded that the influence of external loads on oxidation products and kinetics has still not been clarified.

The aim of this paper was to investigate the thermal oxidation behaviour of Ti-6Al–4V alloy as well as pure titanium under external bending strains. The effect of external strains on the growth of oxide layer and ODZ was experimentally identified. Moreover, an analytical model was developed to predict the growth stress within the oxide layer.

2. Experimental procedure

2.1. Materials

The as-received Ti-6Al–4V alloy and pure titanium in the form of plate was provided by Baoji Titanium Industry CO., LTD, China. Prior to oxidation, the as-received plate of Ti-6Al–4V alloy was solution-treated for 1 h at 1073 K, and then annealed at 973 K for 2 h to relieve residual stress. The nominal chemical compositions (in wt.%) of Ti-6Al–4 V alloy were 5.87 Al, 4.04 V, 0.125 Fe, 0.022C, 0.17 O, 0.03 N, 0.01 Si and balanced Ti. The pure titanium was annealed at 823 K for 2 h to relieve residual stress. Chemical analysis showed the nominal chemical compositions (in wt.%) of pure titanium were 0.86C, 0.33 N, 0.3 O, 0.14 Si and balanced Ti. The cross-sectional microstructures of Ti-6Al–4V alloy and pure titanium were shown in Fig. 1. The Ti-6Al–4V alloy consisted of equiaxed primary α-grains and lamellar transformed β-grains. The pixel analysis of the binary image revealed that the area fractions of alpha phase and beta phase were respectively 67% and 33%, as seen in Fig. 1b. According to Delesse's equation, the volume fraction of a specific phase is approximately equal to its area fraction [35]. The pure titanium was entirely composed of alpha phase. The uniaxial tension testing results indicated that the yielding strength, ultimate strength, and Young's modulus of Ti-6Al–4V alloy were respectively 912.5 MPa, 980.6 MPa and 119.5 GPa, as shown in Fig. 2. For pure titanium, they were respectively 293.3 MPa, 219.8 MPa and 115.9 GPa.

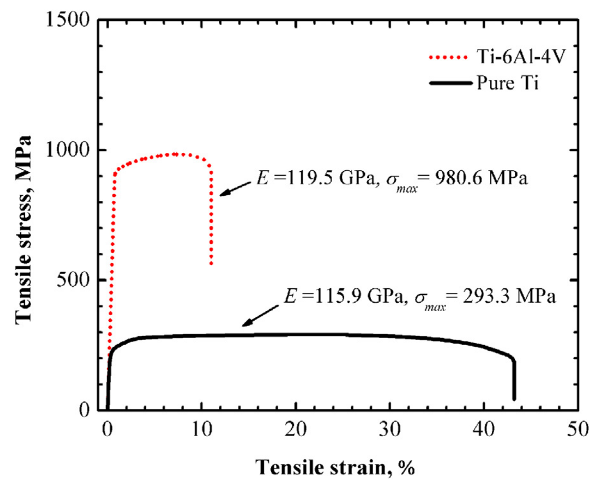

Fig. 2. Tensile stress-strain curves of Ti-6Al-4V alloy and pure titanium.

2.2. Oxidation experiments

Isothermal oxidation of Ti-6Al–4V alloy and pure titanium was conducted at 873 K for up to 96 h in air. The specimens used in oxidation experiments were cut into plates with the dimensions of 68 × 30 × 2 mm^3 by using wire electrical discharge cutting machine. The oxidation behaviour at the 68 × 30 mm^2 surface was investigated. Before oxidation, the specimen surface was ground with 1200 grit SiC papers, and then cleaned ultrasonically in ethanol.

Bending strains were applied at the 68 × 30 mm^2 surfaces to investigate the effect of external strains on the oxidation behaviour. The experimental set-up was designed according to ASTM G39-99 standard guideline [36], as shown in Fig. 3. The maximum deflection of specimens was kept to be 1 mm prior to oxidation experiments, which was monitored by a micrometre. The initial elastic strain, ε_0, was calculated according to the following equation [36],

$$\varepsilon_0 = 12hy\left(3H^2 - 4A^2\right)^{-1} \tag{1}$$

where h is the specimen thickness, y is the maximum deflection, H and A are the distance between outer supports and that between outer and inner supports. In the present work, h, H and A were respectively 2.0, 50.8 and 12.7 mm. Hence, the initial elastic strains were respectively 0.0034 and −0.0034 at the tensile and compres-