Influence of Alloying Elements on Laser Powder Bed Fusion Processability of Aluminum: A New Insight into the Oxidation Tendency

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Abstract

This study focuses on the influence of alloying elements (Si and Mg) and the process parameters on the laser powder bed fusion (LPBF) processability of aluminum (Al). In this regard, pure Al, AlSi12, and AlSi10Mg parts with and without single tracks on their top surface were fabricated using a wide range of process parameters. The oxidation tendency, laser absorptivity, and powder attributes were evaluated to justify the densification level and the processing window of the fabricated parts. The starting powders were subjected to the Auger electron spectroscopy to characterize the nature of the oxide compounds participating in the melt pool. The measurement of the oxygen content in pure Al (2260 ppm), AlSi12 (1299 ppm), and AlSi10Mg (740 ppm) powders, as well as their printed parts (90, 220, and 130 ppm, respectively at laser power of 300 W), proved that the level of oxide removal outweighs any possible in-situ oxidation of the molten Al/Al alloys. A mechanism was proposed to explain the release of oxygen, confirmed by microstructural observations and oxygen elemental map analysis. This study indicates that neither the laser absorptivity of AlSi12 (58.4%) and AlSi10Mg (56.1%) alloys nor the high oxidation affinity of pure Al adversely affects their processability.

Keywords: Laser powder bed fusion (LPBF); Pure Al, AlSi12, and AlSi10Mg alloys; laser absorptivity; Oxygen content/Oxide nature; In-process oxide evaporation.

1 Introduction

Additive manufacturing (AM) is an exceptional manufacturing route in which industrial parts with complex geometries and intricate features can be easily produced in a single processing step without the need for expensive assemblies [1-4]. For instance, the laser powder bed fusion (LPBF) process, as one of the most promising AM techniques, has enabled the production of lattice structures [5, 6], which were not feasible to be produced before the emergence of AM. In other words, AM has changed the design concept from design-for-manufacturing to design-for-performance [7]. Breakthrough in the AM has been applied not only to generate new designs but also to redesign the existing industrial and engineering components. In recent years, topology optimization [8] and generative design [9] methods have been implemented to produce light and/or highly efficient dies and molds [10], biomaterial scaffolds [11], and aircraft brackets [12], while maintaining their overall initial size to meet the service requirements. In addition, the successful fabrication of heat exchangers and heat sinks with lattice structures [13], cooling channels [14], and pins/fins with functionally graded geometries [15] has significantly enhanced their cooling efficiency.

In many of the abovementioned applications in the automotive, aerospace, and heat exchanger industries, aluminum (Al) and Al alloys are believed to be potential candidates owing to their high specific mechanical strength and thermal/electrical conductivity [16, 17]. Given the fact that the manufacturing process directly influences the microstructure and hence the properties of the parts, microstructural characterization of the additively manufactured Al and Al alloys is essential prior to their reliable application. For Al and its alloys, their incredibly high oxidation tendency and relatively low laser absorptivity have been claimed to be the main obstacles to achieving sound oxide-free parts using the LPBF process [16, 18]. Figure 1(a) shows the overview of the LPBF process in which a laser beam is directed onto the powder bed in specific regions to fuse the powder track-by-track and layer-by-layer [19]. In the case of Al/Al alloys, Louvis et al. [16] proposed that the consolidation of a track is accompanied by the formation of oxide layers since being highly prone to oxidation (Figure 1(b)). Given the fact that certain amounts of inter-track and inter-layer overlaps are required to ensure obtaining defect-free parts, the in-situ developed oxide layers on a track must break down during the printing of the subsequent tracks and layers (Figure 1(c)). Even if the oxide film's breakdown happens successfully during the LPBF process, the disrupted oxide inclusions will be trapped within the consolidated material. Therefore, the LPBF-processed Al/Al alloys should have higher oxygen concentrations and more oxide inclusions than their cast or wrought counterparts, originating from the stepwise nature of this manufacturing technique. If this is the case, parts with inferior mechanical and thermal properties are expected to be obtained. However, based on the numerous research studies conducted on mechanical properties [7, 20-22] and a few articles on thermal properties [23, 24] of the LPBF-processed Al/Al alloys, the former is superior (up to 40% improvement in yield and tensile strength for AlSi10Mg and up to 400 and 200% improvement in the corresponding values for AlSi12

alloy), and the latter is almost equal to that of the conventionally manufactured parts after heat treatment.

Figure 1. Schematic illustration of (a) LPBF process, (b) in-situ oxidation of aluminum/aluminum alloys during the formation of each track, and (c) breakdown of the oxides of the previous layer during the consolidation of the subsequent layer in the overlap regions. By deep etching of the printed samples, Louvis et al. [16] observed a continuous oxide film between the laser scan tracks and concluded that the inter-track oxides do not break during the printing of the subsequent tracks.

The Al/Al alloy oxidation investigation has not been renewed since 2010, when the abovementioned mechanism was proposed [16]. The current generation systems have two main differences with the old ones, which noticeably change the oxidation condition: (i) the output laser powers are increased from 50 W [16] (old systems) up to 1 kW [25], and (ii) the allowable oxygen content of the processing chamber during the printing of Al/Al alloys is reduced (from about 0.2 to less than 0.1 wt%). At relatively low laser powers, employment of relatively slow scan speeds was inevitable to produce dense parts. However, the possibility of applying relatively high laser powers in the new systems is accompanied by noticeably shorter scanning time [25], and therefore, the lower chance of in-situ oxidation. Moreover, it is expected that the lower oxygen content in the building chamber mitigates the oxidation reaction during the printing process. Therefore, it is essential to determine whether or not the in-situ oxidation of Al/Al alloys during the LPBF process is a serious issue under the processing condition of the current generation systems. It should be mentioned that for most of the materials, the optimization of process parameters has been done based on the densification level, surface roughness, and/or mechanical properties [26-29]. However, for materials prone to oxidation (i.e., Al/Al alloys), the samples also need to be optimized in terms of the oxygen/oxide content. It is especially crucial for applications where fatigue [30] or thermal/electrical properties of the Al/Al alloys [31] are of interest. However, this vacancy in the literature has not been filled so far to the best of the author's knowledge.

In many of the research studies that targeted the challenges during the LPBF processing of Al and Al alloys, the in-situ oxidation of the molten material during this layer-wise manufacturing process has been acknowledged. Some examples of these studies can be found in [16-18, 30, 32]. They have referred to the work conducted by Louvis et al. [16], which was published at the early stages of the LPBF process, or cited articles that were published before the emergence of the LPBF process. On the other

hand, owing to the complicated physics of the LPBF process with non-equilibrium melting and solidification nature, oxidation of melt pool has hitherto received only scant attention within the literature. This study calls into question the previously proposed mechanisms and proves that the level of the pre-existing oxygen in the starting powder can significantly decrease during the LPBF processing of Al/Al alloys under specific conditions. As will be discussed, neglecting the oxygen originating from the oxide layer of the starting powder has led to misleading conclusions in the literature. It should be borne in mind that the level of oxygen release is highly sensitive to the manufacturing process parameters. Nevertheless, any evolution related to the oxides in Al alloys is preeminently influenced by the chemistry of the alloy. The addition of alloying elements to Al can alter the nature of the oxide compounds and, therefore, their formation kinetics (i.e., the thickness of the oxide layer in the starting powder), evaporation temperature, and breakdown tendency; in a word, processability.

This study investigates the role of alloying elements (i.e., silicon (Si) and magnesium (Mg)) as well as the process parameters on the processability of Al. For this purpose, pure Al, binary Al-Si (AlSi12 alloy), and ternary Al-Si-Mg (AlSi10Mg alloy) were fabricated in a wide range of process parameters both in bulk and single track forms. Different contributing factors, namely, laser absorptivity of the powder, oxidation affinity, and powder characteristics, were thoroughly examined to justify the densification level and the processing window of the fabricated parts. The oxide compounds existing on the surface of the starting powders were characterized via Auger electron spectroscopy. The oxygen level was measured both in the starting powders and the final printed parts to understand whether or not in-situ oxidation occurs during the process. A mechanism governing the oxide diminishment during the LPBF process was proposed. By simultaneous consideration of the abovementioned contributing factors, the processability of pure Al, AlSi12, and AlSi10Mg was justified in detail, and the influence of Si and Mg alloying elements were scrutinized. Implications of the findings in this study are also essential for other Al alloys and materials with high oxidation affinity.

2 Materials and Experimental Procedure

EOSM280 and EOSM290 LPBF machines were utilized to build samples made of Al alloys (AlSi12 and AlSi10Mg) and pure Al, respectively. Both machines use a 400 W Yb-fiber laser with a nominal beam diameter of 100 μm . The nominal chemical composition of the powders is provided in Table 1. The AlSi12 and AlSi10Mg powders were supplied by LPW Technology Ltd. (a subsidiary of Carpenter Technology Corporation), and pure Al powder was provided by American Elements. All of the powders were manufactured by the gas atomization process. Three sets of samples were built for each material, with 36 cubic coupons per set corresponding to 4 different laser powers and at each power, 9 different scan speeds. The other process parameters such as hatch spacing and nominal powder layer thickness (Platform displacement) were kept constant. The individual process parameters are shown in Table 2. Two subsets were replicas with dimensions of $10\times10\times10\text{ mm}^3$ and one subset having samples

dimensions of $10 \times 10 \times 4.2 \text{ mm}^3$. The shorter coupons had six single tracks printed on their top surface using the same process parameters. These single tracks were used to measure the melt pool dimensions. The employed process parameters spanned volumetric energy densities from 33.33 to 308.33 J/mm³. A stripe hatch pattern was used for in-layer exposure, while a 67° rotation was employed between subsequent layers. The build plate was preheated to 180 °C to reduce residual stresses, and the build chamber was filled with argon gas to reduce the oxygen content to less than 0.1%.

Table 1. The nominal chemical composition of pure Al, AlSi12, and AlSi10Mg powders.

Powder	Elements [wt%]					
	Al	Si	Mg	Fe	Cu	Others
Pure Al	Bal.	-	-	-	-	1
AlSi12	Bal.	11	0.1	0.25	0.3	0.1
AlSi10Mg	Bal.	9.76	0.21	0.07	0.08	1.5

The apparent packing density of powders was measured using the Hall method. The optical absorption of powders was measured using the diffuse reflectance spectroscopy (DRS) technique as thoroughly explained in [33]. To determine the nature of the oxides existing in each powder system, Auger electron spectroscopy (AES) was utilized. Auger electron spectra in this study were acquired at 10 keV and 30 nÅ with a JEOL JAMP-9500F Field Emission Auger Microprobe. The spectra were acquired from each powder particle using a slightly defocused beam and processed using the JEOL Spectra Investigator software. The composition was determined by deconvolution of the acquired Auger spectra by curve fitting standard reference spectra of Al, Al₂O₃, Si, SiO₂, Mg, and MgO (Figure 2(a)).

Table 2. Process parameters used for the fabrication of test coupons.

Laser power, <i>P</i> [W]	Scan speed, <i>v</i> [mm/s]	Hatch spacing, <i>h</i> [mm]	Nominal powder layer thickness, <i>t</i> [mm]
200, 250, 300, 370	400, 600, 800, 1000, 1200, 1400, 1600, 1800, 2000	0.1	0.03

The density of LPBF-fabricated cubic samples was measured using the Archimedes method in accordance with the ASTM B296-17 standard. The theoretical bulk density was selected to be 2.7 g/cm³ for pure Al and 2.67 g/cm³ for both AlSi10Mg and AlSi12 alloys. For pure Al samples, the ImageJ software was also utilized to calculate the area fraction (volume fraction) of the porosities in the printed samples. For this purpose, 12 optical micrographs with a magnification of 50X and a field of view of 1.75×1.25 mm² were used. The reported relative densities (100 - Vol% porosities) achieved by the image analysis are the average of 12 distinct measurements. The top surface of the LPBF-fabricated parts was characterized using a Vega Tescan scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS) analysis. The chemical composition of the top surface was also analyzed using EDS in the elemental mapping mode. To reveal the microstructures,

the AlSi10Mg and AlSi12 samples were etched chemically using Keller's Reagent. For pure Al, a reagent containing 5 mL HNO₃, 5 mL HCl, 5 mL HF, and 95 mL distilled water was used to etch the samples chemically. The etched cross-sections of the laser scan tracks were observed by means of a Keyence (Osaka, Japan) VHX digital optical microscope as well as a Nikon LV100 optical microscope. The dimensions of the tracks were measured by analyzing the optical micrographs taken from the single tracks of each sample using the ImageJ software (Figure 2(b,c)). The reported dimensions are the average of at least six distinct measurements. The depth of the melt pool is defined as the distance between the surface of the part and the root of the scan tracks. In other words, any section rise above the part surface is not considered in the depth measurements. It is worth noting that in some of the laser scan tracks, a depression with respect to the part surface (rather than a rise) was observed. In these cases, the distance between the highest point of the track and the root was defined as the track depth.

The oxygen/hydrogen (O/H) content of the powders and the fabricated samples was measured using an Instrumental Gas Analyzer (IGA). The equipment used for analyzing O and H were EMGA-920 and EMGA-921, respectively (HORIBA, Ltd., HORIBA Techno Service Co.,Ltd. HORIBA Advanced Technology Center, Japan). The oxygen content in this technique is measured as carbon monoxide and carbon dioxide by a non-dispersive infrared detector. The hydrogen is extracted as Hydrogen gas (H₂), and its concentration in the specimen is determined by a thermal conductivity detector. The reported O/H concentrations for each powder or printed sample represents the average of two distinct measurements. Before the test, specimens were heated to 150 °C for 30 minutes. All samples were then ultrasonically cleaned in acetone and petroleum benzene.

A Java-based materials properties program (JMatPro software) was used to calculate the properties and behaviors of the Al/Al alloys, such as the density of pure Al and AlSi12 alloy as a function of temperature by utilizing the "Aluminum Alloy" database. The derivative of the density with respect to the temperature has been calculated between the melting point and 973 K using data acquired from JMatPro Software. In all of the simulations, the chemical compositions provided in Table 1 were defined for the JMatPro software by excluding the elements that exist in trace amounts and elements referred to as "others".

Figure 2. The schematic view listing the analysis performed on: (a) powder, (b) single tracks, and (c) cubic coupons.

3 Results and Discussion

3.1 Processability of Al/Al alloys

The processability of pure Al and Al alloys was studied in a wide range of process parameters through relative density-volumetric energy density ($E_v = P / vht$) plots provided in Figure 3. It should be noted that these plots fail to reveal the role of powder attributes and physical properties in the processability of different materials since the utilized E_v only considers the effect of process parameters. In section 3.2, another volumetric energy density equation is used in which not only the process parameters but also the powder attributes (effective powder layer thickness) and laser absorptivity are taken into account.

Figure 3. Relative density versus E_v of the LPBF-processed: (a) Pure Al, (e) AlSi12, and (i) AlSi10Mg. The density results are the average of two distinct measurements. The standard deviation from the average values was in the range of 0.04-0.98 for pure Al (a), 0.03-0.48 for AlSi12 (e), and 0.03-0.56 for AlSi10Mg (i). The zones designated in (a), (e), and (i) by the ovals with the dotted, dashed, and dash-dotted outlines represent the samples with large irregular pores (and delamination in (a)), highly-dense samples (with relative density higher than 98.5%), and samples with large spherical pores, respectively. The region named as (1) in (a), (e), and (i) shows the samples having relative densities higher than 99%. The region named as (2) in (e) shows the samples with relative densities between 98.5 and 99%. The optical micrographs in (b-d) show examples of pure Al samples with large irregular pores, delamination, and almost no defects (zone (1)), respectively. The optical micrographs in (f-h) show examples of AlSi12 samples with large irregular pores, almost no defects, and large spherical pores, respectively. The optical micrographs in (j-i) show examples of AlSi10Mg samples with large irregular pores, almost no defects, and large spherical pores, respectively. The process window for each material leading to relative densities higher than 99% is shown in (m).

Figure 3(a) shows the relative density versus E_v for pure Al samples. Generally speaking, the densification level first increases with heat input up to the $E_v \sim 50-70 \text{ J/mm}^3$, where the maximum relative density is achieved (99.5%), then decreases slightly up to the $E_v \sim 100 \text{ J/mm}^3$ (98% < relative density < 99.5%), and finally levels off when higher E_v is applied (97% < relative density < 98%). The only exceptions to this general trend are the samples processed by $P = 200 \text{ W}$ at E_v levels higher than 50 J/mm^3 , in which large irregular porosities and delamination decreased the density significantly (Figure 3(b, c)). It is worth noting that such delaminations were detected in almost all samples of $P = 200 \text{ W}$ family, regardless of the employed v (dotted oval in Figure 3(a)). Samples with relative densities in the range of 97 to 98% featured large/small irregular pores even at extremely high E_v levels (no spherical pores were observed). Samples with relative densities higher than 98.5% are referred to as the highly-dense samples (dashed oval). Almost defect-free samples with relative densities higher than 99% are highlighted as zone (1) in this region. It is self-evident that high P should be exploited in LPBF processing of pure Al to fabricate almost defect-free parts. Only three pure Al samples with relative densities higher than 99%¹ could be obtained at $P = 370 \text{ W}$ and $v = 1600 - 2000 \text{ mm/s}$ (Figure 3(d)).

According to Figure 3(e, i), the addition of Si or Si + Mg could significantly change the processability of Al. The relative density of the fabricated AlSi12 and AlSi10Mg samples first shows an ascending trend with increasing E_v up to 50 J/mm^3 . Then, it reaches a steady-state region in the range of $\sim 50-100 \text{ J/mm}^3$, where a considerable number of highly dense samples (relative density > 98.5% shown in dashed oval) are achieved. Finally, it follows a sharp decrease by a further increase in the E_v . Despite the pure Al, lower P (250 - 370 W) can also lead to the almost defect-free AlSi12 (Figure 3(g)) and AlSi10Mg (Figure 3(k)) parts (zone (1)). No delamination was observed in samples subjected to the P of 200 W.

¹ Based on the 2D image analysis of the non-etched cross-section of the pure Al samples, some of the samples processed at $P = 300 \text{ W}$ also had relative densities higher than 99%.

In the group of samples designated by dotted oval and dash-dotted oval in Figure 3(e, i), large irregular (Figure 3(f) for AlSi12 and Figure 3(j) for AlSi10Mg) and large spherical pores (Figure 3(h) for AlSi12, and Figure 3(l) for AlSi10Mg) were identified, respectively. While the low E_v causes the former, excessive E_v is the reason behind the latter.

Figure 3(m) compares the overall processability of pure Al, AlSi12, and AlSi10Mg samples by depicting the range of E_v in which almost defect-free samples with relative densities higher than 99% were obtained. It is crystal clear that the addition of Si and Mg could noticeably enhance the processing window of Al, the reason behind which is discussed in detail in the following sections. The Al alloys can benefit from such improved processability in several ways. It is indisputable that complex and various physical phenomena are involved in the LPBF process, and the formation/reshaping of the molten material is a dynamic process [34]. Therefore, the top surface of each consolidated track/layer shows a stochastic nature [35], resulting in the formation of peaks and valleys on the surface (surface roughness). The surface roughness and the powder segregation during the powder spreading cause non-uniformities in the powder layer deposited on each consolidated substrate, making the powder layer thickness and thus the actual heat input location-dependent. When the processing window is narrow (i.e., pure Al), there is a high chance for the formation of isolated defects in random locations due to the minor changes in the actual heat input, even if the optimum set of process parameters is employed. The contrary is the case for AlSi12 and AlSi10Mg alloys with a wide processing window. Besides, the solidification mode and cooling rate are dictated by process parameters during the LPBF processing of a specific material. Being processable in a wide range of E_v (50-100 J/mm³ for AlSi12 and AlSi10Mg alloys) enables fine-tuning of the microstructure or implementation of various process parameters for the printing of different layers (without being worried about the formation of defects) by using a suitable controller to end up with components having functionally graded microstructures [36] and/or heterogeneous grain structures benefiting from multiple strengthening mechanisms [37].

The reasons behind the significantly enhanced processability of Al alloys caused by the addition of Si and Si + Mg were assessed from different viewpoints, including (i) powder-laser interactions, (ii) powder bed packing density, (iii) powder and sample oxygen content, and (iv) nature and estimated thickness of the oxide compounds existing on the surface of powder particles. In the following, each factor is thoroughly discussed for pure Al, AlSi12 and AlSi10Mg. By considering these contributing factors simultaneously, the processability and densification level of the fabricated parts are explained in detail in the following sections.

3.2 Influence of Powder attributes and laser absorptivity on the processability

Figure 4(a) shows the particle size distribution and the SEM micrographs of the pure Al, AlSi12, and AlSi10Mg powders used in this study as the starting material. The SEM micrographs reveal that the

morphology of particles is almost identical in all cases (all powders are gas atomized). While most of the powder particles are nearly spherical, semi-spherical, and irregular-shaped particles were also occasionally observed in the powder systems. According to the particle size distribution analysis results, all powders featured almost the same d_{90} (62.4, 62.3, and 66.5 μm for pure Al, AlSi12, and AlSi10Mg, respectively), though the d_{50} and d_{10} of the pure Al powder ($d_{50} = 34.9 \mu\text{m}$ and $d_{10}=18.3 \mu\text{m}$) were slightly lower than those of the AlSi12 ($d_{50} = 38.8 \mu\text{m}$ and $d_{10}=23.9 \mu\text{m}$) and AlSi10Mg ($d_{50} = 40.0 \mu\text{m}$ and $d_{10}=23.7 \mu\text{m}$) alloys. According to the optical absorption measurement results shown in Figure 4(b), regardless of the tested wavelength, the optical absorption of Al alloy powders is significantly higher than that of pure Al. Having almost the same powder morphology, the observed differences in the optical absorption are mainly referable to their chemistry and powder particle size. At the wavelength of 1070 nm, which is the wavelength of the laser used in this study, the optical absorption of pure Al, AlSi12, and AlSi10Mg is 38.6, 58.4, and 56.1%, respectively, meaning that the addition of Si and Si + Mg to the Al significantly enhanced its optical absorption. It is worth noting that although pure Al powder had finer powder particles compared to the Al alloys, which act to enhance the optical absorption of the powder system, the influence of the chemistry on the optical absorption was dominant.

Figure 4. (a) Particle size distribution and SEM micrographs, and (b) optical absorption versus wavelength of the pure Al, AlSi12, and AlSi10Mg powders.

The apparent packing density of the powders was measured by means of the Hall flow method. As confirmed in [38], in the size range of the powder used in this study, the apparent packing density is almost equal to the powder bed packing density, which was measured on a single powder layer with the thickness of 100 μm using the computed tomography (CT) technique. Therefore, the powder bed packing density can be reasonably estimated by measuring the apparent density by the Hall flow method. As listed in Table 3, both Al alloy powders possessed higher packing densities (1.27 and 1.29 g/cm^3 for AlSi12 and AlSi10Mg, respectively) than that of the pure Al (1.17 g/cm^3). The relative powder packing densities are also provided in Table 3. Due to the presence of interstices in the powder bed, the melting of powder particles and the subsequent consolidation of the molten material during the LPBF process is accompanied by a contraction, creating a gap between the tip of the recoater and the top of the consolidated layer. This gap will be filled during the deposition of the next powder layer, leading to the deviation in the powder layer thickness from its nominal value (30 μm in this study). The increase in the powder layer thickness continues during the printing of several layers until the powder layer thickness approaches a constant value known as the effective powder layer thickness (t_{eff} in μm) [39]:

$$t_{\text{eff}} = \frac{t}{\rho} \quad \text{Eq. 1}$$

in which t is the nominal powder layer thickness [μm] and ρ is the relative powder packing density. Using Eq. 1 and the data provided in Table 3, t_{eff} was calculated to be 70 and 62 μm for pure Al and Al alloys, respectively. By taking the powder bed packing density and laser absorptivity (Figure 4(b)) into consideration, a modified volumetric energy density equation has been proposed as follows [33, 40]:

$$e_v = \frac{AP}{vht_{\text{eff}}} = \frac{\rho AP}{vht} = (\rho A)E_v \quad \text{Eq. 2}$$

where A signifies the laser absorptivity of the powder. Implementation of Eq. 2 to calculate the heat input for a specific material would only shift the values obtained by E_v to lower values. However, when comparing the heat input of different materials in a fixed set of process parameters, the E_v would be misleading. According to Eq. 2, the actual heat input in pure Al and Al alloys is $0.17E_v$ and $0.28E_v$, respectively. Under printing conditions with a fixed set of process parameters, the heat input in pure Al would be $\approx 65\%$ lower than that of the AlSi12 and AlSi10Mg alloys. That is why as opposed to the pure Al, which required P levels higher than 300 W to end up with highly-dense parts, lower P (250 W) could lead to the almost defect-free AlSi12 and AlSi10Mg components (Figure 3). Therefore, it can be concluded that the addition of Si and Si + Mg to the Al significantly improves the processability by enhancing the laser absorptivity. Although the literature assumes the relatively low laser absorptivity of AlSi12 and AlSi10Mg alloys as one of the main contributing factors behind needing relatively high

P for their LPBF processing [18], the optical absorption measurements in this study clearly revealed that their absorption is relatively high and comparable to that of other materials such as H13 tool steel [40], and Ti-6Al-4V [41]. For pure Al, on the other hand, the relatively low laser absorptivity plays a significant role in its inferior consolidation kinetics.

Table 3. The apparent packing density of the powders measured by the Hall flowmeter funnel.

Powder	Apparent Packing Density [g/cm ³]	Relative powder packing density
	Hall Funnel	
Pure Al	1.17±0.00	≈ 0.43
AlSi10Mg	1.29±0.00	≈ 0.48
AlSi12	1.27±0.02	≈ 0.48

It should be highlighted here that the absorptivity of not only the powder but also the consolidated material is of utmost importance during the LPBF process [42] since reasonable inter-track and inter-layer overlaps are required in the LPBF-processed parts to ensure high densification levels. Therefore, a portion of the laser beam is in direct contact with the previously consolidated material in the overlap region where not the power, but the bulk is present (see section 0). Bramson et al. [43] proposed an empirical equation correlating the laser absorptivity of the bulk material (n_s) to the wavelength of the laser beam (λ) and electrical resistivity of the material (μ):

$$n_s = 0.365\sqrt{\frac{\mu}{\lambda}} - 0.0667\left(\frac{\mu}{\lambda}\right) + 0.006\sqrt{\left(\frac{\mu}{\lambda}\right)^3} \quad \text{Eq. 3}$$

By substituting $\lambda = 1070$ nm and μ of 2.85, 4.32, and 4.26 $\mu\Omega\cdot\text{cm}$ into the above equation [44, 45], n_s of 5.8% for pure Al, and 7% for AlSi12, and AlSi10Mg alloys would be obtained. The laser absorptivity of the bulk Al alloys is also considerably higher than pure Al ($\approx 20\%$ higher) but not as significant as the case of powder ($\approx 50\%$ higher). Based on the calculated results, it can be concluded that due to the extremely low bulk laser absorptivity of pure Al and Al alloys, they are noticeably prone to the formation of inter-track and inter-layer defects. Nevertheless, it can be claimed that the formation probability of such defects in pure Al is more pronounced. It should also be underlined that the μ values used in Eq. 11 to calculate the n_s are for conventionally manufactured pure Al/Al alloys. Silbernagel et al. [46] reported that the μ of the LPBF-processed AlSi10Mg samples is in the range of 7.8 to 9.9 $\mu\Omega\cdot\text{cm}$ (orientation dependent) in the as-built condition. Substituting the current values in Eq. 11 yields n_s of 9.4-10.5%, which is considerably greater (up to 50%) than the n_s calculated by using the data on the conventionally manufactured AlSi10Mg alloy.

3.3 Influence of the chemical composition on the oxidation tendency and processability

3.3.1 Nature of the oxide compounds in the starting powder

As it is well-known, metal powder particles (i.e., pure Al, AlSi12, and AlSi10Mg) are covered by an ultra-thin oxide layer, developed on the surface of the particles during the atomization process or maintaining in an oxygen-containing atmosphere [47]. The nature of these oxide layers can play a crucial role during the LPBF processing of pure Al and Al alloys by influencing the direction of convectional flows within the melt pool, thermo-physical properties of the melt, and the evaporation temperature of the oxides. To investigate the surface chemical composition of pure Al, AlSi12, and AlSi10Mg powders, they were analyzed by Auger electron spectroscopy (the acquired spectra and their derivatives are individually available in the supplementary materials). Figure 5 shows the derivative of the acquired data (intensity) as a function of the binding energy along with the reference spectra of Al, Al₂O₃, Si, SiO₂, Mg, and MgO for the sake of comparison. Quantifications were also made on the derivative of the acquired data, the results of which are summarized in Table 4. Al, Si, and Mg concentrations are the combination of their metal and oxide components obtained by curve fitting the references for each acquired peak.

Figure 5(a) shows the spectrum of the pure Al powder. The shape of the oxygen peak in the acquired data fit well with oxygen from the Al₂O₃ reference spectrum (Figure 5(d) and Figure 5(j)). The Al peak shape showed characteristics of both the typical Al metal (Figure 5(e) and Figure 5(l)) and Al₂O₃ (Figure 5(d) Figure 5(k)) peak shape. This suggests that the thickness of the oxide layer is less than the depth at which Auger electrons are collected, which is about 6 nm. There is also the possibility that the atomic scale boundary between the oxide and metal is a bit diffuse rather than perfectly sharp, so there may be an oxygen gradient. In both cases, it is impossible to pinpoint the thickness of the oxide layer based on the point spectra. However, it can be claimed that the identified material is not pure Al₂O₃ oxide in the full 0-6 nm depth since the peak shape is a convolution of Al and Al₂O₃ rather than only shaped like the Al peak of Al₂O₃. Therefore, one shall not expect to observe a spectrum (Figure 5(a)) and chemical composition (Table 4) that perfectly fits stoichiometric Al₂O₃ since it contains some amount of pure Al (with no oxygen) as well.

Figure 5. The first-derivative Auger spectra for: (a) Pure Al, (b) AlSi12, and (c) AlSi10Mg powders. The reference spectra of Al₂O₃, Al, SiO₂, Si, MgO, and Mg, are provided in (d-i), respectively. The higher magnification of the designated colored box in each reference spectrum is shown in (j-r).

Figure 5(b) shows the Auger electron spectrum of AlSi12 powder. The particles, in this case, had less Si on the surface than expected. The concentration was very low, so it was difficult to break down Si into metal and SiO₂ (Si4+) peak shape since the differences are subtle. However, the Si reference (Figure 5(g) and Figure 5(o)) fits the data a little better than Si4+ (Figure 5(f) and (n)) or a combination of the two, suggesting that the oxide is only/mainly Al₂O₃, and most of the Si in the data comes from the metal below the oxide. Similarly, the Al metal fraction of the Al peak was quite high. As a general rule, the thinner the oxide layer, the larger the Al metal contribution to the Al peak, and this applies to Si and Mg as well in other samples. So the sharp Al peak in the spectrum of AlSi12 powder serves as a token of the existence of an oxide layer, thinner than that of the pure Al sample. The oxygen peak fits very well with just the Al₂O₃ reference (Figure 5(d) and Figure 5(j)) rather than a mix of Al₂O₃ and SiO₂ (Figure 5(f) and Figure 5(m)). This is a further indication that, most probably, the Si is not significantly in the oxide.

Figure 5(c) shows the spectrum of AlSi10Mg powder. Similar to the AlSi12 sample, the Si peak here in AlSi10Mg tends to resemble Si (Figure 5(g) and Figure 5(o)) more than Si⁴⁺ (Figure 5(f) and (n)), although it is a small peak, so it is hard to be sure through the noise in the data. The Si peak seemed to fit a little better if SiO₂ was also included in the fitting, but it still mostly resembled Si metal. This might indicate some Si oxide in the oxide layer, but some of the metal below is also being collected, which would have metallic Si. The Mg concentration at the surface is much higher than the bulk metal concentrations, and the peak shape fits almost exclusively as MgO (Figure 5(h) and (q)) rather than Mg (Figure 5(i) and (r)). According to Table 4, the concentration of Mg on the surface of the AlSi10Mg powder was 6 at.%, which is ≈ 10 times greater than the bulk concentration of this element. The oxygen peak for these particles fit best as a combination of all three oxide references, namely, Al₂O₃, SiO₂, and MgO. Any other combination of these (trying just one, or any two such as Al₂O₃ + MgO) did not fit the peak shape as perfectly as using all three.

Table 4. Surface chemical composition of the pure Al, AlSi12, and AlSi10Mg powders

Powder sample/Element	O [at%]	Al [at%]	Si [at%]	Mg [at%]	Nature of oxide layer
Pure Al	57.6	42.6	-	-	Al ₂ O ₃
AlSi12	49.4	48.2	8.4	-	Al ₂ O ₃
AlSi10Mg	48.5	36.6	8.9	6	Al ₂ O ₃ -MgO-SiO ₂

3.3.2 Oxygen content of the initial powders and printed parts

Not merely the nature but also the thickness of the oxide layers is a significantly important contributing factor in the processability of Al and Al alloys since it affects the concentration of oxygen in the final printed part. Figure 6 shows the oxygen content of the pure Al, AlSi12, and AlSi10Mg starting powders as well the parts printed with these powders using two different sets of process parameters, corresponding to low density ($P = 200$ W) and highly-dense ($P = 300$ W) samples. These results provide an insight into the initial content of oxygen in the powder, as the main source of oxygen, and the oxide evolutions during the LPBF process. Before anything else, the data give strong evidence that the oxygen in the pure Al powder (2260 ppm) is conspicuously higher than that of the AlSi12 and AlSi10Mg powders. The oxygen content in AlSi12 (1299 ppm) and AlSi10Mg (740 ppm) powders was found to be 42.5 and 67.3% lower than that of the pure Al powder, which is consistent with the higher intensity of the metallic constituents detected in the Auger electron spectra of Al alloys compared to the pure Al powder (Figure 5). Simultaneous consideration of the powder oxygen content (Figure 6) and the Auger electron spectroscopy findings give evidence that the addition of Si and Mg has significantly changed either the nature of the oxide layers or their formation kinetics. While not changing the nature of the oxide layer (Figure 5(b) and Table 4), Si in AlSi12 remarkably decreased the oxygen content, and, therefore, the thickness of the oxide layer in this alloy by obstructing the oxidation of Al. Incorporation of a minor percentage of Mg along with Si to the Al (AlSi10Mg) showed a

pronounced influence not only on the oxidation tendency but also on the nature of the oxide layers (Figure 5(c) and Table 4). It is worth noting that the observed differences between the oxygen content of the different powder systems are not merely attributable to the chemistry of them but also their particle size distribution. Referring to Figure 4(a), the pure Al powder had finer particles than the Al alloy powders. This is accompanied by a higher surface area to the volume ratio of the particles in the former, resulting in the greater oxygen content.

Figure 6. The oxygen content (mass ppm) of the starting powders as well as the pure Al, AlSi12, and AlSi10Mg parts fabricated by P=200 W ($v=2000$ mm/s) and P=300 W ($v=1400$ mm/s). The reported O concentrations for each powder or printed sample represent the average of two distinct measurements. Error bars represent the standard deviation from the average values.

By having the oxygen percentage in the powders and knowing the nature of the oxide layers existing on their surface, it is feasible to calculate the average thickness of the oxide layer with reasonable accuracy. Even though the oxide layer thickness calculation is pretty straightforward for pure Al and AlSi12 powders in which the oxide layer is merely Al_2O_3 , such a calculation seems to be trickier for AlSi10Mg powder since the combination of Al_2O_3 , MgO, and SiO_2 was detected on the powder surface. To render it possible even for the AlSi10Mg case, it was attempted to separate the contribution of oxygen in each oxide based on the deconvolution of the acquired data by curve fitting the references of the pure oxides for the oxygen in the acquired peak. It appeared to have 8.9, 15.9, and 23.7 at.% (from the total of 48.5 at.% shown in Table 4) of oxygen from Al_2O_3 , MgO, and SiO_2 , respectively. By assuming that the oxygen is fully concentrated in the oxide layer on the surface of the powder (the concentration of oxygen in the bulk of powder is assumed to be negligible because the oxygen content

of the typical wrought pure Al ingots used to produce the melt for the gas atomization process is around 4 ppm [48]), the thickness of the oxide layers in pure Al (Eq. 4), AlSi12 (Eq. 5), and AlSi10Mg (Eq. 6) powders can be calculated as follows:

$$t_{oxide} = \frac{f_o \rho_{Al} D_{ave} M_{Al_2O_3}}{18 M_o \rho_{Al_2O_3}} \quad Eq. 4$$

$$t_{oxide} = \frac{f_o \rho_{AlSi12} D_{ave} M_{Al_2O_3}}{18 M_o \rho_{Al_2O_3}} \quad Eq. 5$$

$$t_{oxide} = \frac{f_o \rho_{AlSi10Mg} D_{ave}}{6[0.18(\frac{3M_o}{M_{Al_2O_3}} \rho_{Al_2O_3}) + 0.33(\frac{M_o}{M_{MgO}} \rho_{MgO}) + 0.49(\frac{2M_o}{M_{SiO_2}} \rho_{SiO_2})]} \quad Eq. 6$$

In all of the above equations, f_o is the fraction of oxygen detected in each powder (Figure 6) and D_{ave} is the average diameter of the powder (the median particle diameter (d_{50}) in Figure 4 is used as the average diameter). The M , and ρ represent the molar mass and theoretical density, respectively. Putting some data into the equations, the t_{oxide} in pure Al, AlSi12, and AlSi10Mg is ≈ 19 , 12, and 8.5 nm, respectively, which is in line with the Auger electron spectroscopy findings, where the oxide layers were predicted to be thinner in Al alloys compared to the pure Al case. This shows the significant contribution of alloying elements in reducing the kinetics of oxide layer formation. The calculated t_{oxide} for all of the powders exceeds the depth at which the electrons were collected during the Augers electron spectroscopy analysis (~ 6 nm), suggesting that the oxide layer is not uniform in thickness and/or the boundary at the atomic scale between the oxide and metal is a bit diffuse.

The oxygen content of the printed pure Al, AlSi12, and AlSi10Mg coupons at low and relatively high P are also provided in Figure 6. Surprisingly, the oxygen content in the LPBF-processed samples is considerably lower than that of the starting powder, regardless of the employed process parameters and the studied material. Moreover, the oxygen content in samples processed by $P = 300$ W was tremendously lower than that of the $P = 200$ W in pure Al and AlSi12. In AlSi10Mg, the oxygen content of the printed parts was found to be less sensitive to the P level. Kimura et al. [48] have also detected lower oxygen levels in the printed pure Al samples than the starting powder, though the reason behind it has not been discussed. Such a finding leads to a very valuable conclusion that either oxidation does not happen during the LPBF processing of Al and Al alloys or the rate of the oxide diminishment is significantly higher than that of any possible in-situ oxidation since the oxygen content of the final components is noticeably lower than that of the starting powders. In the following section, a mechanism governing the oxygen release during the LPBF process is proposed. By implementing this mechanism,

the results shown in Figure 6 are discussed in detail, and the influence of Mg and Si on the processability of Al/Al alloys is elaborated by considering the nature and content of oxide/oxygen.

3.3.3 Oxide diminishment mechanism

A mechanism is proposed for the oxide diminishment based on the findings of Cunningham et al. [49] on surface vaporization of the melt pool and Zhao et al. [50] on Marangoni thermocapillary flow directions, which were confirmed through ultrahigh-speed X-ray imaging of the melt pool during the LPBF processing of Ti-6Al-4V alloy and in-situ observation of the laser spot welds (Fe-Cr-Ni alloy) using a high-speed camera, respectively. Based on [49], regardless of the process parameters employed and the corresponding melting mode (conduction or keyhole mode), the evaporation occurs at least on the surface of the melt pool and leaves behind a vapor depression. The latter study proved that the direction of the Marangoni thermocapillary force in the presence of aluminum oxide would not change unless the oxides find enough time to dissolve within the weld pool.

Spallation of the oxide layer- Step 1: During the LPBF process, prior to the melt pool formation, the laser irradiates the powder particles, which can be assumed as pure Al or Al alloy spheres covered by an ultra-thin oxide shell. Olakanmi [32] suggested that the disparity in the coefficient of thermal expansion of the oxide shell (α_{oxide} , $7.4 \times 10^{-6} / K$ for Al_2O_3) and the metal core (α_{core} $27.4 \times 10^{-6} / K$ for pure Al) will generate huge circumferential stress (σ_c) during the heating stage, which is responsible for the separation and breakdown of the oxide layers:

$$\sigma_c = E \Delta T (\alpha_{core} - \alpha_{oxide}) \quad Eq. 7$$

in which E signifies Young's modulus of the oxide. Trunov et al. [51] explained the oxide layer's cracking during the heating with a diverse approach to the subject. They proposed that upon heating, the Al_2O_3 layer goes through a series of phase transformations accompanied by volume decrease, promoting the chance of oxide layer fracture. However, both mechanisms fail to address the oxide breakdown during the LPBF process with a non-equilibrium heating nature. The fast heating ($\sim 10^6 K / s$) prevents the breakdown of the oxide shell before melting of the metal core [52] on the one hand and the diffusion-controlled phase transformations on the other hand. The fracture of the oxide layer can be explained by considering the pressure build-up within the powder particles as a result of the core melting while the covered oxide layer is still in the solid form [52] (Figure 7(a-c)). The solid to liquid phase transformation in pure Al, AlSi12, and AlSi10Mg from solidus to the liquidus temperature is accompanied by a volume change corresponding to 4.9, 3.7, and 3.1 vol.%, respectively. The magnitude of the pressure applied to the oxide shell as a result of this volume strain can be calculated as follows [53]:

$$P_r = B \varepsilon_v \quad Eq. 8$$

in which P_r , B , and ε_v denote the pressure due to the volume change, bulk modulus, and volume strain, respectively. Assuming the B to be 70 GPa for Al and Al alloys, the P_r exerted to the oxide shell would be 3.7, 2.8, and 2.3 GPa for pure Al, AlSi12, and AlSi10Mg, respectively. By knowing the P_r , the hoop stress (σ_θ) in the oxide shell is calculated as [54]:

$$\sigma_\theta = \frac{P_r r_{ave}}{2t_{oxide}} \quad Eq. 9$$

where r_{ave} is the average particle radius. By substituting the calculated t_{oxide} (Eq. 3, Eq. 4, and Eq. 5), and the average particle radius (Figure 4), the magnitude of σ_θ would be astronomically high (thousands of GPa) for all powders, meaning that the rapid melting of the metal core is the governing mechanism explaining the fracture and spallation of the oxide layer (Figure 7(a-c)). It needs to be noted that the presence of cracks in the oxide shell can significantly reduce the calculated σ_θ by decreasing the chance of liquid pressure build-up within the particle.

Figure 7. The schematic illustration of: (a) Al/Al alloy powder particles having an oxide shell, (b) melting of the core before its separation from the oxide shell caused by the non-equilibrium rapid heating of the powder particles, (c) oxide fracture and spallation through the core melting and pressure build-up mechanism, (d) buoyancy force and (e) Marangoni thermocapillary force in the melt pool causing the nano-sized oxide particles to concentrate on the surface of the melt pool, (f) evaporation of the oxides, especially in the zone (I) as a result of their direct interaction with the laser beam, (g) the solidified melt pool and trapped oxides after the laser travels away, and (h) second chance of oxide evaporation during the printing of the subsequent tracks where the oxides in the zone (II) of previous track locate in the zone (I) of the new track.

Formation of a melt pool covered by nano-sized oxides- Step 2: As mentioned in the previous section, the laser-powder interaction would create a melt pool from metal powders, which contains solid nano-sized (at least in one dimension) oxides formed due to the severe fracture at the heating stage. The temperature gradient within the melt pool leads to the formation of surface tension (γ) gradient between the warmer (center of the pool surface) and cooler (edges of the pool) regions. Since the surface tension of the molten Al/Al alloys decreases by increasing the temperature ($d\gamma/dT < 0$), the shear stress induced by the surface tension gradient would result in an outward fluid flow from the center of the surface toward the edges of the melt pool, returning beneath the surface [55] (known as Marangoni thermocapillary fluid flow, Figure 7(e)). On the other hand, the temperature gradient also causes density

gradients within the melt pool, developing buoyancy forces. Given the fact that the density of molten Al decreases by increasing the temperature ($d\rho/dT < 0$), the heavier Al (cooler region) at the edges moves inward (sink) along the melt pool boundary, and the lighter liquid (warmer region) undergoes an upward movement along the melt pool axis [55] (Figure 7(d)). Therefore, it can be concluded that the buoyancy forces facilitate the transfer of solid nano-sized oxides from the bulk of the melt pool toward the surface. Accordingly, the melt pool of Al/Al alloys during the LPBF process is not a bare pure metal/alloy molten phase in which the oxidation can occur, but is a melt pool covered by the solid nano-sized oxides which act as a barrier to the oxidation (Figure 7(f)). While it cannot guarantee the lack of melt pool oxidation during the LPBF process, it can definitely reduce the activity and affinity of the melt pool to react with the existing oxygen in the processing chamber. The lower tendency for oxidation plus the short laser-powder interaction time in the order of microseconds significantly reduces the chance of in-situ oxidation.

Evaporation of the nano-sized solid oxide particles- Step 3: Figure 8, Figure 9, and Figure 10 show the width, and depth of the printed single tracks as a function of v at each P for pure Al, AlSi12, and AlSi10Mg, respectively. As it is evident, regardless of the material studied and the process parameter employed, the width of the tracks was found to be higher than the nominal laser spot diameter (100 μm). Accordingly, it is fair to conclude that the melt pool can be divided into two different zones regarding the laser beam interaction. In zone (I), the melt pools of pure Al and Al alloys with solid nano-sized oxides on their surface directly contact the laser beam. In zone (II), the opposite is the case (Figure 7(f)). The solid nano-sized oxides will undergo evaporation in zone (I) due to the direct interaction with a heat source having a high power intensity ($P/A = 2.5\text{-}5 \times 10^{10} \text{ W/m}^2$ in this study). Based on the data available for the oxides of pure Al (Al_2O_3), AlSi12 (Al_2O_3), and AlSi10Mg ($\text{Al}_2\text{O}_3\text{-MgO-SiO}_2$), their melting temperatures are considerably higher than that of the pure Al and Al alloys. Except for the SiO_2 , they all possess a higher boiling temperature as well. Therefore, the evaporation of the oxides in zone (I) might seem impossible at first glance, even after considering their direct interaction with the laser beam. However, the melting-point depression phenomenon caused by the extremely high surface area-to-volume ratio (A/V) of the nanoscale oxide particles can explain the rationale behind their easier evaporation at noticeably lower temperatures during the LPBF process. The melting point of a particle (T_m) can be calculated using the following equation [56]:

$$\frac{T_o - T_m}{T_o} = \frac{A}{\rho_s V \Delta H_m (\gamma_{sv} - \gamma_{lv})} \quad \text{Eq. 10}$$

in which T_o , ρ_s , ΔH_m , γ_{sv} , and γ_{lv} denote the bulk melting temperature, density of the solid material, latent heat of fusion, solid/vapor surface energy, and liquid/vapor surface energy, respectively. In the nano-sized oxides with an extremely high A/V ratio, copious surface atoms with unsaturated bonds

(reduced number of cohesive bonds) exist in the particle, reducing the overall thermal energy required to free the atoms from the solid and, therefore T_m . Joshi et al. [56] studied the T_m of Al_2O_3 films having a thickness in the order of nanoscale and an infinite length (1 μm), which can be the case for the fractured oxide shells during the spallation stage. They reported that the T_m of Al_2O_3 varies in the range of 727 – 2000 °C when the film thickness increases from 1-10 nm ($T_0 = 2072$ °C). The same statement should be valid for the evaporation of nano-sized particles in which their high A/V facilitates their evaporation. Therefore, if P is sufficiently high during the LPBF process, the oxide evaporation can occur in zone (I), decreasing the oxygen concentration in the printed component (Figure 6).

The reduction in the oxygen content of the fabricated parts is not merely due to the evaporation of oxides in zone (I) but also zone (II). However, the oxide evaporation takes place on a smaller scale in zone (II) since the maximum temperature experienced by the solid nano-sized oxides is lower than zone (I), in which the oxides are in direct contact with the laser beam (Figure 7(f, g)). It should be noted that the nano-sized oxides are accumulated more at the edges of the melt pool surface (zone (II)) than the central region (zone (I)) because of the outward direction of the Marangoni thermocapillary fluid flow (Figure 7(d-f)). Thus, conditions enabling the evaporation of oxides in this zone are expected to significantly decrease the overall oxygen of the fabricated part. Although the complete evaporation of the nano-sized oxides in zone (II) is not effectively possible during the printing of an ongoing track, they will undergo evaporation during the printing of the very next track, which has an overlap with it. Simply put, the edges of the previous track (zone (II)) are located in the central region (zone (I)) of the new one, where the oxides effectively evaporate (Figure 7(h)). Due to the higher temperature of the melt pool surface, high P provides more favorable conditions for effective evaporation of the oxides. It should also be borne in mind that during the LPBF process, each consolidated layer might experience repeated remelting, the number of which is dictated by the applied heat input. This provides an opportunity for the evaporation of oxides in the previous layers, which did not find the chance to escape from the melt pool surface. The depth of the laser scan tracks as a function of the v at each P for pure Al, AlSi12, and AlSi10Mg alloys are shown in Figure 8, Figure 9, and Figure 10, respectively. As it is evident, the depth of the melt pool shows an ascending trend with increasing P . At $P = 300$ W, sometimes the depth of the laser scan tracks in AlSi10Mg (the same is valid for pure Al and AlSi12) reached 165 μm . By assuming that the nominal thickness of the consolidated track is 30 μm , such a depth corresponds to five times remelting of any consolidated layer. This factor also plays a major role in reducing the oxygen concentration in the LPBF-processed parts at high P levels.

According to the results provided in Figure 6, as well as the abovementioned discussion, it cannot be concluded that the in-situ oxidation of Al/Al alloys does not happen at all during the LPBF process. In other words, the observed decrease in the oxygen content can also be caused by the fact that the level of oxide removal has outweighed any possible in-situ oxidation of the molten Al/Al alloys under the

processing condition employed in this study. Nevertheless, it seems that the in-situ oxidation was negligible during the LPBF process of Al/Al alloys based on the oxygen content of the samples printed at the laser power of 300 W and scanning speed of 1400 mm/s. For instance, in the case of pure Al, the oxygen content of the printed sample at such process parameters was 90 ppm, while it was 2260 ppm in the starting powder. Even if it is assumed that all of the oxides in the starting powder (source of oxygen) are evaporated during the LPBF process and the 90 ppm oxygen detected in the printed part is originated from the in-situ oxidation, it can be concluded that the rate of oxidation was only 4% of the that of the oxide evaporation. It means that the rate of oxidation at high temperatures (high laser power of 300 W) and relatively long interaction time (relatively low scanning speed of 1400 mm/s) is not significant. Then the rate of oxidation at the lower laser power of 200 W and shorter interaction time associated with the faster scan speed of 2000 mm/s should be even less than 4%. The reason behind the detection of higher oxygen content in the samples printed at the laser power of 200 W is not the higher rate of in-situ oxidation but the lower chance of oxide evaporation at lower temperatures and shorter interaction times. This is also valid for the AlSi12 and AlSi10Mg alloys with lower oxidation tendencies than the pure Al.

Figure 8. The size measurement results of pure Al single tracks: (a) scan track width, and (b) scan track depth as a function of v at different P . The reported values are the average of at least six distinct

measurements, and the error bars are the standard deviations from the average values. The cross-sectional view of the tracks processed at high ($P = 370$ W, $v = 400$ mm/s), medium ($P = 370$ W, $v = 1600$ mm/s), and low ($P = 200$ W, $v = 1400$ mm/s) heat inputs are shown in (c-e), respectively.

Figure 9. The size measurement results of AlSi12 single tracks: (a) scan track width, and (b) scan track depth as a function of v at different P . The reported values are the average of at least six distinct measurements, and the error bars are the standard deviations from the average values. The cross-sectional view of the tracks processed at high ($P = 370$ W, $v = 800$ mm/s), medium ($P = 300$ W, $v = 1400$ mm/s), and low ($P = 200$ W, $v = 1600$ mm/s) heat inputs are shown in (c-e), respectively.

Figure 10. The size measurement results of AlSi10Mg single tracks: (a) scan track width, and (b) scan track depth as a function of v at different P . The reported values are the average of at least six distinct measurements, and the error bars are the standard deviations from the average values. The cross-sectional view of the tracks processed at high ($P = 370$ W, $v = 800$ mm/s), medium ($P = 300$ W, $v = 1400$ mm/s), and low ($P = 200$ W, $v = 1800$ mm/s) heat inputs are shown in (c-e), respectively.

3.3.4 Verifying the proposed oxide diminishment mechanism through microstructural observations

The proposed mechanism in section 3.3.3 was confirmed by the microstructural analysis. Figure 11(a-d) shows the top surface SEM micrographs along with the EDS maps showing the oxygen distribution on the top surface of the LPBF-processed pure Al samples at different P and constant v . As it is evident, the oxygen (of oxides) is mainly concentrated in the inter-track (overlap) regions rather than the center of the laser scan tracks. As explained earlier, this is mainly attributable to the upward and outward fluid flow directions caused by the buoyancy and Marangoni thermocapillary forces, respectively, causing the pile-up of oxides on the surface, especially at the edges of the melt pools. The center of the laser scan tracks and the overlap regions are zone (I) and zone (II), shown in Figure 7. At relatively low P of 200 W (Figure 11(a)), in addition to zone (II), oxygen was also detected in the zone (I) since the surface temperature of the melt pool was not high enough even for the complete evaporation of oxides in the zone (I), where they are in direct contact with the heat source. However, at P levels

exceeding 250 W (Figure 11(b-d)), almost no oxide is perceptible in zone (I). In contrast, the amount of oxides in zone (II) is strongly dependent on the employed P . For instance, at P levels of 300 and 370 W, the melt pool surface temperature is considerably high, and the oxides in zone (II) are negligible. It should be noted that the oxides shown in Figure 11(a-d) can undergo evaporation during the printing of subsequent layers only for the laser power of 300 W and 370 W, since the depth of laser scan tracks for samples shown in Figure 11(a-d) is 35, 36, 50, and 71 μm , respectively. Therefore, not only the population of oxides is significantly low in the as-consolidated layers processed at high P , but also the remaining oxides are given another chance to evaporate.

The same trend as that of the pure Al was also observed for AlSi12 and AlSi10Mg alloys, the only difference being that the oxygen was not mainly concentrated in the edges of the laser scan tracks. The top surface SEM micrographs and oxygen EDS maps of one of the AlSi12 and AlSi10Mg samples processed at $P = 250$ W are shown in Figure 11(e, f). The obvious pattern in the pure Al could not be detected in Al alloys, especially for AlSi10Mg. This can be ascribed to the Marangoni thermocapillary forces in the melt pool of AlSi12 and AlSi10Mg alloys. The driving force of Marangoni thermocapillary flow in the melt pool, which directs the oxides toward the edges is $d\gamma/dT$, reported to be -0.15 and $-0.03 \text{ mN} \cdot \text{m}^{-1} \text{K}^{-1}$ for pure Al and AlSi12, respectively [57]. No data is available on AlSi10Mg, but it is fair to assume the same $d\gamma/dT$ as that of the AlSi12 for this alloy [58]. The weaker Marangoni thermocapillary forces in Al alloys are the major reason behind the more uniform distribution of oxides on the top surface of the laser scan tracks. The higher concentration of oxides on the surface of the AlSi12 alloy is consistent with the oxygen content analysis provided in Figure 6.

Figure 11. Top surface SEM micrographs of pure Al samples processed using $v=1400$ mm/s and P of: (a) 200 W, (b) 250 W, (c) 300 W, and (d) 370 W. (e) and (f) Top surface of AlSi12 and AlSi10Mg samples processed using $v =1400$ mm/s and P of 250 W. There are two insets in each SEM micrograph, the top one is the EDS map shows the oxygen distribution on the top surface, and the bottom one shows the ESD map merged with the corresponding SEM micrograph.

3.3.5 Rationalization of the lower oxygen content in the printed parts based on the proposed mechanism

The abovementioned discussion can be utilized to justify the oxygen content analysis results provided in Figure 6. In the range of the applied P (200 - 370 W), the oxygen content of the LPBF-processed parts was found to be considerably lower than that of the starting powder, proving that not only oxidation did not happen during the LPBF process, but also the employed P levels were enough for the evaporation of nano-sized oxides, especially in the zone (I). According to Eq. 10, higher P can provide higher melt pool temperatures (T) [27]:

$$T = \frac{AP}{\sqrt{2}r_0k\pi^{3/2}}\exp\left(\frac{-r^2}{2r_0^2}\right)\tan^{-1}\left(\sqrt{\frac{2\alpha}{\nu r_0}}\right) \quad \text{Eq. 11}$$

in which A , k , α , r_0 , and r denote the laser absorptivity, thermal conductivity, thermal diffusivity, beam radius, and radial position in the melt pool, respectively. Higher P can lead to higher temperatures for oxide evaporation in zone (I)/zone (II). Moreover, higher laser powers can enhance the chance of remelting of the previously consolidated layers and, therefore, releasing oxygen. That is why lower oxygen contents were detected in the samples processed by higher P (300 W versus 200 W in Figure 6) in both pure Al and Al alloys. For pure Al, 55% and 96% of the oxygen in the starting powder were released at $P = 200$ W and $P = 300$ W, respectively. The corresponding values were 26% and 83% for AlSi12 alloy, intimating that the release of oxygen happened to a less extent in AlSi12 than pure Al. This finding is attributable to the lower magnitude of buoyancy forces in AlSi12 than pure Al ($d\rho/dT = -0.00039$ and -0.00073 g.cm⁻³.K⁻¹ for AlSi12 and pure Al, respectively²). Hence, a lower fraction of oxides is expected to reach the surface of the melt pool and evaporate due to the upward movement along the melt pool axis. It means that the lower oxygen content in the AlSi12 sample processed by $P = 200$ W is not due to the more oxide evaporation but lower oxygen concentration in the starting AlSi12 powder (Figure 6). The influence of the stronger buoyancy forces in the melt pool of pure Al is reflected in the oxygen content results of the samples processed by $P = 300$ W, in which even though its starting powder had higher oxygen content than Al alloys, the fabricated sample had less oxygen content (90 ppm for pure Al versus 220 ppm for AlSi12). For AlSi10Mg alloy, 80% and 82% of the oxygen in the starting powder were released at $P = 200$ W and $P = 300$ W, respectively, meaning that a high fraction of oxides could evaporate at relatively low P levels. This can be explained by considering SiO₂ (Figure 5 and Table 4) in the AlSi10Mg powder. The bulk melting and boiling temperatures of SiO₂ are significantly lower than those of Al₂O₃ and MgO oxides. These temperatures can be even lower than those of the bulk for nano-sized SiO₂. Therefore, even at lower temperatures (lower P levels), the conditions for SiO₂ evaporation can be satisfied. Since in pure Al and AlSi12 alloys, the SiO₂ oxide is absent, their oxygen reduction percentage at $P = 200$ W was lower than that of AlSi10Mg alloy. However, the increase in the P had the least influence on AlSi10Mg alloy. This is mainly attributed to the presence of MgO oxides in this alloy. The bulk melting and evaporation temperatures of MgO are noticeably higher than Al₂O₃ and SiO₂ oxides, and therefore, they require higher P levels to evaporate. Moreover, according to the Ellingham diagram [59], the Al₂O₃ and SiO₂ oxides can transform to MgO if enough time is available for their reactions with Mg in the melt pool, further decreasing the chance of oxygen release in light of this scenario.

² The $d\rho/dT$ values have been calculated between the melting point and 973 K using data acquired from JMatPro Software.

As a conclusion, although it was expected to have a lower oxygen content in AlSi12 and AlSi10Mg samples due to the lower oxygen content in their starting powder (thinner oxide layers), the opposite was the case. This finding clearly proves that the nature of the oxides, which is dictated by the chemistry of the material, has a crucial impact on the oxygen concentration in final printed parts since it affects their melting/boiling/evaporation temperature during the LPBF process. Nevertheless, the oxygen content of all of the Al/Al alloys processed under $P = 300$ W was noticeably low. The oxygen level of the AlSi10Mg alloy was negligible even at P of 200 W. However, such a P did not lead to almost defect-free parts, meaning that the presence of the oxides is not the factor controlling the densification level of the LPBF-processed AlSi10Mg parts. For pure Al and AlSi12, on the other hand, application of high P seems to be essential to achieve almost oxide-free parts since the level of oxygen is strongly dependent on the P level in these materials. This can also explain why high P levels are required to achieve highly-dense pure Al parts. It is worth noting that the application of relatively high P would also increase the chance of material evaporation and consequently defect formation. Therefore, care must be exercised in selecting the appropriate set of process parameters (e.g., relatively high v in the range of 1600 to 2000 mm/s in this study) to achieve sound oxide-free pure Al parts. These results suggest that reliable, pure Al components with complex geometries meeting the requirements of thermal and electrical applications can be successfully fabricated via the LPBF process. Although not being in the scope of this study, the melt viscosity, thermal conductivity, and melting point are also among the important factors affecting the processability of materials during the LPBF process. Both higher thermal conductivity and melt viscosity of pure Al compared to Al alloys are believed to adversely affect the processability of pure Al.

3.4 Comments on the inability of decomposition and reduction reactions to decrease the oxygen content

According to the literature in chemistry, two other possible reactions can lead to the release of oxygen upon activation, namely, reduction and decomposition reactions. To prove that the evaporation of the nano-sized oxides on the surface of the melt pool is the only reason behind the decrease in the oxygen content, it should be proved that the reduction and decomposition reactions are impossible during the LPBF process of Al/Al alloys. Dooley et al. reported that the Al_2O_3 could be reduced by hydrogen through the following reaction [60]:

This reduction reaction can proceed spontaneously at temperatures lower than 2100 K [61]. The temperature in a major portion of the melt pool (not the surface) meets this condition during the LPBF process. To investigate the possibility of such a reaction during the LPBF processing of Al/Al alloys, the hydrogen content of the starting powders was measured. The measurement results are shown in Figure 12. As it is evident, the concentration of hydrogen detected in the powders is not negligible, especially for pure Al. However, the hydrogen content in the starting powders is significantly lower

than the oxygen content (Figure 6) and cannot explain the noticeable decrease in the oxygen content of the starting powder after melting and consolidation, especially at high laser powers. Besides, the abovementioned reaction does not happen during the LPBF processing of Al/Al alloys since the hydrogen detected in the powder is not in the form of H (atomic hydrogen) but moisture (H_2O). Therefore, the reduction of Al_2O_3 with hydrogen can proceed only if the thermal decomposition of H_2O ensues:

Jellinek et al. [62] studied the possibility of such a reaction at high temperatures and concluded that at temperatures as high as 3000 K, only 14% of the H_2O is in the decomposed form. Since this reaction activates effectively at very high temperatures (exceeding 4000 K), H will not be available in the melt pool during the LPBF process to reduce Al_2O_3 and release the oxygen.

The oxygen release can also occur through the partial or complete thermal decomposition of Al_2O_3 based on the following reactions [63]:

The first and second reactions were reported to get activated at temperatures higher than 4000 K and 4400 K [63]. Since the oxides evaporate at significantly lower temperatures than the thermal decomposition temperature of H_2O and Al_2O_3 , it can be concluded that only the evaporation mechanism proposed in section 3.3.3 can explain the decreased oxygen content of the LPBF-processed parts.

Figure 12. The hydrogen content in ppm (by mass) in the pure Al, AlSi12, and AlSi10Mg powders.

4 Conclusions

This research study realizes the importance of the laser absorptivity, powder characteristics, powder oxygen content and oxide nature on the processability of Al/Al alloys. The addition of Si and Mg to the Al was found to significantly enhance the laser absorptivity and consolidation kinetics. Moreover, the AlSi12 and AlSi10Mg powders featured a higher packing density than pure Al powder, leading to a slightly lower effective powder layer thickness and consequently lower heat input required for the melting. By obstructing the oxidation of Al, the presence of Si in AlSi12 powder resulted in noticeably lower oxygen content and a thinner oxide layer than pure Al. The addition of a minor amount of Mg along with Si to the Al (AlSi10Mg) could not only significantly reduce the powder oxygen content but also change its nature. Regardless of the material studied and the process parameters employed, the LPBF-fabricated parts had oxygen contents lower than their starting powders, meaning that either oxidation does not happen during the process or the rate of oxide diminishment (evaporation) overweighs any possible in-situ oxidation. The parts obtained at relatively high laser powers contained lower oxygen content compared to their counterparts processed by lower laser powers. However, the release of oxygen in pure Al and AlSi10Mg showed the highest and lowest sensitivity to the change in the laser power, respectively. While the pure Al powder had the highest oxygen content among all powders, the oxygen level in the pure Al parts fabricated by the optimum process parameters was lower than that of the AlSi12 and AlSi10Mg alloys. This is attributable to the (i) more intense Marangoni thermocapillary fluid flow of pure Al, and (ii) absence of MgO with extremely high melting/evaporation temperature. Therefore, when it comes to the LPBF processing of Al/Al alloys, the nature of the oxides in the starting powder must also be considered to justify the processability. Although pure Al showed a narrower processing window compared to the Al alloys, still sound oxide-free parts could be obtained by careful selection of the process parameters.

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Data availability statement

The data will be made available upon request.

Authorship contribution statement

Ali Ghasemi, and Eskandar Fereiduni: Investigation, Conceptualization, Methodology, Writing - original draft; Mohamed Balbaa: Methodology, Conceptualization and Writing - original draft; Suraj Dinkar Jadhav: Investigation and Writing - original draft; Mohamed Elbestawi, and Saeid Habibi: Supervision, Writing - review & editing.

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