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DEPARTAMENTO DE ENGENHARIA DE MATERIAIS

OVERVIEW OF Al-Si ALLOYS FOR ADDITIVE MANUFACTURING AND PROSPECTS

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OVERVIEW OF Al-Si ALLOYS FOR ADDITIVE MANUFACTURING AND PROSPECTS

Trabalho de conclusão de curso apresentado ao Departamento de Engenharia de Materiais da Universidade Federal de São Carlos, como requisito para obtenção do título de bacharel em Engenharia de Materiais.

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Certifico que a defesa de monografia de TCC realizou-se com a participação a distância dos membros Prof. Dr. José Eduardo Spinelli e Prof. Dr. Piter Gargarella e depois das arguições e deliberações realizadas, os participantes à distância estão de acordo com as informações redigidas nesta ata de defesa.

Prof. Dr. José Eduardo Spinelli

Dedico este trabalho a todos que contribuíram em minha trajetória acadêmica até aqui, especialmente a minha mãe, que lutou contra tudo pelo meu ensino.

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“As pessoas podem tirar tudo de você, menos o
seu conhecimento”
Albert Einstein

RESUMO

A manufatura aditiva (MA) ganhou espaço nos últimos anos por possibilitar a geração de peças com geometrias de alta complexidade. Devido à natureza do processo de MA, que faz as ligas experimentarem um complexo histórico térmico durante seu processamento, há a necessidade de desenvolver ligas que sejam adequadas ao processo. As ligas Al-Si são amplamente empregadas em diversos setores industriais, como o automotivo e aeroespacial, sendo de grande interesse por suas ótimas propriedades mecânicas e baixa densidade. Ao longo dos últimos anos diversos trabalhos reportaram bons resultados com ligas baseadas no sistema Al-Si em processos de manufatura aditiva. Entretanto, as algumas composições de ligas Al-Si ainda precisam ser estudadas mais profundamente em manufatura aditiva, envolvendo o efeito de elementos de liga em suas propriedades, e aspectos microestruturais, especialmente na morfologia do silício eutético e formação de outras fases secundárias. Este trabalho de conclusão de curso avaliou as principais ligas do sistema Al-Si que estão em destaque para processos de manufatura aditiva, assim como elementos de liga empregados e novas opções para a composição de ligas que se adequem melhor ao processo de MA. São discutidas as principais técnicas de manufatura aditiva, apontando quais as vantagens de cada uma e os desafios inerentes ao processo. Elementos de liga foram avaliados quanto as suas influências na morfologia do Si e nas propriedades mecânicas de peças produzidas por manufatura aditiva, e em comparação com outros processos. Dentre os elementos estudados, adições de Ni e Zn mostraram-se efetivas no aumento da durezas e resistência mecânicas das ligas avaliadas. Zr e terras raras como Sc e Ce apresentaram excelente influência como agentes refinadores da morfologia do Si, o que também eleva as propriedades da liga. Dois tratamentos térmicos se mostraram muito efetivos, T6 e T73, envelhecimento e envelhecimento em duas etapas, respectivamente. Ambos tratamentos elevaram as durezas das ligas tratadas, entretanto, mais investigação é necessária. Avaliando todos os aspectos, a liga mais utilizada atualmente é a Al-10%Si-Mg, que possui propriedades ótimas se processada dentro de uma janela de processamento com energia do laser variando de 170 a 200 W e velocidade de varredura de 700 a 1400 mm/s. Além disso, os elementos Ni, Zn, Zr e as terras raras Sc e Ce mostraram-se promissores como elementos de liga para o sistema Al-Si, sendo um excelente foco para estudos futuros mais aprofundados. A combinação de Sr com as terras raras apresentou uma ótima sinergia em termos de refinamento microestrutural, sendo uma boa alternativa para composição de ligas a serem aprimoradas.

Palavras-chave: Al-Si, Manufatura aditiva, Microadições, Terras raras, Elementos de liga.

ABSTRACT

Additive manufacturing (AM) has emerged in recent years for enabling the generation of parts with highly complex geometries. Due to the nature of the AM process, which causes alloys to experience a complex thermal history during processing, there is a need to develop alloys that are suitable for this process. Al-Si alloys were widely used in many industries, such as automotive and aerospace, being of great interest for their excellent mechanical properties, processability and low density. Over the last years, several studies have reported suitable results Al-Si based alloys processed by AM. However, some Al-Si alloys compositions need to be further investigated, encompassing the effects of alloying elements on the properties of interest as well microstructural features, especially on the eutectic silicon size/morphology and growth of other secondary phases. This study evaluated the main Al-Si alloys that are highlighted for AM processes, as well as used alloying elements and new options for chemistries that would be suitably employed. The main AM techniques are discussed, pointing out their advantages and the challenges according to the inherent characteristics of the process. Alloying elements were evaluated considering their impact on Si morphology and mechanical properties on produced parts.. Among the evaluated elements, Ni and Zn additions proved to be effective in increasing the mechanical strength of the analyzed alloys. Zr and rare earths such as Sc and Ce demonstrated efficiency as refining agents for Si morphology, which also enhances the alloys properties. Two heat treatments showed to be effective, T6 and T73, aging and two-stage aging, respectively. Both treatments increased the hardness of treated alloys, however, more investigation appears to be needed. Evaluating all aspects, the most used alloy nowadays is the Al-Si10Mg due to its optimal properties if processed within a processing window having laser power ranging from 170 to 200 W and scanning speeds from 700 to 1400 mm/s. In sum, Ni, Zn, Zr and rare earth elements such as Sc and Ce demonstrated to be promising as alloying elements for the Al-Si alloys, being excellent topics for future investigations. Combining Sr with rare earths presented a great synergy in terms of microstructural refinement, being a suitable alternative for alternatives alloys to be developed.

Keywords: Al-Si based alloys, Additive Manufacturing, Microadditions, Alloying elements, Rare earths.

LIST OF ILLUSTRATIONS

LIST OF TABLES

LIST OF ACRONYMS

AM – Aditive Manufacturing
CAD - Computer Aided Design
Al - Aluminum
Si - Silicon
Mg - Magnesium
EB - Electron Beam
L-PBF - Laser Powder Bed Fusion
SLM - Selective Laser Melting
Ce – Cerium
Zn - Zinc
Cu – Copper
Ni - Nickel
Zr - Zirconium
Sc – Scandium
Sr – Strontium
WAAM – Wire Arc Additive Manufacturing
TS – Tensile Strength
MS – Melt Spinning
CMC – Copper Mould Casting
UTS – Ultimate Tensile Strength
YS – Yield Strength
VED – Volumetric Energy Density
DA – Direct Aging

SUMMARY

1 INTRODUCTION

Additive Manufacturing (AM) consists of an innovative technique to build parts from the scratch using CAD (Computer-Aided Design). AM processes are well known in the industrial field, but it is still among the most challenging methods for manufacturing materials. This occurs because of the great number of variables attached to the process itself, like powder and energy source characteristics. Even though AM has been a means of processing materials for about two decades, it just emerged as a commercially relevant manufacturing technique recently. Despite that, it is still one of the most important methods created in this new era of industry, because it allows the manufacturing of complex geometries parts and almost zero waste in the process, so it becomes an environment-friendly operation (FRAZIER, 2014).

In recent years AM is still progressing and being relevant to all classes of materials, including metals, polymers, ceramics, and even biological components. It's known that AM is quite advanced in the polymeric materials field, but when it comes to metals more understanding is needed to turn the actual techniques into processes that are economically and technically viable. It's needed a better comprehension of all the mechanisms involved in additive manufacturing processes, for each alloy that is viable to work with, because it's vital to understand the link between processing, microstructure, and properties of all alloys. Nowadays a just few alloys are available, mostly pertaining to the 3XX.X and 4XX.X series of Al casting alloys, used in AM processes to produce structural parts that are projected with this purpose. These Al series have been used due to the similarities between casting and additive manufacturing processes, as for the good properties obtained from adding Si and Mg, like good weldability, corrosion resistance and suitable ductility. Adding Si and Mg also turns possible hardening the alloy by heat treatments like natural aging or precipitation hardening (FRAZIER, 2014).

The development of metals to additive manufacture has been quite challenging because the process itself is physically complex, due to the rapid interaction between energy source (laser or electron beam) and the micrometric metallic powders. This results in a very fast melting followed by rapid solidification. That dynamic provides refined microstructures that is a very positive factor since that kind of microstructure tends to generate suitable mechanical properties. However, all parameters need to be precisely controlled to guarantee adherence between the melted and the consolidated layers (MANFREDI, 2017).

Aluminum alloys are widely used in the industry as structural materials once they have a good balance between mechanical properties and weight, as well as good weldability, suitable ductility and high corrosion resistance, so it is very desirable to use these alloys in additive manufacturing. Despite that, just a few Al alloys are used commercially on AM, most of them Al-Si based, so this work will focus on the benefits, limitations and challenges of using Al-Si on these processes, including evaluation third elements additions as well as powder characteristics. Additive manufacturing has three main techniques systems that are most common: Powder Bed Systems, Powder Feed Systems, and Wire Feed Systems. This first mentioned is the most used and best accepted on industrial operations (MANFREDI, 2017).

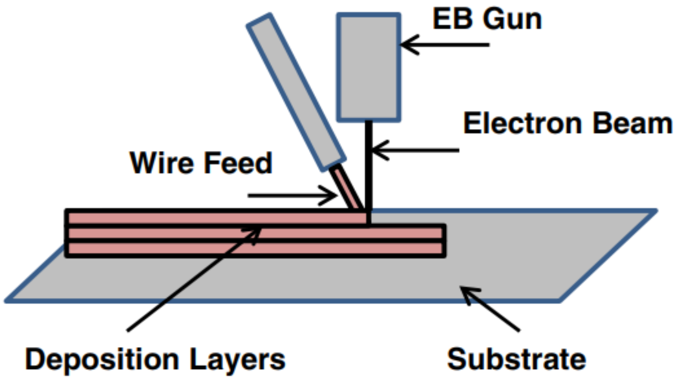
2 MAJOR ADDITIVE MANUFACTURING TECHNIQUES FOR METALS

2.1 Wire Feed Systems

To build a three-dimensional structure, this process consists in deposit a single wire filament on the initial layer and keep adding more wires in the subsequent passes. The energy sources that could be used are electron beam (EB), plasma arc, or laser beam.

The wire feed systems have a high deposition rate, so it suits well on processes that have the need to build large volumes of parts. Despite that, structures built by this method need extensive machining, more than other processes that used powder materials. Fig.1 shows an image of a Wire Feed System.

Figure 1. Illustration of a generic AM Wire Feed System

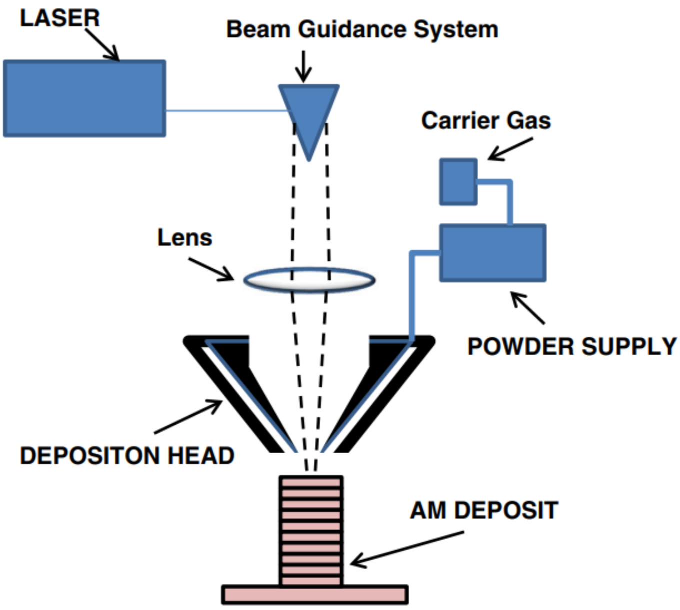


Source: (FRAZIER, 2014)

2.2 Powder Feed Systems

Powder feed systems use a powder supply attached to a tank of carrier gas that conveys the powder through a nozzle to the surface of the substrate, where it is melted by the energy source (commonly a laser beam) and creates a monolayer. This process will be repeated until the component is done. This system can use a stationary feeder, and then the building component will move. Or the component can be stationary and the deposition head will move. This technique allows building a larger scale of components than powder bed systems. Despite that, this process shows more difficulty to control the parameters. One of the biggest advantages of using powder feed systems is that it allows the refurbish of damaged or worn components. Fig. 2 illustrates a generic Powder Feed System.

Figure 2. Illustration of a generic AM Powder Feed System

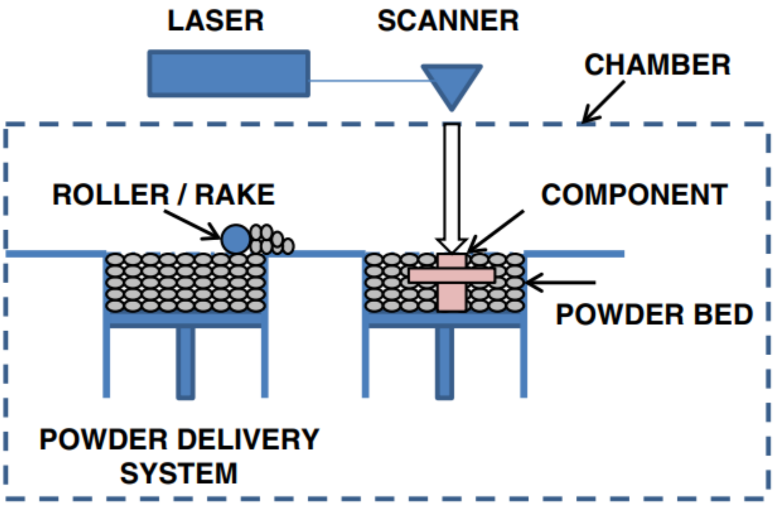


Source: (FRAZIER, 2014)

2.3 Powder Bed Systems

Powder bed systems are the most advanced and widely used when it comes to additive manufacturing. Laser Powder Bed Fusion (L-PBF), as known as Selective Laser Melting (SLM), is the most widespread technique used. It consists in creating a thin powder bed layer by raking the powder uniformly using a roller. Then the energy source (electron beam or laser beam) melts or sinters the layer on the desired shape. This operation is repeated with more layers of powder until the three-dimension component is built. Powder bed systems produce high-resolution features, maintain better dimensional control, and generate high quality surface parts, so, almost no machining is needed. These advantages turn it into the best technique to build small components, or high precision parts.

Figure 3. Illustration of a generic AM Powder Bed System.



Source: (FRAZIER, 2014)

2.4 AM Systems Challenges

Additive manufacturing processes are sufficiently evolved to be used on an industrial scale in some sectors. However, it is necessary to pay attention to the fact that there are still some difficulties that must be overcome so that this process will be more economically viable to be used widely in industrial sectors. These problems can be faced from two different perspectives so it will be easier to solve them. The scientific/engineering perspective and the economic perspective.

From a scientific point of view, many tests are needed to generate robust and reliable statistical data, to be able to parameterize and standardize the additive manufacturing process, making the resulting parts free from defects such as porosities, cracks, or unwanted microstructures. Creating a database with this information is essential since there is a huge variety of alloys available on the market for many processes, but just a few viable for additive manufacturing. Inevitably, by standardizing the additive manufacturing processes, the cost of producing parts will drop considerably and the time for their production will be optimized, turning viable to fit AM processes on the production of many other parts.

3. ESSENTIAL PARAMETERS FOR ADDITIVE MANUFACTURING PROCESSES

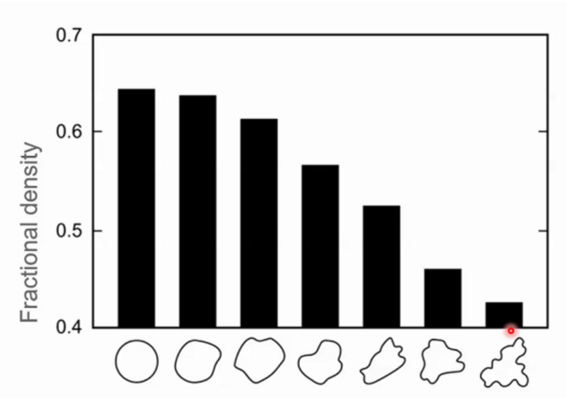
Building up three-dimensional parts, layer by layer, is not an easy task. It requires control over a lot of variables. Some of the most critical parameters on additive manufacturing processes will be presented in this topic, pointing the optimal conditions that produce high-performance Al-Si alloys.

3.1. Powder size and morphology

As the main material to produce additive manufacturing parts, metal powders need to be carefully designed to produce high quality and properties parts. Powders that could achieve those properties on produced parts present good flowability and densities (NALIVAIKO, 2019). Other characteristics that metal powders need to achieve in order to become adequate for AM: proper particle size and particle distribution, spherical shape with regular surface.

It can be seen in Figure 4 that the near a powder shape is of a spherical shape the higher the fractional density that will be achieved processing this powder by AM. It is also necessary that the particle surface of the powder exhibits low roughness, otherwise interlocking between particles will severely decrease the powder flowability (KEMPEN, 2014).

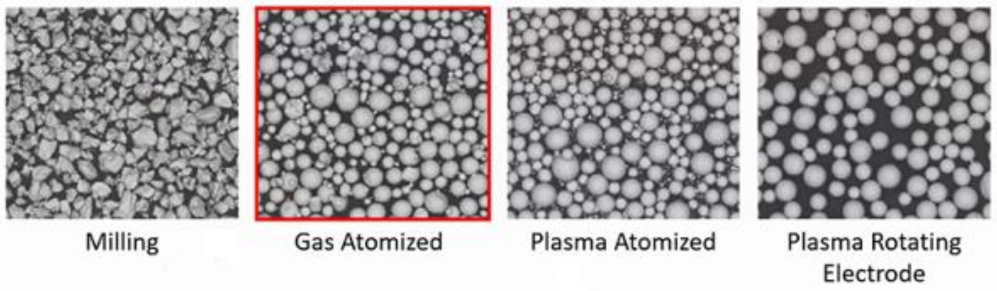
Figure 4. Fractional density depending on powder particle shape.



Source: (MALVERN PANALYTICAL PRESENTATION, 2021)

Figure 5 depicts some images emphasizing powder’s shape produced by different methods. It can be noted that the milling process does not produce suitable powders for AM. Gas atomization may produce powder with desirable properties, but plasma atomization and plasma rotating electrode produce powders with minor roughness surfaces.

Figure 5. Morphologies of powders produced by different techniques.



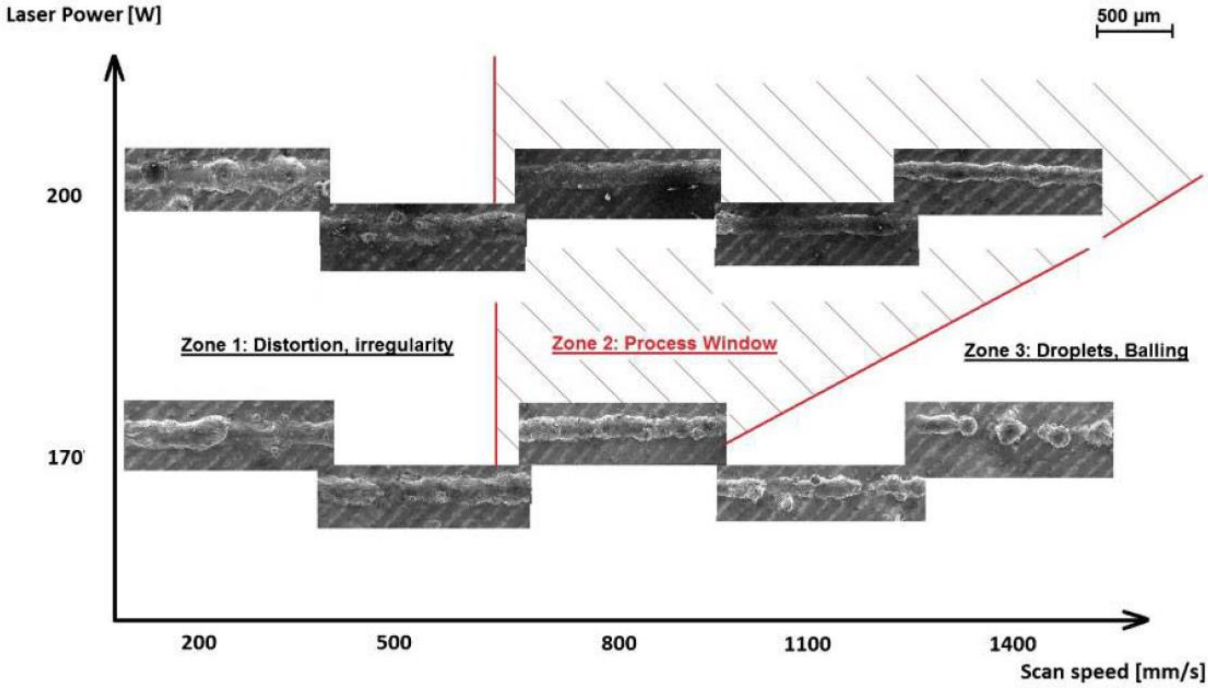
Source: (MALVERN PANALYTICAL PRESENTATION, 2021)

Powders for additive manufacturing also need to present a narrow particle size distribution, containing finer and coarser particles, but only in small fractions. This size distribution is optimized to obtain almost full dense produced parts. On the whole, spherical shaped powders with low roughness on their surface, presenting a suitable particle size distribution will result in higher values of flowability and packing, being able to produce dense and flaws-free parts by additive manufacturing (OLAKANMI, 2015).

3.2 Optimized parameters for AM of Al-based alloys

Additive manufacturing processes submit produced parts to complex thermal histories, so it’s not simple to determine optimal parameters that fit for a great number of alloys. KEMPEN (2014) developed optimized parameters that suit well for aluminum alloys, avoiding the main problems found in this process, like distortion of the produced layers, irregularities, or balling effects. Figure 6 shows the most common problems caused by unappropriated processing conditions. Excessive energy on the process, caused by exceeding laser power and/or low scan speeds tends to deform the layer tracks. Low energy allied to fast scan speeds may not melt the substrate, causing the layer to balling due to the Marangoni effect (KEMPEN, 2014)

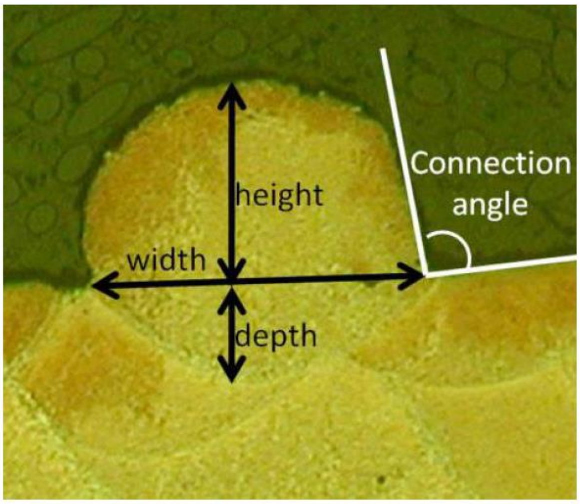
Figure 6. Top view of selective laser melting scan tracks produced through different laser parameters.



Source: (KEMPEN, 2014)

To produce stable layers on additive manufacturing, by selective laser melting, each melted track must exhibit a connection angle close to 90°, so it will fit well to next scan tracks and layers, avoiding distortions on the final produced parts. Figure 7 shows the protocol used to measure a single track, to understand the quality of a single scan track. Figure 8 presents the laser parameters related to the produced tracks. Using higher powers and low scan speed tend to generate a bigger melt pool turning impossible to build other layers on top of that. Lower powers combined with high scan speeds will not melt the subtract or previous layer, which is enough to achieve good bound between layers.

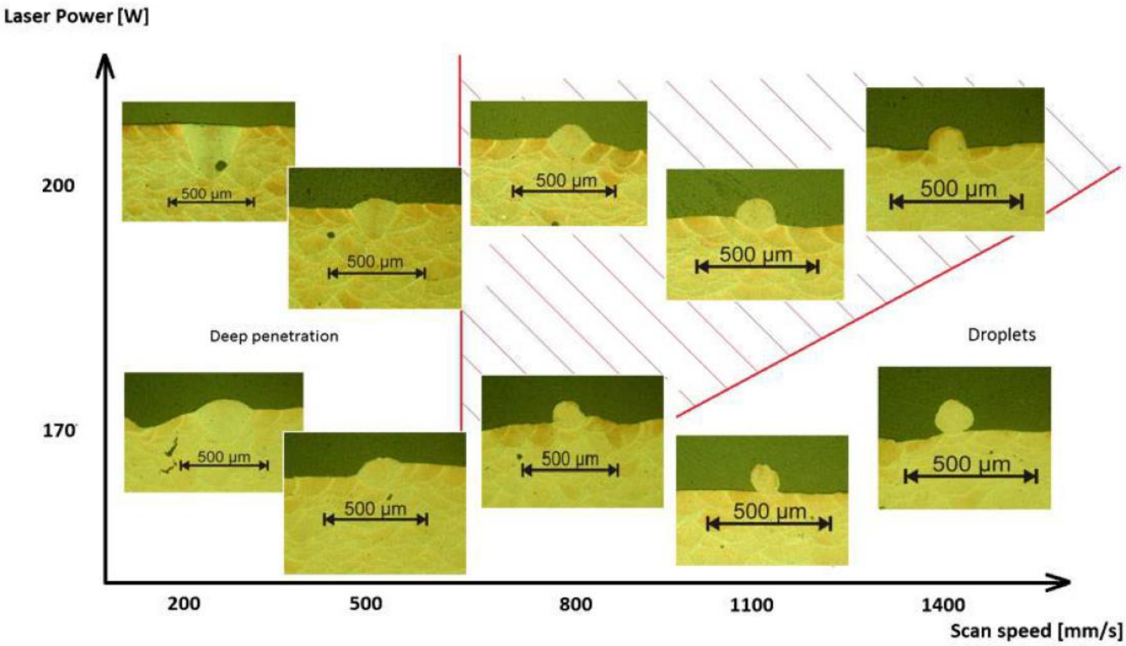
Figure 7. Requirements for single laser scan tracks: measurement protocol for AM



Source: (KEMPEN, 2014)

As it can be seen on the graphics presented by (KEMPEN, 2014) there are an optimal process window to produce parts by selective laser melting, with laser power between 170 W and 200 W, combined with scan speeds varying from 650 mm/s to 1400 mm/s. These parameters present a good start point to many future works that will evaluate modified Al-Si alloys on AM processes.

Figure 8. Transversal view of selective laser melted scan tracks of the AlSi10Mg alloy produced by different parameters.



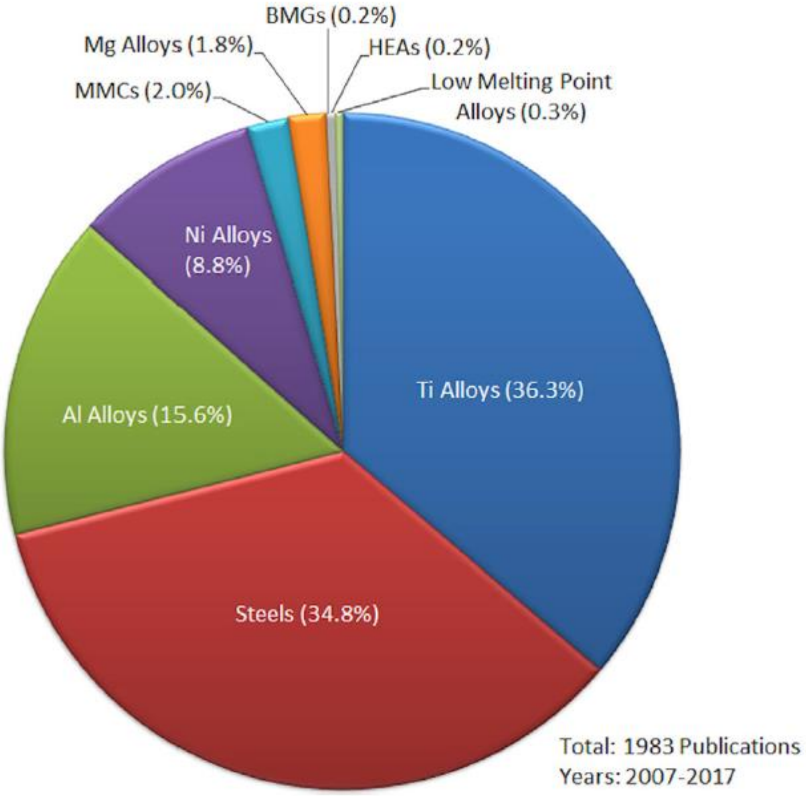
Source: (KEMPEN, 2014)

4. Al-Si ALLOYS ON AM: INFLUENCE OF TERNARY AND QUATERNARY ELEMENTS

Aluminum alloys have been widely used in industry for a long time because of their good balance between mechanical properties and weight, with a specific density of approximately 2.7 g/cm³ that is less than half the value for steel. It also has good corrosion resistance due to the fine layers of Al2O3 that covers the surface of Al pieces (MONDOLFO, 1976). Because of that, these alloys are great to compose structural parts. In additive manufacturing processes, aluminum alloys are highlighted. Despite that, due to the high heat diffusivity of Al-based alloys, high focused energy sources are required to melt the layers. Initially, Al alloys that were already used in casting processes were chosen to AM processes, however, with recent improvements many alloy elements were made possible to create Al alloys with improved properties for the AM process. It's extremely necessary to develop specific alloys for AM due to the complex thermal history that produced parts will experience, like rapid solidification, repeated melting, and directional solidification. These factors will contribute to generate complex microstructures and properties that are not typically found on conventional manufacturing processes (OLAKANMI, 2013).

The last decade resulted in approximately 2000 publications with topics related to metals in additive manufacturing. 15.6% of the papers were related to Al alloys development for AM, as shown in Fig. 9. Over these 10 years many studies reported the development of ternary and quaternary Al-Si based alloys or adaptation of the commonly used chemistries on processes like casting, for example. These developing works used many of the most common elements found on composition of Al alloys as object of study (ZHANG, 2018). Even so, understand the effects of alternative elements on Al-Si alloys is also critical in order to develop materials with properties that fit on the extreme conditions of AM. Aiming on that purpose, the effects of addition of some rare earth elements like Sc and Ce on properties of Al alloys have been investigated in the last 4 years.

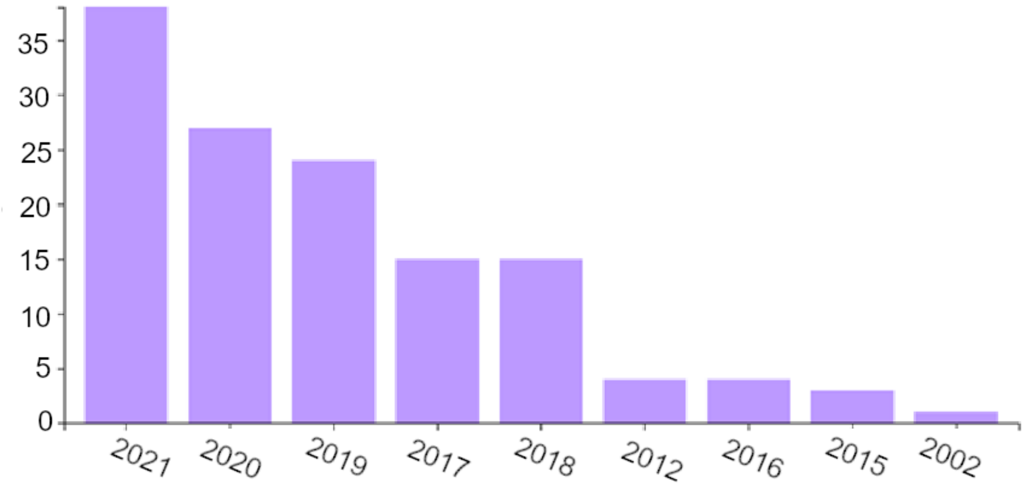
Figure 9. Pie chart of recent 10 years publications related to alloys on AM.



Source: (ZHANG, 2018)

Many works were published discussing topics related to metals on AM, but when it comes to Al-Si Alloys and alternative elements all published papers are recent. For that reason, some data about research developed these years on that topic was brought up, using the Web of Science tool, since a bibliometric analysis was made using method by SOLER (2020). This analysis aimed including all publications with topics involving Al-Si alloys and additive manufacturing. It shows an increase on the number of papers published about it, as shown in Figure 10 over the last 4 years.

Figure 10. Publications over the years regarding research on Al-Si alloys and AM.



Source: Web of Science

The present work will discuss the relations between Al-Si alloys (tested as AM alloys), elements that already are proposed to compose ternary or quaternary alloys, and alternative elements that are highlighted to compose Al alloys on AM.

4.1 Traditional alloying elements on Al-Si alloys

Many elements are already used to compose Al alloys suitable for additive manufacturing processes, being most of them typically employed in commercial as-cast Al-Si alloys. It’s since the available Al alloys systems are those related to the casting alloys group (MANFREDI, 2017).

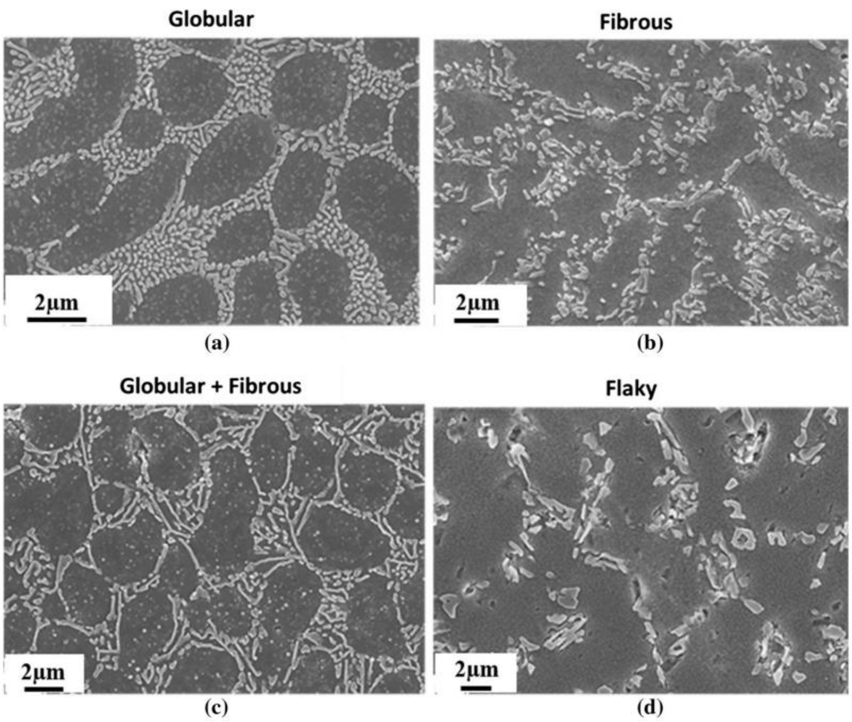
4.1.1 Si influence on Al alloys

Silicon already became a traditional element when it comes to Al alloys due to the great number of alloys based on this system. With a eutectic composition for this system at 12.6% wt.%, Si addition improves the properties of the pure aluminum, lowering alloy levels of contraction on solidification, increasing the fluidity, providing good weldability, and outstanding corrosion resistance. This excellent combination of suitable mechanical properties, low weight and high heat conductivity grants it numerous applications in many industries, like aerospace, automotive or electronics.

The addition of Si on Al alloys also provides many improvements when allied to more elements on the alloy's composition. One of the most relevant mechanisms on Al-Si alloys is the hardening through precipitation (heat treatment T6) by adding elements such as Mg. It provokes precipitation of Mg_2Si particles, that significantly strengthen the alloy, by refining its microstructure, without decreasing other mechanical properties (KEMPEN, 2015). The eutectic Si morphology is also very relevant for the mechanical properties of the alloys that belong to the Al-Si system and adding new alloying elements may modify it and change significantly it's properties. The more refined the Si morphology the better are the mechanical properties reported in the literature.

Hearn (2019) reported the influence of Si refinement/morphology on hardness for the hypoeutectic binary alloy Al-10wt.%Si. Fig. 11 shows different morphologies for the eutectic silicon found in the as-atomized Al-10wt.%Si alloy. These microstructures are related to the process and the parameters used to manufacture Al-Si alloys. The finer microstructures (globular and globular +fibrous) are more desirable by their relation with better mechanical properties. Previous works also reported that the transition in Si growth from bulky/faceted plates to smooth/globular fibers are related to the solidification process kinetics. The higher the cooling rates that the alloy is subjected to, the finer the eutectic silicon microstructure (HEARN, 2019).

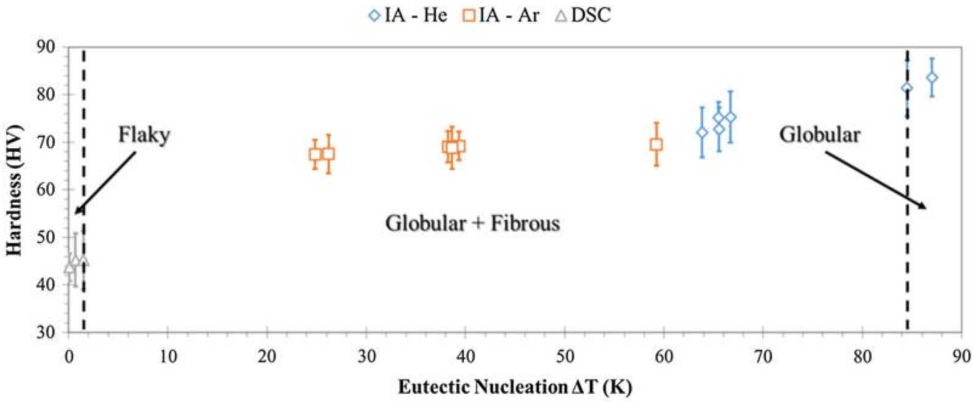
Figure 11. FE-SEM images outlining the four observed morphologies of the eutectic Si phase in the as-impulse-atomized Al-10wt.%Si alloy: (a) ‘‘Globular’’ Si morphology for 212 to 250 μm sample size (under He). (b) ‘‘Fibrous’’ Si morphology, for 125 to 150 μm sample size (under Ar). (c) ‘‘Globular + Fibrous’’ Si morphology, for 300 to 355 μm sample size (under He) and (d) ‘‘Flaky’’ Si morphology, for 300 to 355 μm sample size (under Ar).



Source: (HEARN, 2019)

Figure 12 shows the relation between hardness and eutectic Si morphology. The higher values of hardness are related to finer microstructures found on the samples. To achieve these high hard alloys is desirable to use appropriate processing conditions (with high cooling rates permitting fibers and globules formation) and add alloying elements, so the Si morphology will be finer and enhance the alloy mechanical properties (HEARN, 2019).

Figure 12. Influence of the eutectic nucleation undercooling and Si morphology on the Al-10wt.%Si alloy hardness.



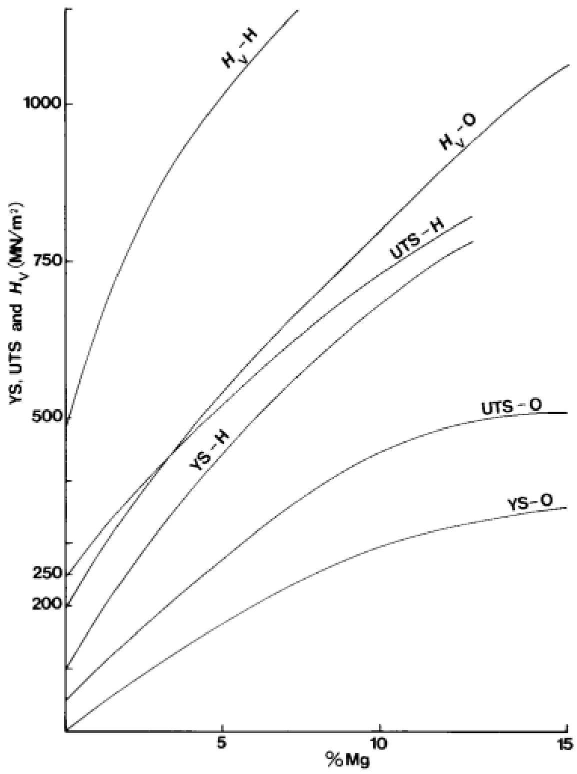
Source: (HEARN, 2019)

4.1.2 Mg influence on Al-Si alloys

Magnesium is a well-known element added to Al alloys. It is already largely employed on many applications related to Al alloys in a great number of industries. Adding Mg on Al alloys grants high mechanical properties, without considerably decreasing ductility, as good weldability, and corrosion resistance. Combining Mg to Al-Si system turn these alloys heat treatable (commonly with T6 heat treatment) increasing their mechanical properties by refining their microstructure, precipitating Mg_2Si, and modifying Si morphology. Mg also has good synergy with the Al-Zn system (granting superior mechanical strength) and Al-Cu (improving aging heat treatments), for example. Aluminum alloys with some content of Mg are also hardenable through cold work but lost some of their ductility over this process (VASUDEVAM, 1989).

Adding magnesium to Al alloys significantly increases the hardness, ultimate tensile strength, and yield strength. Figure 13 shows the improvements of some properties varying the magnesium content.

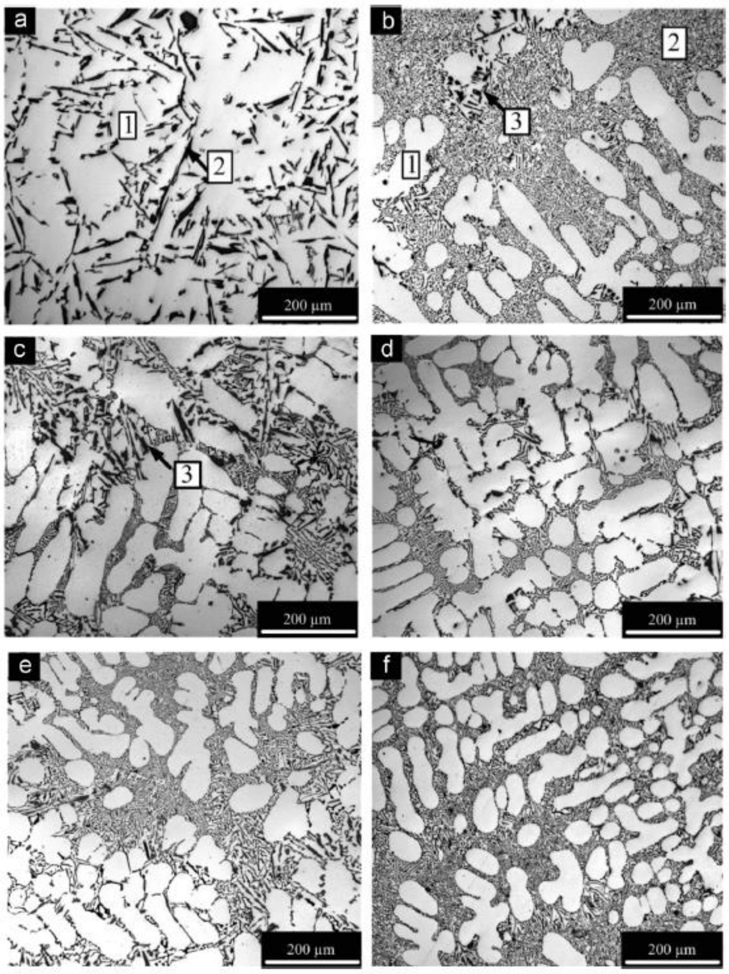
Figure 13. Mechanical properties of Aluminum-Magnesium alloys as function of Mg content. Hv = Vickers hardness; UTS = Ultimate tensile strength; YS = Yield strength; H = Cold worked; O = Annealed.



Source: (MONDOLFO, 1976)

DARLAPUDI (2016) reported the influence of ternary alloying elements on Al-10Si alloys as well as in a modified Al-10Si-350(ppm)Sr. This work compared the effects of increasing magnesium content in the final microstructure of cast and quenched parts. As shown in figure 14 increasing the magnesium content on the Al-10Si alloy refined its microstructure considerably. The modified Sr alloy showed a better level of refinement compared to the Al-10Si-*X*Mg, which indicated that Sr improved the effect of Mg content on the microstructure of the samples.

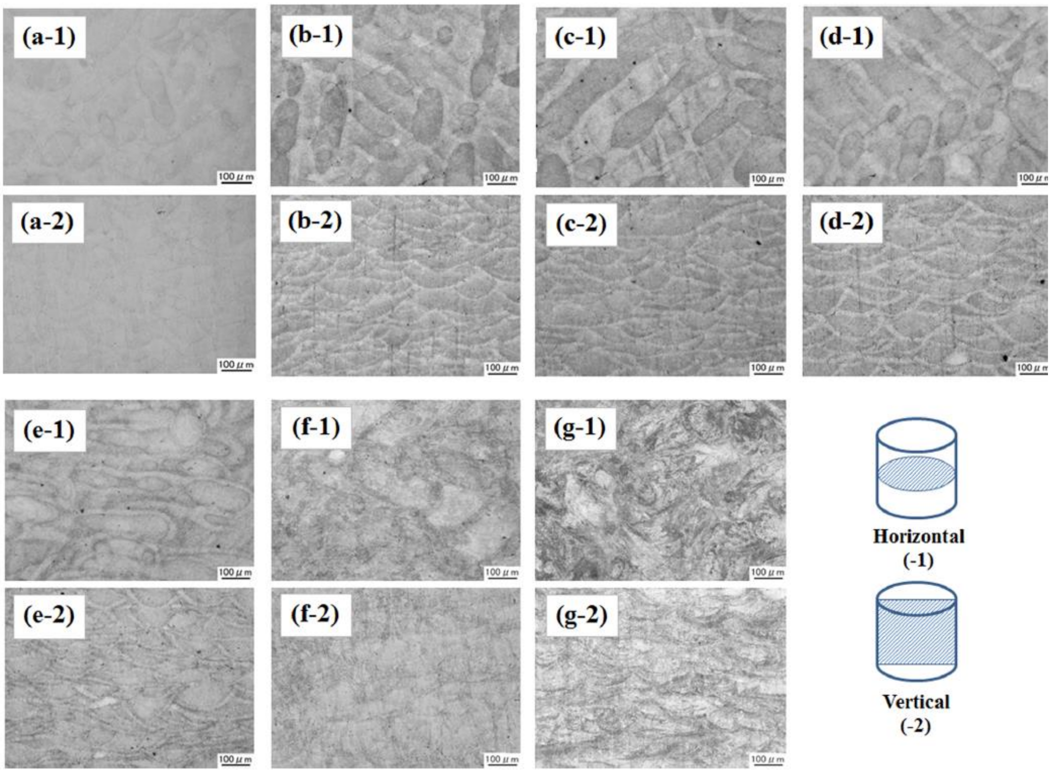
Figure 14. Microstructures of the Al–10%Si–(a) 0.5%Mg, (b)0.5%Mg–350ppm Sr, (c)1.5%Mg, (d)1.5%Mg–350Sr, (e)2.5%Mg and (f)2.5%Mg–350Sr alloy samples produced by casting. α-Al dendrites are labelled as 1, eutectic silicon is labelled as 2 and Al–Si–Mg_2Si ternary eutectic is labelled as 3.



Source: (DARLAPUDI, 2016)

Once atomization and additive manufacturing are processes that submit produced parts to high cooling rates, the synergy between magnesium and silicon suits well to refine microstructure and produce good properties parts. This is evidenced in the paper by Kimura (2019) that evaluated the microstructural features of Al-4Si-*X*Mg (*X* indicates the magnesium content) alloys, processed by Selective Laser Melting (SLM), with increasing magnesium content, as can be seen in Figure 15.

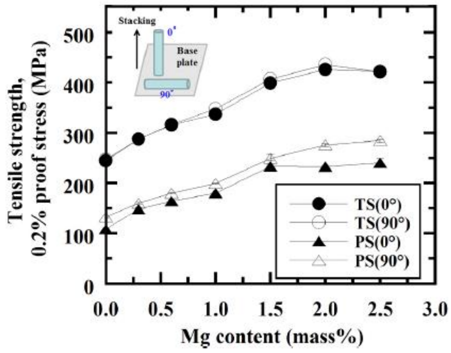
Figure 15. Optical microscopy images on the horizontal (-1) and vertical (-2) planes of the Al–4Si–Mg SLM specimens: (a) Al–4Si, (b) Al–4Si–0.3Mg, (c) Al–4Si–0.6Mg, (d) Al–4Si–1.0Mg, (e) Al–4Si–1.5Mg, (f) Al–4Si–2.0Mg, and (g) Al–4Si–2.5Mg.



Source: (KIMURA, 2019)

Kimura (2019) also reported that the yield tensile strength and ultimate tensile strength significantly increases with the addition of higher percentages of Mg, as presented in figure 16. It was ascribed to factors like the solubility of Mg on the α-Al matrix and the grain refinement. Increasing the content of magnesium also increase the porosity of the Al-4Si-*X*Mg alloys. This was attributed to the gas pores generated by the evaporation of Mg. Specimens with less than 2wt.% of Mg presented relative densities of more than 99.5%.

Figure 16. Ultimate tensile strength (TS) and yield tensile stress (PS) in the Al–4Si–Mg SLM specimens fabricated under the optimum processing conditions: Laser power (200 to 370W) and Scanning Speed (400 to 3400 mm/s).



Source: (KIMURA, 2019)

Park (2021), by evaluating the AlSi10Mg via selective laser melting, reported high mechanical properties obtained by this process. The Al-Si-Mg samples were also heat treated by two different methods: T6 heat treatment and direct aging (DA). Treating the alloys with DA demonstrated to be effective to enhance the tensile properties of the samples. The T6 heat treatment decreased the mechanical properties of the alloy, reaching values below those related to the as-built condition, as can be seen in Table 1.

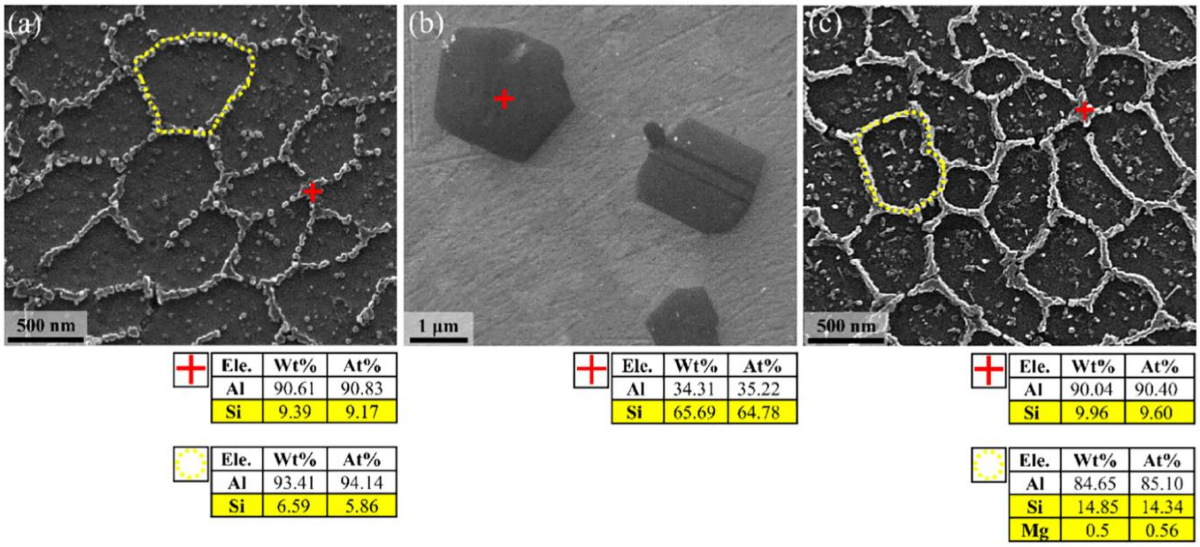
Table 1. Tensile properties of as-built, T6 and DA alloys.

	Y·S [MPa]	U.T.S [MPa]	Elongation [%]
As-built	263.6	448.0	9.8%
T6	180.3	241.7	9.6%
DA	310.2	451.7	6.2%

Source: (Park, 2021)

By examining Figure 17 and Table 1 is possible to make a comparison between the achieved microstructures and the respective mechanical properties values for each condition. The SLM process itself produced a refined microstructure containing eutectic Si, on the as-built alloys. A higher fraction of Si nanoprecipitates can be seen on DA-treated samples, proving the efficiency of this treatment. However, T6 heat treatment coarsened the microstructure of the samples, decreasing their properties (PARK, 2021).

Figure 17. SEM images showing the microstructures of AlSi10Mg alloys; (a) as-built alloy, (b) T6 heat-treated alloy and (c) Direct aging (DA) treated alloy.



Source: (Park, 2021)

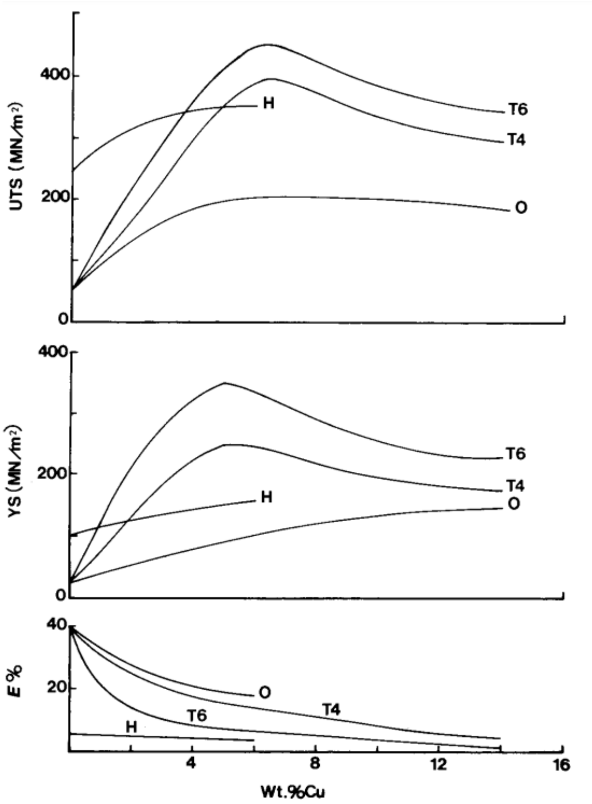
Marola et al. (2018) reported a comparison between rapid solidification techniques, evaluating the obtained microstructures in order to identify processing effects on the resulting microstructures. By evaluating copper mold casting (CMC), melt spinning (MS), and selective laser melting (SLM) samples, it was demonstrated that SLM presented finer microstructures and Si morphology.

By comparing the aforementioned studies is possible to infer that the AlSi10Mg is the most known and suitable alloy used on AM processes, once its properties and solidification mechanisms allow it to perform well on fast cooling processes.

4.1.3 Cu influence on Al-Si alloys

Copper already has its uses in many industries as a component of Al alloys and is commonly added to it to improve the strength at low temperatures, by precipitation heat treatments, or through the formation of compounds with other elements like manganese, nickel, or iron, at high temperatures, and also the creep resistance. However, such an increase in mechanical properties decreases the electrolytic potential and the corrosion resistance of the alloy. Copper-bearing alloys, when age-hardened maybe susceptible to stress or intergranular corrosion, as demonstrated by (MONDOLFO, 1976). As shown in figure 18, ultimate tensile strength (UTS) and yield strength (YS) presents continuous improvement as the copper content increases until about 5.7 wt.% Cu, but the ductility decreases with the increase of Cu content. Nonetheless, strength and mainly ductility strongly depend on whether the copper is on a solid solution, and due to the complex thermal history that parts go through during AM process it may be hard to control this occurrence.

Figure 18. Mechanical properties of aluminum-copper alloys as a function of copper content. H = work-hardened; O = annealed; T_4 = quenched and naturally aged; T_6 = quenched and artificially aged.



Source: (MONDOLFO, 1976)

When it comes to the Al-Si-Cu alloys system, no ternary compound is formed, coexisting in equilibrium only $CuAl_2$ and Si. Copper slightly reduces the thermal expansion coefficient of aluminum, and silicon additions improve this effect. Al-Si-Cu have increased fluidity by adding of Si when compared to Al-Cu alloys. Moreover, adding Cu to Al-Si alloys does not improve their thermal conductivity, so it does not differ from other Al alloys. The copper content also improves the castability on Al-Si-Cu alloys, the machinability decreases severely, though (DARLAPUDI, 2016). It is critical to understand the effects of alloying elements on Al alloys so it would be possible to develop optimized compositions that, combined to optimized processing parameters, will fit most to the additive manufacturing processes.

4.1.4 Ni influence on Al-Si alloys

Nickel is usually found as a minor constituent in Al alloys, and is commonly added to Al-Cu alloys to which it promotes high strength at high temperatures and added to Al-Fe alloys it improves the corrosion resistance on high pressure steams environments. Moreover, nickel has a limited grain refinement effect on Al alloys that is caused by hindering of grain growth process much than nucleation processes. On ternary alloys based on the Al-Si system, nickel has just little effect on the strength at room temperature, although it increases the hardness at high temperatures (VASUDEVAM, 1989).

The studies on Al-Si alloys with the addition of nickel processed by additive manufacturing processes are very recent. As such, Ni is promising as an alloying element to AM, as reported by (AVERSA, 2017) when comparing an Al-Si-Ni alloy to the most used Al alloy on additive manufacturing nowadays: Al-10Si-Mg. The same optimized parameters reported by (KEMPEN, 2014) to process Al-10Si-Mg alloys were used on the Al-Si-Ni alloys: Laser Power (170 to 200 W) and can speed (700 to 1400 mm/s).

In this work AVERSA et. al related the level of porosity found on the samples with the volumetric energy density (VED) in order to identify the optimal parameter that produces dense parts with the minimum energy. It was found a minimum value of VED in which denser parts could be produced. Consequently, these samples were used to the next evaluations. Equation 1 shows the equations used to obtain VED values, where: laser power (P), scan speed (v), hatching distance (h), and layer thickness (d).

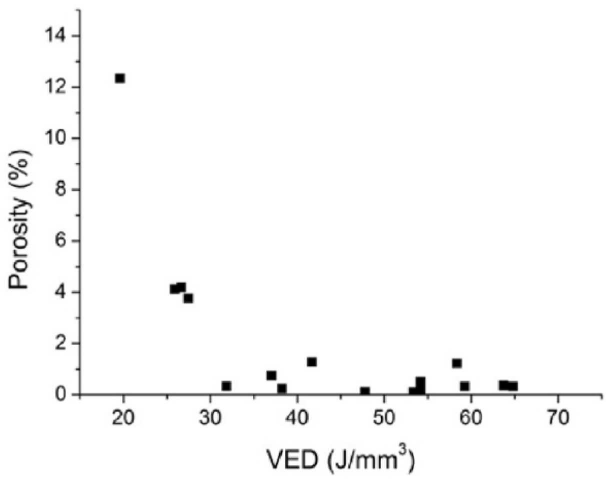
Equation 1. VED equation

$$VED = \frac{P}{vhd}$$

Source: (AVERSA, 2017)

Fig. 19 shows the obtained levels of porosity on the samples where values of VED higher than 50 J/mm³ presented stability on producing dense parts. Below these values the final density of parts is unstable and with VED less than 30 J/mm³, pieces tend to be much porous and suffer from a reduction in their mechanical properties.

Figure 19. Porosity values of the Al-Si-Ni samples were produced with different VED values.



Source: (AVERSA,2017)

The effects of Ni addition in rapidly solidified SLM samples were investigated through hardness as well. Table 2 presents values of Brinell hardness and Vickers micro-hardness for some samples having similar compositions processed by different methods. The Al-Si-Ni alloy presented the higher hardness values among the presented alloys, overcoming the Al-Si10-Mg, also processed by SLM. Such difference was attributed to the different grain sizes between samples, with the finer grains being obtained via selective laser melting, due to the rapid solidification nature of the process.

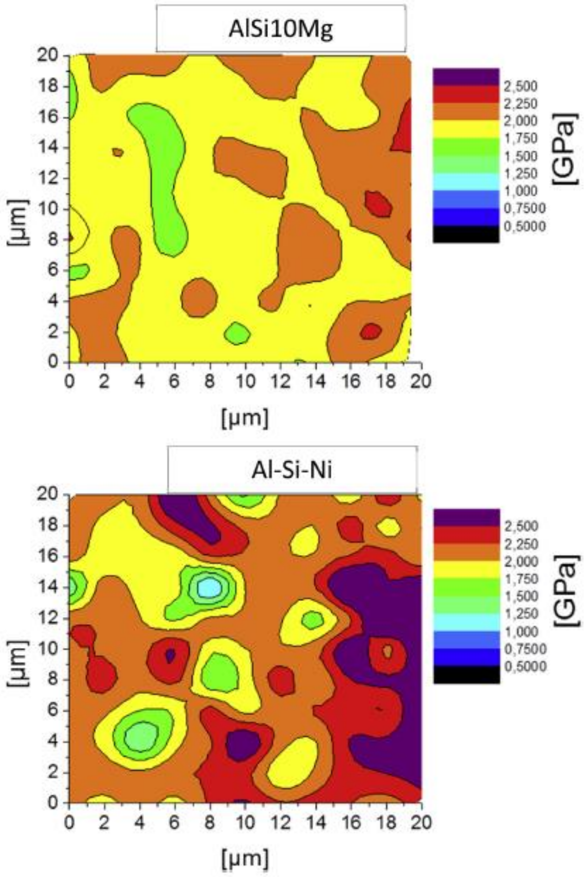
Table 2. Brinell and micro-Vickers hardness values for the Al-Si-Ni and Al-Si10-Mg alloys compared with literature data regarding melt-spun and as-cast alloys with similar composition.

Composition	Technology	HB		HV	
		Value	St. Dev.	Value	St.Dev.
Al–Si–Ni	SLM	158.7	3.0	179.5	3.0
AlSi10Mg	SLM	128.6	1.9	135.0	0.9
Al–Si12.5-Ni1 [38]	Melt spun	–	–	139.0	9.3
Al–Si12.5-Ni1 [38]	As cast			75.5	5.2

Source: (AVERSA,2017)

Hardness maps, presented on fig. 20, were built showing values of nano-hardness for each microstructural region. In the Al-Si10-Mg alloy, the highest nano-hardness value was recorded in regions where a finer microstructure was observed, with values around 2.4 GPa. The Si segregated at the boundaries of α-Al dendrites implied an increase in local hardness. The Al-Si10-Mg alloy sample presented a more homogeneous hardness along with the microstructure. The Al-Si-Ni alloy sample presented much higher values for hardness in some regions, reaching 3.0 GPa, although in other zones the nano-hardness was observed to be around 2.2 GPa. This effect and increase on hardness for the Al-Si-Ni samples was attributed to the Al_3Ni precipitates that were identified on regions where the highest hardness values were measured.

Figure 20. Nano hardness maps obtained for the rapid solidified AlSi10Mg and Al-Si-Ni alloys.



Source: (AVERSA,2017)

4.1.5 Zn influence on Al-Si alloys

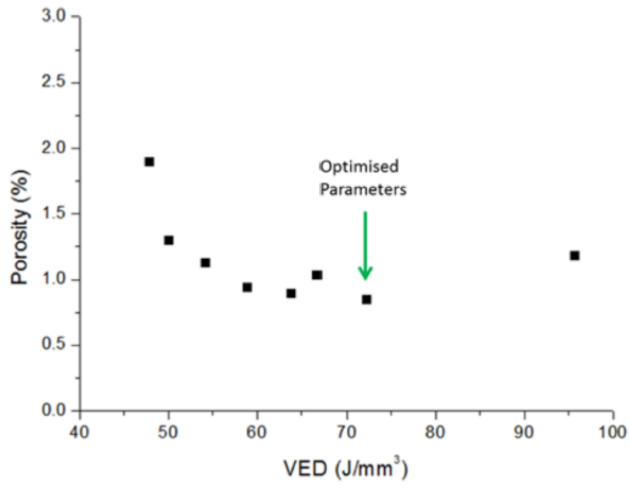
Al-Zn alloys were those to be first developed as Al-based alloys for applications. However, their use was reduced with the development of Al-Cu and Al-Si alloys. Al-Zn alloys, without the addition of other elements present high susceptibility for hot cracking and corrosion, so adding elements to improve their properties is necessary. There are just a few papers with topics evolving Al-Si-Zn alloys and additive manufacturing, being most of these works concerning Al-Zn alloys with the addition of other elements like magnesium and copper (VASUDEVAM, 1989).

There are two papers that will be discussed on this topic, the first one reported the characterization of an Al-10Si-Mg alloy mixed to a 7075 commercial alloy to produce a high strength Al-Si-Zn-Mg-Cu by laser powder bed fusion (LPBF). Another study reported the characterization of an Al-Zn-Mg-Cu alloy produced by Wire Arc additive manufacturing. It is possible to make a comparison between these two studies and discuss some relevant issues.

Al-Zn alloys do not show suitable properties to most of the applications, so adding other elements to improve them is desirable. Aiming at that purpose (AVERSA, 2018) reported an Al-Si-Zn-Mg-Cu alloy, named “50% 7075”. In this work, some important properties for additive manufactured parts, like porosity, hardness, yield strength (σ_y) and ultimate tensile strength (UTS) were evaluated on either as built or heat-treated parts.

In order to evaluate porosity and be able to make a comparison with other findings Aversa et al. (2018) (AVERSA, 2018) used the same method as reported in their previous work, using the volume energy density (VED) to correlate with porosity values. VED was calculated with the same equation 1. Fig. 21 shows that the smallest value for porosity was obtained using approximately 70 J/mm³ of VED. In this process the optimized parameters to process Al-based alloys by AM reported by (KEMPEN, 2014) were used. However, none of the samples presented density values higher than 99.2%.

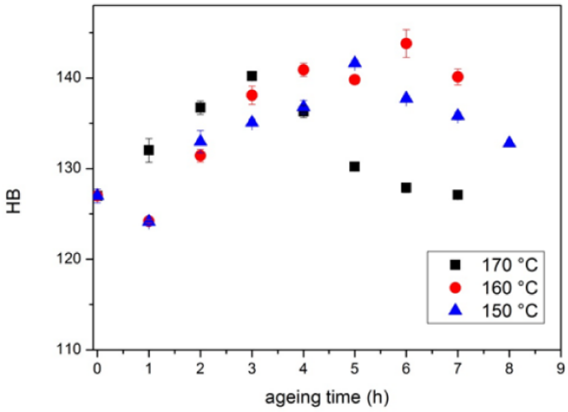
Figure 21. Porosity versus Volumetric Energy Density (VED) plot for the 50% 7075 alloy processed by L-PBF.



Source: (AVERSA, 2018)

Figure 22 shows Brinell hardness measurements obtained to compare the mechanical properties improvements from the different thermal histories. Aging heat treatments presented to be very effective on enhance hardness, reaching the best value for 6h and at 160 ºC, evidencing the precipitation of silicon phase and some Cu-Zn-Si intermetallics.

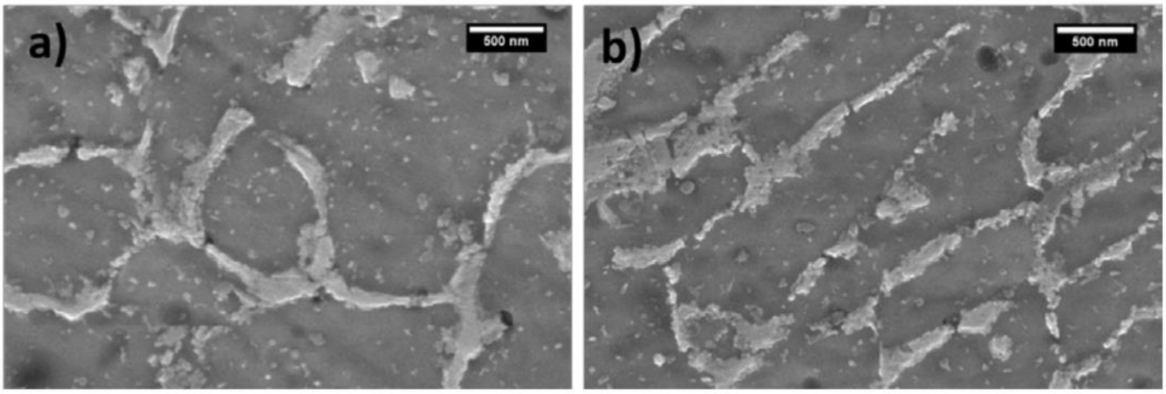
Figure 22. Brinell hardness as a function of the aging time for the 50% 7075 alloy processed by L-PBF.



Source: (AVERSA, 2018)

Figure 23 shows two images obtained by scanning electron microscopy (SEM) comparing two samples with distinct heat treatment times and temperatures. As can be seen, the image “b” presented a higher fraction of precipitates than image “a”. The microstructure is very similar to that found in previous works with the Al-10Si-Mg alloys, constituted by fine α-Al cells (dark grey) surrounded by an eutectic network (bright grey). Furthermore, there are small particles of Si precipitates and intermetallic phases, which became coarse with higher heat treatments times.

Figure 23. FE-SEM micrographs of 50% 7075 alloy built with the optimized L-PBF parameters and aged for (**a**) 3 h at 170 ºC and (**b**) for 6 h at 160 ºC.



Source: (AVERSA, 2018)

Table 3 compares values of mechanical properties between the 50% 7075 samples analyzed, the Al-10Si-Mg alloy (most used on AM) and commercial alloys with similar compositions. It is important to highlight the influence of optimal heat treatments on the final properties of the samples processed by laser powder bed fusion, which improved the mechanical properties for the condition for 6h at 160 ºC. It must be mentioned that the stress-relieving heat treatment (300 ºC for 2h), commonly used on Al-10Si-Mg alloys, is not suitable for this composition, once it decreases severely its properties.

Table 3. Mechanical properties of 50% 7075 samples built with the optimized parameters compared with literature data related to other Al alloys.

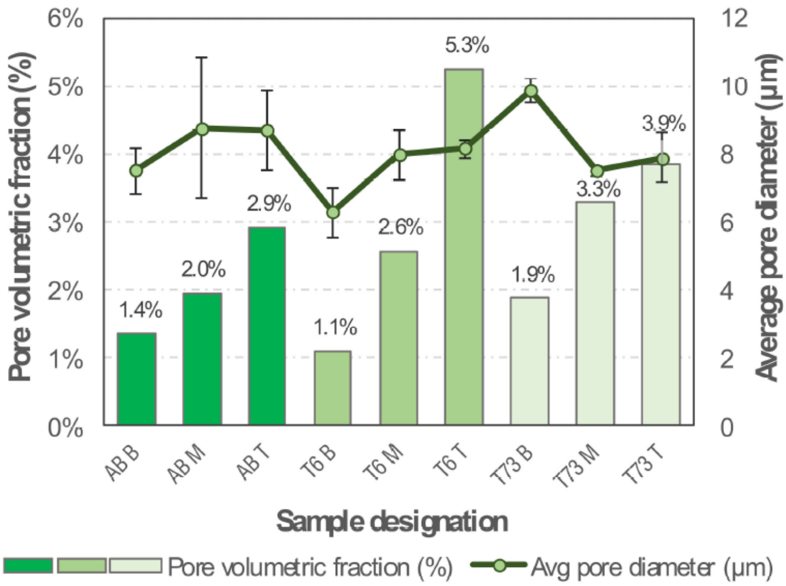
Material	Process	*HB*	*HV*	σ_y (MPa)	*UTS* (MPa)
AlSi10Mg [12]	LPBF	128.6	135.3	250	362
50% 7075	LPBF	126.9	135.8	315	387
50% 7075	LPBF stress relieved	65.0	73.4	-	-
50% 7075	LPBF 3 h 170 °C	140.2	148.8	315	370
50% 7075	LPBF 6 h 160 °C	143.8	152.9	350	415
7075 [11,21]	Extruded and T6	165–169	175.0	406	582
7050 [21]	Cold rolled and T6	150–155	-	430	606
4% Si modified 7075 [11]	LPBF	-	160.0	-	-
4% Si modified 7075 [11]	LPBF and aged (150 °C 6 h)	-	171.0	-	-
7075 + Zr [14]	LPBF and aged	-	~130-140	-	-

Source: (AVERSA, 2018)

Morais (2020) reported the microstructure and properties of an Al-3.58Zn-5.87Mg-0.33Cu alloy processed by wire arc additive manufacturing (WAAM). The samples were divided into three groups: as-built (AB), post T6 heat treated (obtained by a solution heat treatment at 470 ºC for 5 h, followed by rapid cooling in water and a subsequent aging treatment at 120 °C for 24 h) and T73 heat treated (obtained by a solution heat treatment at 470 °C for 5 h, followed by rapid cooling in water and a subsequent two-stage aging treatment at 120 °C for 24 h, and then 160 °C for 24 h.). Each sample had three of its layers evaluated: Bottom (B), middle (M) and top (T). It is important to know how the processing thermal history affect each formed layer.

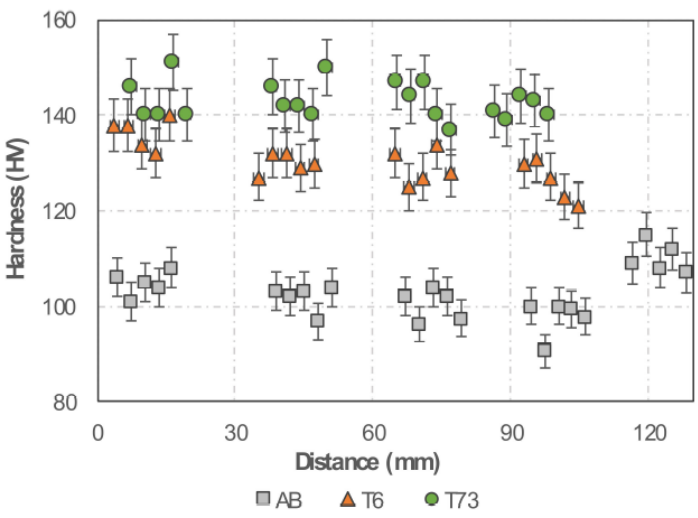
The alloys presented high porosity, and only one layer (T6 B) had approximately 1% pores. The absence of a fully dense part may affect mechanical properties and turn the part vulnerable to cracks.

Figure 24. Pore volumetric fractions and average diameters of pores of the Al-Zn-Mg-Cu alloy samples in the AB, T6 and T73 conditions.



Source: (Morais, 2020)

Figure 25. Evolutions of Vickers hardnesses from the bottom (first layer) to the top for three different conditions (as-built, T6 and T73) of the WAAM processed Al-Zn-Mg-Cu alloy.



Source: (MORAIS, 2020)

As shown on the graphic above, T73 presents a better improvement on hardness for all samples and layers tested. This occurred because of the two-stage aging treatment (T73) which promoted the full formation of precipitates and the development of very fine precipitates, such as $MgZn_2$ and $Al_2Mg_3Zn_3$ (MORAIS, 2020).

By comparing obtained values of hardness for the Al-Si-Zn-Mg-Cu (50% 7075) and Al-Zn-Mg-Cu alloys is possible to note that both present very similar values if considered the optimized heat-treated samples. It may indicate that Si addition does not affect severely the hardness of this alloy system. However, a complementary study comparing these alloys with the same heat treatments is necessary to have a better comprehension of Si influence on hardness. The samples with some Si content present lower porosity values, though. AVERSA (2018) also reports that adding silicon, probably by reducing the solidification range and the coefficient of thermal expansion, strongly reduces the solidification crack occurrences.

Zinc addition improved the alloy's mechanical properties when compared with the results for the Al-10Si-Mg alloy. It appears to be a promising element in the development of alternative aluminum alloys for additive manufacturing.

4.2 Alternative elements added to Al-Si alloys (rare earths and Zr)

Aluminum alloys have been widely used in additive manufacturing processes in the last decade. However, it is still hard to process and just a few limited alloys are considered viable. In this scenario adding new alloying elements emerges like an excellent alternative to improve Al and mainly Al-Si alloys properties and processability. Some of the most common elements used on casting Al alloys were already applied to additive manufacturing processes due to the similarities between them, despite huge differences in the cooling rate severities. Since AM exposes the produced parts to more extreme conditions, it requires different characteristics and needs other post-treatments, such as heat treatments.

The corrosion resistance and mechanical properties of Al-Si alloys are severely affected by the existence and growth of irregular primary silicon phases. In this context, it's extremely necessary to use some mechanisms to refine Si morphology and improve Al-Si system alloys properties. The rapid solidification during the powder productions as well as additive manufacturing processes has become an effective method to refine primary Si morphology, but some more improvement is needed (MAROLA, 2018). The rare earth elements and Zr emerge like good options as alloying elements on Al-Si alloys once they can react with aluminum and form fine precipitates, like Al_3Sc and Al_3Zr, that could have a positive effect as second phase strengthening.

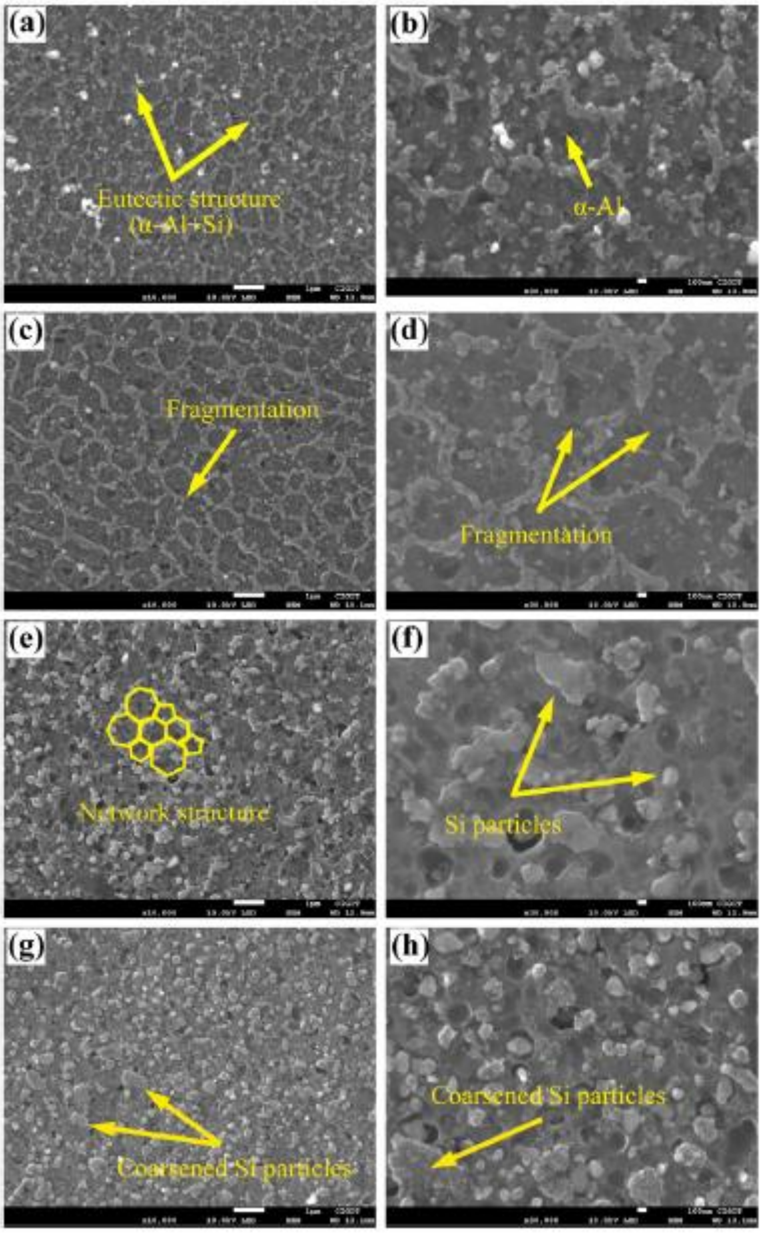
4.2.1 Sc on Al-Si alloys

Scandium is highlighted as a new element to compose Al-Si alloys in the last years, considering that rare earth elements have gained visibility and employment in recent years. Some works reported great improvements on mechanical properties of Sc-modified Al-Si alloys, based on the conclusion that rare earths can enhance aluminum alloys properties precipitation of phases on aging heat treatments (CHEN, 2021). Numerous researches have been carried out on topics related to Sc-modified aluminum alloys, mainly focusing on casting processes, like that reported by (ZHANG, 2019). Despite that, the addition of scandium on additive manufactured Al-Si parts as well knowledge on its effects remain very recent and limited.

In their work CHEN (2021) and coauthors reported the effects of heat treatments on the microstructure and mechanical properties of Sc-modified Al-10Si-Mg alloy (0.26wt.% Sc), produced by selective laser melting. The samples were evaluated in the as-built condition and after some selected heat treatments that presented suitable results thanks to rare earth added on Al-Si alloys.

Results demonstrated that scandium added on Al-10Si-Mg alloy in combination with the fast cooling promoted a refinement on the eutectic microstructure of the samples. As shown in figure 26 of the as-built condition, the microstructure formed a network eutectic structure due to the rapid cooling process provided by selective laser melting. It happened because silicon atoms were pushed out to the solid-liquid interface during the cooling process, leading to an increase of Si concentration on the $\alpha-$Al grain boundaries. It can be seen from “c” and “d” images that the heat treatment on 225 ºC turns the eutectic microstructure more refined when compared to as-built condition. However, in the case of higher temperatures heat treatments the eutectic silicon started to dissolve and grow, resulting in coarser Si. Furthermore, at 275 °C Si eutectic network turns into separated Si particles and at 325 °C it was completely transformed into Si blocks, with a coarser final microstructure.

Figure 26. Microstructures of the AM Sc-modified AlSi10Mg alloy after different heat treatment: a, b As-built; c, d 225 °C for12 h; e, f 275 °C for12 h; g, h 325 °C for 12 h



Source: (CHEN, 2021)

Analyzing table 4, it is possible to compare the influences of the heat treatment conditions on some properties of interest. The coarsening of the eutectic Si is strongly related to the decrease in hardness, tensile strength and elastic modulus. Only the plasticity of the post-treatment alloys presented higher values, once the strengthening effect on grain refinement and eutectic Si network almost disappeared. The Sc-modified Al-10Si-Mg alloys presented better mechanical properties than those observed for the non-modified Al-10Si-Mg alloy (CHEN, 2021).

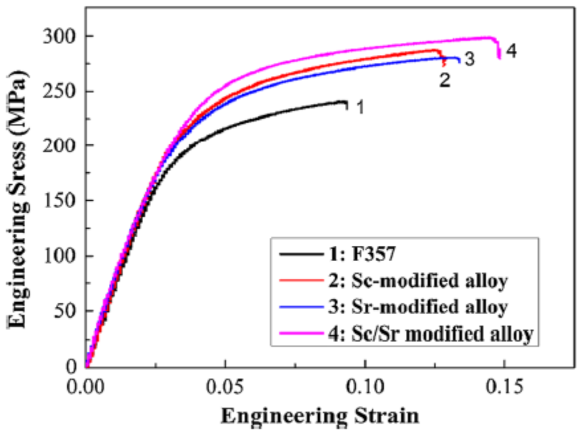
Table 4. Mechanical properties of the AM Sc-modified AlSi10Mg alloy after different heat treatments.

Heat treatment	Microhardness (HV)	Tensile strength (MPa)	Elastic Modulus (GPa)	Elongation (%)	Impact energy (J)
As-built	100 ± 3.4	438 ± 10	33.6 ± 3.2	6 ± 0.2	1.4 ± 0.2
225 °C, 12 h	100 ± 3.5	335 ± 6	3.5 ± 1.1	14.3 ± 0.3	2 ± 0.2
275 °C, 12 h	81.9 ± 2.6	264 ± 9	1.7 ± 0.5	25.8 ± 0.5	4.3 ± 0.5
325 °C, 12 h	78 ± 1.7	208 ± 6	1.4 ± 0.3	30.2 ± 1.2	6 ± 0.5

Source: (CHEN, 2021)

To compare and discuss some results, figure 27 below presents plots of engineering stress and strain for the F357 (Al-7Si- 0.6Mg) commercial casting, Sc-modified and Sr-modified F357 alloys, as reported by XU (2017). The Sc and Sr additions promoted a significant improvement in the evaluated mechanical properties after T6 heat treatments.

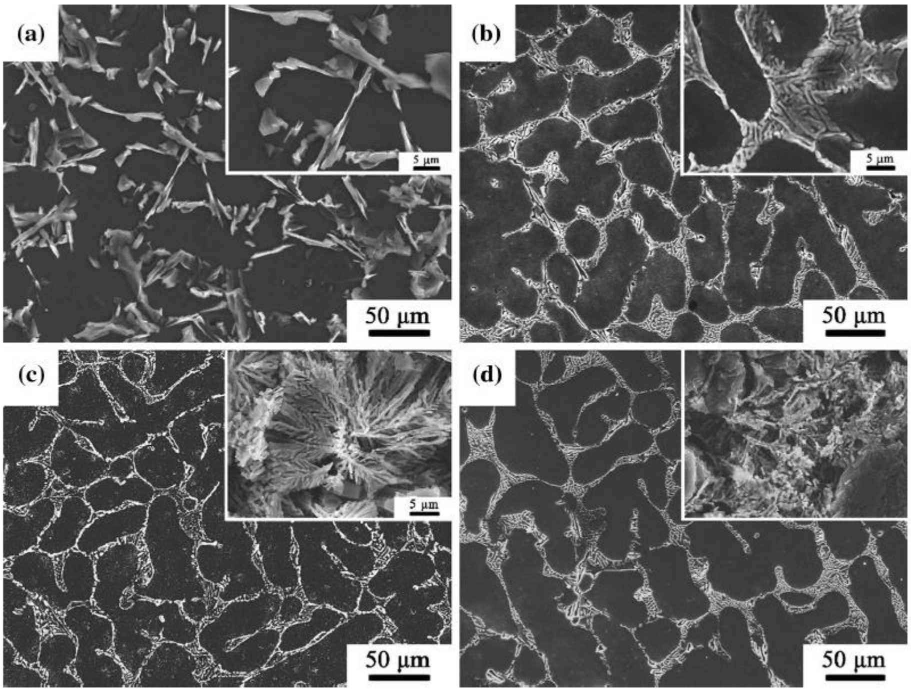
Figure 27. Engineering tensile stress–strain curves of various T6 tempered alloys: F357, F357-Sc and F357-Sr.



Source: (XU, 2017)

Figure 28 shows the found microstructures for all evaluated samples. It can be seen that the F357 alloy presented a platy-like Si morphology while scandium and strontium modified chemistries turned the silicon eutectic into more refined particles, reaching the best refinement when adding Sc and Sr together.

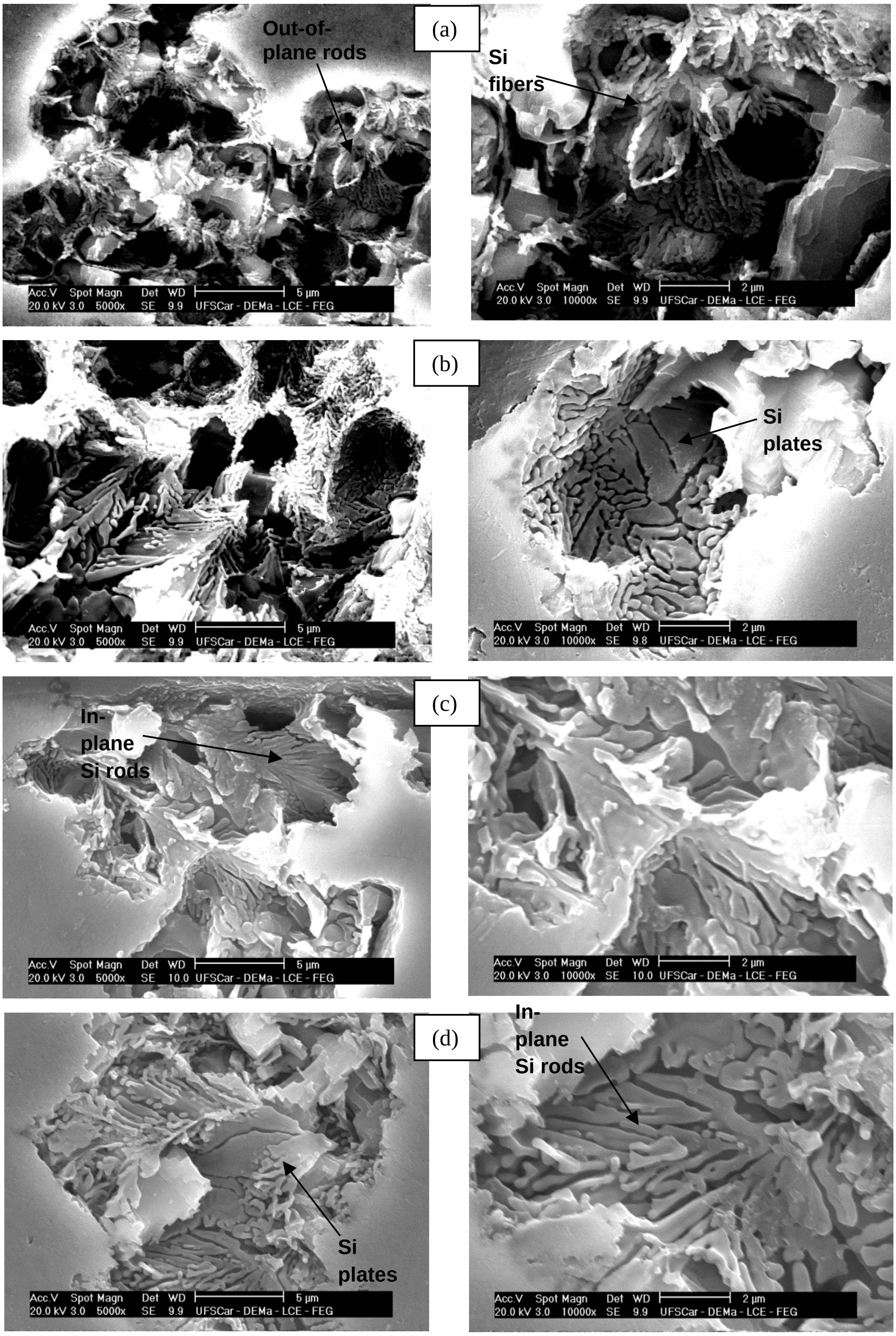
Figure 28. Microstructures of the F357, F357-Sc and F357-Sr alloys: (a) unmodified; (b) 0.4 wt.% Sc; (c) 0.04 wt.% Sr (d) 0.4 wt.% Sc + 0.04 wt.% Sr.



Source: (XU, 2017)

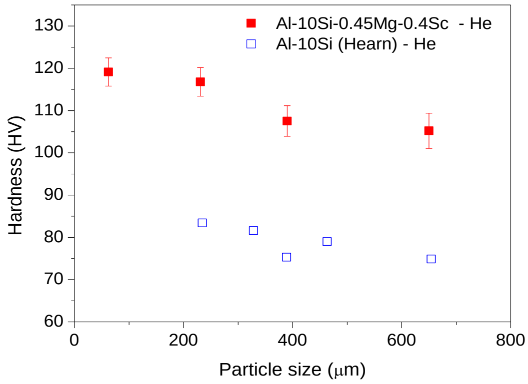
Fig. 29 and 30 show the variations of Si morphology and hardness as a function of particle size of an Al-Si-based alloy produced by impulse atomization (IA). As can be seen, the samples that present Si morphology as a plate-like and in-plane rods (coarser) resulted in lower hardness compared to those having Si morphology as out-of-plane rods and fibers (coral-like).

Figure 29. SEM micrographs of the Al-Si-Mg-Sc powder samples after deep etching revealing the Si morphology: (a) <125 µm, (b) 230 µm, (c) 390 µm and (d) 650 µm;



Source: (Santos Jr, 2021)

Figure 30: Variations in Vickers hardness with the particle size of the Al-10Si-0.45Mg-0.4Sc alloy produced by IA in He, compared to those related to the Al-10Si alloy.



Source: (Santos Jr, 2021)

For the presented reasons it's extremely necessary that adding elements on Al-Si alloys don't result in coarsening the Si particles, otherwise, mechanical properties of the produced parts could be decreased, turning inviable to fit these alloys on high requisites applications, for example as structural parts.

Scandium added on Al-Si-Mg alloys appears to be an excellent option to refine the eutectic network microstructure because of the Al_3Sc particles on the grain boundaries (CHEN, 2021). However, to achieve more understanding of the influence of the rapid cooling and complex thermal history of additive manufacturing processes on these modified alloys, further research needs to be performed, especially regarding to the following topics:

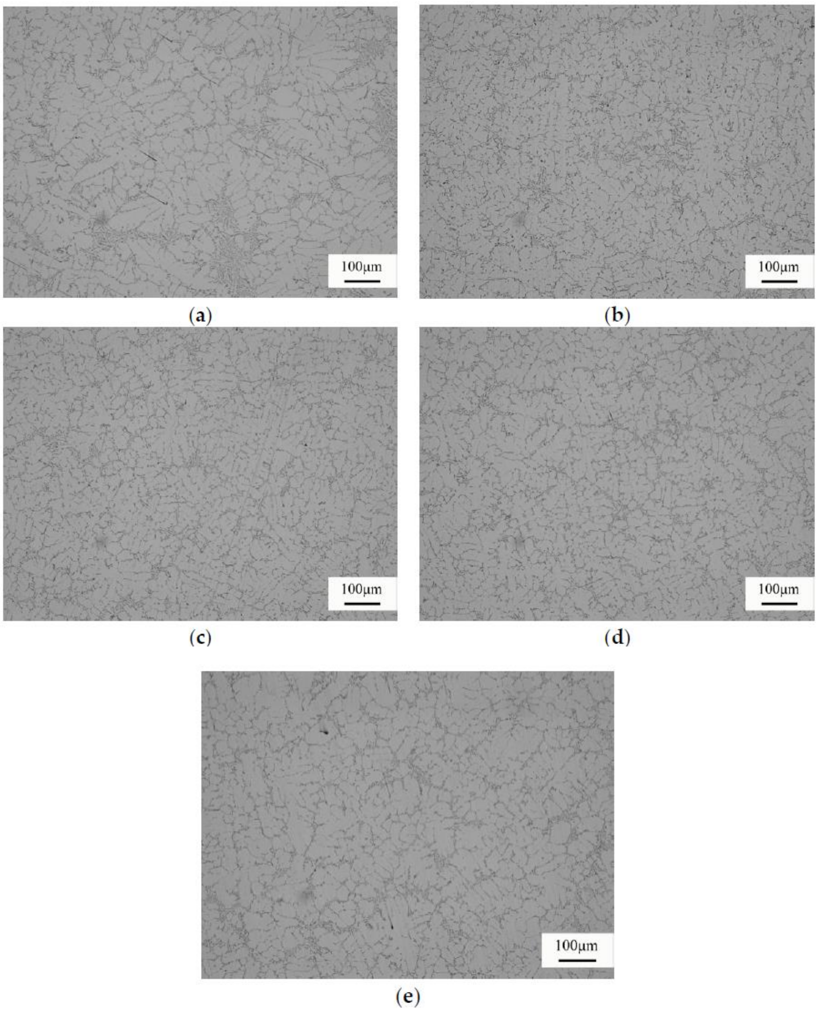
- Compare the impact of Sr addition on Sc-modified Al-Si-Mg alloys manufactured by additive manufacturing technologies with other alloying elements.
- Evaluate effects of more heat treatment conditions for samples processed by AM.

4.2.2 Ce on Al- alloys

Following the same as for other elements of addition, cerium has been barely studied on additive manufacturing processes yet. However, this rare earth element may be promising to this application as will be discusses later. Studies evaluating Ce addition on Al and Al-Si alloys produced by casting will be presented next. Once additive manufacturing processes have many similarities with casting, these works may rather indicate if Ce fits on AM.

Figure 31 shows that cerium addition implied in the microstructural refinement of a 357 alloy. This was because of the formation of an intermetallic compound containing cerium, which was formed thanks to heterogeneous nucleation activity. Comparing to the unmodified 357 alloy with those containing Ce, grain size of the Ce-containing chemistries was reduced on average (WANG, 2020). These authors also reported that the T6 heat treatment applied to the samples improved mechanical properties.

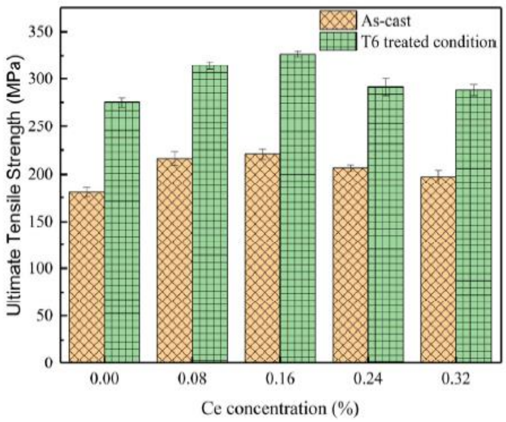
Figure 31. As-cast microstructures for the A357 alloy with different Ce contents (wt.%). (**a**) 0%, (**b**) 0.08%, (**c**) 0.16%, (**d**) 0.24%, and (**e**) 0.32%.



Source: (WANG, 2020)

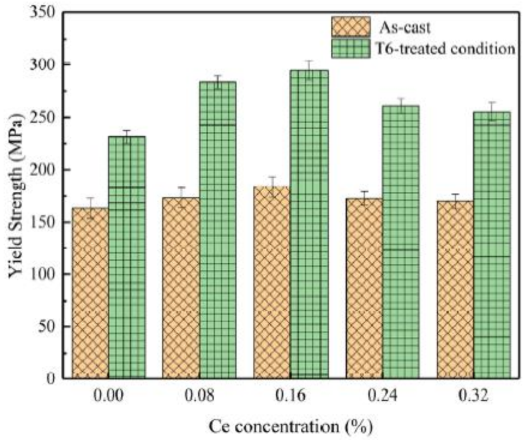
It can be seen in figures 32 and 33 that the tensile and yield strengths of the heat-treated samples showed considerably higher values when compared to the as-cast ones. This is because of the successful precipitation of strengthening phases due to the T6 heat treatment.

Figure 32. Tensile strength values of the A357 alloy with different Ce contents.



Source: (WANG, 2020)

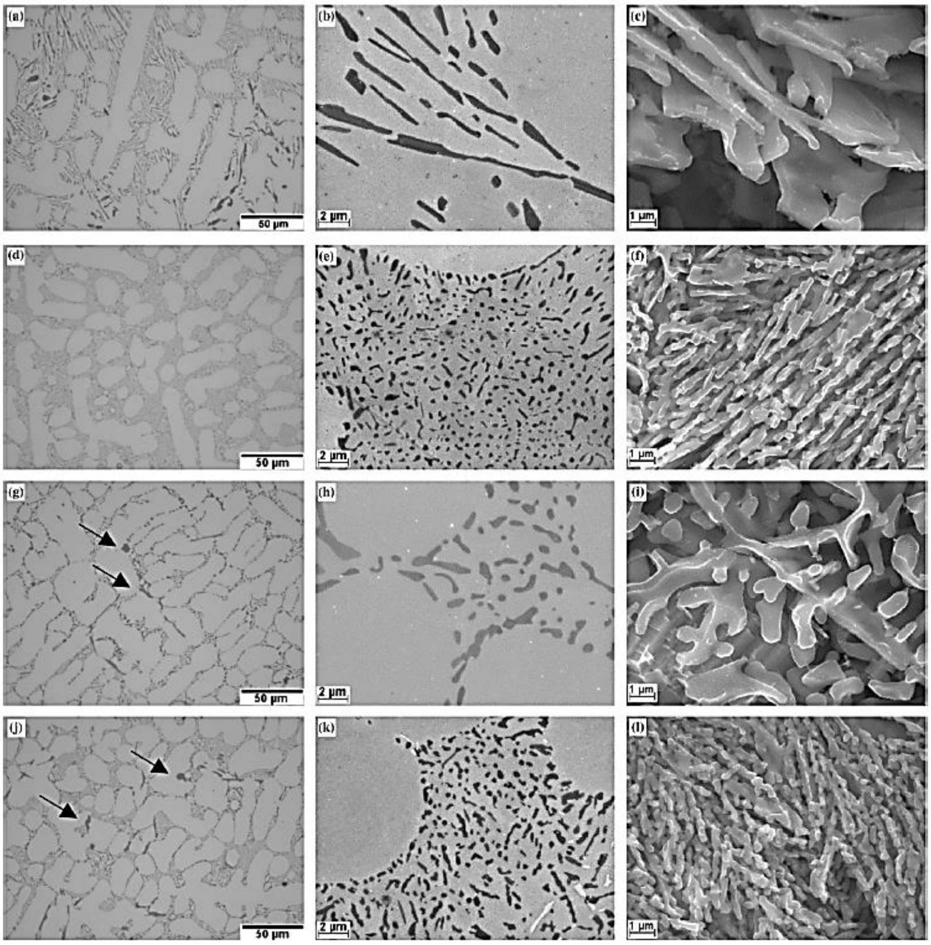
Figure 33. Yield strength values of the A357 alloy with different Ce contents.



Source: (WANG, 2020)

A study by DEGIOVANNI, 2019 evaluated the addition of Ce, Sr and Ce with Sr on Al-Si alloys to understand the effects of these elements on the Si eutectic morphology. As shown on Figure 34 the unmodified alloy was associated with primary Al and eutectic Si morphology in the form of elongated plates. The modified alloys presented a lower average grain size and a refined silicon morphology. Sr and Ce+Sr additions need to be highlighted once these compositions generated a fine fibrous structure for the eutectic Si morphology, which may improve the mechanical properties, according to the literature.

Figure 34. Optical microscopy images (a, d, g, j) and scanning electron microscopy images on unetched (b, e, h, k) and etched (c, f, i, l) samples of Al-Si (a–c), Al-Si-Sr (d–f), Al-Si-Ce (g–i), and Al-Si-Ce-Sr (j–l) alloys.

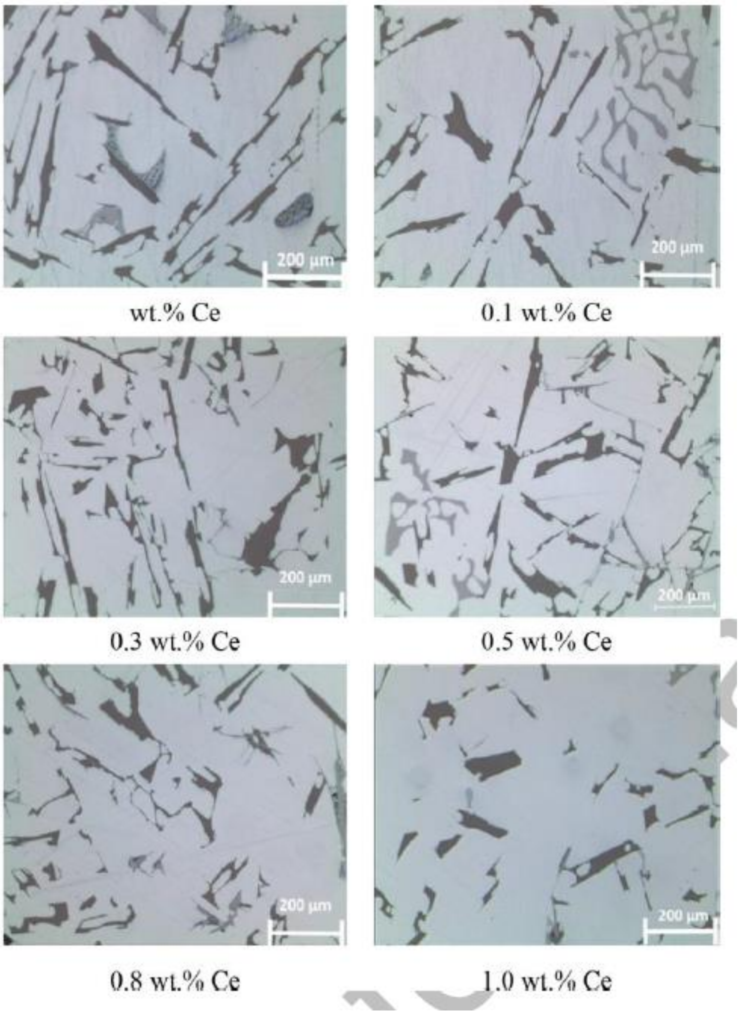


Source: (DEGIOVANNI, 2019)

WANG, (2020) demonstrated that suitable results could be attained when adding Ce to A357 casting alloys as DEGIOVANNI (2019) did. Both studies reported considerably microstructural refinement of the α-Al and eutectic Si morphologies by adding Ce and/or Sr. It is important to mention that the T6 heat treatment was also relevant and could be promising for applying on additive manufacturing produced parts.

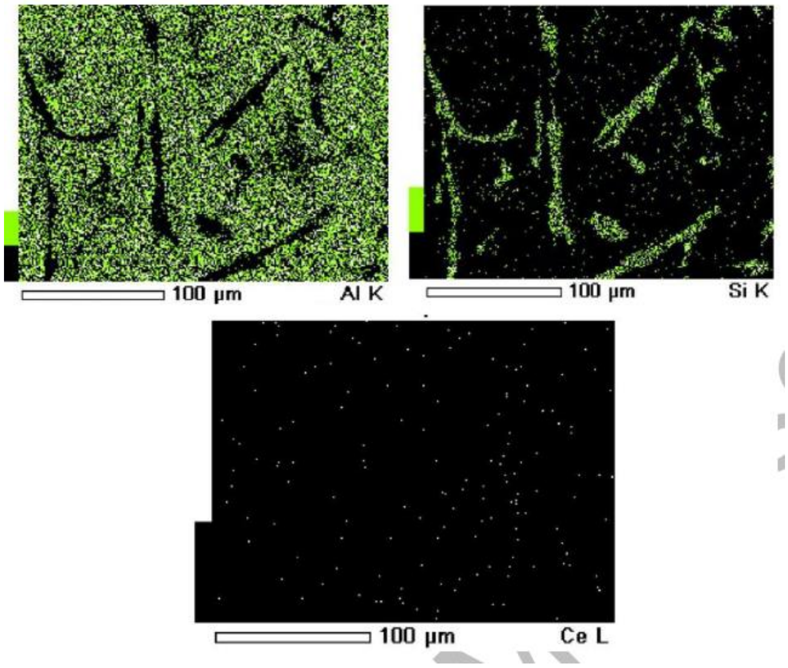
Ahmad (2015) reported that Ce additions up to 1wt.% may act as a refiner for the Al-Si alloy by decreasing its nucleation and growth temperatures. Increasing Ce content also decreased Si particle size, altering its morphology. Cerium additions above 0.3wt.% reduced the formation of eutectic Al-Si phases, as seen comparing Figures 35 and 36. Al-Si alloys with Ce content above 0.5wt% demonstrated a significant decrease in the solidification temperature range. Adding Ce also produced Al-Si-Ce intermetallics, which affected the modification degree of the base alloy. Moreover, AlCu intermetallics, the last phase to be solidified, had its solidification temperature increased with Ce content, changing its morphology to needle-shaped. This analysis reported by (AHMAD, 2015) indicated that Ce content may boost the mechanical properties of Al-Si alloys.

Figure 35. Microstructures of base alloy and Ce-modified alloy samples with (0.1, 0.3, 0.5, 0.8 and 1.0 %wt) additions.



Source: (AHMAD, 2015)

Figure 36. EDS Mapping of the evaluated Al-Si-Ce alloy.



Source: (AHMAD, 2015)

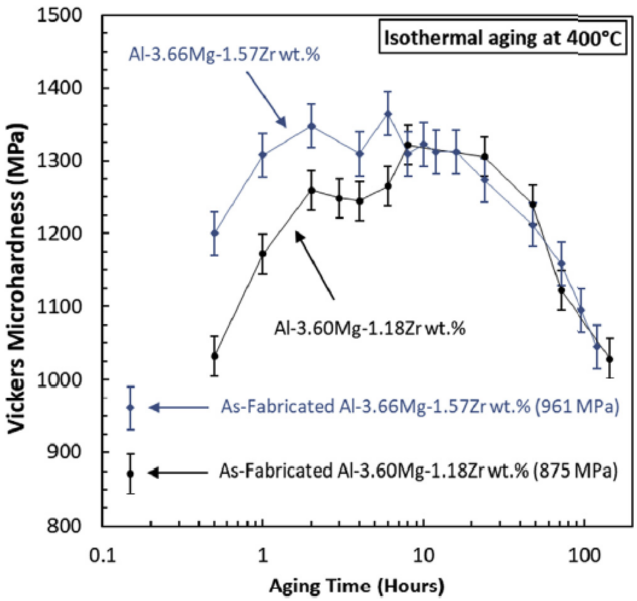
Related to the additions of Ce and/or Sr on Al-Si alloys, more investigation is needed to evaluate their effects on mechanical properties as well the influences on heat-treated samples. The same heat treatment used on previously mentioned works may be suitable for this application.

4.2.3 Zr on Al-Si alloys

Zirconium is promising to be a suitable element to compose aluminum alloys designed for additive manufacturing. However, its application in this field is recent, so there are just a few works relating Zr addition to AM processed parts. To the best of the author's knowledge, none study was found specifically devoted to modification of additively manufactured Al-Si alloys with Zr. The conducted researches have a focus on the microstructure and mechanical properties of Al-Mg(-Zr) alloys. These compositions are already applied on additive manufacturing, which may indicate a path to the next works on Al-Si alloys, including Zr addition. CROTEAU, (2018) evaluated two gas atomized alloys with similar compositions (Al-3.60Mg-1.18Zr and Al-3.66Mg-1.57Zr) that were processed by selective laser melting and then heat treated.

CROUTEAU (2018) reported improvements on many mechanical properties of the samples due to Zr presence. Heat-treated parts showed superior properties compared to the as-built ones. There were some optimal parameters for selective laser melting for producing the better parts: Laser power of 200W, and scanning speed of 200 to 800 mm/s. Other parameters resulted in a severe decrease of mechanical properties due to concurrent mechanisms like grain growth, coarsening of the microstructure, and relieving of internal stresses.

Figure 37: Hardness evolution upon isothermal aging at 400 °C of Al-3.60Mg-1.18Zr wt.% (black circles) and Al-3.66Mg-1.57Zr wt.% (blue diamonds).



Source: (CROTEAU, 2018)

Table 5: Average tensile properties for two Al-Mg-Zr alloys processed by laser powder bed fusion AM in the as-fabricated and peak-aged conditions

As-Fabricated		
Alloy Composition (wt.%)		Yield Strength (MPa)
Al-3.60Mg-1.18Zr	Z	221 ± 1
	XY	220 ± 3
Al-3.66Mg-1.57Zr	Z	282 ± 8
	XY	290 ± 6
Post Heat Treatment		
Al-3.60Mg-1.18Zr	Z	350 ± 7
	XY	353 ± 5
Al-3.66Mg-1.57Zr	Z	349 ± 15
	XY	365 ± 11

As-Fabricated			
Alloy Composition (wt.%)		Ultimate Tensile Strength (MPa)	Elongation (%)
Al-3.60Mg-1.18Zr	Z	287 ± 1	25.6 ± 0.8
	XY	292 ± 2	29.0 ± 1.6
Al-3.66Mg-1.57Zr	Z	332 ± 2	24.0 ± 1.0
	XY	329 ± 3	25.2 ± 1.8
Post Heat Treatment			
Al-3.60Mg-1.18Zr	Z	382 ± 5	17.1 ± 2.0
	XY	386 ± 3	18.6 ± 0.9
Al-3.66Mg-1.57Zr	Z	383 ± 5	19.5 ± 4.4
	XY	389 ± 4	23.9 ± 4.4

Source: (CROTEAU, 2018)

As reported by (CROUTEAU, 2018) all the samples precipitated phases that improved their mechanical properties, as seen comparing figure 37 and table 5. Magnesium act like a solid-solution strengthener and zirconium creates two types of Al_3Zr that act like grain refinement agent, nucleating thin aluminum grains, and strengthening the alloy, leading to values about 40% higher when compared to the as-building samples.

5. COMPARATIVE ANALYSIS FOR AM PARTS

A clear comparison among all data presented on this study regarding to AM parts has been summarized in Table 6. By evaluating this table is possible to identify the heat treatment conditions and their effects on mechanical properties of the aforementioned alloys. The impact of adding alloying elements also became clear.

Direct aging showed better results when compared to other heat treatments. This increase on mechanical properties is due to the absence of a solutionizing step on aging. Discarding solutionizing allows DA to maintain the refined eutectic Si particles as well as generating fine precipitates that enhance the alloy properties. Annealing heat treatments resulted in decreasing some mechanical properties, while increasing the alloy ductility. Zn and Ni elements appear to the most promising in order to improve yield strength, ultimate tensile strength, and hardness.

Table 6. Alloys, conditions and mechanical properties of additively manufactured samples considering all studies evaluated in the present contribution.

Composition	AM Process	Heat Treatment	Y.S. (Mpa)	U.T.S. (Mpa)	HV
Al-4Si-2Mg	SLM	None	280	440	N/A
Al-10Si-Mg	SLM	DA 6h 180 °C	310.2	451.7	N/A
Al-10Si-5.1Ni	SLM	None	N/A	N/A	179.5
Al-10Si-Mg	SLM	None	250	362	135.8
Al-Si-Zn-Mg-Cu	SLM	DA 6h 160 °C	350	415	152.9
Al-5.87Mg-3.58Zn-0.33Cu	WAAM	T73	345	480	155
Al-9.9Si-0.53Mg-0.26Sc	SLM	None	N/A	430	100
Al-9.9Si-0.53Mg-0.26Sc	SLM	Annealing 12h 325 °C	N/A	208	78
Al-3.66Mg-1.57Zr	SLM	None	290	329	98
Al-3.66Mg-1.57Zr	SLM	Aging 6h 400 °C	365	389	138.8

Source: (Santos Jr, 2021)

6. CONCLUSIONS

This work evaluated many different elements that were used on additive manufacturing processes of Al-Si based alloys, as the elements that could fit in this application. The low number of published works on additive manufacturing in modified Al-Si alloys made it necessary to evaluate works with alloys produced by different processes, mainly casting. Selective laser melting remains still the best option for producing Al-Si based alloys nowadays due to its intrinsic high cooling rates, that generates parts with finer microstructures and suitable mechanical properties, as for building higher precision parts than other AM techniques. The process window proposed by Kempen (2014) suits well to many Al-Si alloys, so is desirable to maintain these parameters in future works. By comparing mechanical properties of Al-Si alloys with the evaluated ternary alloys was possible to conclude that Ni additions allied to AM processes made possible to achieve an improvement of about 110% on hardness. Direct aging (DA) and two-stage aging presented to be the most effective heat treatments evaluated, refining the microstructure and altering positively the Si morphology. DA enhanced yield strength by 17% and two-stage aging improved hardness by 48%, when comparing treated to as-built alloys. Small strontium additions combined with cerium or scandium presented to be desirable in order to obtain finer microstructures produced by AM.

Future works should focus on evaluating nickel additions combined with rare earths, especially cerium. Ni and Zn significantly enhanced the hardness, while Ce reduced the solidification range. Therefore, adding Zn, Ni and Ce as alloys elements on Al-Si alloys designed for AM may result in some improved microstructures, with increased mechanical properties, and producing high-quality parts.

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