Thermodynamic analysis of oxidation during selective laser melting of pure titanium

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Abstract

Purpose – When a pure titanium component is fabricated in a selective laser melting (SLM) process using titanium powder, the oxygen concentration of the SLM sample increases compared to the initial powder. The purpose of this paper is to study the reason for increasing oxygen concentration after SLM.

Design/methodology/approach – To understand this phenomenon, the authors analyzed the oxidation behavior during the SLM process thermodynamically.

Findings – Based on the laser parameters used in this study, the temperature of the Ti melt during the SLM process was expected to rise to 2,150°C. Based on the thermodynamic analysis, the equilibrium oxygen partial pressure for oxidation was 2.32×10^{-19} atm at 2,150°C when the dissolved oxygen concentration in the titanium is 0.2 wt.%. However, the oxygen partial pressure inside the SLM chamber was 1×10^{-3} atm, which is much higher than the equilibrium oxygen partial pressure. Therefore, oxidation occurred during the SLM process, and the oxygen concentration of the SLM sample increased compared to the initial powder.

Originality/value – Most studies on fabricating Ti components using additive manufacturing (AM) have been focused on how the changes in the microstructures and mechanical properties depend on the process parameters. However, there are a few studies that analyzed the oxygen concentration change of Ti during the AM process and its causes. In this study, the authors analyzed the oxidation behavior during the SLM process thermodynamically.

Keywords Titanium, Selective laser melting, Oxygen concentration, Oxygen partial pressure

Paper type Research paper

1. Introduction

Ti has a high strength-to-weight ratio and excellent corrosion resistance and is therefore widely used in the aerospace and chemical plant industries (Park *et al.*, 2019). Ti is also used in biomedical implants owing to its good bio-compatibility. However, Ti has poor machinability owing to its low thermal conductivity (Sun *et al.*, 2010).

Manufacturing technology for making Ti components using additive manufacturing (AM) is being actively pursued. AM is a new technology that fabricates products by adding materials in a layer-by-layer fashion. The AM process allows the manufacture of components with complex internal structures and near-net shapes. Owing to these advantages, research on the manufacturing of Ti parts by AM is being actively carried out; however, most studies have focused on how changes in microstructures and mechanical properties depend on the process parameters, such as the laser power and laser scan speed (Attar *et al.*, 2014; Gu *et al.*, 2012).

The mechanical properties of titanium are strongly influenced by oxygen concentration (Ouchi *et al.*, 1998). As oxygen concentration increases, strength and hardness increase, while elongation decreases. When the oxygen concentration of titanium is more than 0.3%, elongation rapidly decreases, and

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the toughness is also reduced (Yan *et al.*, 2014). However, there are few studies that focus on the oxygen concentration changes in Ti during the AM process and the causes of such changes.

Therefore, in this study, we investigated the oxidation behavior of commercial pure Ti (CP-Ti) during the selective laser melting (SLM) process. In addition, the causes of oxidation were studied based on a thermodynamic analysis.

2. Experimental procedures

Spherical CP-Ti powders (ASTM F67 Grade 2, supplied by LPW, England) were used as the initial material. The Grade 2 CP-Ti powders used in this study had an oxygen concentration of 0.197 wt.%. The morphology of the initial CP-Ti powders was observed by a field emission-scanning electron microscope (FE-SEM) (FEI, QUANTA FEG 250), and the powder size distribution was examined using a powder size analyzer (Malvern, Mastersizer 3000). The result of morphology and powder size distribution of the initial powder is shown in Figure 1. The powders had a spherical shape and their d_{10}, d_{50} and d_{90} values were 19.6, 29.0 and 41.6 μm, respectively.

A bulk Ti sample with dimensions of 20 × 20 × 20 mm^3 was fabricated by the SLM process using a Farsoon Technologies FS271M machine. The SLM machine used in this study is equipped with a 500 W Yb-fiber laser, and the laser motion is controlled by a dynamic focusing galvanometer scanning system. In the SLM process, the laser spot size, hatching distance and layer thickness were set to 120, 120 and 30 μm, respectively.

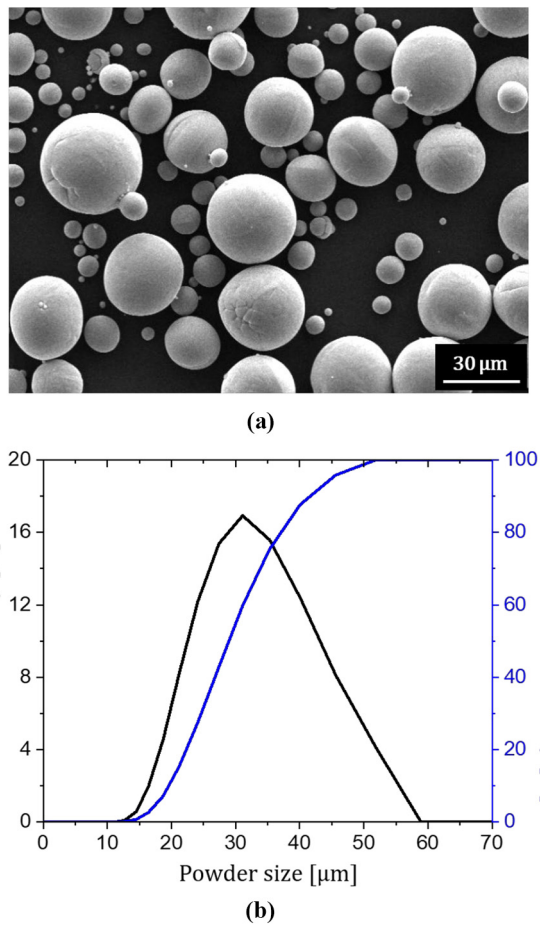
In the SLM process, high purity argon gas (99.999%) was first injected into the chamber to remove oxygen. The oxygen concentration inside the chamber was analyzed using an oxygen sensor (GS Yuasa, KE-25) located at the top of the SLM chamber. The oxygen sensor is capable of measuring the oxygen concentration in the atmosphere from 0% to 100% and has an accuracy of ± 1% of the measured value. The SLM process was started when the oxygen concentration in the chamber reached 0.1 wt.% (1,000 ppm) by substituting it with argon. During the SLM process, argon was continuously injected into the chamber, and its flow rate was automatically controlled to keep the oxygen concentration at 0.1 wt.%. After adjusting the atmosphere inside the SLM chamber, the SLM process was performed with a laser power of 120 W and a laser scan speed of 220 mm/s. These values for the laser power and the scan speed were selected because the Ti powder is fully melted under these conditions (Na *et al.*, 2018). After SLM process, the relative density of as-built SLM samples was analyzed by Archimedes methods, and its value was measured to 99.9%.

The concentrations of oxygen in the powder and the SLM sample were analyzed using an inert gas fusion infrared absorption method using an O/N analyzer (LECO, 736 series) with a graphite crucible. Oxygen concentration was obtained by averaging five measurements. To investigate the phase of the initial CP-Ti powder and the SLM samples, the samples were examined by X-ray diffractometer (XRD) (PANalytical, Empyrean) with Cu Kα in a 2θ range from 30° to 80°.

3. Results and discussion

To investigate the change of oxygen concentration after the SLM process of the CP-Ti powders, the oxygen concentration of the initial powders and the SLM sample were analyzed using the oxygen analyzer, and the results are shown in Figure 2. In the case of CP-Ti, the mechanical properties vary greatly depending on the oxygen concentration, so the grade of CP-Ti is determined by the oxygen concentration. That is, the criteria require oxygen concentrations of not more than 0.18 and 0.25 and 0.35 wt.% for Grades 1, 2 and 3 CP-Ti, respectively (Pohler, 2000). The ranges of the oxygen concentrations corresponding to the grade are shown in Figure 2.

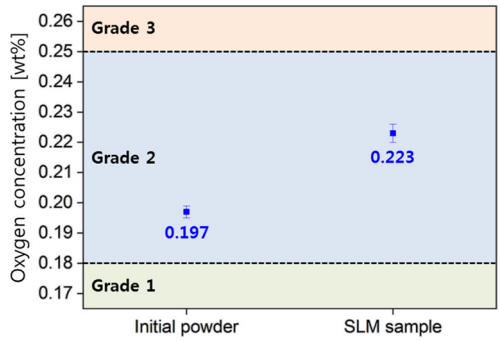
Figure 1 (a) Morphology of the initial Ti powders and (b) their powder size distribution



Based on the result of the oxygen analysis, the oxygen concentration of the initial powders was 0.197 wt.%. For Grade 2 CP-Ti, the criteria of oxygen concentration range are between 0.18 and 0.25 wt.%, and therefore the oxygen concentration of the initial powders corresponds to Grade 2 CP-Ti. However, the oxygen concentration for the SLM sample was 0.223 wt.%, which met the Grade 2 standard but was increased compared to the initial powder. In the case of CP-Ti, the strength and hardness increase and elongation decreases as the oxygen concentration increases. Therefore, it is important to analyze the cause of increased oxygen concentration after the SLM process because the mechanical properties of Ti can be controlled through the oxygen concentration.

To analyze the phase change after SLM process, the initial Ti powder and the SLM sample were analyzed by XRD, and the result is shown in Figure 3. Both the powder and the SLM

Figure 2 Oxygen concentration of the initial powder and the SLM sample

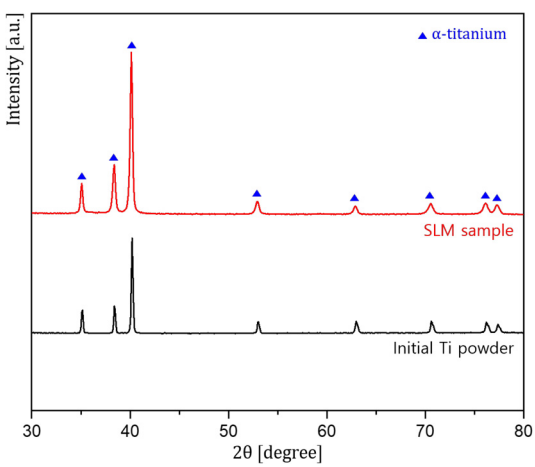


sample were composed of α-Ti phase having hexagonal close packed structure and no other phase was observed. Although the oxygen concentration was increased during the SLM process, oxide phase was not formed after the process. Ti has a high oxygen solubility and can retain up to 30 at.% (~12.5 wt.%) oxygen (Hautaniemi *et al.*, 1992). The oxygen concentrations of the powders and the SLM sample were lower than the maximum oxygen solubility of Ti, so oxygen would exist in a dissolved state. Therefore, the oxidation in the SLM process was likely not caused by the formation of Ti oxide but by an increase in the concentration of oxygen dissolved in Ti.

Oxidation and reduction reactions of metals are determined by the temperature and the oxygen partial pressure. In the SLM process, the temperature of Ti melts increased as the amount of incident laser energy increased. The laser energy irradiated on the sample can be evaluated based on linear energy density (LED), which is defined as the ratio of laser power to scan speed (LED [J/mm] = laser power [W]/scan speed [mm/s]) (Gu *et al.*, 2012).

Roberts *et al.* (2009) reported the temperature change in the Ti melt based on the values of the laser power and scan speed in the SLM process using a 3 D finite element analysis. They performed the calculations under conditions where the laser power and the scan speed were 120 W and 220 mm/s, respectively. The maximum temperature of the Ti melt was determined to be 2,150°C under these conditions. In this study, the laser power and the scan speed in the SLM process were set at 120 W and 220 mm/s, respectively. The LED value used in this study is the same as the LED value considered in Robert's research. Therefore, the maximum temperature in our SLM process was expected to reach 2,150°C.

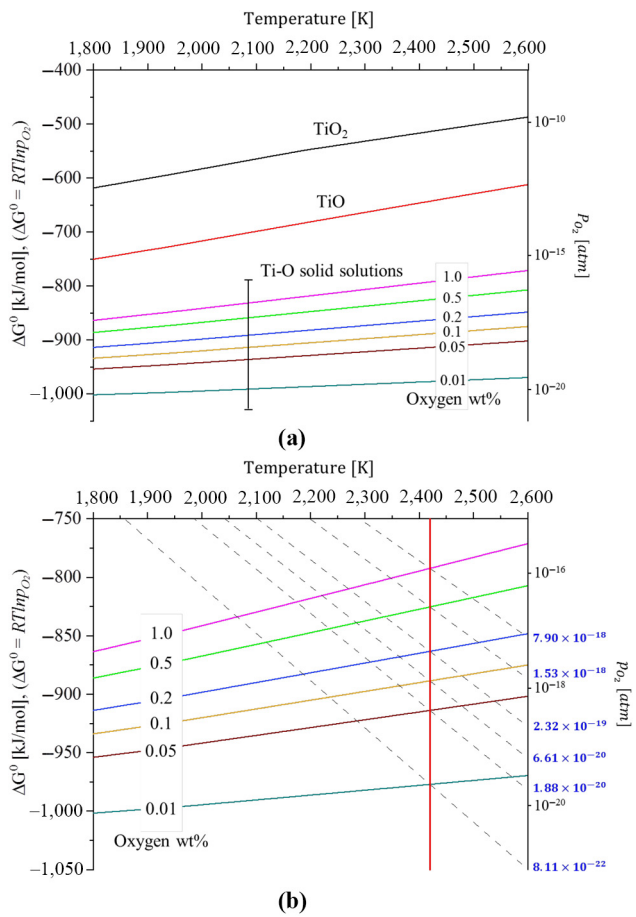
Figure 3 XRD patterns of the initial Ti powder and the SLM sample



The Ellingham diagram for Ti oxidation was calculated to obtain the equilibrium oxygen partial pressure at a particular temperature, and the results are shown in Figure 4. Figure 4(a) shows the Ellingham diagram for the Ti oxides and Ti-O solid solution system at temperatures between 1,800 and 2,600 K. The standard Gibbs free energy change (ΔG^0) with respect to the temperature of TiO_2 and TiO was calculated via Thermo-Calc using an SSUB5 database and that of the Ti-O solid solution was calculated based on the data in Mah *et al.* (1955). As shown in Figure 4(a), a lower value of the standard Gibbs free energy change was observed when oxygen was dissolved in Ti than when Ti oxide was formed. In addition, the driving force for oxidation changed according to the oxygen concentration in the Ti-O solid solution, and the driving force increased with decreasing oxygen concentration.

As mentioned above, the oxygen concentration in the initial powders and the SLM sample corresponded to the level of oxygen that can be dissolved in Ti. The corresponding equilibrium oxygen partial pressure in the Ti-O solid solution state is shown in Figure 4(b). The vertical red solid line represents 2,150°C

Figure 4 Ellingham diagram for the Ti oxides and Ti-O solid solution system at temperatures between 1,800 and 2,600 K



(2,423.15 K), which is the temperature of the Ti melt during the SLM process. As shown in Figure 4(a), the values of the standard Gibbs free energy change for oxidation reaction are determined by the temperature and the oxygen concentration dissolved in Ti. If the temperature is constant, the oxidation and reduction are determined according to the oxygen partial pressure. The equilibrium oxygen partial pressure at a specific temperature can be calculated by following equation, $\Delta G^0 = RTlnP_{O_2}$.The equation shows that the P_{O_2} value at the intersection of the ΔG^0 value and the $RTlnP_{O_2}$ value is equilibrium oxygen partial pressure. Therefore, the $RTlnP_{O_2}$ values with respect to the temperature are shown as dotted lines in Figure 4(b), and values in blue color on the right *y*-axis are the equilibrium oxygen partial pressures according to the oxygen concentration in Ti at 2,150°C.

The oxidation of Ti is determined by the oxygen partial pressure at the corresponding temperature. Oxidation occurs when the oxygen partial pressure in the SLM chamber is higher than the equilibrium oxygen partial pressure, and reduction occurs when the oxygen partial pressure is lower. The oxygen concentration of the initial powder used in this study was 0.197 wt.%. Therefore, the equilibrium oxygen partial pressure was calculated to be 2.32×10^{-19} atm assuming an oxygen concentration in Ti of 0.2 wt.%.

In this study, the oxygen concentration was kept at 0.1 wt.% during the SLM process. Therefore, the oxygen partial pressure inside the chamber was determined to be 0.001 atm (1×10^{-3} atm). The oxygen partial pressure of 1×10^{-3} atm is much higher than the equilibrium oxygen partial pressure of 2.32×10^{-19} atm at 2,150°C, so oxidation occurs and the oxygen concentration increases during the SLM process of Ti.

As mentioned above, in the SLM process that proceeds above the melting temperature of Ti, oxidation occurs owing to the residual oxygen gas in the chamber. Therefore, the longer the high temperature holding time of the sample, the higher the oxygen concentration will be. The energy irradiated in the SLM process is determined by the LED value. Therefore, as the process proceeds at a high LED value, the high temperature holding time would be increased and the oxygen concentration would be increased. In addition, even with the same LED value, the slower the laser scan speed, the higher the temperature holding time. However, when the LED value is low, there is a problem that the powder is not completely melted so that pores are formed and the relative density is lowered. Therefore, further research is needed to derive the appropriate LED value considering the relative density and the oxygen concentration of SLM components.

4. Conclusions

In the SLM process, the temperature of the Ti melt reaches 2,150°C. At this temperature, the equilibrium oxygen partial pressure for the oxidation of Ti with an oxygen concentration of 0.2 wt.% was 2.32×10^{-19} atm. During the SLM process, the oxygen partial pressure was kept at 1×10^{-3} atm. Therefore, the oxygen concentration increased during the SLM process of Ti, as the oxygen partial pressure in the chamber was much higher than the equilibrium oxygen partial pressure.

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