Phase transformation sequence of Ti-6Al-4V as a function of the cooling rate

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Abstract. The growth kinetics of allotriomorphic α along the prior β grain boundaries and of globular primary α in Ti-6Al-4V during continuous cooling is described. A physical model is developed based on classical nucleation and growth of platelets for the allotriomorphic α. The growth of the primary α is modelled based on the growth of spherical particle immersed on a supersaturated β-matrix. Continuous cooling tests at two different holding temperatures in the α+β field, 930°C and 960°C, and five different cooling rates, 10, 30, 40, 100 and 300°C/min, are conducted to validate the proposed models and elucidate the growth sequence of those α morphologies. Additionally, interrupted tests at different temperatures are conducted to determine the progress of growth of primary α and formation allotriomorphic α during cooling. The size of primary α increases while its size distribution broadens with a decrease in cooling rate. Area fractions of primary α decrease with increasing cooling rate and increasing holding temperature. Moreover, the lower the cooling rate, the thicker the plates of allotriomorphic α. At the beginning of the cooling, growth of primary α, as well as formation of allotriomorphic α plates is observed. The experimental and modelled results show good agreement.

Introduction

The mechanical properties of Ti-6Al-4V, especially fatigue resistance, toughness and ductility, are strictly correlated with its microstructure formed during the industrial thermo-mechanical treatments [1]. Different microstructures can be achieved, i.e. martensitic, lamellar, equiaxed or bimodal, and they are mainly related to the cooling rate during thermo-mechanical treatment. A bimodal microstructure consisting of lamellar α and globular primary α (αp) is normally desired owing to the combination of high ductility and high toughness [1]. The globular αp phase grows during cooling, and the allotriomorphic α phase is formed along the grain boundaries.

The growth of αp phase is a diffusion-controlled process. For very slow cooling rates, the β phase transforms mainly into αp. Thus, the resulting microstructure consists almost entirely of large equiaxed αp with small amounts of retained β phase [2]. The amount of αp decreases for increasing cooling rates and other morphologies of α phase are formed [3]. Semiatin et al. [4] observed that αp exhibits epitaxial growth for Ti-6Al-4V, and that it is controlled by the diffusion of vanadium. The presence of a rim-α phase in a near α Ti60 [3] surrounding the αp during cooling with the same crystallographic orientation, evidences the epitaxial growth of αp phase. The nucleation and growth of allotriomorphic α (ααB) is dependent on the cooling rate and follows a platelet-like formation [2],[4]. Extensions from αp with same crystallographic orientation were observed preferentially along the β/β boundary suggesting symbiotic growth from the αp phase [3].

Semiatin et al. [4] proposed a model for the growth of αp that uses exact solutions of the diffusion equation and takes into consideration: a) the diffusion coefficients with a thermodynamic correction for the specific composition of the material, and b) the large super-saturation formed during cooling [4]. Meng et al. [5] complemented the model proposed in [4] by considering the effect of the thermal history on the diffusion field of growing particles, and the overlap of these diffusion fields [6].

The development of robust, accurate but computational simple models to simulate the β→α transformation are of great importance to predict and control the evolution of the microstructure in complex shape and variable cross sections components during thermomechanical processing. A coupled model for the growth of primary α and formation of allotriomorphic α phases is here proposed. The results are compared with the measured data acquired for different continuous cooling experiments.

Experimental procedures

Material

A coggled Ti-6Al-4V in the β and α+β fields with further annealing at 730°C for 1 hour followed by air cooling was used for this investigation. The estimated β transus is ~1020°C [7]. Cylindrical samples with a diameter of 5.5 mm and a length 10 mm were utilized for the heat treatments in a dilatometer.

| Al  | V   | Fe  | O   | C   | N   | H   | Y   |
|-----|-----|-----|-----|-----|-----|-----|-----|
| 6.54 | 4.21 | 0.20 | 0.185 | 0.028 | 0.023 | 0.000335 | <0.001 |

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Heat treatments

A dilatometer DIL 805A/D (TA Instruments, Hüllhorst, Germany) was used to perform continuous cooling heat treatments. The tests were carried out in a protective atmosphere of argon. After heating with a rate of 30°C/min, the samples were held for 1 h at two different holding temperatures in the α+β field, 930 and 960°C, followed by continuous cooling until room temperature. The cooling was conducted using five different cooling rates: 10, 30, 40, 100 and 300°C/min. Interrupted continuous cooling heat treatments were carried out in order to elucidate the mechanism(s) governing the transformation during cooling. After heating with 30°C/min, the samples were held for 60 min at a constant temperature of 930°C or 960°C. The subsequent cooling was performed with 10 and 100°C/min. The samples were quenched using Argon at four different temperatures, 900, 875, 850 and 800°C.

Metallography and microstructure investigation

The samples were polished using OP-S (oxide polishing suspension) after a conventional grinding procedure from grit 500 until 2000. The samples were etched with Kroll’s reagent, 91 ml water, 6 ml HNO₃ and 3 ml HF. The metallographically prepared and etched samples were investigated using light optical (LOM) and scanning electron (SEM) microscopy. The SEM analysis were conducted using a Tescan Mira3 microscope using an acceleration voltage of 10 kV and working distance of 12 mm. A minimum of five representative micrographs were analysed for each cooling rate and holding temperature for the quantification of globular αₚ. The globular phases were marked using the software GIMP (GNU Image Manipulation Program) and analysed with ImageJ software.

Modeling strategy

The growth of αₚ during cooling in heat treatments conducted below the β-transus temperature was modelled based on [4]. The growth of allotriomorphic α was modelled based on a classical model of nucleation and diffusion equation for growth of platelet. The microstructure is modelled as consisting of three major components: αₚ, αSEC and αGB, as schematically shown in Figure 1. The nucleation and growth of αSEC is not considered in the present model.

\[ \frac{dR}{dt} = 2\lambda^2 \frac{D}{R} \]  \hspace{2cm} \text{Equation 1} 

Where R is the radius of the particle, D is the diffusion coefficient and λ is a parameter that can be calculated according to Equation 2.

\[ \left\{ \lambda^2 e^{\lambda^2} \right\} \left[ e^{-\lambda^2} - \lambda \sqrt{\pi} \text{erf} \left( \lambda \right) \right] = \Omega/2 \]  \hspace{2cm} \text{Equation 2} 

The parameter Ω denotes supersaturation, and can be calculated according to Equation 3.

\[ \Omega = \frac{(C_M - C_I)}{(C_P - C_I)} \]  \hspace{2cm} \text{Equation 3} 

Where Cᵢ is the composition of the matrix-particle interface, Cₚ is the composition of the αₚ phase, Cₗ is considered as the equilibrium phase composition of the alloy at the actual temperature, and C₀ is considered as the equilibrium phase composition of the α phase. The equilibrium phase fraction as well as the chemical composition were calculated using the software JMatPro® v.10. In order to account for the soft impingement on the “far-field” matrix composition, Cₘ is calculated using a usual mass balance between the fraction of α (f₀) and β phases, as given by Equation 4.

\[ f_β = \frac{C_M - C_I}{C_M - C_P} \]  \hspace{2cm} \text{Equation 4} 

Figure 1: a) Schematic representation of the different morphologies of the alpha phase: primary (αₚ), secondary (αSEC) and allotriomorphic (αGB), formed during cooling of a typical Ti-6Al-4V alloy; b) growth of a spherical particle of radius R and composition Cₚ immersed in a matrix of composition Cₘ in which Cᵢ is the chemical composition at the interface.
\[ C_M = \frac{(C_0 - f_{\alpha}C_\alpha)}{(1 - f_{\alpha})} \]

Where \( C_\alpha \) is the nominal concentration of V in the material and \( C_\alpha \) is the concentration of V in the \( \alpha \) phase. Similar to the growth of \( \alpha_p \), the partial enrichment of V along the formed \( \alpha/\beta \) phase boundary is observed. However, this phenomenon stabilizes locally the \( \beta \) phase. Thus, a plate-like morphology of \( \alpha \) phase is obtained along the \( \beta/\beta \) grain boundaries. When the nucleation time is neglected, the rate of nucleation of precipitates can be given according to Equation 5.

\[
\frac{dN}{dt} = N_0 (1 - f_{\alpha p} - f_{\alpha GB}) \exp \left( -\frac{Q}{RT} \right) \exp \left( -\frac{\Delta G_{\text{Nuc}}^*}{RT} \right)
\]

Equation 5

Where \( N_0 \) is a pre-exponent term and considered as 4.5 \( \times \) 10^4 for a prior \( \beta \) grain size of 200 \( \mu \)m, \( Q \) is the activation energy for diffusion, \( \Delta G_{\text{Nuc}}^* \) is the energy barrier for heterogeneous nucleation, \( R \) the molar gas constant and \( T \) the temperature. \( f_{\alpha p} \) and \( f_{\alpha GB} \) are the volume fraction of \( \alpha_p \) and allotriomorphic \( \alpha \) formed along the prior beta grain boundaries, respectively. The energy barrier for heterogeneous nucleation can be calculated according to Equation 6.

\[
\Delta G_{\text{Nuc}}^* = -\frac{(A^*)^3}{(RT)^2 \left[ \ln \left( \frac{C_\alpha}{C_I} \right) \right]^2}
\]

Equation 6

Where \( A^* \) is a parameter obtained according to the nucleation at grain boundary, or sympathetic nucleation [9], or a sum of contributions of both (adopted in the current model).

The critical thickness (\( B_{\text{crit}} \)) for a disk-like \( \alpha_{GB} \) to nucleate can be calculated according to Equation 7.

\[
B_{\text{crit}} = -\frac{A_{\gamma\alpha\beta}}{\Delta G_{IV}}
\]

Equation 7

Where \( \gamma_{\alpha \beta} \) is the interface energy between \( \alpha \) and \( \beta \) phases, \( \Delta G_{IV} \) is the chemical free energy of phase transformation obtained using Equation 8 [9].

\[
D \Delta \ln G_V = \frac{C_I - C_{\alpha GB}}{1 - C_I} \frac{RT}{(1 + \frac{\partial G_V}{\partial C_I}) \ln \left( \frac{C_I}{C_M} \right)}
\]

Equation 8

Where \( C_{\alpha GB} \) is the concentration of V in the \( \alpha_{GB} \), considered to be equal to the V concentration in the \( \alpha_p \) (\( C_{\alpha GB} = C_p \)).

The nucleus of \( \alpha_{GB} \) will grow by diffusion process, and it is considered to be similar to the growth of the platelets, i.e. thickening of a planar disordered boundary via ledge growth mechanism. In this case, the lengthening of a platelet is significantly faster than the thickening due to high anisotropy in interfacial energy. Therefore, the volume fraction of \( \alpha_{GB} \) is only dependent on the number density and its thickness. The thickening of the \( \alpha_{GB} \) can be then modelled according to Equation 9.

\[
\frac{dB}{dt} = \frac{2m \sqrt{\kappa_{GB}} D}{B}
\]

Equation 9

Where B is the thickness of the \( \alpha_{GB} \), \( m \) is a ledge coefficient to account for the planar disordered growth, \( D \) is the diffusivity of V in the \( \beta \) matrix and \( \kappa_{GB} \) is parameter that can be calculated according to Equation 10.

\[
\sqrt{\pi} e \exp \left[ \frac{\lambda_{GB}^2}{\langle B \rangle} \right] \exp \left[ \frac{\lambda_{GB}}{\langle B \rangle} \right] = \Omega_{\alpha GB}
\]

Equation 10

Where \( \Omega_{\alpha GB} = (C_I - C_M) / (C_I - C_{\alpha GB}) \) is a dimensionless supersaturation parameter, and considered equal to \( \Omega \) because \( C_{\alpha GB} \). Similar to the growth of precipitates, the mean thickness of the platelets \( \langle B \rangle \) is calculated according to Equation 11 [10].

\[
\frac{d\bar{B}}{dt} = \frac{dB}{dt} + \frac{1}{N} \frac{dN}{dt} \left( B_{\text{crit}} - \bar{B} \right)
\]

Equation 11

The first term corresponds to the growth of the existing platelets of allotriomorphic \( \alpha \), while the second represents the contribution of new nuclei of critical size calculated according to Equation 7.

A Matlab® routine was developed to implement the model for the growth of the \( \alpha_p \) previously described.

**Results and discussion**
Figure 2 shows the microstructure of the Ti-6Al-4V argon quenched after 1 h holding at 960°C. Sparsely and nearly separated αp particles are found in a matrix of martensite (α’), originally a matrix of β phase.

From the microstructure shown in Figure 2, different fractions and sizes of α phase are formed during cooling, as shown in Figure 3. The cooling rate of 10°C/min (Figure 4a) lead to a nearly fully equiaxed microstructure, thus mostly growth of αp is exhibited. It is difficult to distinguish the lamellas of αSEC from the globular αp for the cooling rate of 10°C/min. The increase in cooling rate leads to formation of αSEC, as well as αGB phase. For 30°C/min and 40°C/min (Figure 3b and Figure 3c, respectively), αGB exhibits irregularities in the interface surface, as well as the αp phase. Higher cooling rates lead to less pronounced growth of αp and αGB (Figure 3d and Figure 3e). Moreover, regular plate-like morphology of αGB is observed for 100 and 300°C/min.
Figure 3: Representative light optical micrographs of the investigated Ti-6Al-4V after holding at 960°C for 1 h followed by continuous cooling at: a) 10°C/min; b) 30°C/min; c) 40°C/min; d) 100°C/min; e) 300°C/min.

Figure 4 exhibits the typical micrographs after interrupted continuous cooling heat treatments. The $\alpha_{GB}$ is highlighted in red dotted line, and the $\alpha_{SEC}$ in dotted green circles. The formation of $\alpha_{GB}$ initiates from the globular $\alpha_p$, i.e. symbiotic growth. The 2D interconnectivity of the plates of $\alpha_{GB}$ along the grain boundaries is very low for 900°C (Figure 4(a,b)). At 850°C the grain boundaries are nearly decorated with $\alpha_{GB}$. Irregular growth of $\alpha_{GB}$ seems to occur at ~800°C, and is more pronounced for 10°C/min cooling rate (Figure 4g). The nucleation and growth of $\alpha_{GB}$ do not seem to be significant at temperatures higher than 900°C for the two investigated cooling rates, leading to comparable evolution behaviour of the $\alpha_{GB}$ after holding at temperatures of 930°C and 960°C (Figure 4a). Formation of $\alpha_{SEC}$ is not pronounced until ~850°C. Although Figure 4e and Figure 4g show the presence of $\alpha_{SEC}$ for 10°C/min cooling rate, its area fraction is notable small. Similar conclusions can be obtained comparing Figure 3a with Figure 3d.
Figure 4: Representative SE-SEM micrographs of the interrupted heat treatments after holding at 960°C for 1 h followed by continuous cooling at 10°C/min (a,c,e,g) and 100°C/min (b,d,f,h). The tests were interrupted at: a,b) 900°C; c,d) 875°C; e,f) 850°C; g,h) 800°C.

The mean $\alpha_p$ diameter, area fraction of $\alpha_p$ and the mean thickness of $\alpha_{GB}$ is compared for the simulated and measured results in Figure 5. The diameter of $\alpha_p$ increases with decrease of cooling rate and the model predicts with good accuracy this behaviour. The increase in area fraction of $\alpha_p$ is pronounced for decreasing cooling rates. The developed model describes well the area fraction evolution apart from 30 and 40°C/min for
The holding temperature of 960°C. The thickness of the αGB was in the range of 1-4 µm for the investigated conditions and it increased with decreasing cooling rates. The differences between 930°C and 960°C are not significant.

![Figure 5: Measured and simulated microstructural features for the investigated cooling rates for the holding temperatures of 930°C and 960°C: a) mean αP phase diameter, and b) area fraction of αP; c) measured and simulated thickness of the αGB](image)

To illustrate the results of the developed model, the evolution of the mean diameter of αp, mean thickness of αGB and vanadium supersaturation is exhibited in Figure 6 for the holding temperature of 960°C. A significant growth of αp as well as αGB is predicted down to 800°C, which was also observed in Figure 4. The supersaturation of V in β phase matrix is predicted to increase sharply until ~850°C, when the αSEC is observed to be formed more pronounced (Figure 4).
Summary and conclusions

The sequence of growth of the α phases (primary, secondary and allotriomorphic) during cooling from an isothermal temperature below the β-transus is clarified and modelled for Ti-6Al-4V. Nucleation of α_{GB} starts at the globular α_p, as well as in other regions. A coupled physical model for the growth of α_p phase and the growth of the α_{GB} is developed and the following conclusions can be drawn:

- Growth of α_p is more pronounced for low cooling rates and occurs more notable until ~800°C.
- Regular (planar) interface shape of α_{GB} is observed decorating the prior β grain boundaries for high cooling rates. For low cooling rates irregular shapes are observed.
- α_{GB} nucleates preferentially from existing α_p phase. For higher cooling rates nuclei in triple points and other regions of the prior β/β grain boundary are observed. The higher nucleation rate for those cooling rates can explain the different behaviour.
- A sharp increase of V supersaturation in the β matrix is observed until ~850°C, which is attributed to contribute to the formation of α_{SEC}, especially for cooling rates higher than 10°C/min.

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