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An experimental study of Ti-6Al-4V powder reactivity in gaseous environment: Application to additive manufacturing

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Abstract

Currently, one of the current issues related to the additive manufacturing is the change in the properties of Ti-6Al-4V powder during this process. This change has been attributed to the interaction of this powder with its gaseous environment that can contain a small quantity of oxygen, nitrogen, carbon dioxide and/or water vapour. Therefore, the aim of this work is to study the effect of oxygen and nitrogen partial pressure as well as the effect of the temperature on the corrosion of the Ti-6Al-4V powder. The results show that the temperature and the oxygen partial pressure have an effect on the **corrosion kinetics**, which is not the case of nitrogen partial pressure. This study is a first step towards a better understanding of the **ageing** of Ti-6Al-4V powder during additive manufacturing processes.

Introduction

Additive manufacturing is considered a promising technology for the design of complex metallic pieces, in a rather short timeframe. Various technologies have been developed based on this concept: for instance, Selective Laser Melting (SLM), Electron Beam Melting (EBM) or Direct Metal Deposition (DMD) are the main three technologies deployed in industry. All these techniques are based on the local melting of previously deposited metallic powder under inert atmosphere. Among the various alloys already available for additive manufacturing, Ti-6Al-4V is one of the most used materials due to its numerous applications in industry –aeronautics and biomedical– and its associated high cost of manufacturing and long lead time[1]. However, it is important to notice that in the additive manufacturing processes, only a small amount of powder is actually used for the final piece and it has been observed that the chemical and rheological properties of the reused powder differ from those of the initial one. These changes are associated with the interaction of the powder with the gaseous environment (corrosion, humidity) in combination with the thermal gradient starting from the melting powder (higher than 1600°C) to the chamber room. The kinetics of the corrosion of Ti-6Al-4V alloy has been extensively studied in the literature for the bulk material, especially regarding high temperature oxidation [2–14]. For instance, H.L. Du et al. [4] observed the formation of a multi-layered oxide structure, that consists of rutile TiO₂ (inner layer) and corundum Al₂O₃ (outer layer). The number of layers within this oxide structure increases proportionally with the increase of temperature and time. Furthermore, the authors presented a mechanism of formation of the multi-layered oxide scale based on the activity of the elements existing in Ti-6Al-4V alloy. This mechanism can be summarized as follows: after the growth of the first duplex TiO₂/Al₂O₃ scale, the difference between the molar volume of TiO₂ oxide and Ti-α (Pilling & Bedworth ratio=1.81) leads to compressive stress inside the scale, resulting in cracks at the metal/oxide interface. Similar results were reported by S. Frangini et al. [5] who observed a transition in the oxidation kinetics from a parabolic to a linear behavior with increasing temperature and time. The authors assume that this transition is due to a change in the morphology of the oxide scale. Additionally, F. Pitt & M. Ramulu [11] reported that the microstructure, specifically the grain size of the Ti-6Al-4V alloy, can play an important role in the oxidation kinetics. In contrast, E. Dong et al. [6] showed that the oxide scale is made of an outer layer of Al₂O₃ and TiO₂ and an inner multilayer containing TiO₂ and TiVO₄. On the other hand, few work has been dedicated so far to the study the corrosion and **ageing** of Ti-6Al-4V powder and the effect of the grain geometry which can play an important role in the corrosion kinetics [15],[16]. For example, in the case of a rate-determining step at the internal interface (between the metallic and oxide phases) and if the oxide layer grows inwards, the surface area of the internal interface and thus the reaction rate will decrease with the reaction conversion for spherical particles. For bulk material (plate-like geometry), the surface area of the internal interface remains constant and the reaction rate does not change with time (for a rate-determining step at the internal interface and in isothermal and isobaric conditions). Moreover, M.M. Arafat et al. [16] found an absence of cracks during high temperature oxidation of Ti-6Al-4V spherical particles with a diameter smaller than 20 μm, what they explained by the absence of pores accumulation at the metal/oxide interface. For these reasons, there is a growing interest to understand the oxidation of Ti-6Al-4V powders that takes into consideration both the geometry and the dimensions of the powders. Therefore, the main goal of the present investigation is to study the behavior of Ti-6Al-4V powder during high temperature corrosion in the temperature range 600-750°C, partially simulating the temperature gradient affecting the unused powder during additive manufacturing. **For the oxidizing gaz, and in order to better understand the corrosion kinetics for this powder, the amount of oxidation found in this work does not represent at all the actual finding during additive manufacturing.** The effect of oxygen and nitrogen partial pressure as well as the nature of the oxide scale formed on the Ti-6Al-4V powder will be discussed.

Materials & Methods

Ti-6Al-4V powder manufactured by the TLS company has been used for this study. The powder is obtained by a plasma atomization process under argon, leading to nearly perfect spherical grains with diameter ranging from 10 to 60 μm, in accordance with the safety data sheet provided by the manufacturer. The chemical composition of the alloy has been measured by inductively coupled plasma-optical emission spectrometry (ICP-OES. Model Activa from Horiba Jobin-Yvon).

Table 1: Chemical composition of Ti-6Al-4V powder from TLS

	Ti	Al	V	Fe	O	N	H	C	Y
wt. %	balance	6,36	4,06	0,22	0,11	0,007	0,0026	0,015	<0,001

The study of the corrosion kinetics of Ti-6Al-4V powder as a function of temperature as well as oxygen and nitrogen partial pressures have been carried out using thermogravimetry analysis with a symmetrical thermobalance TAG24 from SETARAM (which allows a direct compensation of Archimedes' buoyancy and thermohydraulic effects). This apparatus allows monitoring the mass change during the high temperature corrosion experiments. The experimental procedure can be detailed as follows: **to avoid the mass and heat transfer**, approx. 15 mg of Ti-6Al-4V powder is weighted into an alumina crucible placed inside the furnace. Once closed this latter is pumped down with a rotary pump for 30 min then filled with commercial helium until reaching atmospheric pressure (10^5 hPa). The furnace is then flushed with helium for 30 min before the heating ramp of $10^\circ\text{C}/\text{min}$. Once the targeted temperature is reached, a mixture of helium and a corroding gas with a controlled partial pressure is injected at a flowing rate of 4 L/h. The temperature and gas partial pressures are kept constant for 5 hours. The time $t=0$ (s) of the mass curves presented here corresponds to the beginning of the isothermal and isobaric conditions.

The results of thermogravimetry analysis have been processed as follows. The mass change as a function of time is normalised according to Eq. 1, where m_0 represents the initial sample mass and m_t the sample mass at a given time.

$$\Delta m = \frac{m_t - m_0}{m_0}, \text{ Eq. 1}$$

The effect of nitrogen and oxygen partial pressures has been studied under 5 hPa and 25 hPa of N_2 and 5, 15, and 20 hPa of O_2 at 700°C , respectively. Moreover, the effect of the temperature has been studied at 600, 700°C and 750°C under 15 hPa of O_2 .

The corroded samples have been characterized with Field-Emission Gun Scanning Electron Microscopy (FEG-SEM) using a Zeiss Supra 55 VP microscope coupled with energy dispersive X-ray spectroscopy (EDX). The Ti-6Al-4V powders are observed either directly or in cross-section. In this latter case the specimen is mounted in a cold resin, then polished using SiC abrasive with grit size ranged from 1000 to 2400 and finally $0.04 \mu\text{m}$ colloidal silica suspension. Afterwards, the mounted samples are ultrasonically cleaned in alcohol and air-dried.

Results and discussion

The mass change of a Ti-6Al-4V powder sample during a typical high temperature treatment at 700°C for 5 hours under helium at atmospheric pressure is presented Figure 1. It is noteworthy that the sample mass increases with time. This mass gain of approximately 5% ($\Delta m=0.05$) of the initial sample mass is explained by the presence of impurities in helium. The helium gas used for this study is actually contaminated by a small amount of impurities which have been quantified: for a total pressure of 1000 hPa, a partial pressure of 0.5 hPa of water vapour, 0.1 hPa of oxygen and 0.4 hPa of nitrogen have been determined. Thus, this mass gain is not surprising since the Ti-6Al-4V alloy is well known to highly react at high temperature with nitriding and oxidising species. From this point of view, these impurities should be taken into account regarding the corrosion kinetics. That is why a minimum partial pressure of O_2 of 2.5 hPa has been imposed for the whole set of experiments, assuming this gas was the main responsible of the mass gain observed on Figure 1.

The influence of the nitrogen partial pressure on the corrosion kinetics of Ti-6Al-4V is presented Figure 2. The plot of normalized mass change of Ti-6Al-4V samples versus time recorded for a heat treatment carried out at 700°C for 5 h for two different partial pressures of nitrogen, respectively 5 hPa and 25 hPa, highlights no evidence of an effect of nitrogen partial pressure in these conditions. One can assume that the mass gain is mainly due to the oxidation of Ti-6Al-4V under the 2.5 hPa partial pressure of O_2 .

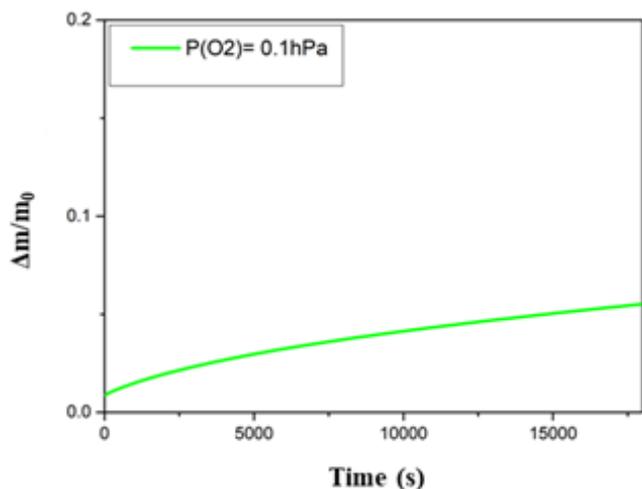


Figure 1: Normalized mass change of Ti-6Al-4V powder heat-treated at 700°C under He with 0.1 hPa of O₂.

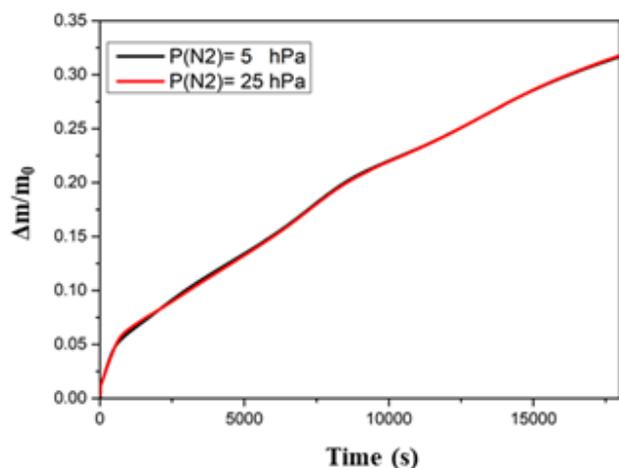


Figure 2: Influence of nitrogen partial pressure on the normalized mass change of Ti-6Al-4V powder during thermal corrosion at 700°C under P(N₂)=5 hPa (black line) and P(N₂)=25 hPa (red line), with P(O₂)=2.5 hPa in both experiments.

Effect of oxygen partial pressure

Figure 3 shows the corrosion tests performed on Ti-6Al-4V powder samples for several oxygen partial pressures (P(O₂)=0.1, 5, 15 and 20 hPa) at 700°C for 5 h.

First of all, two experiments have been carried out at P(O₂)=5 hPa in order to verify the repeatability of the experiments. As it can be noticed comparing the red & turquoise curves plotted in Figure 3, the repeatability of the measurements are very good. Therefore, if the mass gain after 5 h at P(O₂)=0.1 hPa remains relatively low (Δm=0.05), the values increases with the partial pressure of O₂. Indeed, the mass gains after 5 h are 0.38, 0.4 and 0.42 for partial pressure of O₂ equals to 5, 15 and 20 hPa, respectively. This slight increase in mass gain is not surprising since the different oxygen partial pressure are with a comparable order of magnitude. However, when the magnitude of the oxygen partial pressure was 25 time smaller (0.1 hPa), a significant effect of oxygen partial pressure is observable. Focusing on the oxidation under 5, 15, 20 hPa, it is clear that the oxygen partial pressure has a negligible effect for the first 3000 seconds (Δm=0.15 for the four corrosion tests). These similar mass gains are probably due to the dissolved oxygen in the Ti-6Al-4V alloy that represents 27 at.% of the total oxygen amount (after 300 h under air at 700°C) [5]. Beyond 3000 s, the mass gain increases slightly and proportionally with oxygen partial pressure. According to G. Bertrand et al. [18], this slight increase in mass gain is due to a slight difference in the structure of the oxide scale. In order to better understand the reasons of these results, the different oxide scales are currently under study.

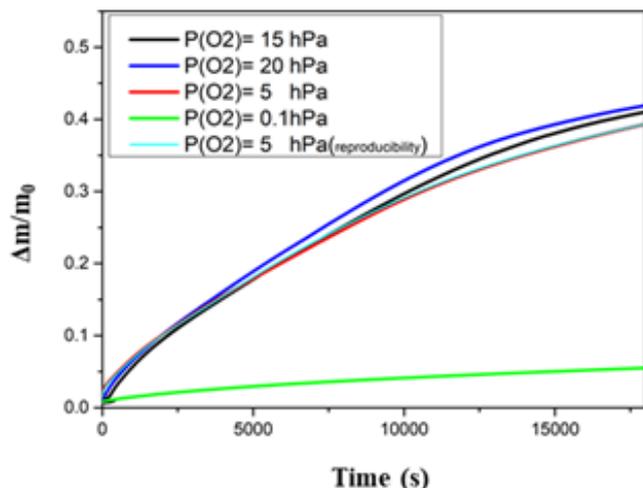


Figure 3: Normalized mass change of Ti-6Al-4V powder samples heat-treated at 700°C, as a function of time for various oxygen partial pressures.

Effect of the temperature

Figure 4 shows the evolution of the normalized weight gain (Δm) versus time at various temperatures for the same partial pressure of O₂. It is evident that increasing temperature causes an **increasing** on the oxidation of the Ti-6Al-4V powder. At 600°C the mass gain is very low ($\Delta m=0.08$), while at 700°C and 750°C it is higher ($\Delta m=0.43$ and 0.58 respectively).

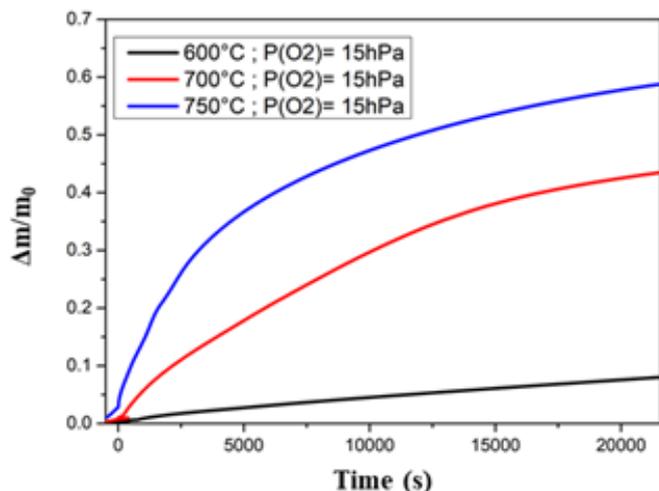


Figure 4: Effect of temperature on the oxidation kinetics of Ti-6Al-4V powder. The oxygen partial pressure is kept constant at P(O₂)=15 hPa.

Figure 5 and Figure 6 show the SEM images and corresponding elemental map of the Ti-6Al-4V powder after high temperature oxidation for 5 h at 600°C and 700°C, respectively. For the corrosion test at 600°C, a single layer of oxide is visible on the surface of the particles (Figure 5-a). EDS elemental map reveals that this oxide scale consists mainly of Ti and O (Figure 5-b & 5-d). Al is less detected in the oxide scale (Figure 5-c). It is interesting to note that despite the high value of the Pilling & Bedworth ratio (PBR) between TiO₂ and Ti-6Al-4V alloy (PBR=1.81 for Ti- α and PBR=1.74 for Ti- β), cracks are not found in this case. On the other hand, cracks are visible on the metal/oxide interface for the powder oxidized at 700°C (see white arrow on Figure 6-a). From the EDS elemental mapping, the presence of O in the whole scale is evident (Figure 6-d). The detection of Al atoms only in the outer oxide scale (Figure 6-c) suggests that this layer is Al₂O₃ whilst Ti atoms detected in the inner oxide scale suggests that this layer is TiO₂ (Figure 6-b). According to H.L. Du [4] who studied the oxidation behaviour of Ti-6Al-4V bulk in the range of 650-850°C under air, cracks are a result of the limited plasticity of the oxide scale. In addition, C. Coddet and al. [17] reveal that the adherence of the oxides layers is relatively high for temperatures below 650°C, while it drops sharply at 700°C.

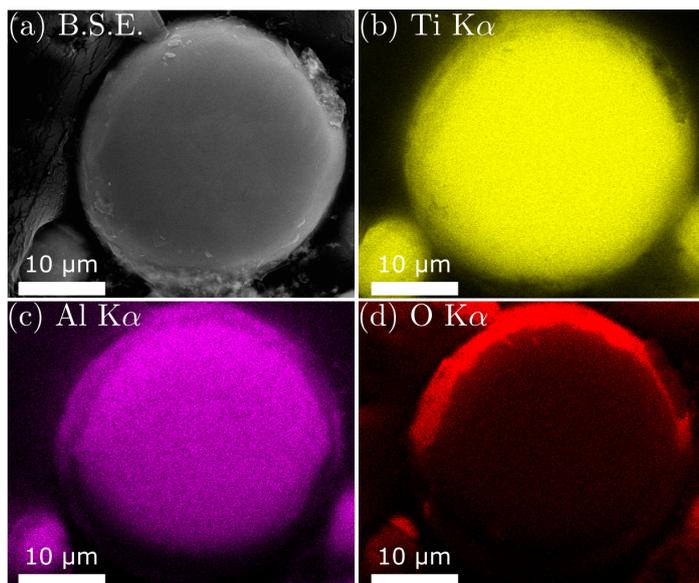


Figure 5: SEM image in back-scattered electron mode (a) and EDX mapping –(b): Ti, (c): Al, (d): O- of Ti-6Al-4V powder oxidized at 600°C for 5 h, with $P(O_2)=15$ hPa.

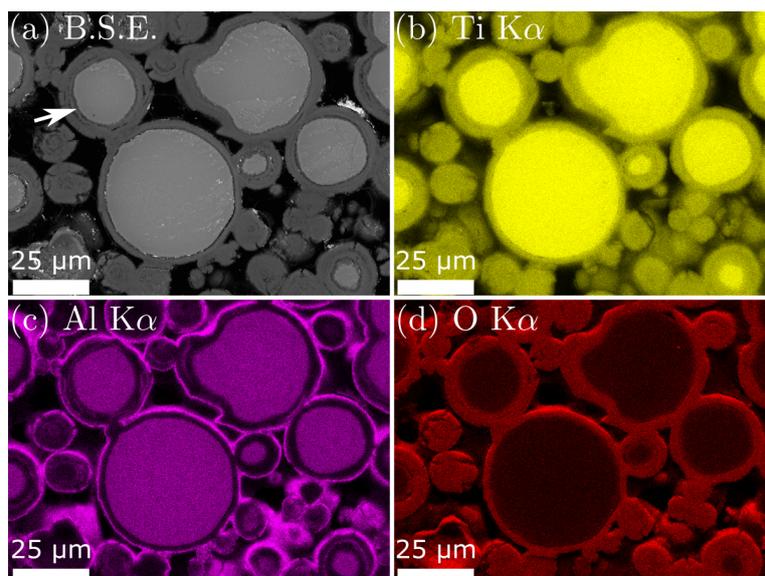


Figure 6: SEM image in back-scattered electron mode (a) and EDX mapping –(b): Ti, (c): Al, (d): O- of Ti-6Al-4V powder oxidized at 700°C for 5 h, with $P(O_2)=15$ hPa.

Conclusion

This study dealt with the effect of thermodynamic parameters such as temperature and partial pressures of O_2 and N_2 on the corrosion kinetics of Ti-6Al-4V powders used in additive manufacturing. This experimental study relied on thermogravimetry analyses in isothermal and isobaric conditions. First, the effect of impurities (namely O_2 , N_2 and H_2O) found in a commercial inert gas has been demonstrated during the heat treatment of Ti-6Al-4V powder. In addition, it has been shown that the variation of nitrogen partial pressure does not influence the corrosion kinetics of Ti-6Al-4V powder heat-treated 5 h at 700°C. On the other hand, the partial pressure of oxygen has a direct influence on the mass gain of Ti-6Al-4V powder, just as the temperature of the heat treatment. Based on these first results, the next phase of this project will be to take into account the partial pressure of H_2O , as well as to quantify the corrosion kinetics of Ti-6Al-4V powders as a function of the partial pressures of the different corroding gases, which may be found in an additive manufacturing apparatus.

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