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Surface treatment effects on chemical milling performance of L-PBF produced Ti6Al4V ELI

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Abstract

Titanium is one of the most preferred engine materials for the cold sections of aircraft engines due to its low density and high strength, but it suffers from oxygen entrapment due to exposure of high temperatures and forming an oxygen-rich layer called the alpha case. Since the L-PBF process produces parts with high surface roughness due to the semi-molten powders formed on the surfaces, it is very difficult to completely remove the alpha case layer on the surface. The motivation of this research is to find out favorable surface treatment parameters by optimization of sand type, size, and pressure on heat treated Ti6Al4V Extra Low Interstitial (ELI) specimens produced in different shapes and geometries. Additionally, the main effects of these selected parameters on surface roughness properties and etch rates were investigated through comparative analysis with the as build and surface treated samples. This study demonstrated that the SB process was improved the chemical milling performance of the specimens fabricated with L-PBF and assist to remove alpha case layer from surface regardless of having complex shapes.

Keywords: Additive Manufacturing, Laser Powder Bed Fusion, Titanium, Alpha Case, Chemical Milling

1. Introduction

Additive manufacturing is a production method in which parts are obtained by adding layers on top of each other. Laser Powder Bed Fusion (L-PBF) is one of the methods of powder bed fusion technology. The main working principle is based on melting powder into the bed by using laser power [1]. Additive manufacturing is mostly preferred to produce the parts as near net shape forms instead of traditional methods such as casting and forging [2]. At temperatures above 427°C, the oxygen in the air diffuses into the titanium lattice structure and forms an oxygen-enriched alpha layer [3]. The alpha case layer is formed on the surface as a result of heat treatment, casting, hot working and exposure to air at high temperature [2, 4]. Since the alpha case layer reduces tensile and the fatigue properties due to the brittle phase and facilitates the crack initiation, the titanium alloys are not used for high load and amplitude applications without its removal [5, 6]. Since it has a detrimental effect on the significant mechanical properties of titanium alloys, precautions must be taken to prevent its formation or, if already present, to completely remove it from the surface [7-8]. The chemical method known as chemical milling or pickling is used in the aerospace industry as an alpha case layer removal process. In addition, machining is also a traditional method used for alpha case layer removal [8, 9]. The chemical milling process involves treating the aviation engine components in chemical baths, usually removing the alpha layer using a mixture of HF and HNO3 acids in an aqueous solution [7]. While HF is responsible for dissolving the oxide residue and titanium metal, HNO3 acts as an oxidizing agent and passivates the surface of the titanium [7]. Since nitric acid has a weaker effect than hydrofluoric acid, the amount of material removed depends mainly on concentration of hydrofluoric acid.

The temperature also plays an important role in material removal caused by titanium and acid reaction [10, 11]. The mechanical and chemical methods are applicable to remove this layer from the casting and wrought parts. Due to the geometric constraints of the parts, the machining method is not always suitable for the additive parts, so the chemical milling is considered to be the best and only option for the removal of the alpha case layer. Due to the porous and poor surface quality of the titanium alloys produced by additive manufacturing, it is difficult to totally remove alpha case by chemical milling method. Therefore, the surface treatment processes are needed. The SB process, which is one of the surface treatments processes, is aimed to activate the surface by igniting the particles as a result of the impact provided by the air pressure. The chemical etching performance is significantly improved depending on the shape, size and kinetic energy of the abrasive particles as well as surface roughness effects [12].

In this study, the effects of the SB process on chemical milling performance were investigated to remove the alpha case layer on the surface of Ti6Al4V ELI specimens fabricated with L-PBF.

2. Material and methods

The specimens intended for alpha case treatment were manufactured in a Concept Laser M2 Series 5 machine under an argon atmosphere. The machine has a dual yttrium fibre laser system and is also capable of heating the build plate up to 200°C. The volumetric energy density of 33 J/mm^3 was used to produce the parts. The direction of gas flow in the process chamber was opposite to the scan direction of the parts. The process was performed below an oxygen content of 1000 ppm.

Production was completed by using Ti6Al4V ELI powder with particle size distributions from 15 to 63 microns. The production specimens conform to ASTM F3001-14. The holed structure and sheet specimens fabricated in the XY build direction and the rectangular specimens were manufactured in the Z build direction. The dimensions of the fabricated as-build specimens (AB) are listed in Table 1. All specimens are shown in Fig. 1.

Table 1. Dimensions and designations of the specimens.

Specimen Identification	AB Specimens	Dimensions (mm)
HS1	Holed Structure	5*20*10
HS2		5*25*15
HS3		2*15*70
HS4		5*25*30
RS1,2,3	Rectangular Shaped Structure	10*10*15
RT1,2,3		5*5*15
RV1,2		2*2*15
ST1,2,3	Sheet Specimens	2*15*55

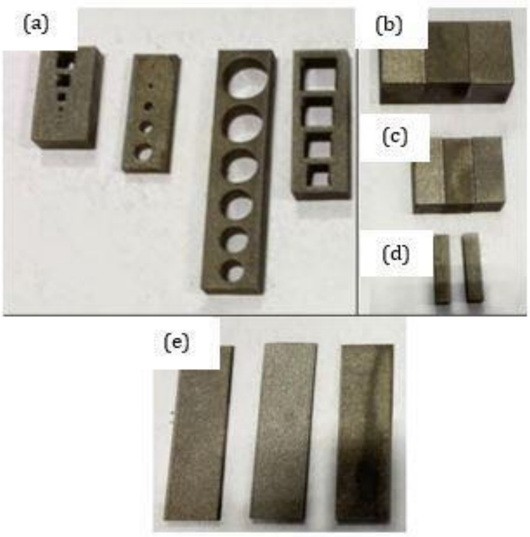

Fig 1. Produced Ti64 ELI specimens from left to right (a) HS1, HS2, HS3, HS4 (b) RS1, 2, 3 (c) RT1, 2, 3 (d) RV1, 2 (e) ST1, 2, 3.

After production, the parts were stress relieved in a vacuum furnace in accordance with AMS 2801. Before removing the alpha case layer, three different SB process parameters were studied. Saykar branded SB machine was used for the parameter studies. The SB parameters are listed in Table 2. Two different sand types were used during the studies, named as X and Y, both are alumina sands and type X sand has a larger particle distribution compared to type Y.

Examinations of the alpha case were performed using a Nikon Exlipse Ma200 optical microscope. Chemical milling was performed as per ASTM B600. According to this specification, the specimens were processed for 5-10 minutes in a bath containing a treatment solution complying with the requirement of a nitric acid/hydrofluoric acid ratio of 10:1 ratio or higher. The coupons were processed under ambient temperature condition (15.5-35°C). The SB and the chemical milled (SC) specimens are shown in Fig. 2. In addition to microstructural examination, Innova test falcon 500 branded hardness machine was used to characterize the alpha case layer from the hardness differences by applying a load of 50 g using with a Vickers indenter which has an indent size approximately 20 µm. Six measurements were taken to investigate the hardness of the alpha case and bulk material.

Table 2. SB parameters.

Parameters	Automatic (A) or Manuel (M) SB Machine	Sand Type	Pressure (bar)
1	A	X-thick	4
2	A	Y-thin	4
3	M	X-thick	5

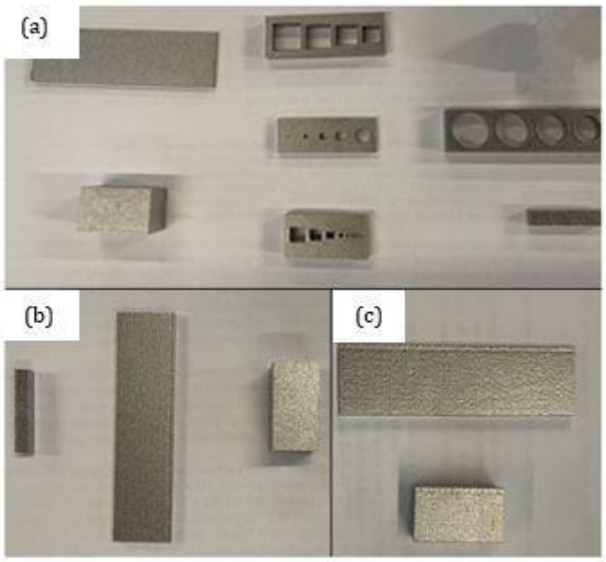

Fig 2. The SC specimens process with a) SB parameter 1, b) SB parameter 2, and c) SB parameter 3.

After chemical milling, specimens were prepared by using a Struers cutting machine mounted, polished, and etched with Kroll's reagent and then ammonium fluoride to examine the alpha case at the proper magnifications. The removal target was selected as 100 microns from the surfaces.

Surface roughness was measured using the Mahr MarSurf M400 machine on specimens AB, SB, SC. The

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probe length is 1X and it measured 5.6 mm across the surface.

The effects of surface roughness on removal efficiency were studied by calculating the etch rate according to (1). The etch rate is a material removal rate calculated on the basis of thickness differences after the parts are placed in the bath for a limited time. Hold time was determined as 5-10 minutes during the etch rate calculations.

$$Etch\ Rate = \frac{First\ thickness - Last\ thickness}{2 * Hold\ time} \quad (1)$$

3. Results and discussion

3.1. Microstructural examinations of AB specimens

The microstructure of the specimen AB is shown in Fig. 3. The alpha case layer thickness was measured as 9 micrometers on average due to the nature of L-PBF methods except for the semi-melted particles. An earlier study concluded that the alpha case was detected as a thin layer on additively manufactured parts [4].

Fig. 3 illustrates the very fine acicular martensitic microstructure, which is due to the high cooling rate of the L-PBF process [13].

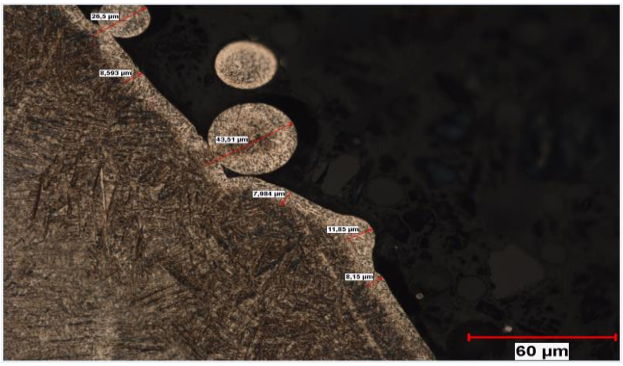

Fig 3. Microstructures of the Ti64ELI L-PBF specimens in the AB condition.

3.2. Etch rate results

Etch rates were calculated using Ti64 sheet material (AMS 4911), specimens AB, and SB. The SB process was shown to increase the chemical milling efficiency and removal rates compared to the as build specimens. It was also observed that the SB specimens had a 29,6% highest removal rate compared to the wrought material. The etch rate differences between as build and wrought specimens can be considered as negligible. The results are shown in Table 3.

3.3. Surface roughness results

ST1, 2, and 3 specimens were investigated under different conditions to observe the effects of as-build, SB and chemical milled conditions on surface roughness. The results and standard deviations (STD) are given in Table 4.

Table 3. % Etch rate comparison between wrought and additive specimens.

Specimen Identification	% Increase in Etch Rates
Ti64 sheet material vs as build RT specimens	1,6
Ti64 sheet material vs of SB ST specimens	29,6

The effects of the three different SB parameters were investigated on both RS1, 2, 3 and ST1, 2, 3 specimens to investigate the thickness effects of specimens.

Three measurements were taken from each specimen.

RA Results of AB Specimens

The average roughness is displayed in Table 4. The as-build specimens demonstrate high results in comparison to the samples with SB and SC [13].

RA Results of SB Specimens

Based on the research conducted during these studies, no research has existed yet that focuses on the removal of the alpha case and the surface effects on it. However, some researchers conducted studies to improve the surface quality of additive parts to diminish the effects on fatigue life and to improve adhesion properties for coating applications [13-14]. The effects of sand grain size and pressure were discussed, and it was concluded that the surface roughness of the samples increased when using larger grain size and higher blasting pressure [15-16]. Based on this research, parameter 2 (big particle size sand and 5 bar pressure) have had the highest roughness. Since a manual machine is mostly dependent on operator experience, the highest value was achieved with parameter 1 that has a lowest particle size and 4 bar pressures. In parallel with research, parameter 1 (big particle size and 4 bar pressure) was shown to have a higher roughness value than the other conditions and roughness value is within the range in comparison to the literature studies [17-20].

RA Results of SC Specimens

The surface roughness results are given in Table 4. The lowest value of surface roughness was obtained from SC specimens with Parameter 1.

Chemical milling has been shown to improve surface quality by reducing the surface roughness value under all conditions. The results of Parameter 1 show that the highest surface roughness value is obtained by the high chemical reaction on the surface. The lowest values of surface roughness after the chemical milling process show that removal of the alpha case was achieved successfully and no wavy surface was observed on the parts. Fig. 4. demonstrates that the specimens processed with Parameter 1 and 3 had high surface quality compared to Parameter 2.

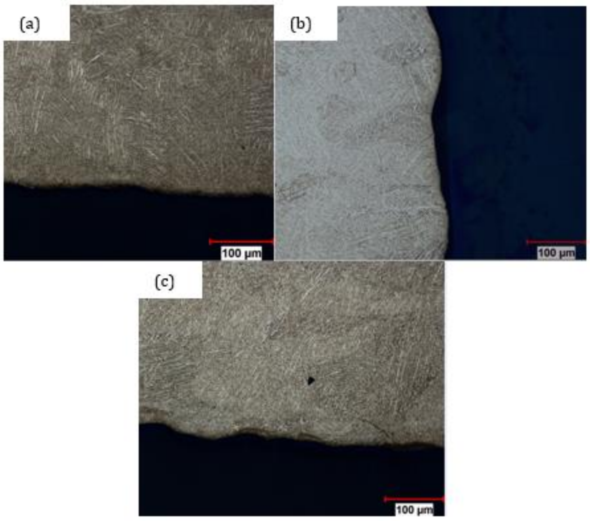

Fig 4. Microstructures of the SC specimens a) for SB Parameter 1 b) for SB Parameter 2 c) for SB Parameter 3.

3.4. Pressure, sand and machine type effects on chemical milling performance

The sand types also showed that the surface activation rate decreased with fine sand type because desired roughness obtains before chemical milling. If the processed surface has a high surface quality before CM, chemicals cannot be attacked the surface properly to remove alpha case due to the losing waviness of the surface. When comparing the delta between the parameter 1 and 2, it is clearly seen that the surface belonging to parameter 2 is activated but not more than having delta of parameter.

In this case, the alpha case layer was removed from all surfaces, it could be changed for complex shaped parts. It can be concluded that the optimal homogeneity of the chemical milling process was observed for Parameter 1 which has high surface roughness values after the application of SB. The highest RA delta between SB and SC samples were also obtained with the application of Parameter 1.

3.5. Alpha case examination before chemical milling process

After stress relief in the vacuum atmosphere and sand blasting process, the alpha case is measured from RT and ST specimens as 20-25 micrometers, on average.

Fig. 5a illustrates that the alpha case layer was not removed from the surface when the as-build surface was chemically milled without the surface treatment process. As shown in Fig. 5b, the semi-melted particles are initiated by the L-PBF method and the alpha case layer was not affected by the SB process.

Table 4. Surface Roughness Results

Specimen Numbers and Conditions	Specimen Identifications	Surface Roughness Results, (STD)	Aim
AB (3 Specimens)	ST1	9,31 (±1,65)	Effects of additive manufacturing process on surface roughness value
	ST2		
	ST3		
SB (3 Specimens)	ST 1 - Parameter 1	5,3 (±0,6)	Effects on sand type/machine type/ pressure differences
	ST 2 - Parameter 2	4,1 (±0,8)	
	ST 3 - Parameter 3	4,8 (±0,7)	
SC specimens process with (6 Specimens)	RS 1- Parameter 1	3 (±0,5)	Effects of dimensions on surface roughness
	RS 2 - Parameter 2	4,1 (±0,7)	
	RS 3 - Parameter 3	3,4 (±0,5)	
	ST1 - Parameter 1	3,1 (±0,7)	
	ST1 – Parameter 2	4 (±0,8)	
	ST3 - Parameter 3	3,2 (±0,5)	

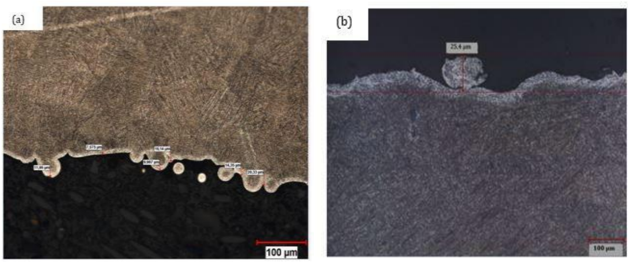

Fig 5. Microstructures of the Ti64ELI L-PBF specimens in the stress relieved condition a) no SB processed b) after SB process.

3.6. Alpha case examination after chemical milling process

After the SC process, Fig. 6 illustrates the alpha case results obtained from the specimens shown in Fig. 2. Based on the results of the optical microscopy, it was shown that no alpha case was found in any of the specimens produced with different dimensions, see Table 5.

The alpha case removal performance from HS1, HS2, HS3, and HS4 specimens was investigated. Fig. 7 points out the result of the alpha case obtained from rectangular and circular-shaped holes. Although it is difficult to process these small parts with small holes in the chemical milling bath, the edges and holes have no alpha case as shown in Fig. 7.

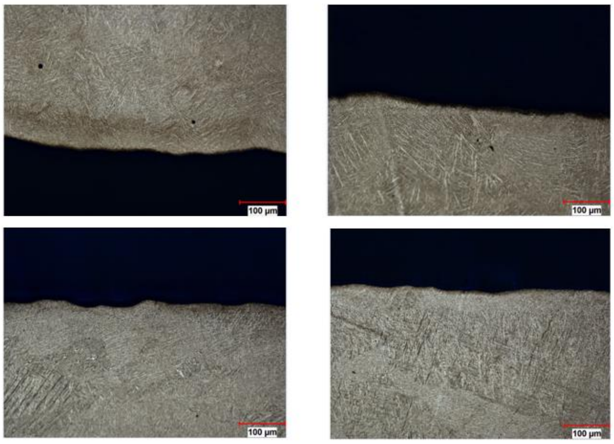

Fig 6. Microstructures of the Ti64 ELI L-PBF specimens after SC.

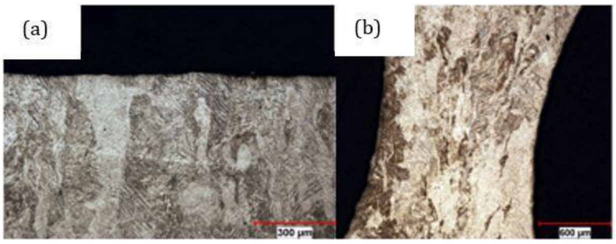

Fig 7. Microstructures of the Ti64 ELI L-PBF specimens after SC a) for rectangular shaped hole specimens (HS4) b) for circular shaped hole specimens (HS3).

Table 5. Alpha case results after chemical milling.

Specimen Numbers and Conditions	Specimen Identifications	Aim	Alpha Case Results (microns)
SC specimens process with 1-SB parameter 1	ST1, RS1, RV1, HS1, HS2, HS3, HS4	The effects of thickness and geometric differences on alpha case removal performance	No alpha case found
1-SB parameter 2	RV2, ST2, RS2		No alpha case found
1-SB parameter 3	ST3, RS3		No alpha case found
SB parameter 1 vs SB parameter 2	ST1 vs ST2 RV1 vs RV2	Sand Type Effects on different thicknesses	No alpha case found
SB parameter 1 vs SB parameter 3	ST1 vs ST3 RS1 vs RS3	SB machine and pressure effects on alpha case removal performance	No alpha case found

3.7. Alpha case characterization with the hardness measurement method

In this study, the hardness results of the bulk material and alpha case layer were measured as 395 (±28) HV and 469 (±20) HV separately, these results are in parallel with the literature studies, see figure 8 and 9. The Hardness of the additive manufactured titanium parts were also measured between 330 to 390 HV [21, 22].

Fig 8. Hardness images of additive specimens after heat treatment.

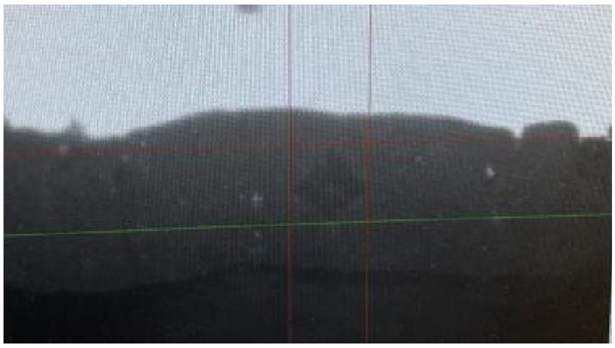

Fig 9. Hardness images of alpha case after heat treatment.

4. Conclusions

The alpha case is a brittle and undesirable layer on the titanium alloys. Due to the brittle structure and crack initiation sides of the parts, titanium components with the alpha case layer are not used in aero engines. In the nature of the L-PBF method, semi-melted particles are seen on the part surface and it is difficult to remove both the semi-melted and alpha case layer from the surfaces without any special surface treatment processes. In this paper, the effects of the three different SB parameters on alpha case removal were comprehensively investigated. The main contributions of this study are summarized as follows:

- Specimens fabricated in XY building directions were heat-treated for stress relief. The amount of alpha case levels resulting from heat treatment was measured as 20-25 microns on average. Additionally, the alpha case layer was found to have 16% higher hardness than the bulk material.
- Without performing the SB process prior to chemical milling, it was shown that alpha case and semi-melted particles were not totally removed from the surfaces.

- Based on the etch rate calculations, the SB process was increased the etch rate by ~30%.
- The highest roughness value was obtained with the type X sand, which has a larger diameter than type Y.
- Since manual sand blasting is a human-dependent method to be more uncontrolled, it can improve the surface roughness undesirably before the CM process.
- The highest chemical reaction was obtained from the specimens which were treated with SB Parameter 1.
- After the chemical milling process, it is clear that the alpha case and semi-melted particles have been removed from the surfaces with the aid of SB and the surfaces are free of the alpha case. The size, thickness, and shape of the specimens have no effects on removal of the alpha case layer.

The future work is planned to investigate the applicability of this process on current aero engine parts. Moreover, the effects of surface roughness on the mechanical properties of the chemical milled, SB and as-build specimens will be investigated.

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Author's statement
Conflict of interest: Authors state no conflict of interest. Informed consent: Informed consent has been obtained from all individuals included in this study. Ethical approval: The research related to human use complies with all the relevant national regulations, institutional policies and was performed in accordance with the tenets of the Helsinki Declaration, and has been approved by the authors' institutional review board or equivalent committee.

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