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# Feasibility of using ground Al-Al<sub>2</sub>O<sub>3</sub> composite powders in laser powder bed fusion

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## Abstract

The reincorporation of residues in the productive cycle helps reduce CO<sub>2</sub> emissions and non-renewable resources extraction. Therefore, the present work studies the feasibility of reincorporating an aluminum residue in the productive cycle by means of an additive manufacturing technique. In this context, other issues considered are the importance of aluminum alloys, the improvement of their properties by adding alumina making composites materials, and issues that must be overcome when printing parts by laser powder bed fusion using a mix of Al and alumina powders. This work evaluates the suitability of Al alloy - alumina composite powders obtained by grinding Al alloy chips from sawing. Laser power and scanning speed were varied until the designed samples were obtained. The findings show that it is possible to use powder obtained by grinding Al chips in the laser powder bed fusion technique to obtain Al-Al<sub>2</sub>O<sub>3</sub> composites which exhibit hardness of 226 HV ± 34.3.

## 1. Introduction

Laser powder bed fusion (LPBF) is an additive manufacturing technique that consists of fabricating parts layer by layer after designing the parts by computer-aided design (CAD) and placing a powder bed inside an inert gas chamber. A roller places a layer of powder on the bed and the laser selectively melts a layer of material, according to the indications of the CAD model. The bed goes down, the feeder roller places another layer of powder on top, the laser selectively sinters by fusion and solidification, and the process is repeated until the whole piece grows [1]. Coalescence between particles is achieved after the molten state, since the laser partially melts the area where it impacts. Because of the nature of the technique, cast alloys such as AlSi10Mg and AlSi12 have been considered good candidates for LPBF- manufacturing, considering that eutectic composition provides good weldability and fluidity and reduces the melting temperature [2,3]. The small size of the melting pool, the extremely short life of the liquid state and the resultant fast heating and cooling rates produce a characteristic superfine microstructure which increases the hardness [4] according to Hall-Petch theory. Additionally, magnesium content plays an important role in hardening by second phase precipitation [5]. Taking this into account, a large body of investigation about the manufacturing of AlSi10Mg alloys by LPBF has been reported.

Despite the better results found with cast alloys in LPBF, further study of LPBF of aluminum matrix composites is required, taking into account the need for materials which combine properties that cannot be met by conventional materials such as cast alloys. In some industry sectors, such as automotive, marine and aerospace, there is interest in the production of aluminum matrix composites because of the potential to obtain through these superior properties such as high stiffness/weight ratio. However, the future of the processing of this kind of composites by LPBF strongly depends on the ease of fabrication and the final properties of products, which can be varied through controlling the

process parameters [6].  $\text{Al}_2\text{O}_3$  particles in particular improve thermal stability, maintain phase composition [7], and increase Young's modulus and wear and corrosion resistances [8]. These composite materials can be manufactured by die pressing [9], casting [10] stir casting [11] or, recently, by additive manufacturing [12]. The main problems associated with die pressing and casting are porosity and low wettability, respectively, and the emergence of particle clusters in both cases.

The preparation of the raw material for manufacturing Al- $\text{Al}_2\text{O}_3$  composites by LPBF require the mixture of  $\text{Al}_2\text{O}_3$  particles with Al powder by milling [12,13]. After melting and cooling the  $\text{Al}_2\text{O}_3$  particles makes barriers for the dislocation movement, which means the distribution of the alumina particles must be uniform. Q. Han, et al [14] mixed 96 vol% Al and 4 vol%  $\text{Al}_2\text{O}_3$  powder and evaluated the printability of the mixture varying the scanning speed. They found that the lower the scanning speed, the higher the maximum temperature variation, 200 and 100 mm/s (laser energy density of 333 and 666  $\text{J}/\text{mm}^3$ , respectively) being the speeds that allowed the melting temperature of the  $\text{Al}_2\text{O}_3$  to be overcome. However, the optimum laser-scanning speed was 300 mm/s (laser energy density of 317.5  $\text{J}/\text{mm}^3$ ), leading to the achievement of uniformly distributed  $\text{Al}_2\text{O}_3$  reinforcement particulates and a 17.5% increase in microhardness (with respect to pure Al). Y. Chen et al [15] approached the obtaining of the composites differently. They mixed Al powder with ZnO powder and used the remelting technique during LPBF, obtaining the oxidation of aluminum by ZnO, resulting in alumina appearing and ZnO disappearing.

Although these aluminum-alumina compounds have been obtained successfully, there are drawbacks still to be overcome, such as microstructural defects caused by lack of melting of the alumina particles. After mixing Al powder with  $\text{Al}_2\text{O}_3$  powder J. Jue et al [12] evaluated the suitability of the mixture for metal additive manufacturing by PLBF using power of 130 W and varying scan speed from 450 to 750 mm/s (linear laser energy density between 289  $\text{J}/\text{m}$  to 173  $\text{J}/\text{m}$ ). Because of the high melting temperature of  $\text{Al}_2\text{O}_3$ , these particles either did not melt or melted partially, reducing the flowability and diminishing the wettability of the underlying previously processed layer, leading to microstructural defects.

Another issue that can be presented is that when printing  $\text{Al}_2\text{O}_3$ -Al some of the  $\text{Al}_2\text{O}_3$  can be lost. In this regard, H. Liao, et al [16] investigated the loss of  $\text{Al}_2\text{O}_3$  in this kind of composites, finding that the loss mechanism of alumina is that the aluminum acts as a reducing agent, causing the  $\text{Al}_2\text{O}_3$  to become a gaseous  $\text{Al}_2\text{O}$  substance during the LPBF process (the higher the laser energy, the higher the loss rate of  $\text{Al}_2\text{O}_3$ ). In another investigation [17] they found that the  $\text{Al}_2\text{O}_3$  that remains is distributed on both sides of the molten pool under the combined action of the Marangoni flow and the evaporation recoil pressure. The laser power, the scanning speed, the hatching space and the layer thickness determine the  $\text{Al}_2\text{O}_3$  loss rate. The higher the scanning speed, the lower  $\text{Al}_2\text{O}_3$  loss, for instance.

Another approach that has been reported is the use of Al- $\text{Al}_2\text{O}_3$  composite powders obtained by hydrothermal oxidation method. A. Y. Nalivaiko et al [18] evaluated LPBF of Al- $\text{Al}_2\text{O}_3$  core-shell composite with 10 wt.% of alumina. They varied the power and the scanning speed between 180 – 220 W and 180 – 220 mm/s, respectively. The results showed that at a low power density (4.5-7  $\text{J}/\text{mm}^2$ ) the alumina did not melt, leading to poor wetting, while a high power density ( $> 8 \text{ J}/\text{mm}^2$ ) led to deoxidation and boiling of the molten bath, both of which in turn caused low density and microcracking of the printed parts.

Although LPBF uses powder obtained by atomization (water, gas or plasma), there is an approach that has not been reported in literature to the best of the author's knowledge, that could minimize the problems presented when the compounds are obtained by mixing aluminum and alumina powders.

This approach involves the use of Al<sub>2</sub>O<sub>3</sub>-Al composite powders obtained by grinding in air atmosphere. Although the rate at which powders are obtained by grinding chips is lower than in the case of those obtained by atomization, in the first-mentioned process, alumina is well distributed along the aluminum matrix. In this regard, L. M. Rojas-Díaz et al [19] subjected Al chips from a sawing process to grinding in a hermetic mill in air atmosphere, varying the grinding time. They found that the morphology of the obtained powder depends on the grinding time: short times (up to 30 hours) lead to a flake-like morphology, while longer times lead to a more rounded morphology. All the powders were composed of Al<sub>2</sub>O<sub>3</sub> in addition to Al and the compacted-sintered samples obtained with the powders showed Al<sub>2</sub>O<sub>3</sub> and Al on their composition with hardness of 90.6 Rockwell F. Given the above, the objective of this paper is to investigate the suitability of Al<sub>2</sub>O<sub>3</sub>-Al composite powders obtained by grinding chips in air atmosphere in LPBF for printing Al<sub>2</sub>O<sub>3</sub>-Al composite pieces, varying power and speed of printing.

## 2. Materials and Methods

The aluminum alloy from which the chips were taken was characterized by spark Optical Emission Spectrometry – OES. Aluminum alloy chips were obtained as the byproduct of a sawing process and were washed with detergent, rinsed with water at room temperature, and dried at 95 °C for 24 hours to remove coolant used during machining. Some of these chips were compacted in a 12.7 mm diameter matrix using a force of 19,000 lb to obtain a flat sample for the measurement of the chemical composition by spark-OES. After that the chips were subjected to a grinding process to obtain powders using a ball mill with an alumina jar of 5 L and zirconia cylindrical grinding bodies. The ratio of grinding bodies to chips was 10:1 (1000 mL of grinding bodies and 100 mL of chips) and the grinding time was 56 hours at 55 rpm, as used in a previous investigation [19]. The powder was characterized by X-ray diffraction (XRD) using a Brucker D8 Discover X ray diffractometer with a cobalt target. Match! Software was used to index the pattern and FullProf\_Suite software was used to refine, using the Rietveld method. Another sample was encapsulated in bakelite, polished with #2,000 sandpaper and cloth with 3 µm Al<sub>2</sub>O<sub>3</sub> particles in water solution, for evaluation by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) using a JEOL JSM-6490 OLV scanning electron microscope device. EDS measurements were made at 5,000 X inside the particles by mapping. The particle size and particle size distribution were measured in a Hydro 2,000MU (A), with water as dispersant. Additionally, a sample of powder was compacted in a 12.7 mm diameter matrix using a force of 19,000 lb to obtain a flat sample, also for the measurement of the chemical composition by spark-OES.

The 3D printer Renishaw AM250 LPBF that works with a modulated ytterbium fiber laser with a wavelength of 1,071 nm was used to fabricate 5 mm \* 5 mm \* 5 mm cubes. The nominal diameter of the laser spot was 70 µm. The speed of the laser (scanning speed) was varied, keeping constant the layer thickness (25 µm) and the hatch spacing (80 µm) using the formula in equation 1, where  $l_p$  is the point distance,  $v_l$  is the speed of the laser between two points (which was fixed at 5,000 mm/s) and  $t_e$  is the exposure time. The volumetric energy density ( $E_v$ ) was calculated as shown in equation 2, where  $P$  is the laser power,  $v_s$  is the scanning speed,  $l_z$  is the layer thickness and  $l_{hs}$  is hatch spacing.

$$v_s = \frac{l_p \times v_l}{l_p + v_l \times t_e} \dots (1)$$

$$E_v = \frac{P}{v_s l_z l_{hs}} \dots (2)$$

The pattern used for the building was meander. As the machine is usually used for printing aluminum alloy powder from Renishaw (REN-ALSi10Mg), the parameters first tested were chosen taking into account the optimal parameter for this powder (power = 200 W, speed = 500 mm/s). After that, the parameters were varied as follows: power from 10 to 200 W and speed from 25 to 700 mm/s. REN-ALSi10Mg (ALSi10Mg-0403, whose specified process parameter are layer thickness of 25  $\mu\text{m}$  and laser power of 200 W [20]) were printed at 200 W and 500 mm/s for purposes of comparison.

After printing the samples were sandblasted to eliminate remnant powder. Then the surfaces of the samples (top x-y surface) were polished using sandpaper number 600 prior to optical microscopy evaluation. To measure the chemical composition of one of the printed samples by spark-OES creating a seal between the specimen and the spark stand, the sample was embedded in Al alloy powder by compacting (12.7 mm diameter matrix using a force of 19,000 lb to obtain a flat sample). Next, the microhardness was measured using an Innovatest device with a load of 100 g for 100 second each indentation. After that, samples were mounted in bakelite ( $T = 160\text{ }^{\circ}\text{C}$ ,  $P = 2,050\text{ bar}$ ,  $t = 3\text{ minutes}$ ) leaving the y-z surface visible. All the samples were polished with sandpaper from #320 to #2,000 and with cloth using 3  $\mu\text{m}$   $\text{Al}_2\text{O}_3$  particles in solution and etched with Keller's reagent (40 seconds) for evaluation by SEM/EDS. Phases were evaluated using X-ray diffraction with an XRD (Bruker D8 Discover) device with a Cu target. Dislocation density of aluminum phase ( $\rho$  in equation 3) was assessed using Williamson-Hall parameters [21] ( $\eta$  = microstrain and  $d$  = crystallite size from equation 4, where FWHM is the full width at half maximum peak in XRD pattern located at  $2\theta$  angle). Lattice parameter was assessed by Nelson-Riley method [22] for calculating the Burgers vector ( $B$ ).

$$\rho = \frac{2\sqrt{3}\langle\eta^2\rangle^{1/2}}{d \times B} \dots (3)$$

$$FWHM \times \cos \theta = \frac{0.9\lambda}{d} + 2\eta \sin \theta \dots (4)$$

### 3. Results and Discussion

#### 3.1. Bulk alloy and chips

The chemical composition obtained by spark-OES of the bulk from which the chips were taken was (atomic percentages): 97.995% Al, 0.9015% Mg, 0.4989% Si, 0.2520% Cu, 0.1640% Fe, 0.0341% Mn, 0.0210% Zn, 0.0032% Ni and 0.130% other elements (including < 0.005% Zr). Figure 1 shows this chemical composition by weight percentage. This indicates that the aluminum alloy from which the chips come corresponds to a 6xxx Al alloy. The same figure shows the chemical composition of the chips, which does not differ to that of the bulk.

#### 3.2. Powders

Figure 1 shows the chemical composition obtained by spark-OES of the powders obtained by grinding the chips. As can be seen, Al content has decreased by 4.21 % (weight percentage). The increase in the other elements is relative to the Al loss, and does not mean the alloy is gaining these elements. The following explanation for this is proposed, bearing in mind that this phenomenon is not the subject of this work, and that additional studies must be done to corroborate the explanation. It has been reported that metals can evaporate from solid state. For this to happen, the condensation rate, which is the rate of the reverse reaction, must be lower than the rate of vaporization, which occurs mostly at low pressure or in vacuum [23]. Three important factors apply during grinding in the current experiment: **1)** The jar is airtight but not in vacuum, instead containing air when grinding starts, **2)**

Al reacts with O<sub>2</sub> in the jar atmosphere (forming alumina), so no oxygen remains in the air in the jar, only nitrogen and the other elements that make up the air. This consumption of oxygen causes the pressure inside the jar to decrease, and 3) the temperature inside the jar increases [24]. These two factors, namely the lower pressure and the higher temperature, promote the evaporation of some elements of the powder. Moreover, when the grinding time increases, the specific surface is larger, which further promotes the evaporation of species. As can be seen in Figure 1, at the start the chips contain Al, Mg, Si, Fe, Cu and other elements in lower quantity. According to Katsutoshi Ono and Ryosuke O. Suzuki [25] a selective evaporation occurs from a solid multi-component system. Of the chemical elements mentioned above Mg and Al have the lowest evaporation enthalpy (considering that these values of  $\Delta H_v$  correspond to pure metals). These two elements could evaporate in the grinding conditions. Figure 1 shows only the loss of Al, although magnesium could also have evaporated, the greater loss of Al obscuring this result. The evaporated Al is subsequently condensed in the walls of the jar. Additionally, it was found that in the powders Zr increases to > 0.25 % wt. (compared with 0.005% in the bulk material), which could be related to the decrease in Al or to contamination by the grinding bodies.

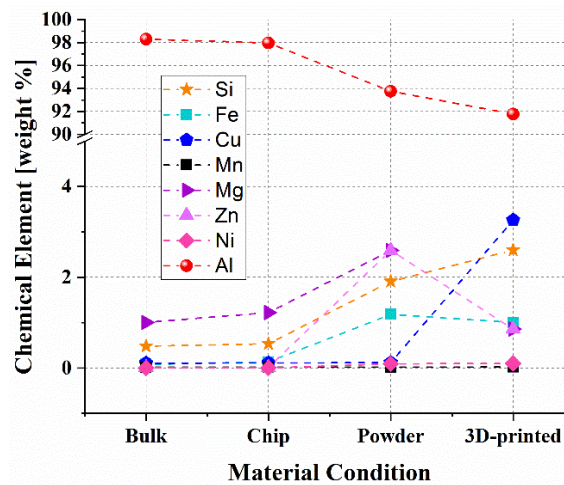


Figure 1. Chemical composition of the materials under study assessed by spark-OES

Figure 2 depicts the SEM images of the powders encapsulated in bakelite, polished and subjected to EDS mapping. The morphology shown by the ground powders is rounded, while the morphology of the REN- $\text{AlSi10Mg}$  powders is spherical. Silicon is well distributed in the REN- $\text{AlSi10Mg}$  powders, and O, Cu, Si and Mg are well-distributed in the powders obtained by grinding. Figure 3-a) shows their granulometric distribution. The maximum particle size of the ground powders was 109.61  $\mu\text{m}$  and  $d(0.5)$  was 42.98  $\mu\text{m}$ . The average particle size of the REN- $\text{AlSi10Mg}$  powders was 45.58  $\mu\text{m}$  and  $d(0.5)$  was 43.77  $\mu\text{m}$ . Figure 3-b) shows the XRD pattern of the powders. As well as the peaks corresponding to aluminum phase in ground powders, peaks corresponding to alumina also appear, which indicates that oxygen shown in EDS forms alumina in the powder after grinding. According to Rietveld Refinement, the content of crystalline alumina is 10.6% by weight. No particles of alumina are visible in the SEM images, although well-distributed oxygen is observed in the EDS mapping, suggesting the presence of small and well-distributed particles of the second phase after grinding. The formation of aluminum oxide during washing and drying is ruled out, bearing in mind that it can be formed at low temperature in the presence of water only when the protective layer is destroyed [26]. In the 1980s, some studies on dispersion strengthened aluminum made by mechanical alloying were performed, by grinding aluminum in high-speed mills. Singer et al [27] explained that the oxide

film is destroyed because of the plastic deformation caused by the grinding bodies. Processes of micro-welding and comminution of the particles lead to the oxide fragments being intruded into the aluminum matrix, resulting in a finer distribution of particles. Benjamin and Bomford [28] found that the alumina dispersoids formed during ball milling were more distributed than those obtained in conventional Al-Al<sub>2</sub>O<sub>3</sub> production. No peaks corresponding to Si, Cu and Mg appear, which could mean that they are in solid solution in Al. On the other hand, XRD pattern of the REN-AlSi10Mg powders exhibits peaks corresponding to Al and Si, which means that some Si is segregated and some of it is in solid solution with aluminum.

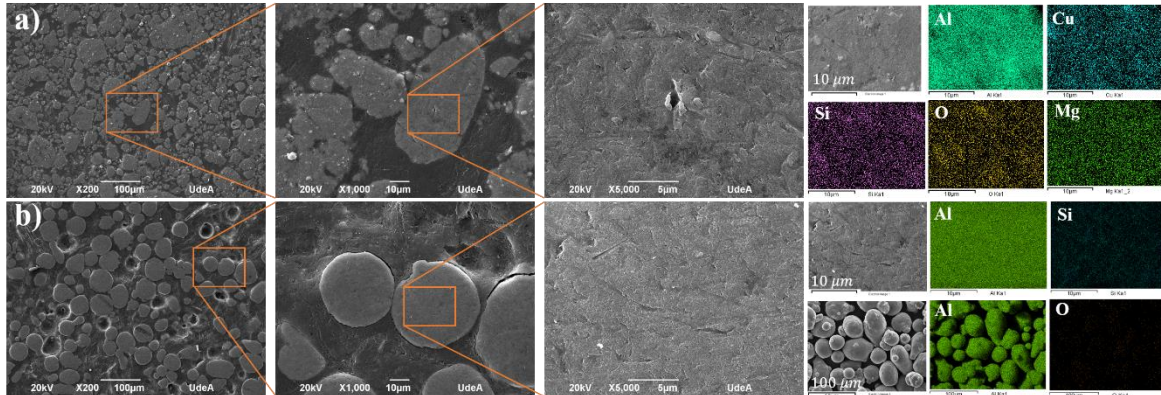


Figure 2. SEM images at 200X, 1000X, 5000X and EDS mapping showing Al, O, Si, Cu and Mg of powders under study, a) Al alloy from grinding chips, b) Renishaw AlSi10Mg-0403

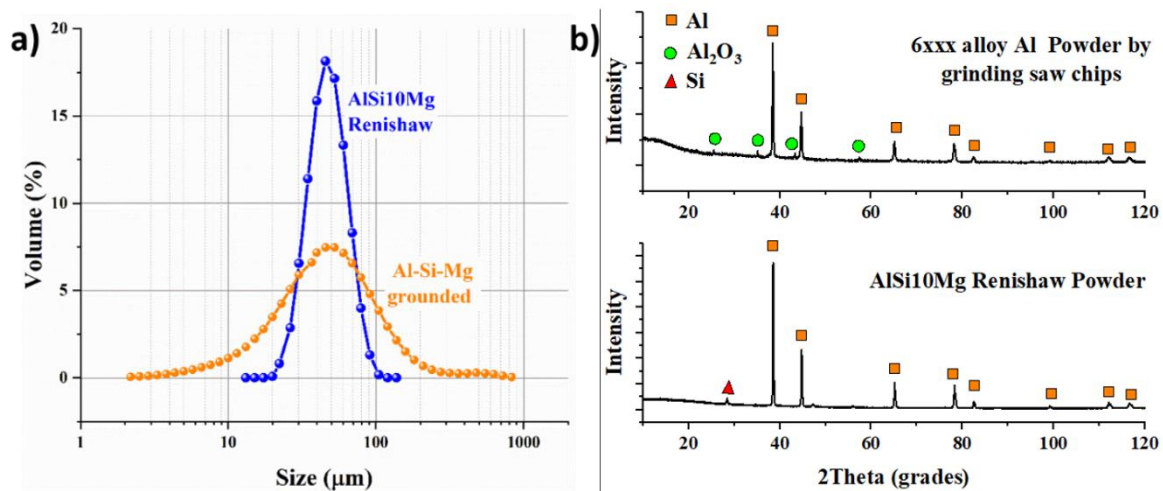


Figure 3. a) Particle size distribution and b) XRD patterns of the powders

### 3.3. Printed samples

#### 3.3.1. AlSi10Mg alloy using Renishaw powder

Figure 4-a) depicts the XRD pattern of the printed part using REN-AlSi10Mg powders at 200 W and 500 mm/s, as well as the x-y top surface after polishing with #600 sandpaper. As can be seen, only Al peaks appear in the XRD pattern, indicating that Si is in solid solution. Parts b) and c) of the same figure show the SEM images, where the characteristic microstructure consisting of Al cell and the Al-Si eutectic microconstituent can be seen. The surface does not show macroporosities or

irregularities, as can be seen in the insert photograph in the XRD pattern. Parts d) and e) of the same figure depicts the Williamson-Hall and Nelson-Riley plots used for determining the dislocation density, which was of  $5.24 \times 10^{13} \text{ m/m}^3$ . The hardness of the sample was  $115.4 \pm 8.9 \text{ HV}$ .

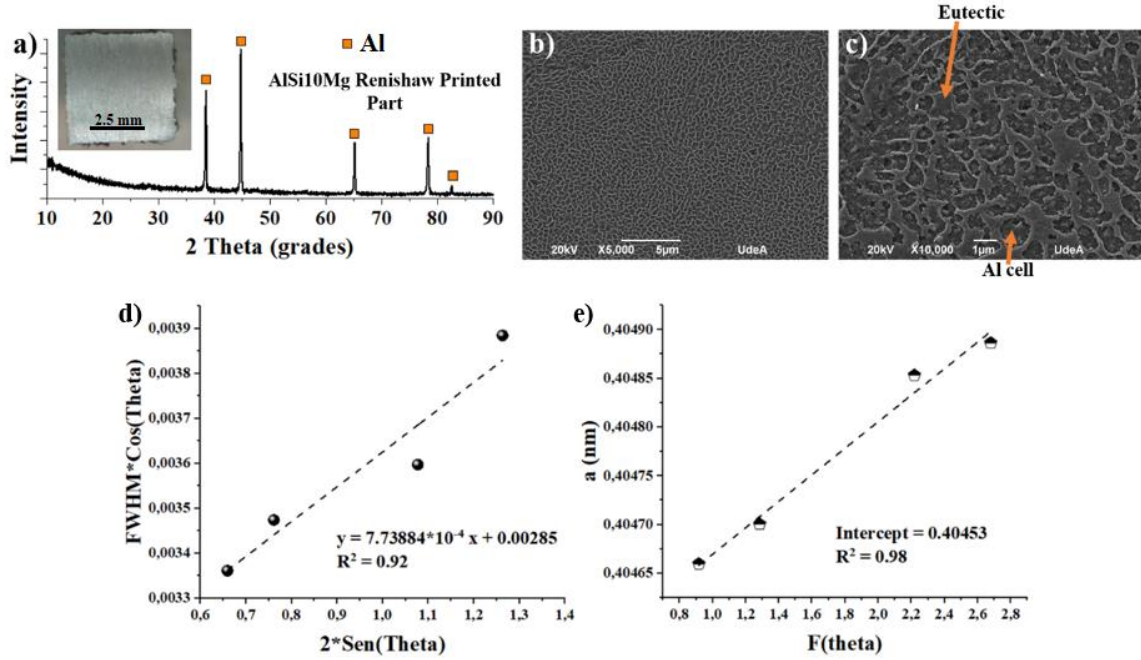


Figure 4. a) XRD pattern (x-y surface polished with #600 sandpaper), b) SEM image of top surface (x-y) at 5,000 X, c) SEM image of top surface (x-y) at 10,000X, d) Williamson Hall and, e) Nelson-Riley plots of printed part, using Renishaw powder at 200 W and 500 mm/s

### 3.3.2. Al-Al<sub>2</sub>O<sub>3</sub> composites using powder from grinding saw chips

#### Chemical composition and microstructure of the phases

The pieces printed using Al-Al<sub>2</sub>O<sub>3</sub> composite powders obtained from grinding the chips can be seen in Figure 5. At the power and scanning speed used for REN-ALSi10Mg powders (200 W and 500 mm/s), a lot of spatter appears, which made the printing impossible. The same occurred at the power and printing speeds bounded in the red space. The Coanda effect [29] is ruled out, since the parts with Renishaw powder were printed successfully. During the laser-powder interaction process, when the energy of the laser is high, there may be instabilities in the melt pool, such as spatter and rapid evaporation of the material [30]. Spatter occurs when the boiling material is expelled by the metal vapor at high pressure. Spatter phenomena has been reported for AlSi10Mg powders when using 300 W and 1150 mm/s of power and scanning speed respectively [31], values which are clearly higher than 200 W and 500 mm/s. However, with the Al-Al<sub>2</sub>O<sub>3</sub> composite powder, values such as 100 W and 200 mm/s led to spatter formation. As can be seen in Figure 2 the morphology of the particles is rounded instead spherical, with a high quantity of Al<sub>2</sub>O<sub>3</sub> (10% wt. according to Rietveld refinement). T. Fedina et al [32] studied the effect of the morphology of the powder particles in LPBF and found that more convoluted powders (compared with near-spherical powders) had more frequent spatter ejection, and they attributed the spattering to, most likely, the high amount of oxygen in the powders, which contributes to instabilities in the melt pool. In our case, the powder obtained by grinding the chips presents both non-spherical shape and a high quantity of oxygen. This effect of sputtering made it impossible to print the samples at high power values. Additionally, the reflectance behavior changes

when Al also contains  $\text{Al}_2\text{O}_3$ . In this regard, D. Garoli [33] reported a reflectance close to 0.9 for Al, and close to 0.1 for  $\text{Al}_2\text{O}_3$ , which also can affect the interaction of the powders with the laser and produce spatter, because the presence of  $\text{Al}_2\text{O}_3$  increases the energy absorbed by the powders.

Lower power (70, 90 and 100 W) and higher scanning speed (700 mm/s) permitted the formation of the walls of the samples (blue zone in Figure 5), while lower speed (200 mm/s) and higher power (100 and 160 W) enabled the floor of the samples to be printed (yellow zone). Moving towards lower power and lower speed led to the formation of the samples (green zone). This means that the morphology and chemical composition of the starting powder led to successful printing of the samples using lower power and lower scanning speed (compared with those used in printing REN-AlSi10Mg). The lower power needed to print the parts could also be related to the reflectance of the powders. As mentioned before, the presence of  $\text{Al}_2\text{O}_3$  diminishes the reflectance of the powders [33], which means that less energy is needed to melt them.

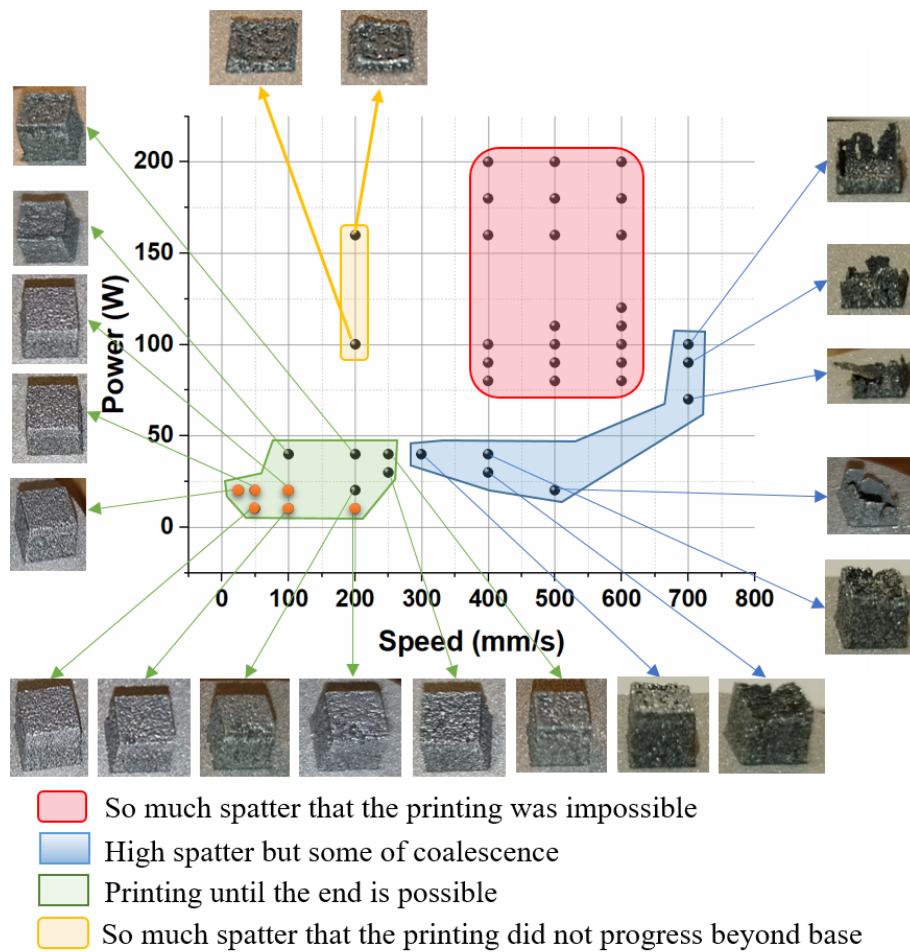


Figure 5. Power and speed of printing map

It was not possible to measure the hardness of some samples because of their high porosity. Figure 6-a shows the polished top surface of the samples whose hardness could be measured (orange points in green area of Figure 5) according to power and scanning speed. In each image, the volumetric energy density ( $E_v$ ) appears. Figure 6-b) shows the SEM images of the top of the y-z surface. As greater volumetric energy implies higher temperature in the melted pool, part c) of Figure 6 shows the temperature trending of the samples. Figure 7-a) shows the SEM images of the matrix (at 10,000 X)

and Figure 7-b) shows the discontinuous phase surrounded by matrix (at 2,000 X). Figure 8 depicts the EDS mapping of three chosen samples (those printed at 50, 100 and 400 J/mm<sup>3</sup>). Meanwhile, Figure 9 shows the XRD patterns of the samples.

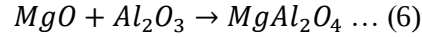
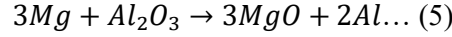
As can be seen in Figure 6-a), there is high macroporosity in all cases. In the top of the *y-z* surfaces shown in part b) of the same figure micropores can be seen, a continuous phase and a discontinuous phase. During the laser-powder interaction process, when the energy of the laser is high, as well as spatter and rapid evaporation, balling and pore formation can occur [30]; hence, porosity is formed at this values of power and scanning speed. Porosity in Al - Al<sub>2</sub>O<sub>3</sub> alloy composites has been also reported by H. Liao et al [16].

The analysis of the chemical composition of the 3D printed part (at 40W and 200 mm/s) in Figure 1 shows that Al, Mg and Fe decrease by in 1.981%, 1.733% and 0.176% wt. respectively. In this regard, Jinge Liu and Peng Wen [34] evaluated metal vaporization and its influence during the laser powder bed fusion process. Using the Langmuir equation, they found that, above 2072 °C (which is the melting temperature of Al<sub>2</sub>O<sub>3</sub> and, therefore, the minimum temperature that was reached in the present study), the evaporation flux tendency is Zn > Mg > Al > Fe. As a result, Al, Mg and Fe decrease during laser/powder interaction as shown in Figure 1. Taking into account the increase in Cu in Figure 1, which means that it is not evaporating during the laser/powder interaction, Jie Yin, et al [35] reported that it does not evaporate until 3000 °C during LPBF, which explains its stability in Figure 1.

Another appreciable difference between the powder and the printed samples is the size of the Al<sub>2</sub>O<sub>3</sub> phase. Particles of alumina are not clearly visible in the starting powder. Taking into account the good distribution of the oxygen, a fine size of the particles could be expected. On the contrary, discontinuous phase in the printed samples is clearly visible in the SEM images. Regarding the continuous phase (Figure 7-a), this is porous mostly in samples obtained by 10 W- 200 mm/s and 20 W – 25 mm/s, and is composed in all cases by Al, Cu, Si, Mg and Fe, according to EDS maps of Figure 8, which shows three of the printed parts as representative results. XRD patterns corroborate the presence of Al (96-901-2429) in all cases (Figure 9) but there are no peaks corresponding to Cu, Mg and Fe, which could mean they are in solid solution in Al. The quantity of Cu is higher than the maximum solubility in Al, which is consistent with C. Shuai, et al [36] who reported that the LPBF technique prevents the precipitation of the supersaturate solute. Additionally, there is a peak corresponding to Si (96-901-1647), which indicates that the silicon particles shown in Figure 8 are crystalline. However, there is also some Si in solid solution in Al, as can be seen in the matrix in samples in Figure 8. Regarding this issue, Y. Ji, et al [37] reported segregation of Si when printing AlSi10Mg powders by LPBF and attributed this to the thermal gradient that formed during laser melting: at low temperatures, the Si clusters were relatively wide, and when the temperature was high, the silicon clusters were narrow.

The discontinuous phase, on the other hand, shows a vermicular morphology (Figure 7-b) suggesting melting and re-solidification of alumina during printing [16]. When melted together, Al and Al<sub>2</sub>O<sub>3</sub> are immiscible, which explains how the well-dispersed alumina observed in the starting powders (Figure 2 and Figure 3-b) forms this vermicular phase in the printed parts: once the two phases are melted, alumina agglomerates. Figure 8 shows that this discontinuous phase is composed of Al, O, Mg, Si, Cu and Fe when the samples are printed at low *E<sub>v</sub>* (Figure 8-a). However, when *E<sub>v</sub>* increases (parts b and c of the same Figure) the discontinuous phase is primarily composed of Al, O and Mg. XRD patterns show the presence of crystalline Al<sub>2</sub>O<sub>3</sub> (96-810-3789) and spinel MgAl<sub>2</sub>O<sub>4</sub> (96-901-0261) which indicate that Al, O and Mg are together in the discontinuous phase, forming a solid

solution between alumina and spinel [38]. An explanation for the formation of this phase may be as follows: once melted, the alumina is in contact with Mg (Figure 2 shows that Mg is well distributed in the starting powders), and when the pool temperature is below the right temperature (1300 °C, according to Ellingham diagram when metals are pure [39]), the Mg reduces the  $Al_2O_3$ , forming MgO (equation 5) and this reacts with alumina, forming spinel (equation 6), which remains in solid solution with the alumina. I. Pasquet, et al [40] fabricated Cu and spinel ferrite by LPBF, mixing oxide and metallic powders, and found the formation of nano spinel ferrite inside copper. Taking this into account and considering that Mg is also present in the continuous phase, as shown in Figure 8, the presence of nano spinel inside the Al phase cannot be ruled out.



On the other hand, the columnar structures that appear in the dashed white box in Figure 6-b) indicate a cellular dendritic structure of the alumina/spinel phase during its growth, which commonly appears in parts printed by laser powder bed fusion [41].

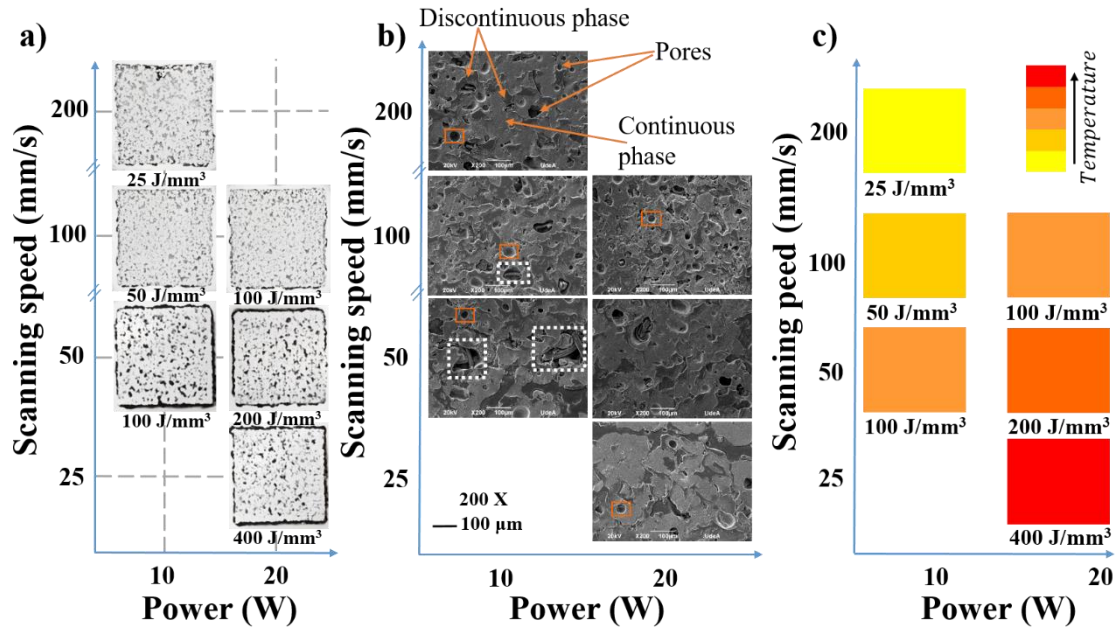


Figure 6. a) printed parts x-y top surface according to power and speed of printing (each sample shows the volumetric energy density), b) SEM images at 200 X of the y-z surfaces (orange solid boxes enclose nearly spherical macropores; dashed white box enclose columnar structures) and, c) schematic temperature in the melted pool during printing

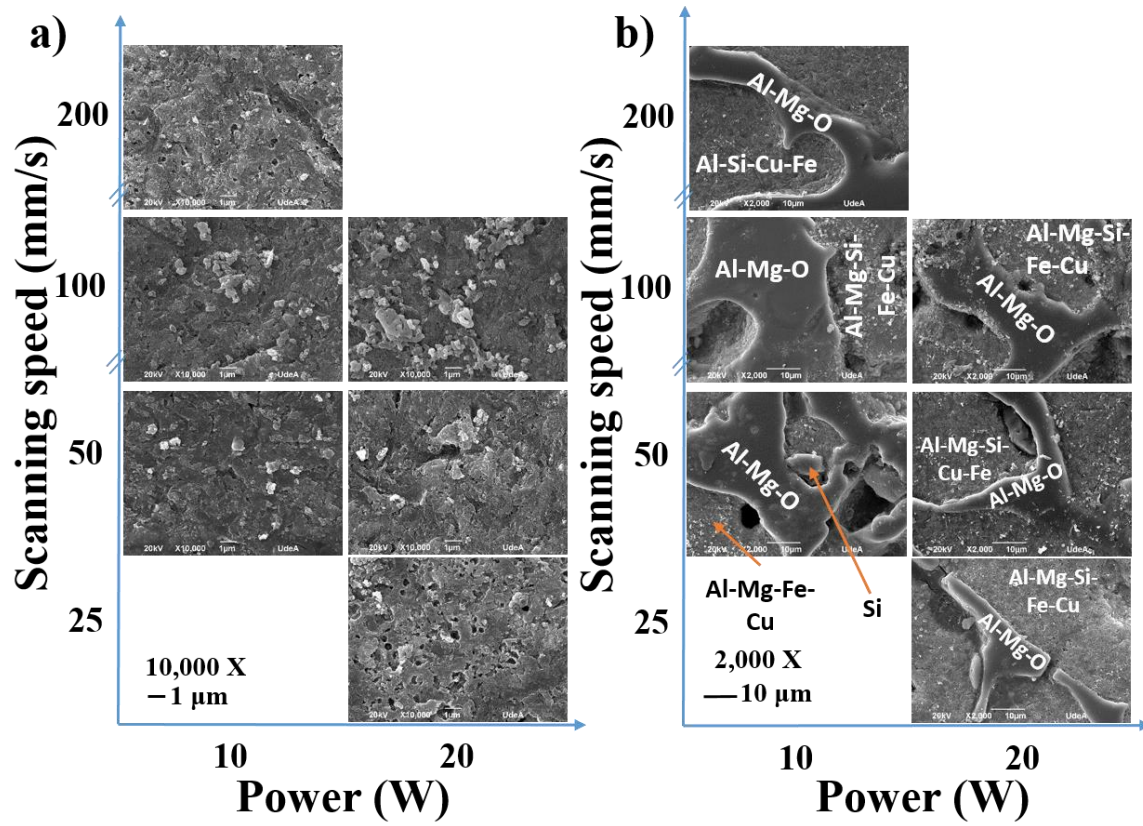


Figure 7. SEM images of a) continuous phase at 10,000X, and b) top sample in z-y growing direction at 2,000X

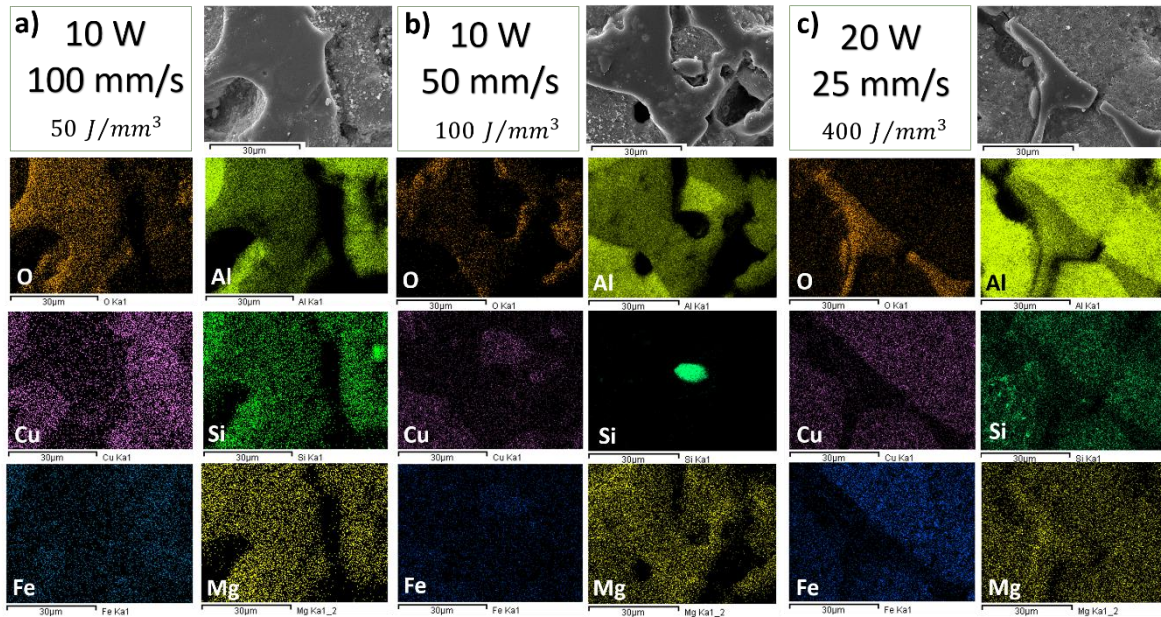


Figure 8. EDS mapping of 10W-100 mm/s, 10W-50 mm/s and 20W-25 mm/s printed samples

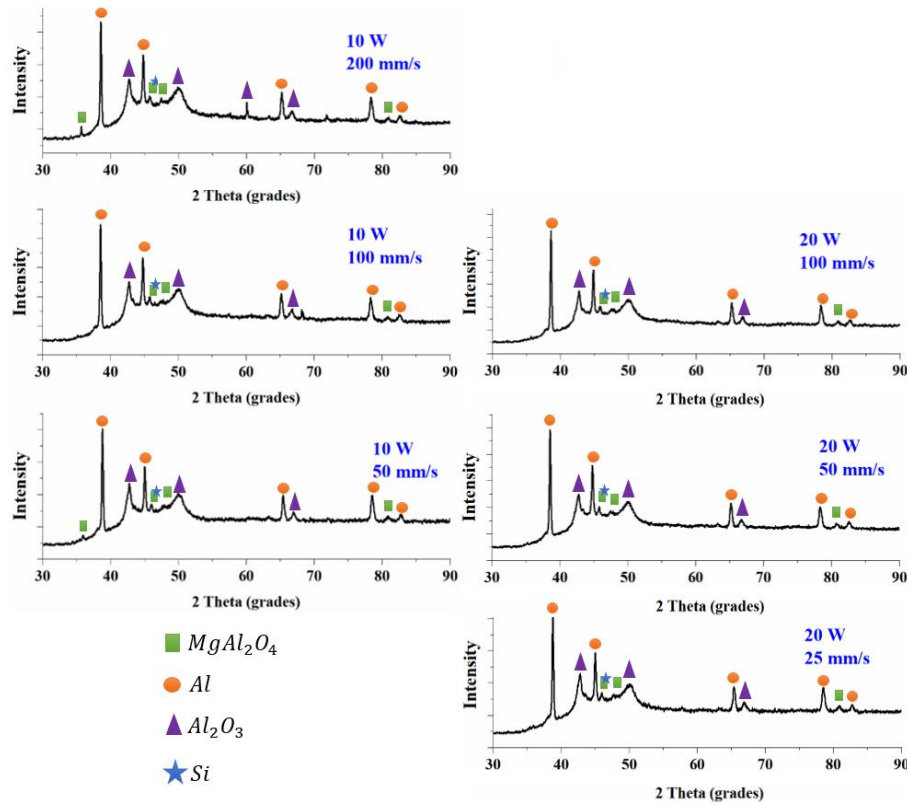


Figure 9. XRD patterns of the printed parts with 6xxx Al alloy from grinding saw chips (power increases from left to right, and scanning speed increases from bottom to top)

When comparing the discontinuous phase of the printed parts in Figure 6-b), it can be seen that the sample obtained with higher  $E_v$  depicts bigger particles of discontinuous phase. This could be related to the maximum temperature of the melted pool during printing (Figure 6-c). The higher the temperature, the higher the movement of the  $Al_2O_3$ , forming larger discontinuous particles. On the other hand, the sample with the highest  $E_v$  in the figure was printed at the lowest speed, which means more time at higher temperature, allowing the  $Al_2O_3$  (and the spinel) to agglomerate, forming larger discontinuous particles. On the contrary, the sample printed with lower  $E_v$  displays shorter particles of discontinuous phase, because the lower temperature in the melted pool led to lower movement capacity of the alumina.

As well as second phases, macro and micropores are other features to be analyzed. The nearly spherical macropores (diameter around  $30\ \mu m$  - orange boxes) observed in SEM images in Figure 6-b) can be explained using the work published by Shuyue Li et al [42], who explained the formation of near spherical pores in CuCrZr alloy obtained by LPBF. As a result of laser energy entering the powder bed, a keyhole pore is formed in the underneath layer. Then, the keyhole temperature is higher than the evaporation temperature, generating enormous recoil pressure and forming a protruding region. The temperature of the protruding region then diminishes and the surface tension increases. This causes the rear wall of the keyhole to collapse, forming a closed pore that moves along the boundary of the molten pool and continually contracts until it becomes almost spherical. In their research, the thicker the layer, the higher the number of porosities. In our case, however, the layer thickness was constant, but it can be observed that the higher the maximum temperature (sample printed at 20 W - 25 mm/s) of the melted pool (Figure 6-c), the lower the number of these macroporosities.

Regarding micropores (around 0.5  $\mu\text{m}$ ), also known as metallurgical pores, in the case of AlSi10Mg alloy it has been found that these tend to be formed at low scan speed values by trapped gases [43]. Something similar occurs in this case, as can be seen in Figure 7-a), with the sample printed at 20 W – 25 mm/s exhibiting the highest quantity of micro-porosities (pores of diameter less than 1  $\mu\text{m}$ ).

Figure 10 summarizes the entire process. When the laser impacts the powder bed, lower melting temperature phase liquefies (a). In the powder, alumina was small and well-dispersed in the Al alloy matrix (Figure 2 and Figure 3-b); however, because of the high temperature of the Al liquid, convection movements can appear and promote the movement of solid  $\text{Al}_2\text{O}_3$ . At this point, Mg presented can chemically reduce  $\text{Al}_2\text{O}_3$ , producing MgO and Al. The Al formed enriches the Al matrix and the MgO reacts with some of the  $\text{Al}_2\text{O}_3$ , forming spinel ( $\text{MgAl}_2\text{O}_4$ ). When the temperature increases, the alumina and the newly formed spinel also liquefy (b). As both liquids are immiscible, alumina/spinel tends to come together and form the vermicular morphology (c). At this temperature keyholes are also formed (c), closing in near spherical pores underneath the layer (d). Moreover, at this temperature, Al, Mg and Fe are evaporated. Here, the evaporation of metallic Al (which is a liquid near to its boiling temperature, which is 2327  $^\circ\text{C}$ ) is more likely than Al in  $\text{Al}_2\text{O}_3$  or spinel (whose bond energy is higher than that of aluminum), because  $\Delta H_v$  is lower in metallic Al. After that, when the laser continues its path, the temperature decreases, and  $\text{Al}_2\text{O}_3/\text{MgAl}_2\text{O}_4$  solidifies while maintaining its vermicular structure (d). Then, the Al alloy solidifies with mostly metallurgical pores when the printing speed is low. In this manner, the microstructure of vermicular  $\text{Al}_2\text{O}_3/\text{MgAl}_2\text{O}_4$  phase embedded in the Al alloy matrix with near spherical macropores and micropores is formed.

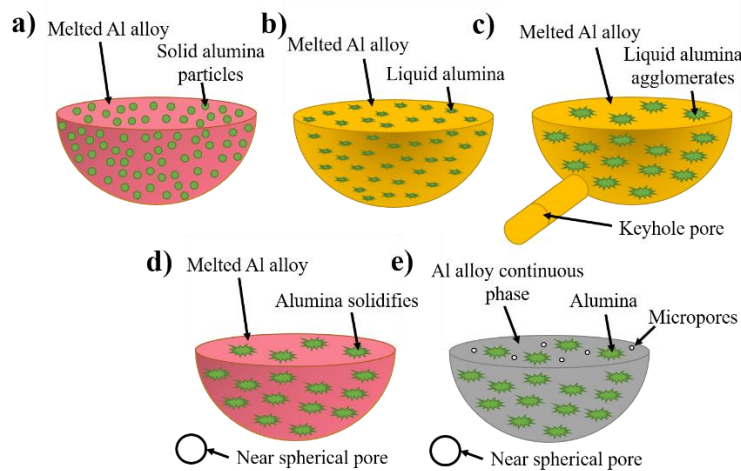


Figure 10. Scheme of the process in a melted pool when the laser impact and after solidification

### Dislocation density of the continuous metallic phase

Williamson-Hall plots for Al alloy phase in printed parts using composite Al- $\text{Al}_2\text{O}_3$  powders are shown in Figure 11-a) and dislocation density is shown in part b) of the same Figure. The standard deviation varied between  $1.06$  and  $1.15 \times 10^{14} \text{ m}^{-3}$ . As can be seen, in all cases the dislocation density is one order of magnitude higher than in the case of AlSi10Mg Renishaw printed parts. Dislocation density value is highest when the printing parameters are 10 W – 100 mm/s and lowest when the printing parameter are 10 W – 50 mm/s. The formation of dislocations has been reported by researchers when obtaining pieces by LPBF [44]. Q. Zhang et al [45] proposed that rapid solidification promotes the formation of solid solution containing high concentration of vacancies, which in turn aggregate to generate a high density of dislocations. Č. Donik et al [41] proposed three

explanations: 1) once the melted pool is formed, the rapid solidification leads to the growing of nano-dendrites, which grow generally in the radial direction with a small misorientation, which is compensated during solidification by the formation of dislocations; 2) the melted pool occupies a bigger volume than its environment and during solidification the newly formed solid phase is affected by local tensile stresses, hence large numbers of dislocations are formed; 3) the dislocations are formed because of the segregation of the alloying elements in the inter-dendritic zones (which solidify last) as a consequence of the dendrites' orientation accommodation during rapid solidification. K.M. Bertsch, et al [46], for their part, explained that dislocations are originated by thermal distortions, affected primarily by constraints surrounding the melt pool and thermal cycling, which is related with the second option proposed by Č. Donik et al. All three explanations could apply in this case; however, a reinforcement to mechanism number two proposed by Č. Donik et al [41] could have occurred, considering the increase in volume of the spinel when it is formed - formation of spinel is accompanied by an increase of 5% of volume [47], which could indicate that, with the spinel formation, there are more constraints surrounding the melt pool, and more dislocation density in the Al alloy phase formed.

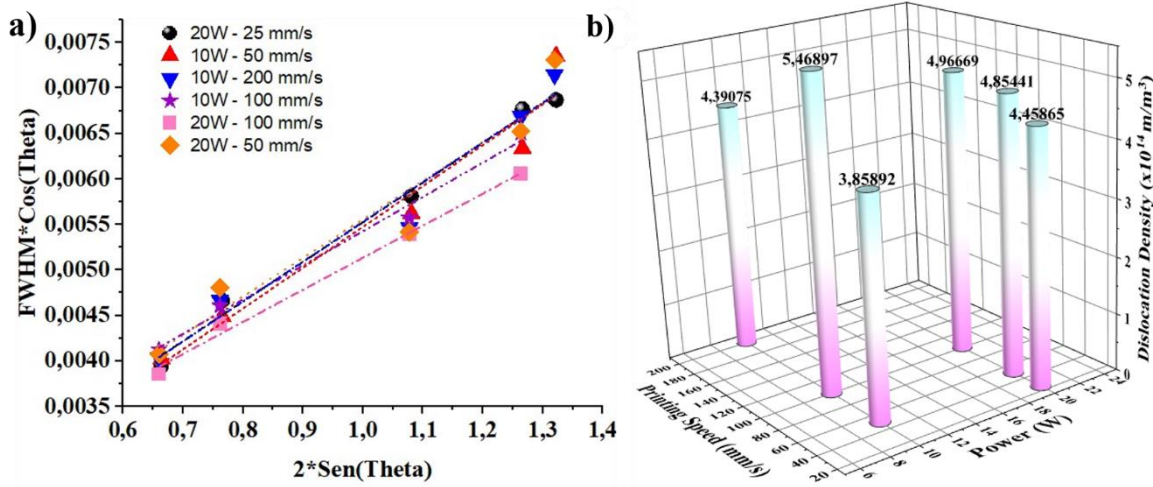


Figure 11. Williamson Hall plots and dislocation density of the printed parts

### 3.3 Hardness

When analyzing micro-hardness, the following aspects are important into explaining the results: porosity, distribution of discontinuous phase, and dislocation density of the continuous metallic phase. All the samples printed with composite powders obtained by grinding Al alloy chips are harder than the sample obtained by REN- $\text{AlSi10Mg}$  powder, which is explained by the presence of discontinuous phase of  $\text{Al}_2\text{O}_3/\text{MgAl}_2\text{O}_4$  and the higher dislocation density, even though REN- $\text{AlSi10Mg}$  samples do not exhibit porosity (Figure 4-b).

Of the samples printed with the powder obtained by grinding chips, the hardest is that printed at 20 W–50 mm/s, which exhibits a hardness of  $226 \pm 34.3$  HV. This sample exhibits the third highest dislocation density (Figure 11-b), low micro-porosity (Figure 7-a) and well dispersed second phase (Figure 6-b). The lowest hardness value is exhibited by the sample printed at 10 W – 50 mm/s. This sample also exhibits the lowest dislocation density, the second highest micro-porosity presence in the metallic matrix, and highest quantity of interrupted growing of the second phase ( $\text{Al}_2\text{O}_3/\text{MgAl}_2\text{O}_3$ ) as shown in Figure 6. The sample with the second lowest hardness value (20 W – 25 mm/s) exhibits a

high dislocation density but also the highest micro-porosity and the biggest particles of second phase, which is the most inefficient morphology in diminishing the movement of dislocations. All these facts mean that, in the present investigation, the micro-porosity, the size of the second phase and the dislocation density collectively explain the hardness.

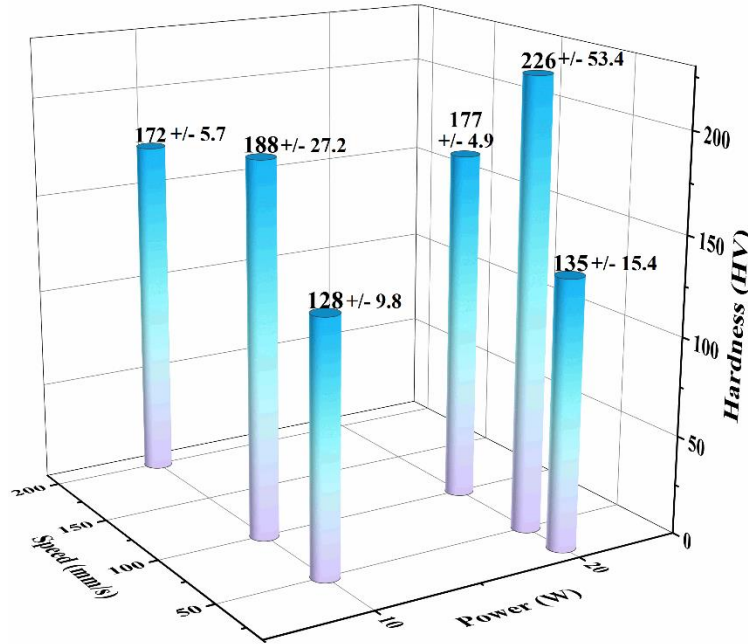


Figure 12. Hardness of the printed samples

## Conclusions

By using aluminum alloy - alumina powder composite obtained by grinding Al alloy chips, samples were printed successfully by the laser powder bed fusion additive manufacturing technique. The printing parameters that were varied were laser power and printing speed. For comparison purposes, samples of REN- $\text{AlSi10Mg}$  were also printed. The following conclusions were established:

- It is possible to obtain composites of  $\text{Al-Al}_2\text{O}_3$  by using oxidized Al alloy powders obtained by grinding Al alloy chips. Alumina phase displayed a vermicular morphology due to the immiscibility between Al and  $\text{Al}_2\text{O}_3$  in liquid state. The successful printing parameters were 10 W – 200 mm/s, 10 W – 100 mm/s, 10 W – 50 mm/s, 20 W – 100 mm/s, 20 W – 50 mm/s, and 20 W – 25 mm/s.
- As the starting powders also contain Mg, spinel  $\text{MgAl}_2\text{O}_4$  was also formed inside the  $\text{Al}_2\text{O}_3$ , which was explained by a chemical reduction of some  $\text{Al}_2\text{O}_3$  forming Al and MgO. Then the formed MgO reacts with the  $\text{Al}_2\text{O}_3$ , forming the spinel.
- Near spherical pores of diameter around 30  $\mu\text{m}$  were also formed during printing due to the formation of keyholes with temperatures higher than the evaporation temperature, forming a protruding region. The temperature diminishes and the surface tension increases, causing the keyhole to collapse and form almost spherical pores underneath the melted pool. Pores of diameter around 0.5  $\mu\text{m}$  were found in some cases in the matrix.
- In all cases of the printed samples with the composite powders, the dislocation density of the metallic phase was one order of magnitude higher than in the case of the sample printed with  $\text{AlSi10Mg}$  alloy Renishaw powders. This was explained by the formation of a spinel phase,

whose volume is 5% higher than the volume occupied by the starting phases, which led to more constraints surrounding the melt pool, and therefore more dislocation density in the Al alloy phase.

- A micro-hardness of  $226 \text{ HV} \pm 34.3$  was achieved in the printed samples at 20 W–50 mm/s. All the analyzed factors, the micro-porosity, the second phase and the dislocation density affected the micro-hardness of the samples.

## Conflict of Interest Statement

On behalf of all the authors, the corresponding author states that there is no conflict of interest.

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## References

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- [1] Pei Wang, Jürgen Eckert, Konda-gokuldoss Prashanth, Ming-wei Wu, Ivan Kaban, Li-xia Xi, Sergio Scudino. A review of particulate-reinforced aluminum matrix composites fabricated by selective laser melting. *Trans. Nonferrous Met. Soc. China* 30(2020) 2001–2034. DOI: [10.1016/S1003-6326\(20\)65357-2](https://doi.org/10.1016/S1003-6326(20)65357-2)
  - [2] Noriko Read, Wei Wang, Khamis Essa, Moataz Attallah. Selective laser melting of AlSi10Mg alloy: Process optimisation and mechanical properties development. *Materials and Design* 65 (2015) 417–424.
  - [3] Panneer Ponnusamy. Mechanical Properties of SLM-Printed Aluminium Alloys: A Review. *Materials* 13 (2020) 4301; doi:[10.3390/ma13194301](https://doi.org/10.3390/ma13194301)
  - [4] N. Qbau, N.D. Nam, N.T. Hien, N.X. Ca. Development of light weight high strength aluminum alloy for selective laser melting. *Journal of Materials Research and Technology* 9(6) (2020) 14075 – 14081. <https://doi.org/10.1016/j.jmrt.2020.09.088>
  - [5] Noriko Read, et al. Selective laser melting of AlSi10Mg alloy: Process optimization and mechanical properties development, *Materials and Design* 65 (2015) 417–424
  - [6] T. B. Sercombe, Selective laser melting of aluminium and aluminium metal matrix composites: review, *Materials Technology: Advanced Performance Materials* 2016 Vol. 31 N. 2
  - [7] K. M. Shorowordi, T. Laoui, A. S. M. A. Haseeb, J. P. Celis, L. Froyen. Microstructure and interface characteristics of B<sub>4</sub>C, SiC and Al<sub>2</sub>O<sub>3</sub> reinforced Al matrix composites: a comparative study. *Journal of Materials Processing Technology* 142 (2003) 738 – 743. [https://doi.org/10.1016/S0924-0136\(03\)00815-X](https://doi.org/10.1016/S0924-0136(03)00815-X)
  - [8] Ivan A. Pelevin, Anton Yu. Nalivaiko, Dmitriy Yu. Ozherelkov, Alexander S. Shinkaryov, Stanislav V. Chernyshikhin, Alexey N. Arnautov, Sergey V. Zmanovsky, Alexander A. Gromov. Selective Laser Melting of Al-Based Matrix Composites with Al<sub>2</sub>O<sub>3</sub> Reinforcement: Features and Advantages. *Materials* 14 (2021) 2648. <https://doi.org/10.3390/ma14102648>
  - [9] Zhiming Zhang, Zan Li, Zhanqiu Tan, Haitao Zhao, Genlian Fan, Yanjin Xu, Ding-bang Xiong, Zhiqiang Li. Bioinspired hierarchical Al<sub>2</sub>O<sub>3</sub>/Al laminated composite fabricated by flake powder metallurgy. *Composites Part A* 140 (2021) 106187. <https://doi.org/10.1016/j.compositesa.2020.106187>
  - [10] Jaswinder Singh, Amit Chauhan. Characterization of hybrid aluminum matrix composites for advanced applications – A review. *Journal of Materials Research and Technology* 5 (2016) 159 – 169. <https://doi.org/10.1016/j.jmrt.2015.05.004>
  - [11] Peng Zhang, Weiyi Zhang, Yunhui Du, Yujie Wang. High-performance Al-1.5 wt% Si-Al<sub>2</sub>O<sub>3</sub> composite by vortex-free high-speed stir casting. *Journal of Manufacturing Processes* 56 (2020) 1126-1135. <https://doi.org/10.1016/j.jmapro.2020.06.016>

- 
- [12] Jiubin Jue, Dongdong Gu, Kun Chang, Donghua Dai. Microstructure evolution and mechanical properties of Al-Al<sub>2</sub>O<sub>3</sub> composites fabricated by selective laser melting. *Powder Technology* 310 (2017) 80-91. <http://dx.doi.org/10.1016/j.powtec.2016.12.079>
- [13] Dongdong Gu, Jiubin Jue, Donghua Dai, Kaijie Lin, Wenhua Chen. Effects of Dry Sliding Conditions on Wear Properties of Al-Matrix Composites Produced by Selective Laser Melting Additive Manufacturing. *Journal of Tribology* 140(2) (2018) 021605. <https://doi.org/10.1115/1.4037729>
- [14] Quanquan Han, Rossitza Setchi, Franck Lacan, Dongdong Gu, Sam L. Evans. Selective laser melting of advanced Al-Al<sub>2</sub>O<sub>3</sub> nanocomposites: Simulation, microstructure and mechanical properties. *Materials Science & Engineering A* 698 (2017) 162-173. <http://dx.doi.org/10.1016/j.msea.2017.05.061>
- [15] Ying Chen, Shiqian Song, Shang Zhu, Xiaosheng Cui, Feng Zhao. Selective laser remelting of in-situ Al<sub>2</sub>O<sub>3</sub> particles reinforced AlSi10Mg matrix composite: Densification, microstructure and microhardness. *Vacuum* 191 (2021) 110365. <https://doi.org/10.1016/j.vacuum.2021.110365>
- [16] Hailong Liao, Haihong Zhu, Gang Xue, Xiaoyan Zeng. Alumina loss mechanism of Al<sub>2</sub>O<sub>3</sub>-AlSi10 Mg composites during selective laser melting. *Journal of Alloys and Compounds* 785 (2019) 286 – 295. <https://doi.org/10.1016/j.jallcom.2019.01.116>
- [17] Hailong Liao, Junjie Zhu, Shijie Chang, Gang Xue, Haihong Zhu, Baijin Chen. Al<sub>2</sub>O<sub>3</sub> loss prediction model of selective laser melting Al<sub>2</sub>O<sub>3</sub>-Al composite. *Ceramics International* 46 (2020) 13414 – 13423. <https://doi.org/10.1016/j.ceramint.2020.02.124>
- [18] Anton Yu. Nalivaiko, Dmitriy Yu. Ozherelkov, Alexey N. Arnautov, Sergey V. Zmanovsky, Alexandra A. Osipenkova, Alexander A. Gromov. Selective laser melting of aluminum-alumina powder composites obtained by hydrothermal oxidation method. *Applied Physics A* 126 (2020) 871. <https://doi.org/10.1007/s00339-020-04029-9>
- [19] L.M. Rojas-Díaz, L.E. Verano-Jiménez, E. Muñoz-García, J. Esguerra-Arce, A. Esguerra-Arce. Production and characterization of aluminum powder derived from mechanical saw chips and its processing through powder metallurgy. *Powder Technology* 360 (2020) 301–311. <https://doi.org/10.1016/j.powtec.2019.10.028>
- [20] <https://www.renishaw.com/media/pdf/en/a5dc91092d694a6a8eb0b472798ae063.pdf> Renishaw, on-line September 2021.
- [21] G. K. Williamson and R. E. Smallman. Dislocation densities in some annealed and cold-worked metals from measurements on the X-ray debye-scherrer spectrum. *Philosophical Magazine* (1955) 34-46.
- [22] D. S. Tsai, T. S. Chin, S. E. Hsu, M. P. Hung. A simple method for the determination of lattice parameters from powder X-ray diffraction data. *Materials Transactions* 30(7) (1989) 474 – 479.
- [23] G. A. Somopja and J. E. Lester. Evaporation mechanism of solids. *Progress in Solid State Chemistry* 4 (1967) 1-52. [https://doi.org/10.1016/0079-6786\(67\)90004-0](https://doi.org/10.1016/0079-6786(67)90004-0)
- [24] Robert Schmidt, H. Martin Scholze, Achim Stolle. Temperature progression in a mixer ball mil. *Int J Ind Chem* (2016) 7:181–186. DOI 10.1007/s40090-016-0078-8
- [25] Katsutoshi Ono and Ryosuke O. Suzuki. Evaporation processes in vacuum metallurgy. *J. Mass Spectrom. Soc. Jpn.* 47 (1) (1999) 38-41.
- [26] John Petrovic and George Thomas. Reaction of Aluminum with Water to Produce Hydrogen. [https://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/aluminium\\_water\\_hydrogen.pdf](https://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/aluminium_water_hydrogen.pdf)
- [27] R. F. Singer, W. C. Oliver, and W. D. Nix, Identification of dispersoid phases created in aluminum during mechanical alloying, *Metallurgical Transactions A* 11 (1980) 1895–1901
- [28] J. S. Benjamin and M. J. Bomford, Dispersion strengthened aluminum made by mechanical alloying, *Metall. Trans. A* 8 (1977) 1301–1305
- [29] Xiaobing Zhang, Bo Cheng, Charles Tuffile. Simulation study of the spatter removal process and optimization design of gas flow system in laser powder bed fusion. *Additive Manufacturing* 32 (2020) 101049. <https://doi.org/10.1016/j.addma.2020.101049>
- [30] Luis E. Criales, Yigit M. Arisoy, Brandon Lane, Shawn Moylan, Alkan Donmez, Tuğrul Özel. Laser powder bed fusion of nickel alloy 625: Experimental investigations of effects of process parameters on melt pool size and shape with spatter analysis. *International Journal of Machine Tools & Manufacture* 121 (2017) 22-36. <http://dx.doi.org/10.1016/j.ijmachtools.2017.03.004>
- [31] M. Lutter-Günther, M. Bröker, T. Mayer, S. Lizak, C. Seidel, G. Reinhart. Spatter formation during laser beam melting of AlSi10Mg and effects on powder quality. *Procedia CIRP* 74 (2018) 33–38.
- [32] Tatiana Fedina, Jesper Sundqvist, John Powell, Alexander F.H. Kaplan. A comparative study of water and gas atomized low alloy steel powders for additive manufacturing. *Additive Manufacturing* 36 (2020) 101675. <https://doi.org/10.1016/j.addma.2020.101675>

- 
- [33] Denis Garoli, Giorgia Giovannin, Sandro Cattarin, Paolo Ponzellin, , Remo Proietti Zaccaria, Andrea Schirato, Francesco D'Amico, Maria Pachetti, Wei Yang, Hai-Jun Jin, Roman Krahne, Alessandro Alabastri. Galvanic Replacement Reaction to prepare nanoporous Aluminum for UV plasmonics. *Nanomaterials* 10(1) (2020) 102. <https://doi.org/10.3390/nano10010102>
- [34] Jinge Liu, Peng Wen. Metal vaporization and its influence during laser powder bed fusion process. *Materials & Design* 215 (2022) 110505.
- [35] Jie Yin, Wenqi Zhang, Linda Ke, Huiliang Wei, Dengzhi Wang, Liangliang Yang, Haihong Zhu, Peng Dong, Guoqing Wang, Xiaoyan Zeng. Vaporization of alloying elements and explosion behavior during laser powder bed fusion of Cu–10Zn alloy. *International Journal of Machine Tools and Manufacture* 161 (2021) 103686.
- [36] C. Shuai, Y. Zhao, C. Li, Y. Deng, Z. Zhao, C. Gao. Supersaturated solid solution enhanced biodegradable Zn-Mn alloys prepared by mechanical alloying and selective laser melting. *Journal of Alloys and Compounds* 943 (2023) 169145. <https://doi.org/10.1016/j.jallcom.2023.169145>
- [37] Yucheng Ji, Chaofang Dong, Decheng Kong, Xiaogang Li. Design materials based on simulation results of silicon induced segregation at AlSi10Mg interface fabricated by selective laser melting. *Journal of Materials Science & Technology* 46 (2020) 145 – 155. <https://doi.org/10.1016/j.jmst.2020.01.037>
- [38] S. Pal, A. K. Bandyopadhyay, S. Mukherjee, B. N. Samaddar, P. G. Pal. MgAl<sub>2</sub>O<sub>4</sub>– $\gamma$ -Al<sub>2</sub>O<sub>3</sub> solid solution interaction: mathematical framework and phase separation of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> at high temperature. *Bulletin of Materials Science* 34 (4) (2011) 859-864.
- [39] Y. Xia, Z. Zak Fang, P. Sun, Y. Zhang, T. Zhang, M. Free. The effect of molten salt on oxygen removal from titanium and its alloys using calcium. *Journal of Materials Science* 52 (2017) 4120-4128. DOI 10.1007/s10853-016-0674-1
- [40] I. Pasquet, V. Baco-Carles, P. Chamelot, M. Gibilaro, L. Massot, Ph. Tailhades. A multimaterial based on metallic copper and spinel oxide made by powder bed laser fusion: A new nanostructured material for inert anode dedicated to aluminum electrolysis. *Journal of Materials Processing Tech.* 278 (2020) 116452. <https://doi.org/10.1016/j.jmatprotec.2019.116452>
- [41] Crtomir Donik, Jakob Kraner, Irena Paulin and Matjaž Godec. Influence of the Energy Density for Selective Laser Melting on the Microstructure and Mechanical Properties of Stainless Steel. *Metals* 10 (2020) 919. [doi:10.3390/met10070919](https://doi.org/10.3390/met10070919)
- [42] S. Li, G. Fu, H. Li, Z. Ren, S. Li, H. Xiao, Q. Peng. Effect of layer thickness on the melt pool behavior and pore defects evolution of selective laser melting CuCrZr alloy. *Journal of Alloys and Compounds* 967 (2023) 171778. <https://doi.org/10.1016/j.jallcom.2023.171778>
- [43] Nesma T. Aboulkhair, Nicola M. Everitt, Ian Ashcroft, Chris Tuck, Reducing porosity in AlSi10Mg parts processed by selective laser melting Reducing porosity in AlSi10Mg parts processed by selective laser melting, *Additive Manufacturing* 1–4 (2014) 77–86
- [44] R. Fang, N. Deng, H. Zhang, G. Wang, Y. Su, H. Zhou, K. Gao, L. Gu. Effect of selective laser melting process parameters on the microstructure and properties of a precipitation hardening stainless Steel. *Materials & Design* 212 (2021) 110265. <https://doi.org/10.1016/j.matdes.2021.110265>
- [45] Q. Zhang, S. Hao, Y. Liu, Z. Xiong, W. Guo, Y. Yang, Y. Ren, L. Cui, L. Ren, Z. Zhang. The microstructure of a selective laser melting (SLM)-fabricated NiTi shape memory alloy with superior tensile property and shape memory recoverability. *Applied Materials Today* 19 (2020) 100547. <https://doi.org/10.1016/j.apmt.2019.100547>
- [46] K.M. Bertsch, G. Meric de Bellefon, B. Kuehl, D.J. Thoma. Origin of dislocation structures in an additively manufactured austenitic stainless steel 316L. *Acta Materialia* 199 (2020) 19 – 33. <https://doi.org/10.1016/j.actamat.2020.07.063>
- [47] Z. Zhang & N. Li. Effect of polymorphism of Al<sub>2</sub>O<sub>3</sub> on the synthesis of magnesium aluminate spinel. *Ceramics International* 31 (2005) 583 – 589. [doi:10.1016/j.ceramint.2004.06.025](https://doi.org/10.1016/j.ceramint.2004.06.025)