HIGH TEMPERATURE OXIDATION OF Ti-6Al-4V ALLOY FABRICATED BY ADDITIVE MANUFACTURING. INFLUENCE ON MECHANICAL PROPERTIES.

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Abstract

Titanium alloys, such as Ti-6Al-4V alloy, fabricated by additive manufacturing processes is a winning combination in the aeronautic field. Indeed, the high specific mechanical properties of titanium alloys with the optimized design of parts allowed by additive manufacturing should allow aircraft weight reduction. But, the long term use of Ti-6Al-4V alloy is limited to 315 °C due to high oxidation kinetics above this temperature [1].

The oxidation behaviour of Ti-6Al-4V alloy at 600 °C of as-built and HIP-ed microstructures was studied. This temperature was chosen to increase oxidation kinetics and to study the influence of oxidation on tensile mechanical properties. In parallel, two other oxidation temperatures, i.e. 500 °C and 550 °C allowed to access to the effect of temperature on long-term oxidation.

Introduction

In the aeronautic field, reducing flight consumption of planes is one of the main objectives. One of the key measures is the weight decrease of the plane. Using lighter metals such as titanium alloys or additively manufactured parts with complex geometry are of interest. Ti-6Al-4V alloy (wt%) is the most used titanium alloy in the aeronautic field and many studies investigating the development of this alloy fabricated by additive manufacturing were published [4-6]. The Electron Beam Melting (EBM) process is a powder bed fusion process used only for conductor materials [5]. The electron beam works in a vacuum environment and is focused on the powder bed using electromagnetic lenses [7]. To avoid the sputtering of the powder, a pre-heating step is used before melting the metallic powder, leading to maintain the powder around 780 °C. Once the melting step is done, the powder bed is recoated by another powder bed and the operation is repeated until the final part is built [5, 6, 8-11]. For Ti-6Al-4V alloy, the high cooling rates and the high building temperature induce a thin lamellar Ti-β phase into a Ti-α matrix microstructure. Hot Isostatic Pressing (HIP) treatment at 920 °C during 2 h at 100 MPa is commonly used on additively manufactured Ti-6Al-4V alloy to close pores and modify microstructure and mechanical properties [12]. Inside or close to plate’s engines, oxidation behaviour of metal alloys is of interest. Kaki et al. showed the modification of tensile properties induced by oxidation [13]. Due to the increase of engines working temperatures in order to increase their efficiency, titanium alloys may face higher oxidation rates. The use of titanium alloys is limited to low temperature areas due to their high oxidation kinetics above 550°C. Temperature is even lower for Ti-6Al-4V i.e. 315°C [1]. Reacting with air, titanium alloys form an oxide and dissolve oxygen in the metallic matrix. The diffusion of the oxygen in the metallic matrix induces a modification of mechanical properties leading to premature failure [13]. Oxidation behaviour of Ti-6Al-4V alloy was essentially reported at temperatures between 600 and 1000 °C and for durations up to 3000 h [14-19]. Sefer et al. and Ciszak et al. published some of the few studies characterizing the oxidation behaviour of Ti-6Al-4V alloys at lower temperatures. Moreover, only two studies were published on the oxidation of titanium alloys Ti-6Al-4V-3Al-5Mo-3Si-0.7Zr [20, 21].

Materials and experiments

Ti-6Al-4V alloy samples were fabricated by EBM using an Arcam Q20 + at IRT Saint Exupéry, France, using Arcam’s parameters and theme 5.2.24. The building chamber was maintained in a partial vacuum of 4.10^-3 mBar and the building plate was pre-heated around 700 °C. Fresh pre-alloyed Ti-6Al-4V grade 23 powder, plasma atomised by AP&C, was used. The particles size was 45-106 µm. The initial powder composition in weight percent was 6.35 Al, 3.68 V, 0.19 Fe, 0.01 C, 0.02 N, 0.01 Mn, 0.08 O (α), 16.75 Ti, 30.5 V, 0.16 Fe, 0.04 C, 0.07 N, 0.05 H, 0.23 O). HIP was carried out on as-built samples at 920 ± 10 °C for 2 h with a pressure of 1020 ± 10 bar. In addition, a rolled β-annealed Ti-6Al-4V alloy was used as comparison point. Microstructure investigations were performed with an Optical Microscope (OM) Nikon Eclipse MA200 after etching with Kroll reagent for 5 minutes. Finer observations were assessed with a Scanning Electron Microscope (SEM) FEI Quantm 450. Oxidation experiments at 600 °C were performed on 28 x 28 x 2 mm³ samples in a pre-heated Carbolite furnace LHT 6/60 with forced convection. In order to study the influence of surface roughness and HIP treatment on oxidation behaviour, 2 samples were kept as-built, 7 samples were polished with SiC abrasive paper of P320 grit size and 5 samples were HIP treated and polished with SiC abrasive paper of P600 grit size. Oxidation was characterized by weight gain, oxide layer and oxygen diffusion zone thicknesses measurements using a Surfotrac LA 75 3200D balance with an accuracy of ± 20 µg, optical and electronic microscopes and microprobe (EPMA) respectively. EPMA measurements of oxygen content in titanium is difficult because of oxygen pollution in the native oxide on its surface. In order to quantify this oxygen pollution, bulk oxygen concentration was measured on a cross section, with an average over 20 points. EPMA signal was corrected to bring back oxygen content between 800 - 1000 ppm (in wt) in the bulk of the TA6V sample. Indeed, the value of 800 - 1000 ppm (in wt) is the oxygen concentration measured in EBM sample when using powder with an initial oxygen content of 800 ppm [22]. This oxygen pollution was removed on all points of the EPMA profiles. Cross-sections were also performed using MEI-FIB FEI HELIOS 600 to observe oxide layers. Tensile tests were performed on a Zwick/Roell 1010 at CIRIMAT using a load scan micrometer Mitutoyo LSM-506 to measure displacement. Gauge area of tensile specimens was 50 x 5 mm² and 1.3 mm thick and was polished with SiC abrasive paper of P600 grit size. In order to investigate the influence of oxidation on tensile properties, two samples were oxidized at 600 °C in the Carbolite furnace LHT5/60 for 500 h, before running tensile tests. Rupture surfaces were observed using LEI 435 VP scanning electron microscope.

Results

Microstructure

Figure 1 (a) and (b) show the EBM Ti-6Al-4V alloy microstructures before and after HIP treatment. HIP erases some of the prior lamellar Ti-β grains into a Ti-α matrix. High temperature oxidation of Ti-6Al-4V alloy at 600 °C of as-built and HIP-ed microstructures was studied. This temperature was chosen to increase oxidation kinetics and to study the influence of oxidation on tensile mechanical properties. In parallel, two other oxidation temperatures, i.e. 500 °C and 550 °C allowed to access to the effect of temperature on long-term oxidation.

Oxidation behaviour

Oxidation kinetics at 600°C of Ti-6Al-4V alloy fabricated by EBM were characterized by weight gain measurements and are presented in Figure 2 (a). Both as-built EBM samples have larger weight gains than polished EBM samples. Figure 2 (b) also shows that oxide layer thicknesses of as-built EBM samples is slightly higher than polished samples. However, these differences in oxide scale thicknesses are not large enough to explain the differences of weight gains. When studying LBM alloy 718, Sanviemvongsak et al. showed that larger weight gains of LBM samples were due to the
higher surface area of as built samples, and to the oxidation of powder grains partially melted at the surface [23]. The same conclusions were reached in a previous study focused on the oxidation of Ti-6Al-4V alloy fabricated by EBM. In this last study, it was shown that powder grains oxidation partially melted at the surface was even more important for Ti-6Al-4V than for alloy 718, because of the breakaway oxidation kinetics of titanium spheres [21]. In the present study, the role of surface roughness on the oxidation kinetics is confirmed by the fact that all 12 samples fabricated by EBM present the same weight gains once ground with P600 paper (7 samples EBM P600 and 5 samples EBM HIP P600), as shown in Figure 2 (a). In addition, it can be observed that the HIP treatment does not influence the oxidation kinetics of Ti-6Al-4V alloy fabricated by EBM.

Figure 2: Ti-6Al-4V alloy fabricated by EBM: (a) Weight gains; (b) Oxide layer thicknesses

Figure 3 (a) exhibits a cross-section of a sample oxidized 500 h at 600°C. The white layer on the top of the oxide scale is a platinum layer used to keep the integrity of the oxide layer during cutting the samples with an ion beam. The oxide layer shows stratification with several layers separated by pores. The oxide layer seems to be composed of a dense layer between two porous layers. For the sample, oxidized 500 h at 600 °C, Figure 3 (b) shows faceted crystals with an elongated morphology of about 40 nm diameter, present at the top of a clearly porous layer. During oxidation, coalescence between independent crystals leads to the formation of larger agglomerates (not shown here). A large density of pores was observed next to and at the oxide/metal interface. This could be the reason for the scale spallation observed for longer oxidation durations.

Figure 3: Oxide layer of a Ti-6Al-4V alloy fabricated by EBM oxidized 500 h at 600 °C: (a) Cross-section; (b) Surface morphology

Figure 4 (a) presents six oxygen diffusion profiles measured by EPMA at different locations on the same sample oxidized for 500 h at 600 °C. It shows that reproducibility is good. A simple diffusion model with the error function represented in Eq (1) was used to fit the experimental data. This allowed to measure an effective oxygen diffusion coefficient D and to estimate the oxygen concentration at the metal/oxide interface. The thickness of the oxygen diffusion zone can be defined using the effective oxygen diffusion coefficient and the time with the relation

\[ ODZ = \frac{1}{\sqrt{D \cdot t}} \]

Where \( C_0 \) is the initial oxygen concentration in the metal, \( C_s \) is oxygen concentration in the metal close to the oxide/metal interface, \( D \) the effective oxygen diffusion coefficient of oxygen in the metal, \( t \) the time and \( C_x \) the oxygen concentration at the depth \( x \).

\[ C_x = C_0 + (C_s - C_0) \cdot \left( 1 - erf \left( \frac{x}{2 \sqrt{D \cdot t}} \right) \right) \]

Eq(1)

Figure 4: Ti-6Al-4V alloy fabricated by EBM and oxidized 500 h at 600 °C: (a) Oxygen concentration profiles; (b) Error fitting function of oxygen concentration profiles and determination of the oxygen diffusion zone thickness

Figure 2 (a) shows that oxidation follows parabolic kinetics in which can be quantified using Eq (2):

\[ \frac{\Delta W}{A} = \sqrt{k_p \cdot t} \]

where \( k_p \) is the parabolic rate constant, \( \Delta W \) the weight gain and \( t \) the time. \( A \) is the surface area of a sample determined from its dimensions. Figure 5 shows that the Arrhenius law, Eq (3), can be used to compare parabolic rate constants \( k_p \) obtained in the present work and in the literature at the same or at different temperatures:

\[ k_p = A \cdot e^{-\frac{E_a}{RT}} \]

Eq (3)
where $E_a$ is the activation energy, $R$ the gas constant and $T$ the reaction temperature.

Results of this study are in good agreement with the literature. Moreover, Ti-6Al-4V alloy fabricated by EBM presents similar oxidation kinetics as fabricated by conventional manufacturing processes.

The effect of oxidation on mechanical properties was studied using uniaxial tensile tests. Figure 6 (a) shows tensile tests of Ti-6Al-4V alloy fabricated by EBM and polished with P600 grit size. Results concerning unoxidized and oxidized specimen during 500 h at 600 °C are given too. During the tensile test, spalling of the oxide layer produces flakes which pass in front of the laser measuring the length of the sample and produce fake deformation jumps on the tensile curves, Figure 6 (a). For the sample size and the oxidation conditions studied, it appears that oxidation significantly reduces the elongation at break but does not influence the yield strength and the ultimate tensile strength, as shown in Figure 6 (a). Study of the fracture surfaces shows an external area with a brittle fracture mode and an inner section with a ductile behavior with cupules, as shown on Figure 6 (b). Oxide scale has spalled during the entire test and was not observed on fracture surface observations. The depth of brittle rupture is $\approx 24 \pm 4 \mu m$. It can be compared with the depth of zone affected by oxygen (Fig. 4b).

EBM Ti-6Al-4V alloy presents a fine lamellar microstructure composed of submicronic $\alpha$ laths into a $\beta$ matrix. HIP treatment is used to reduce porosity and induces the coarsening of $\alpha$ laths. As seen on weight gains and oxide layer thickness measurements, despites its large effect on the alloy microstructure, HIP does not influence the oxidation behaviour, Figure 2. Cross-sections observed with SEM show the presence of pores into the oxide layer and at oxide/metal interface. Tensile tests and SEM observations of fracture surfaces shows that the oxide layer quickly spalled during the tensile test. EPMA measurements were used to determine the oxygen diffusion zone which has an influence on mechanical properties. Tensile tests confirmed that oxygen diffusing into the metal decreases the elongation at break and changes the rupture mode from ductile to brittle. The brittle fracture zone thickness is slightly higher ($\approx 23 \mu m$) than the oxygen diffusion zone thickness which can be determined by EPMA ($\approx 18 \mu m$), Figure 4 (b) and Figure 6 (b). This shows that the critical amount of oxygen necessary to embrittle the alloy is much lower than the minimum amount of oxygen which can be measured accurately by EPMA. It is possible to use the diffusion model to estimate this critical value. The calculated diffusion profile allowed to approximate the oxygen concentration at 23 $\mu m$ deep (Fig 4b). This value is about 0.5 at%. It can be compared to the result obtained by Yan et al. determined a drop of ductility for an oxygen concentration above 0.33 mass% ($\approx 1$ at%) into the metal [27].

Additive manufacturing processes commonly make use of HIP. This high temperature treatment under pressure allows to reduce porosity but also induces microstructure evolutions. It was shown that HIP strongly influences the microstructure of TA6V. Nevertheless, for EBM Ti-6Al-4V alloy, HIP does not influence oxidation kinetics. The oxide layer obtained after 500 h at 600 °C is 7 ± 1 $\mu m$ thick with prismatic needles at its top. This oxide layer presents an inner dense layer between porous layers. Pores in the inner part delimitate oxide scale sublayers which may induce spallation during tensile tests. The oxygen diffusion zone in the metal drastically reduces the elongation at break and changes the rupture mode from ductile to brittle. It was shown that the oxygen diffusion zone which can be measured with the accuracy of EPMA, $\approx 18 \mu m$, is slightly lower than the observed brittle zone which is about 23 ± 4 $\mu m$ after 500h at 600°C. Using diffusion modelling, the critical oxygen content at the transition between the brittle and ductile failure was estimated to be lower than 1 at% determined by Yan et al. [27].

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