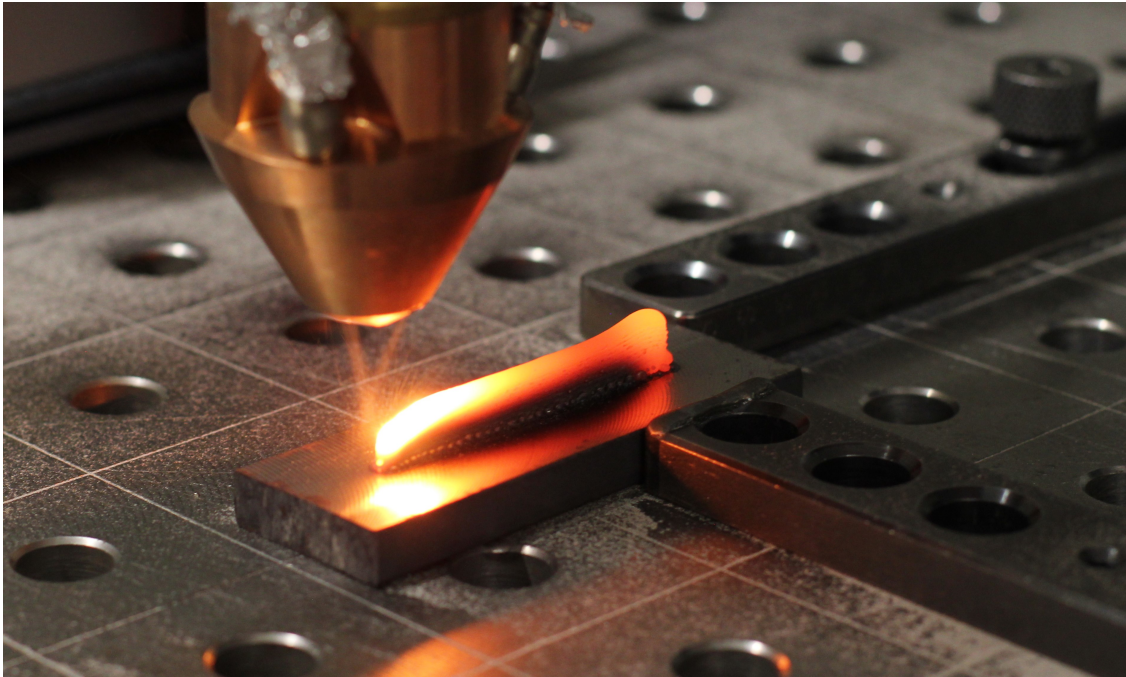




CHALMERS
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Materials for Additive Manufacturing by Direct Energy Deposition

Master's thesis in Materials Engineering

MATTIAS MIEDZINSKI

MASTER'S THESIS 2017:205

Materials for Additive Manufacturing by Direct Energy Deposition

Identification of material properties that can have an influence on
the building process or the resulting component properties

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Gothenburg, Sweden 2017

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Abstract

The interest in additive manufacturing techniques such as direct energy deposition has increased recently. However, the number of alloys that are available for the various processes is very limited. A better understanding of process parameters and material behavior facilitates the design of new materials that can meet future requirements.

This work investigates materials for direct energy deposition, where the focus is on material parameters such as thermal expansion coefficient, thermal conductivity, viscosity and wetting of the materials during printing and examining how these parameters affect the building process. Criteria were identified and used to select materials suitable for direct energy deposition. The selected materials investigated were 316L, which is austenitic stainless steel and 316L HSi which is a variant of 316L with higher silicon in order to improve fluidity of melt pool. These two materials have the same levels of thermal expansion and thermal conductivity but they differ in viscosity of the melt. To have a different material with different properties in thermal expansion and thermal conductivity, one NiFeCrSi (1530-CE) alloy was selected.

The materials were evaluated by manufacturing a single-track wall, consisting of 20 deposited layers for each build. Each material requires its own set of optimum process parameters. Therefore, optimum process parameters for each material were identified so that builds with minimum amount of defects could be manufactured. These samples were then evaluated with using metallography, light optical microscopy and scanning electron microscopy with electron backscattering diffraction imaging.

Single-track walls could be built with 316L, 316L HSi and 1530-CE, without any significant defects.

Keywords: Additive manufacturing, Direct energy deposition, Stainless steel, Nickel alloys

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A handwritten signature in dark ink, appearing to read 'Mattias Miedzinski', with a stylized, flowing script.

Mattias Miedzinski, Gothenburg, September 2017

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1

Introduction

Additive manufacturing (AM) is a process where you build a component from a 3D CAD model, that you split model into many 2D layers. Then the 3D printer builds the component layer by layer. AM has become attractive, because of its potential and benefits, such as design freedom and short production times. The objective of this Master thesis is to investigate how material properties interference the ability to build structures using direct energy deposition (DED).

There are many AM technologies, but the four most common methods using metal powders can be divided into two families, powder bed and blown powder techniques.

Powder Bed Fusion Technology is a technique where a layer of metal powder is spread on the previous layer and a heat source is melting or fusing the metal powder. In Powder Bed Fusion family there are mainly three methods.

- Binder Jetting (BJ) is a method where an inkjet jets binder onto the powder bed in order to glue the powder particles together. Then the finished printed component is sintered in an oven to make the component solid.
- Electron Beam Melting (EBM) is a method where you use an electron beam as a heat source to melt the powder.
- Selective Laser Melting (SLM) is a method where you use a laser as a heat source to melt the powder.

Blown Powder Technology is a technique where the metal powder is deposited on a substrate. A heat source in the form of a laser or an electron beam is used to melt the substrate and the deposited powder. These techniques are mainly called Direct Energy Deposition (DED), Laser Metal Deposition (LMD) or Laser Cladding (LC) [1].

DED is a blown metal powder AM method which uses a focused heat source (typically an electron beam or a laser which in this case has been used in this work) to melt the deposited material on a substrate material and builds three-dimensional objects. It can be used in a similar way for PTA cladding and laser cladding. The difference with this AM process is that the material is melted while you are depositing the powder. Unlike the powder bed fusion process where you add a layer of powder before you melt it [2]. This method is faster, allows larger building volumes and even the waste of material is lower because you will only use the powder to melt to build the component compared with powder bed.

DED has a great potential to build large components within aerospace. However, the area of uses of DED can be divided into three groups:

- Direct additive manufacturing
- Adding of functions or features
- Repairing or remanufacturing

In direct additive manufacturing you build a component from scratch with DED. One such component can be seen in Figure 1.1(a). Adding of functions is where you add features to an existing component. This component may be built with AM or another manufacturing method. This can be seen in Figure 1.1(b), where a spiral is deposited onto a tube. You can use this method to repair components e.g. by building up the worn part. As in figure 1.1(c) where an aerospace part is repaired.

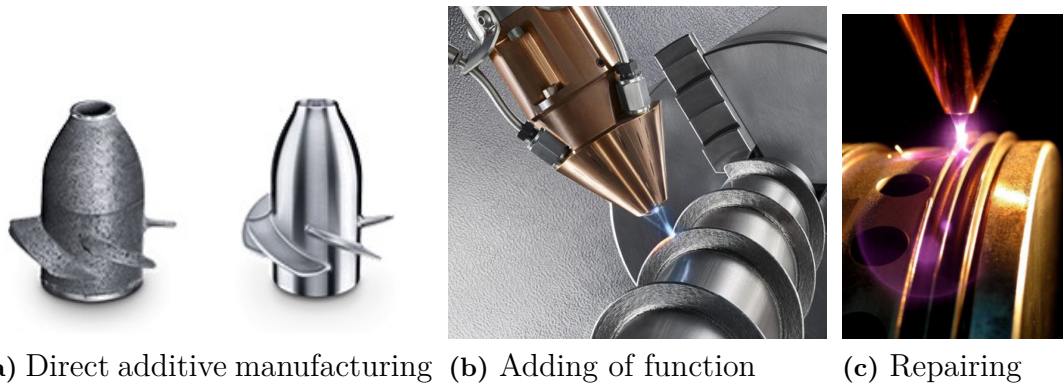


Figure 1.1: The three areas of use of DED

1.1 Background

The easiest way to join (atoms) metallic materials to make a solid 3D component is by forming a liquid which will then solidify and fuse materials together [3]. SLM, LC, DED and (laser) welding are different processes but they have in common that they fuse metallic materials in the same way, forming a liquid that then solidifies in a track. However, studies have shown that you can have different mechanical properties if you manufacture a component with DED or SLM for the same material.

The cooling rate will be at temperatures near the solidification temperature determined by the heat input. The melt pool size and the ability of the surrounding material to transport the heat away from the melt pool region. Within SLM the melt pool size is estimated to be in the micrometer range and for DED the melt pool size is in the millimeter range. However, mechanical properties will not be addressed in this work. This is just something that will have an impact that you must keep in mind. But both SLM DED, LC and (laser) welding have the same main process parameters, that are [4, 5]:

- Laser beam power
- Laser beam diameter
- Powder or wire feed rate
- Scanning speed
- Hatch (x-y) spacing
- Z-increment

These are the most important parameters that will have an influence on the thermal history $T = f(x, y, z, t)$ of the part. This will have an effect on melt pool shape, layer growth and also on the final metallurgical and mechanical properties of the part. Therefore, the material properties should be approximately the same for DED as for welding, LC. But there is a difference in AM process. AM is a uniquely complex process where your component is built by layer-by-layer and the thermal history of a layer may involve multiple solidifications and remelt cycles as well as multiple solid-state phase transformation, during this process [6]. Therefore, an extra weight should be placed on these materials that can handle, multiple solidifications and remelt cycles and multiple solid-state phase transformation.

Effect of layer thickness setting on DED is something to keep in mind when building structures. The single-layers height is influenced by many parameters. According to earlier studies [6], it shows that there is a relationship between the three principal parameters (laser power, powder feed rate, laser scanning speed) and the single-layers height.

According to [4] “Any powder material or powder mixture which is stable in a molten pool can be used for the construction of parts” with DED. Metals that have high thermal conductivities and reflectivity are hard to process, these materials are gold, copper, there are also some aluminum alloys that are difficult to process. Otherwise, most of the materials that do not oxidize as much that the bond between the layers deteriorates can be processable by DED. It is also known that for a successful AM process, the liquid-solid wetting features are critical for DED. Of course, there are lots of other factors that matter also, thermal expansion, shock resistance and phase transformations in the material.

To print a component with good quality requires optimum process parameters and these are material dependent. Therefore, it is important to understand what these material parameters are and what it is that makes some materials more suited for AM by DED than others.

The essence of this thesis is to examine the materials that have a potentiality for DED process. What materials can be easy to process and which materials are difficult to process and create an understanding of why it so.

1.2 Aim

The interest in additive manufacturing techniques such as direct energy deposition has increased recently. The number of alloys that are available for the various

methods is very limited. A better understanding of the requirements on the materials imposed by the methods facilitates design of new materials well adapted to the process in the future.

The aim of this work is to perform detailed investigation by building structures with DED. There are many parameters that can have an effect on building structures. In this work will the focus be on the materials parameters such as thermal expansion, viscosity, thermal conductivity, phase transformation of the material during printing and see how these parameters can have an important effect on building structures. The goal of the thesis is:

- Identify materials parameters that can have an influence on the building process or the resulting component properties.
 - Selecting materials with different (extreme) values of the most important properties.
- Perform simple and more complex builds and determine the influence of the respective material properties on the build process and the resulting component properties.

1.3 Scope

This work will only be done with the DED method that will use a laser as a heat source and the deposited material will be metal powder. Also, materials that will be used are only those found in Höganäs AB's assortment in gas atomized powder.

1.4 Approach to the problem

Today there is already some material for DED. It is important to find the material properties that are important for DED, In order to be able to map various suitable materials that are printable with the DED method. Then a material choice will be made for this work. Therefore, two materials that have similar properties and one that has major differences in properties will be selected to build structures with DED.

Different materials have different optimum process parameters. Therefore one will try to find an optimum process parameter for each material so that they can be compared to each other. Then the materials will be investigated how they behave when building with them. The samples will be evaluated by light optical microscope for investigating porosity and cracks. The microstructure will also be investigated using the light optical microscope (LOM) and electron backscatter diffraction (EBSD). This practice should lead to an understanding of material properties to the ability to build structures using DED.

2

Direct Energy Deposition

Direct energy deposition (DED) can be found by many different names, Laser metal deposition (LMD), Laser engineered net shaping (LENS) and so one. In this report, the method will be called Direct energy deposition (DED). According to ASTM, DED is defined as; “Additive manufacturing process in which focused thermal energy is used to fuse materials by melting as they are being deposited” [7]. Therefore, in this section things like equipment and process parameter will be addressed for DED.

2.1 Equipment

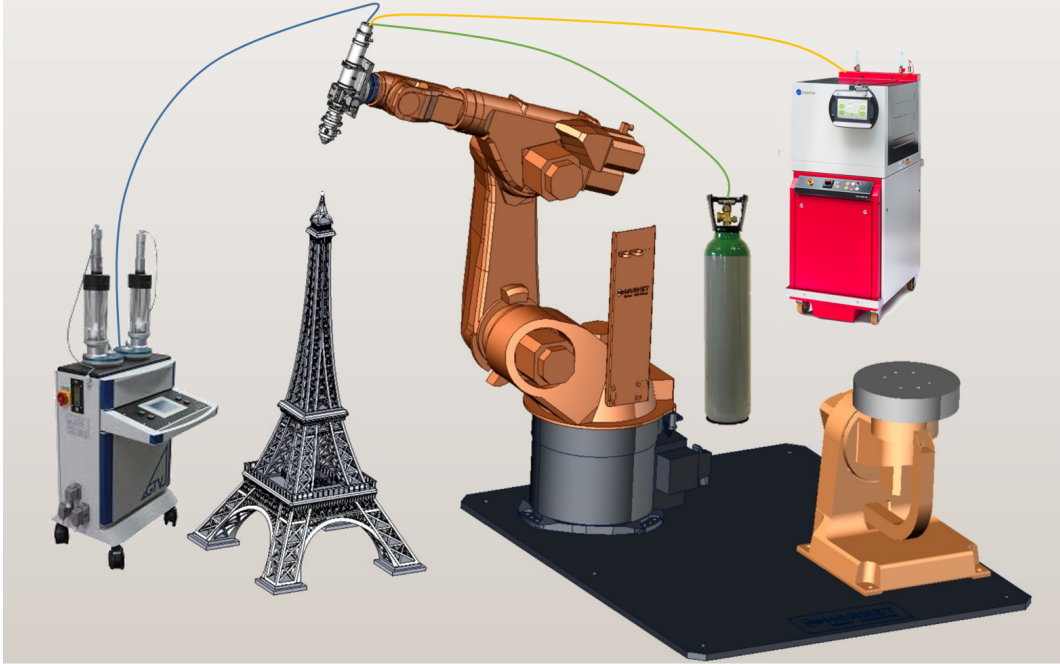


Figure 2.1: DED system with a powder feeder furthest to the left, industrial robot with a nozzle, to the right of the industrial robot shielding gas and a laser source can be seen. An Eiffel tower is visualized to demonstrate the possible building size.

DED equipments are usually custom-made and usually consists of a powder feeder, laser source, shielding gas, powder nozzle and an industrial robot. An overview

2. Direct Energy Deposition

of how such an assembled system can be seen in Figure 2.1. Therefore, an process parameters can normally not be directly transferred between systems. Each material has also its own process parameters, but also all applications and geometry may require special settings. The important parameters in DED are laser power, powder feed rate and track scan speed and laser beam spot size. In the Table 2.1 you can see how the various process parameters affect the different properties [2].

A schematic description on how the powder, laser beam and shield gas is deposited with DED, which creates a melt pool on the workpiece in Figure 2.2(a). And a schematic description of the cross-section of the deposited single track can be seen in Figure 2.2(b). With a corresponding height h , new layer height h_0 , track width w and surface roughness R_{max} . Width w_m and depth d_m it that gets remelted. In this area, you get the remelted bulk area A_m . On this, a new layer is deposited and due to materials surface tension, you will get a circular cross-section.

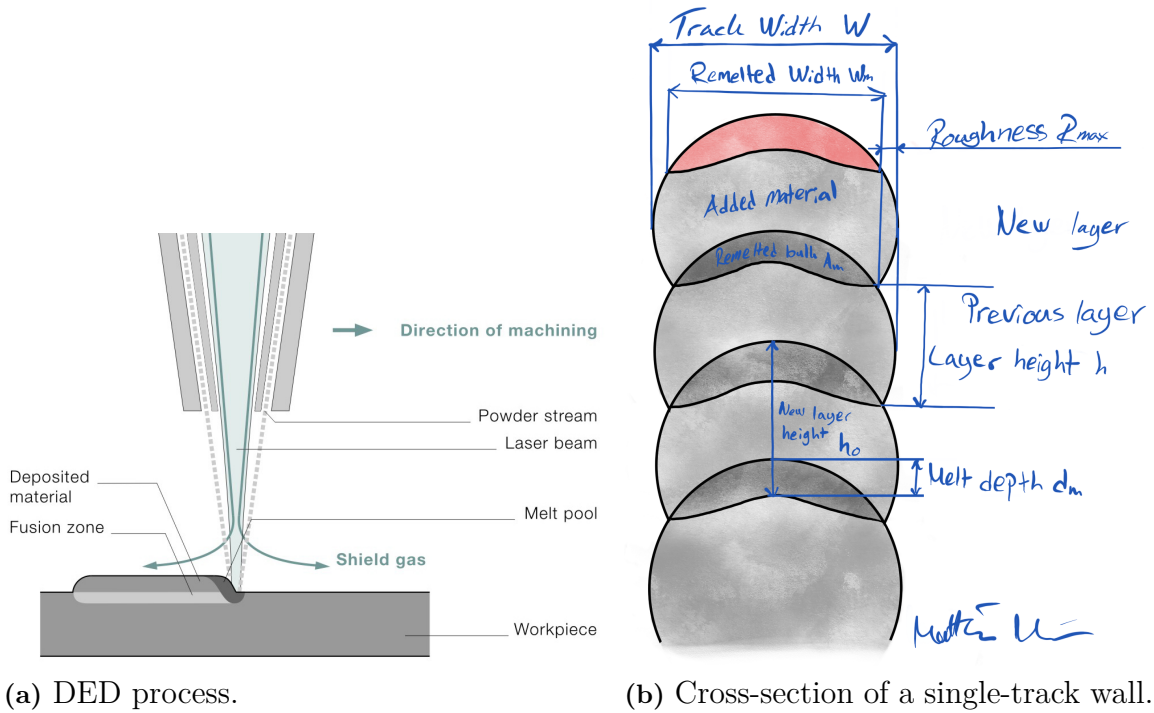


Figure 2.2: (a) schematic diagram of DED process. (b) schematic description of the formation of layers as cross-section.

2.2 Process

The quality of a component made with the DED method is mainly influenced by process parameters. Therefore optimum process parameters are key to a good result [6, 8]. The parameters can be changed by the operator. Laser power, scanning speed and powder feed rate (at fixed spot size) are the core process parameters that can be changed between the runs, and they have the biggest impact on the

end of the process final product. The previous investigation looked at the effect of different process parameters and found out that the single-layer height was affected by almost all process parameters. While the single-layer width was mainly affected by the scanning speed, laser power and spot size.

Table 2.1: Influence of main process parameters on selected deposit characteristics.

Parameters \ Properties	Clad height	Clad thickness	Dilution
Laser Power	↓	↑	↑
Laser spot size	↑	↓	↓
Powder feed rate	↑	↑	↓
Scanning speed	↑	↓	↓

2.2.1 Laser power

Laser power affects both height and width of the single-layer clad. According to [5] the width increases with an increased laser power, which can be seen in Figure 2.3(a). The studies were done on nickel-base alloy Ni20 and stainless-steel. According to [6], the height increases with an increased laser power which can be seen in Figure 2.3(b). But after 1800 W it shows a decrease in single-layer height and this is because more energy goes into melting the metal powder and too little goes to melting the substrate that creates to small melting pool for the powder. The studies were done high-speed tool steel M4.

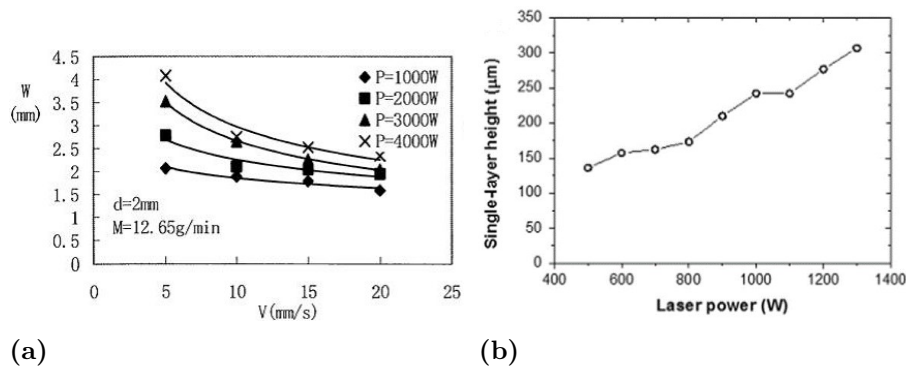


Figure 2.3: (a) Effect of laser power on track width from [5]. (b) Effect of laser power on track height from [6].

The laser power has a major impact on the efficiency, the surface finish, the height and width of the deposited track. When the laser power increases so does the width of the deposited track, there is, even more, energy to fully melt of all powder particles that are depositing on the substrate which is improving the surface finish. But the deposited height is reduced if the powder feed rate, scanning speed and laser spot size are constant. This is a dilemma because you want to keep a good

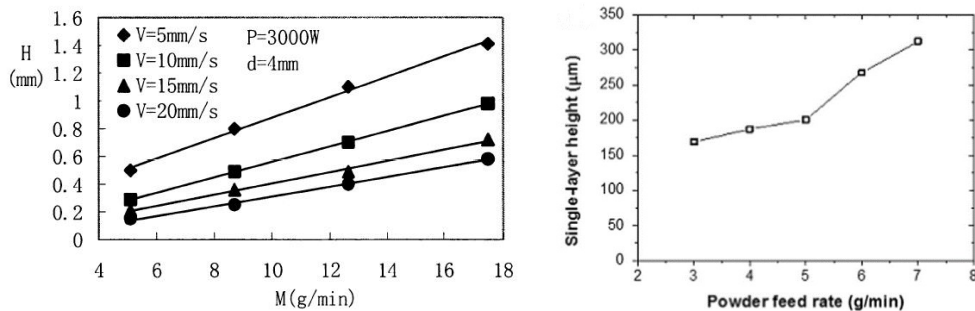
balance between height and width as you build your desired component but also want a good surface fineness.

2.2.2 Scanning speed

Low scanning speed can lead to too high heat buildup because of too long interaction time between the laser and the substrate. This is, of course, opposite if you have too high scanning speed. Speed also affect the shape of the melt pool, low speed gives a circular shape to the melt pool and high speed gives a teardrop shape to the melt pool. Teardrop shape can contribute to unwanted microstructure and crack formation in the center of the deposited track [2].

2.2.3 Powder feed rate

As the scanning speed and the powder feed rate determine the amount of powder feed into the melt pool, they are the dominating factors in determining the single-layer height in the DED process. In [6, 8] it is found that the single layer height increased with increasing powder feed rate, see Figure 2.4 The quality of the nozzle and the balance between powder feed rate. [6, 8] previous works looked at the effect of different process parameters and found out that the single-layer height was affected by almost all process parameters. While the single-layer width was mainly affected by the scanning speed, laser power and spot size. An increase in powder feed rate results in an increase in roughness, height and width of the single-layer clad [8]. Effect on layer thickness with powder feed rate can be seen in Figure 2.4(b) to the right as investigated by [6] on high-speed tool steel M4. In Figure 2.4(a) nickel-base alloy Ni20 and stainless-steel 316L exhibit a linear relationship between powder feed rate and single-layer height.



(a) Height on a nickle-base alloy Ni20 and with different scanning speeds. (b) Height on a high-speed-tool M4.

Figure 2.4: The influence of powder feed rate [g/min] on the single-layer height of a laser clad track.

The powder feed rate also affects the laser energy available for the substrate, since powder particles absorb part of the laser energy. This can be a delicate balance

between energy absorbed by powder and energy used to maintain the melt pool without other heating [2].

2.2.4 Energy density and powder density

The operating head with a selected laser spot diameter (D) will also have an impact on the process combined with laser power (P) and laser scanning speed (v) on the height of the single-layer. Energy density is the energy that is actually responsible for melting the powder and the substrate. The maximum height of the single-layer is therefore also dependent on the energy density.

$$E = \frac{P}{vD} [J/mm^2] \quad (2.1)$$

Too high amount of energy density and then dilution is too large, too low energy density and then no fusion bond can be formed. Powder feed density is defined as:

$$F = \frac{G}{vD} [g/mm^2] \quad (2.2)$$

Where G is the powder feed rate. These two parameters are used quite often within DED studies. And by calculating powder feed density and energy density input the height of the single-layer can be predicted [6].

3

Materials for Direct Energy Deposition

Any powder material or powder mixture can be used for 3D printing with DED method if they are stable in a molten pool. Metals that have high thermal conductivities and reflectivity are hard to process, these materials are gold, copper, there are also some aluminum alloys that are difficult to process. Otherwise, most of the materials that do not oxidize as much that the bond between the layers deteriorates can be processable. Of course, there are lots of other factors that matter also, for example: thermal expansion, thermal shock resistance, phase-transformations in the material.

Powders used for DED are normally gas-atomized because these powders require low oxygen levels. Powders for DED have a particle size usually between 50 to 150 μm . Because, these powders sizes exhibit very consistent flow in a carrier gas. Smaller particles down to 20 μm can be used but then increases the risk for inconsistent flow or clogging in the nozzle. Particle sizes below 20 μm should normally be avoided since the risk of clogging increases and the risk for spreading of the powder particles in the air increases quickly with decreasing powder size. The risk for dust explosions and inhalation of particles must be considered.

Alloy composition is an important factor that will play a role in printability. In [9] it has been found that a high carbon content in tool steel has a negative influence on printability using SLM. The carbon segregated up to the surface of the melt, and like oxides they reduce wettability.

Metals suitable for AM with direct melting, have the same characteristics as for welding. Therefore, we have not seen so much of material like 440C stainless steel and 2024 aluminum, they are more difficult to weld because they tend to crack [10]. DED is quite similar to laser cladding. In laser cladding, it is known that there are materials that are easier and harder to clad. Some materials require preheating to avoid coating cracking. Some materials like tool steels, Inconels and stainless steels have no problem to coat three layers without cracking [11].

Welding and laser cladding are two processes that have similarities to DED by laser. Two material groups that exhibit very good processability in these processes are stainless steels and nickel alloys. They are generally easy to process, allow good control of the melt and are not sensitive to cracking.

3.1 Microstructure

The final microstructure after DED is dependent largely on the chemical composition of the alloy and the solidification process, cooling rate of the melt, remelting of the material, but it is also affected by the heat history from the previous layers. [3, 12]. The solidification structure in AM with metals can be planar, cellular, columnar dendritic or equiaxed dendritic, depending on G/R value and cooling rate. G/R is a ratio of temperature gradient G and the solidification rate R at the solid-liquid interface [13]. Metals with high purity have a planar solid-liquid interface or extremely high values of temperature gradient or solidification rate have a planar solid-liquid interface and solidify as a single crystal. However, for alloys it is more complicated, redistribution of alloy elements leads to concentration gradients near the liquid-solid interface, which in turn affect the solidification morphology.

If a metal contains impurities or alloying elements, the melt at the solidification front enriches with them during solidification and the planar solidification front breaks down, causing a cellular or dendritic solidification. A cellular structure is generated when the crystals grow in columns without formation of secondary dendrite arms, otherwise, the structure is called dendritic.

High solidification and cooling rates result in fine solidified clad microstructures, which result in superior wear and corrosion properties to those of coarse microstructure. High cooling rates can result in the formation of beneficial metastable phases and extended solid solubility, which also enhances properties. However, high cooling rates increase the sensitivity of the clad and HAZ to cracking, and precautions such as preheating might be necessary. However, pre-heating decreases the temperature gradient.

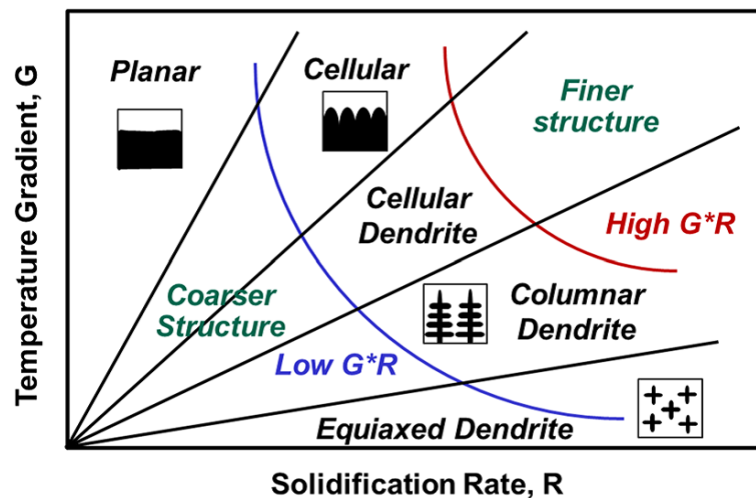


Figure 3.1: The effect of temperature gradient (G) and solidification rate (R) on the solidification morphology and size.

3.2 Surface tension and wettability

For a successful AM process, the liquid-solid wetting features are crucial for forming a consistent bead geometry. The wetting of a solid by a liquid is related to the surface tension of the solid-liquid (γ_{sl}), solid-vapor (γ_{sv}) and liquid-vapor (γ_{lv}) interface. Wettability can be defined by the contact angle θ [14]:

$$\cos(\theta) = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \quad (3.1)$$

The liquid wets the substrate as $\cos(\theta) \rightarrow 1$. To describe wetting behavior, [15] has defined a spreading coefficient

$$S = \gamma_{sv} - \gamma_{sl} - \gamma_{lv} \quad (3.2)$$

A large positive S causes to a good spreading of the liquid. On the other hand, if the $\gamma_{sl} > \gamma_{sv} > 90^\circ$ and accordingly, this causes the liquid to spheroidizing itself instead of wetting the substrate in order to have a minimal surface energy. Das has also described in its report [15] that contamination of oxides on the surface of the melt, severely prevents good wettability and causes defects such as balling. In order to prevent oxidation, the AM process must be performed so that the melt is protected with a protective atmosphere by using high purity inert gas. However, welding with protective gas cannot fully guarantee complete wetting due to the high reactivity of the melt at welding temperatures. Most metals will easily form oxides even at very low levels of oxygen [15]. Under normal AM conditions, a certain amount of oxidation cannot be avoided. To obtain a good wetting a reduction of surface oxides is required to form clean metal-metal interfaces. When choosing material for AM, additives like in situ deoxidizers or fluxing agents can be given in small quantities by alloying it with the material or mixing it with the powder to improve the wetting [16].

3.3 Viscosity

In addition to a good wetting, It is required that the viscosity of the melt is low enough so that it can successfully spread onto the previously processed layer. The viscosity μ of molten metal can be described as [14]:

$$\mu = \mu_0 \left(1 - \frac{1 - \varphi_l}{\varphi_m}\right)^{-2} \quad (3.3)$$

Where μ_0 is the viscosity of the liquid, φ_m is volume fraction of solids above which the liquid-solid mixture has a essentially infinite viscosity μ and φ_l is the volume fraction of the liquid.

As for a DED process system with a complete liquid formation, the dynamic viscosity of the liquid is defined by [9]:

$$\mu = \frac{16}{15} \sqrt{\frac{m}{kT}} \gamma \quad (3.4)$$

Where k is Boltzmann constant, T is the temperature, m is the atomic mass and γ is the surface tension of the liquid. From the equation you see when the temperature increases, the dynamic viscosity decreases. Which leads to better rheological properties of the liquid. Dynamic viscosity μ should be high enough to prevent balling phenomena [16].

3.4 Residual stresses

According to the ASTM standard E6-09B residual stress can be defined as “stress in a body which is at rest and in equilibrium and at uniform temperature in the absence of external and mass forces”. The dynamic temperature change and the cooling/heating rate of the building component of DED, cause great temperature changes in the component and is known to cause residual stresses in DED components. Thermal residual stresses in parts made with DED are highly influenced by the properties of the material for example; phase transformations, thermal expansion, thermal conductivity, Young’s modulus, and yield stress affects residual stresses from the material point of view. But also other things can affect size and pattern of residual stresses within the manufactured part by DED, like; Process parameters, scanning pattern, size and geometry of the part.

Deposition of molten metal that solidifies on top of solid material (metal) will result in tensile stresses in the deposited layer and compressive in the material below. The magnitude of these stresses is of or near the yield strength, unless relaxing processes, like stress relieving heat treatment, can be applied. In DED process layers are applied consecutively on top of each other. To some degree, this means that the next layer will stress relieve the previous layer.

3.5 Thermal shock resistance

Thermal shock resistance describes how sensitive the material is to damage if exposed to a sudden change in temperature. Thermal shock occurs when a thermal gradient causes different parts of an object to expand by different amounts. This difference in expansion can be understood in terms of stress or strains. At some point the stress overcomes the strength of the material, causing to a crack to form. If nothing stops this crack from propagating through the material, it will lead to the object’s structure to fail. Where k is Thermal Conductivity ($W/m.K$), E is Young’s Modulus (GPa), α is Thermal Expansion Coefficient ($\mu strain/^\circ C$), σ is Yield Strength of Material (MPa) and ϑ is Poisson-Ratio (*Constant*). In DED almost all materials used so far are very shock resistant: stainless steel, nickel alloys, etc. The thermal shock resistance parameter is detailed below.

$$R_T = \frac{\sigma(1 - \vartheta)k}{E\alpha} \quad (3.5)$$

3.6 Stainless steel

Stainless steels are steel alloy that contains of least 12 % Cr to prevent corrosion in difficult environments. This corrosion resistance is obtained by that a thin chromium oxide film formed on the surface of the steel that prevents oxidation between the steel and surroundings. Stainless steels are divided into groups based on their microstructure at room temperature [17]. The five most common groups of stainless steel are; Martensitic, Precipitation Hardening (PH), Ferritic, Duplex, and Austenitic. Their chemical composition can be seen in Table 3.1, which was taken from [17]. In this work, only stainless steels from the austenitic group are presented. Therefore, only information about austenitic stainless steels will be addressed.

Table 3.1: Chemical composition of stainless steels.

Steel type	Composition wt%					Harden-ability	Magne-tism
	C	Cr	Ni	Mo	Others		
Martensitic	>0,10	11-14	0-1	-	V	Yes	Yes
Precipitation-hardening		15-17	7-8	0-2	Al	Yes	Yes
		12-17	4-9	0-2	Al, Cu, Ti, Nb	Yes	Yes
Ferritic	<0,08	12-29	0-5	<5	Ti, Nb	No	Yes
Duplex	<0,05	18-32	1-7	1-5	Mn, N, W, Cu	No	Yes
Austenitic	<0,08	16-30	8-35	0-7	Mn, N, Cu, Ti, Nb	No	No

As can be seen from the Table 3.1 different alloying elements have different effects on the microstructure. In the Schaeffler-Delong diagram, which can be seen in Figure 3.2, one can see the impact of the various alloy element. The Schaeffler-Delong diagram is based on the fact that alloying elements are either austenite or ferrite stabilizers and their phases are a relation to the chromium and nickel equivalent, calculated by using these expressions:

$$\text{Cr equivalent} = \%Cr + \%Mo + 1,5\%Si + 0,5\%Nb \quad (3.6)$$

$$\text{Ni equivalent} = \%Ni + 0,5\%Mn + 30(\%C + \%N) \quad (3.7)$$

In this way, it is possible to take into account different alloying elements. The Schaeffler-Delong diagram was developed for welding, to describe the structure for rapid cooling from 1050°C to room temperature.

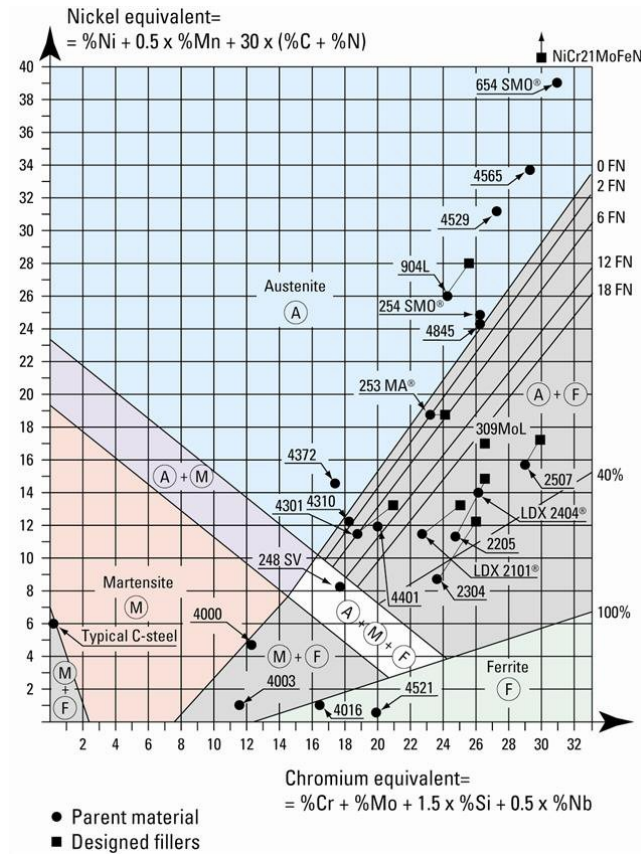


Figure 3.2: Schaeffler-Delong diagram.

Austenitic stainless steel exhibit the austenitic structure at room temperature thanks to the stabilizing effect of Ni (Mn, N in sometimes). Austenitic stainless steel are not heat-treatable, but shows a good work-hardenability. To eliminate weldability problems that are related to carbides that prencipitatic during welding, low carbon austenitic stainless steels (marked with L) have been developed. The microstructure is mostly austenitic in austenitic stainless steel but they contain a small amount of δ -ferrite, which is the first solid phase after liquid phase. The δ -ferrite amount is usually below 1%. The presence of δ -ferrite increases strength and decrease grain growth properties of steel. δ -ferrite has an important role for austenitic steels in welding to prevent the occurrence of hot cracks [18].

3.7 Ni base alloy

1530-CE is gas atomized powder of 50Ni-7Cr-1.5B-2.5Si-Fe and it is self-fluxing nickel alloy. This material is used in laser cladding, the microstructure of the coating consisted of austenitic dendrites. [19]

4

Experimental

Experimental part is divided into three sections. In section 4.1 material are selected for DED, in section 4.2 the samples are built with DED with selected materials and in section 4.3 experimental part of metallography is explained.

4.1 Material selection

The first part of the project was to investigate which materials are used in AM to build a structure using the DED method. By investigation DED manufacturer and AM material manufacturer. This was done by examining various websites. These materials were then placed into Table 4.1 to see what these materials have in common. Properties as melting point, thermal conductivity and thermal expansion, and more were used in the CES Selector which is a material selection software or on the material manufacturer if this was a possibility. These materials were plotted and used as a guideline in CES Selector.

Table 4.1: Selected list of some materials used for DED process.

Stainless steels	Other steels	Nickel	Cobalt	Titanium
304L [20, 21]	1018 [20]	IN625 [20, 21, 22]	Stellite 6 [21]	CP Ti[21, 20]
316L [20, 21, 22]	4140 [21]	IN713 [22]	Stellite 21[21]	Ti6Al4V [22]
410 [20]	300 Maraging[21]	IN718 [20, 21, 22]	Stellite 31[21]	
420 [20, 21]	H13 [20, 21]	IN738 [22]	Co6	
15-5PH [21, 22]	M4 [6]	Hastalloy X [20]		
17-4PH [20, 21, 22]	S7 [20, 21]	Waspalloy[21, 20]		

4.1.1 Selection criteria

The selection criteria are chosen in order to be generic regarding component properties, but specific for the DED process. There were many material parameters which were of interest to investigate like viscosity, thermal expansion, thermal conductivity, the volume change of the material during solidification, phase transformation. The thermal history of a layer may involve multiple solidifications and remelt cycles. Therefore you want a material that has good thermal shock resistance and

dimensional stability. You also want a low volume change and not many phase transformations during DED.

The selection criteria may be divided into following groups: Powder, laser heating, melt behavior, Solidification and post-solidification.

- **Powder:** It should be possible to atomize the material and the powder should have sufficient flow behavior to facilitate robust powder feed through the nozzle.
- **Laser heating:** The material should have sufficient absorption of the laser light in order to effectively heat and melt the powder. It should have a low vapor pressure to avoid vaporization during heating.
- **Melt behavior:** Once melted the material should have sufficient wetting to itself. The melt should also have good fluidity and not oxidize to suddenly or too much.
 - Wetting angle.
 - Viscosity.
- **Solidification:** The solidification temperature interval $\Delta T = T_l - T_s$ should not be too large. If a significant fraction of solid is formed in the melt $> 20\%$ the fluidity drops strongly. The heat conductivity of the solid material must be considered. A low heat conductivity concentrates the heat to the vicinity of the melt pool but lowers the effective cooling rate. A high heat conductivity will need more laser power to melt and maintain the melt pool.
 - ΔT of liquid solid range.
 - Heat conductivity.

4.1.2 CES Selector

The first step in the material selection with CES Selector is to define the design requirements, see Table 4.2 where function, constraints and objectives for the materials are described.

Table 4.2: Design requirements for materials for DED.

Function	A component that will built by layer-by-layer deposition.
Constraints	High thermal shock resistance
	High dimensional stability
	Low thermal conductivity
	Low thermal expansion coefficient, near T_m
	Low liquid-solid range $\Delta T = T_l - T_s$
	No large or many phase,transformations
	Sufficient laser absorption
	Do not oxidize during the process
	Should be possible to atomize the material
Objectives	Good weldability
	Does not crack

A screening process was done with CES Selector, which examined nickel cobalt-chromium, steel and titanium alloys. Five plots (Thermal expansion coefficient vs oxidation at 500 °C, Thermal conductivity vs weldability and three Thermal shock resistance vs. Thermal conductivity) were obtained and a handful of materials passed the design requirements. These plots can be seen in section 5.1. For Thermal shock resistance vs. Thermal conductivity (Figure 5.6) it was decided to only include materials with excellent weldability and resistance from oxidation at 500 °C. Liquid-solid range, phase transformations, laser absorption, viscosity and wettability had also been desirable to investigate but this data does not exist in this edition.

4.1.3 JMatPro

JMatPro is a program that can investigate material properties from a material melting point down to solid in room temperature. JMatPro can also simulate the phase transformation of the desired material. Therefore, the following materials that were used in this work were simulated to find out the properties of the materials such as liquid-solid range, viscosity, surface tension of the liquid material, thermal conductivity and volume change from melting down to room temperature. This result can be seen in section 5.2. Materials 316L and 316L HSi were simulated. It was not possible to make simulations for 1530-CE since the databases available could not cover this composition. Alloy content for 316L and 316L HSi that has been simulated with JMatPro can be seen in Table 4.3.

4.2 Direct Energy Deposition

Using the identified criteria in section 4.1 it would be desirable to have materials with high/low values of all parameters. However; due to time constraints it was decided to limit investigations to the materials in Table 4.3. From material selection it was decided to test 316L, 316L HSi and 1530-CE. Chemistry of the powders which have been used in this experiment is shown in Table 4.3. The substrate which has been used for all DED experiments was a low alloy steel, SS-EN S 235 JR.

Table 4.3: Chemical composition of materials used for DED.

Materials	Fe %	C %	Ni %	Mo %	Cr %	Si %	Mn %
316L	Bal	0,03	12,1	2,8	16,7	0,6	1,5
316L HSi	Bal	0,02	13,3	2,6	17,9	1,9	
1530-CE	39		Bal		6,9	2,3	

In order to compare the materials with each other, we had to determine a geometry that would be used to print our materials. This geometry was determined to be a single track wall, consisting of 20 deposited layers. Figure 4.1 shows the single-layer wall. The walls were produced at Höganäs AB in the ArcX Thermal Surfacing lab

4. Experimental

using a 7 kW (Laserline) fiber coupled diode laser. Powder feeder (GTV), 5 mm nozzle were mounted on a 5 axis industrial robot (KUKA). This workstation can be seen in Figure 4.2.

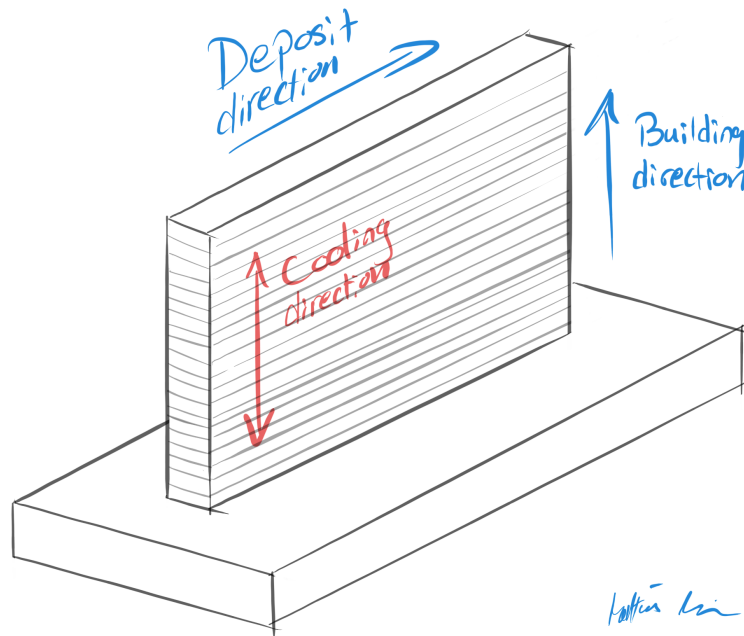


Figure 4.1: Schematic of the building direction and deposition direction of the wall structure.

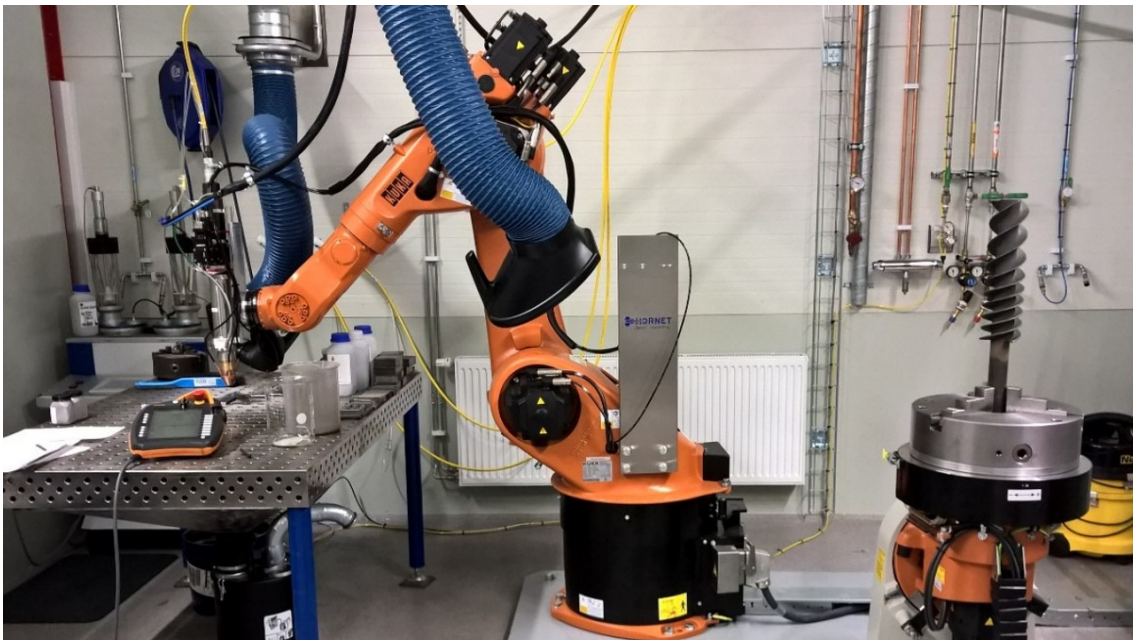


Figure 4.2: working station at Arcx.

The robot deposited a single track on the substrate, after that the robot was raised in the z-direction (which is the building direction) to deposit a new layer and so on until 20 layers have been built up.

The nozzle travels between the start and the stop position at a constant velocity. However, it accelerates from a standing start and decelerates to a complete stop at the stop position. It was not possible to achieve a “flying start and stop” without the robot having to accelerate at start and retard at stop, during the project, due to difficulties in programming the laser and the robot. When you change the material or every time you restart the machine, you had to measure the powder flow. The powder flow was measured by spraying powder into a container for one minute and weighing the sprayed material, then you got a value with a g/min unit.

Each material requires its own optimum process parameters, to find a suitable process window for each material by trying out various parameter combinations as laser power, powder feed rate, scanning speed and raising the robot to the next layer.

Powder feed is a difficult parameter to change all the time because this parameter has to be adjusted manually and takes a long time. Therefore, the powder flow rate is set as a fixed parameter. Raising the robot is used only to maintain even focus on each layer of the laser during deposition.

In order to find the optimum process parameter for each material in the Table 4.3, different process parameters were tested. The main process that was tested were; laser power between 1000 and 2200 W, scanning speed between 10 and 20 mm/s and two different powder feed rates 20 and 30 g/min were tested. Secondary process parameter that is a movement of the robot in the z-direction (building direction) was set to 0.6 mm to increase per layer. The movement of the robot in z-direction was corrected for the component that had optimal laser power, scan speed and powder feed rate. First, one layer was deposited on the substrate and then it was measured with a micrometer. Then the robot was calibrated that it would move in z-direction after the first layers height to maintain the focus point. Then five layers were deposited and then measured to see if these layers were deposited in focus. This was done by measuring the single-layer height and then dividing it by the number of the layers that were deposited. When you got the same number as the first deposited layer then each layer was built with the same focus point. Then new 10 layers were tested and if they were good, then new 20 layers were tested one last time to see if the single-layer wall were built so that each layer was deposited with the same laser focus. Some components achieved defects like; edge effect, lack of fusion, satellites and waviness these defects can be seen in section 5.3.1. Therefore, it was decided to not proceed further for metallography with these samples. Samples which were free from defects were chosen to be examined in the optical microscope. Process parameters for these samples can be seen in section 5.3.

4.3 Metallography

Selected samples were prepared for optical microscopy. This was done by cutting out a 5 mm long piece from the middle of the samples. Then the samples were molded into a polymer such that the cross-section could be investigated. Later the samples were ground with a grinding stone to level the samples and remove unwanted polymer. Then the samples were ground with Alegro, which is a finer grinding disc for 6 minutes. After this, the samples were polished with polishing cloth MOL for 6 minutes and then NAP for 30 seconds. Then the samples were washed with ethanol and polished one last time with cotton. Between each grinding and polishing the samples are cleaned in ultrasonic baths.

After sample preparation, the samples were observed under a stereo microscope. Both the length and the width were measured at the bottom center and end of the wall. After the measurements in a stereo microscope, the porosity and the cracks were examined in an optical microscope. After investigating the porosity and cracks, the microstructure was investigated for grain structure. Therefore, the samples were etched, 316L and 316L HSi were etched in Glyceregia and 1530-CE were etched in N1. But before the samples were etched, they were polished again with NAP for 30 seconds.

4.3.1 EBSD

Samples preparation was the same as for metallography, but after the polish with NAP the samples were polished with OP for 3 minutes. After that, the samples were taped with conductive tape to prevent charging in the SEM. The EBSD scans were performed at Chalmers using their FEG-SEM (LEO 1530). The EBSD investigation was operating at 20 kV and 10 mm working distance and the samples were tilted at 70°. An 8 μm step size was used. For 316L the material consists mainly of austenite and a small amount of δ -ferrite, therefore phases selected to investigate were bcc and fcc. For 1530-CE the material consists of mostly austenite and some different carbides. It was a fairly low magnification which should be mapped, therefore, it was decided to investigate only the fcc phase.

5

Results

5.1 Material selection

This section shows charts created with CES Selector. Figures 5.2 to 5.6 shows different properties of materials that are compared to each other. Figure 5.5 was made to show clearer the stainless steels. Figure 5.6 only shows materials that have passed the criteria for oxidation and weldability.

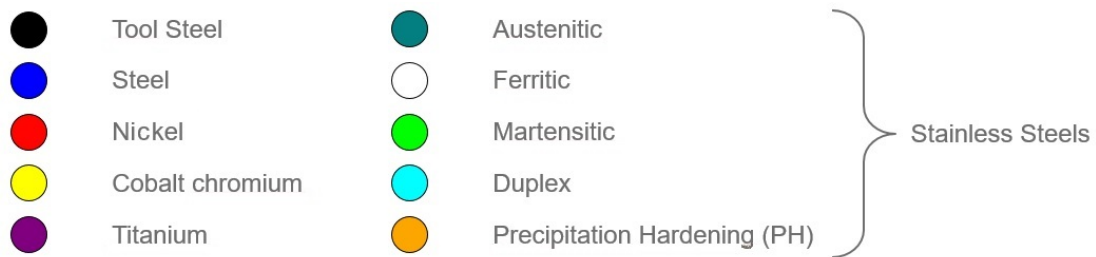


Figure 5.1: Corresponding colors for each metal as shown in Figures 5.2 to 5.6 for easier reading of the figures.

5. Results

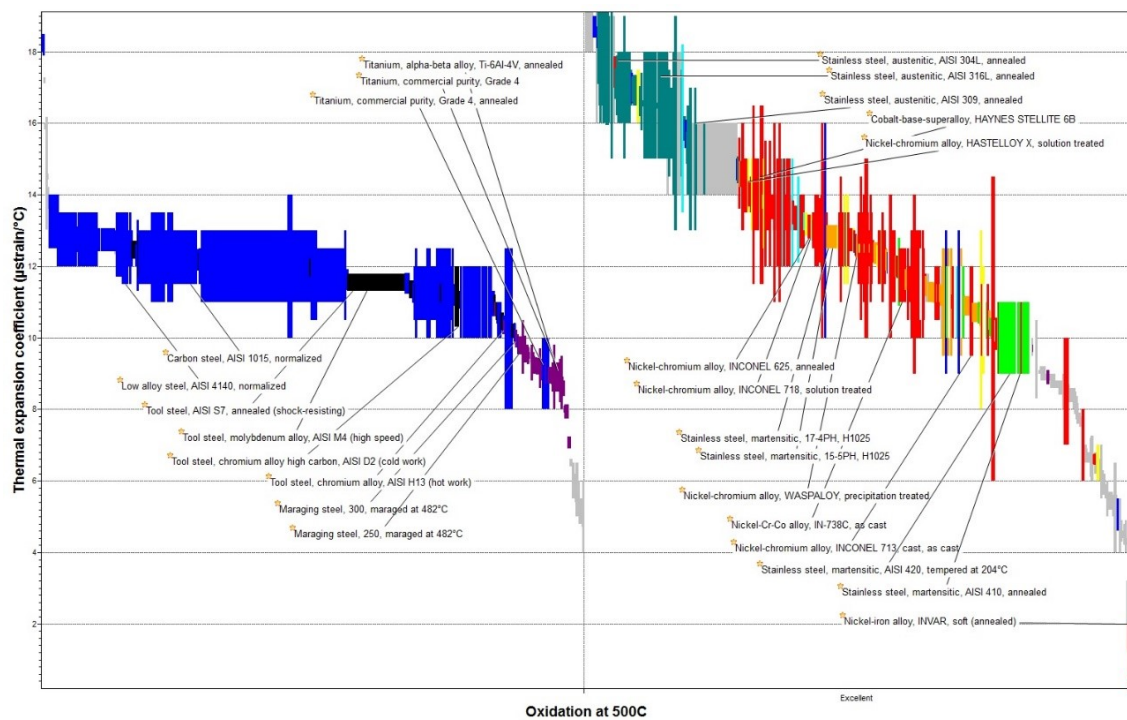


Figure 5.2: Thermal expansion coefficient vs oxidation at 500 °C, where oxidation is a qualification, created by CES Selector. There only Acceptable (left half) and Excellent (right half) are included.

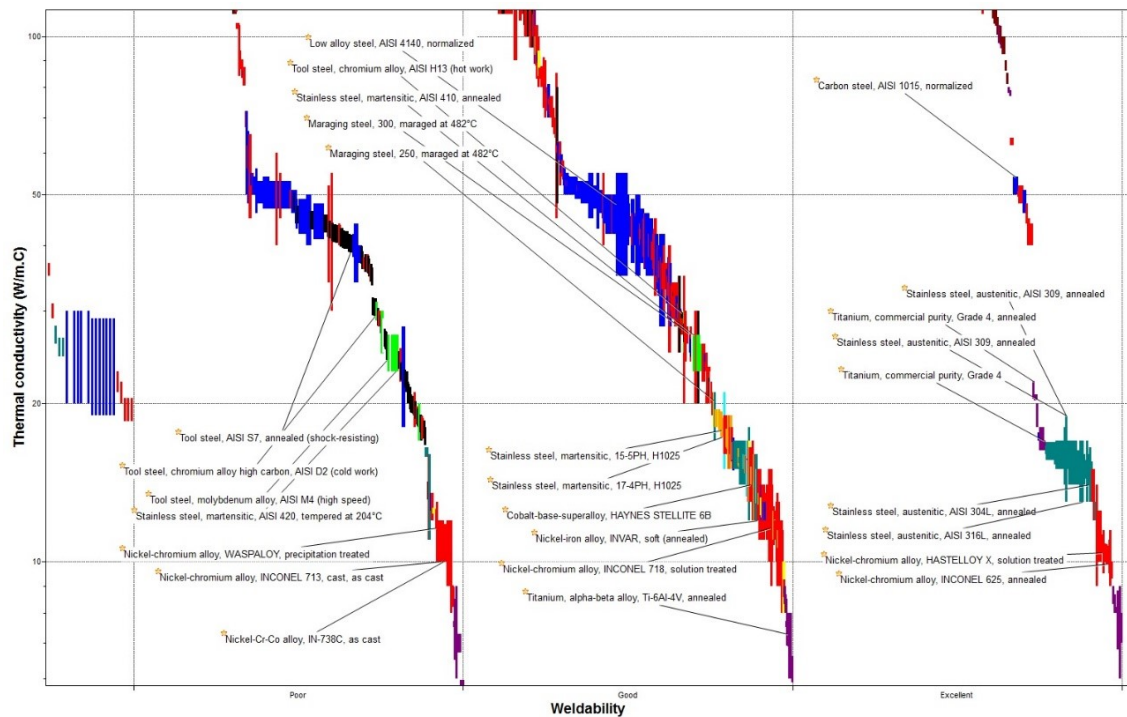


Figure 5.3: Thermal conductivity vs weldability, where weldability is a qualification, created by CES Selector. Were three halves are included; Poor (left), Good (middle) and Excellent (right).

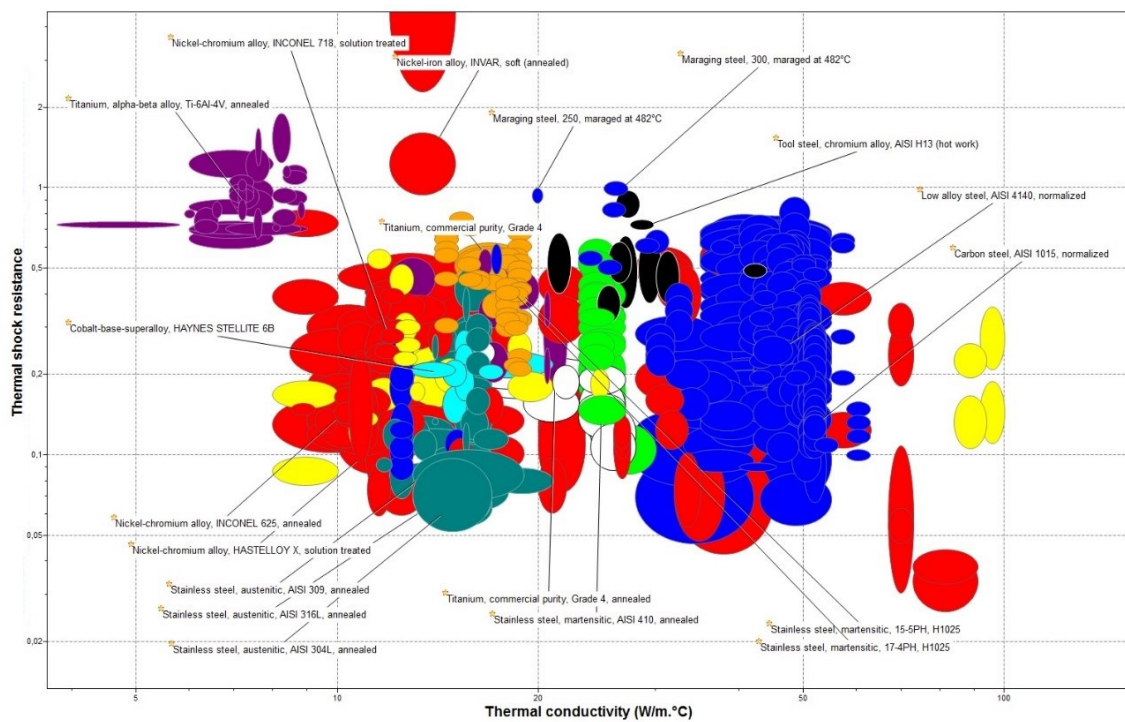


Figure 5.4: Thermal shock resistance vs thermal conductivity, created by CES Selector. The size and shape of the "bubbles" represent the ranges of the properties for the particular material in question.

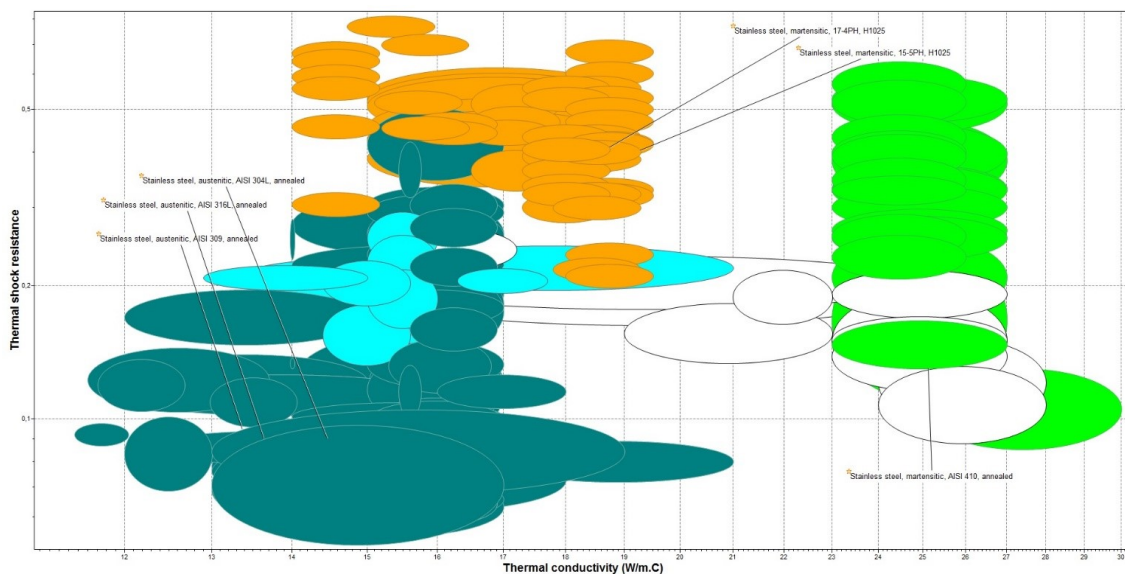


Figure 5.5: Thermal shock resistance vs thermal conductivity for stainless steels, created by CES Selector.

5. Results

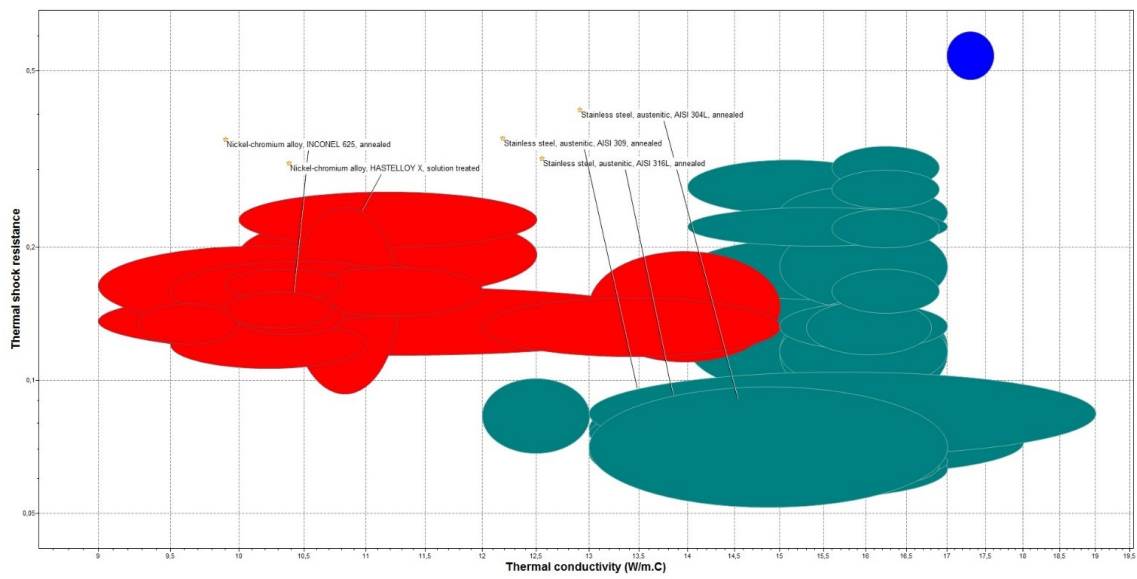


Figure 5.6: Thermal shock resistance vs thermal conductivity for materials with excellent weldability and oxidation at 500 °C, created by CES Selector.

5.2 Thermal calculations

This section shows thermodynamic calculations by JMatPro for 316L and 316L HSi. Figures 5.7 to 5.9 show that they have similar properties during solidification. However, Figures 5.10 and 5.11 shows that liquid viscosity and surface tension in the solid liquid region is significantly different for the two materials.

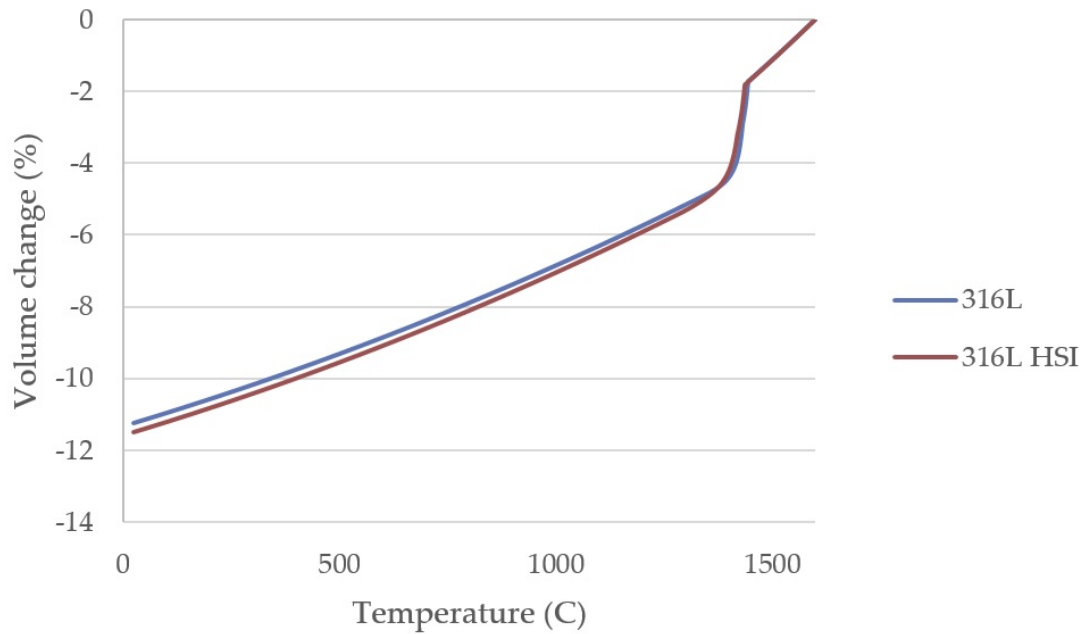


Figure 5.7: Volume change during solidification and cooling to room temperature. The properties of 316L and 316L HSi are simulated from 1600 °C down to 25 °C by JMatPro.

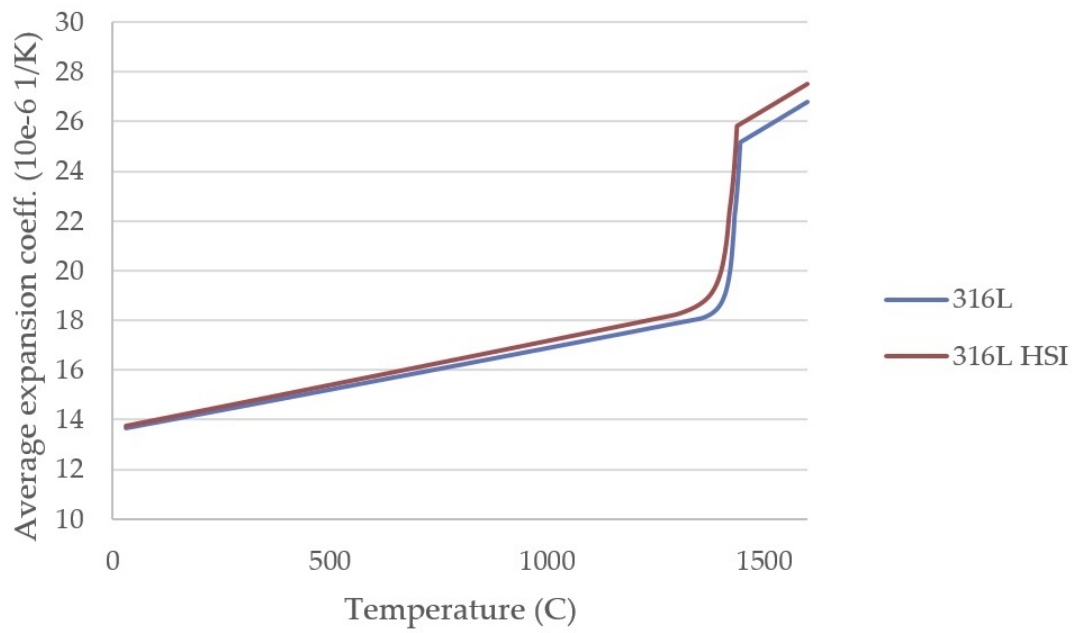


Figure 5.8: Average expansion coefficient during solidification and cooling to room temperature. The properties of 316L and 316L HSi are simulated from 1600 °C down to 25 °C by JMatPro.

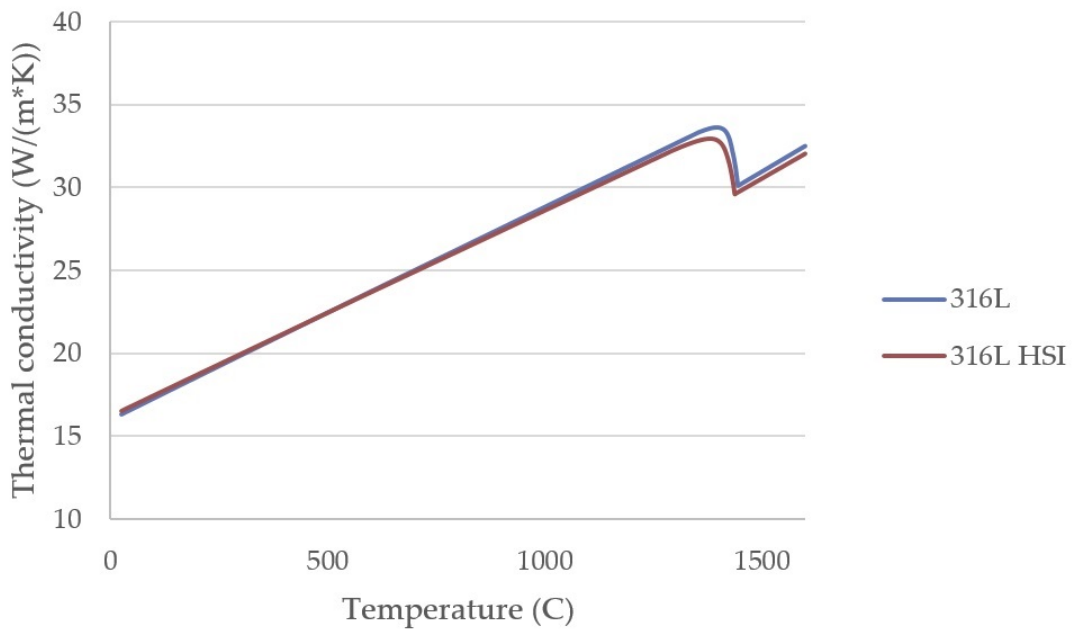


Figure 5.9: Thermal conductivity during solidification and cooling to room temperature. The properties of 316L and 316L HSi are simulated from 1600 °C down to 25 °C by JMatPro.

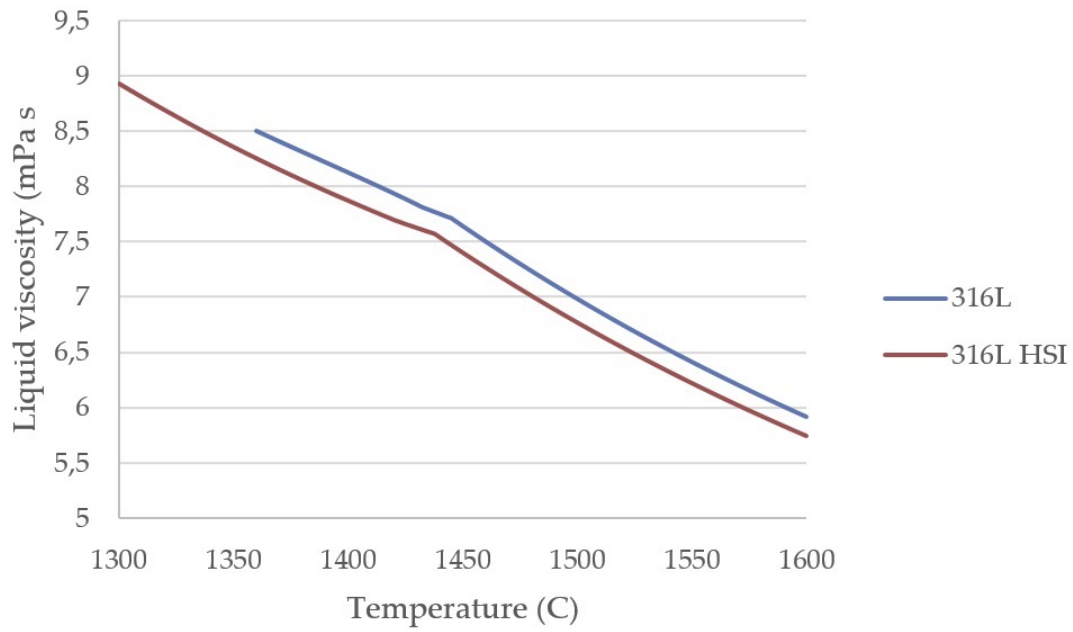


Figure 5.10: Liquid viscosity during solidification and cooling to room temperature. The properties of 316L and 316L HSi are simulated from 1600 °C down to 1300 °C by JMatPro.

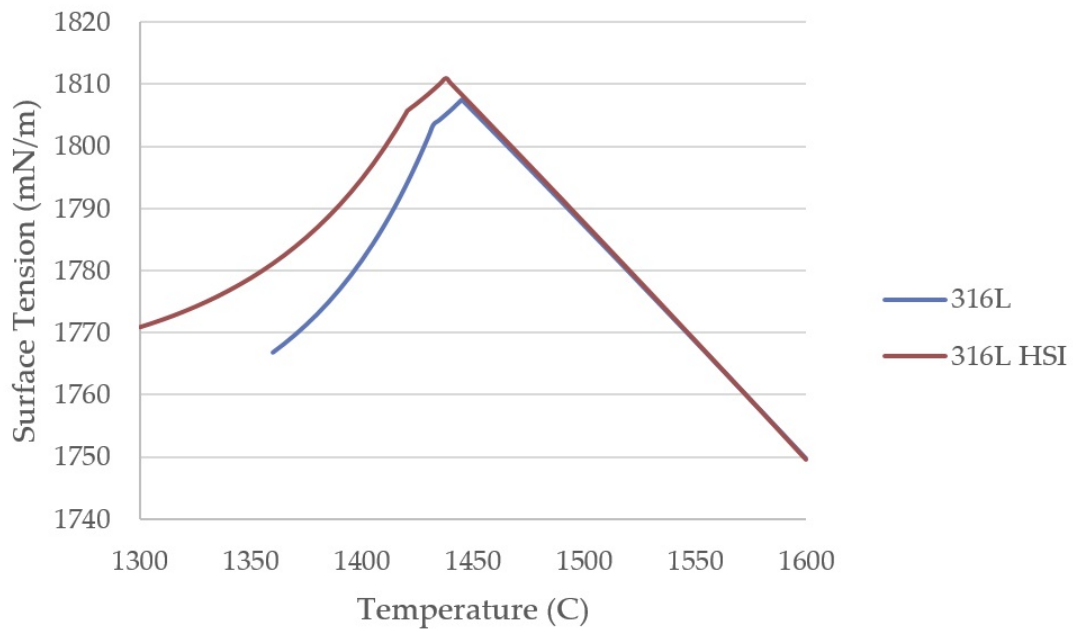


Figure 5.11: Surface tension during solidification and cooling to room temperature. The properties of 316L and 316L HSi are simulated from 1600 °C down to 1300 °C by JMatPro.

5.3 DED

This section shows process quality from the DED experiment section 4.2. All parameters for all results can be seen in the Table 5.1, each sample has a sample code to be easier to identify the parameters for the sample that are presented in sections 5.3.1 to 5.5. Figures 5.12 to 5.14 show the samples with minimal defects for 316L, 316L HSi and 1530-CE. The Figures 5.15 to 5.18 shows common defects that occurred during DED. Figure 5.15 shows a defect called egde effect, it has a peak at the start of the deposit and a valley at the end of the deposit. Figure 5.16 shows lack of fusion, the deposit material does not fuse to the substrate. Figure 5.17 shows a defect called waviness, the deposited layers are wavy. Figure 5.18 shows many small satellites that are fused to the single-track wall. Figures 5.19 and 5.20 shows how the heat flows out from the sample during DED, you can see that lack of fusion will affect how the heat will flow out from the sample.

Table 5.1: Process parameters for DED.

Material	Sample code	Laser power [W]	Scanning speed [mm/s]	Powder feed rate [g/min]	Substrate distance [mm]	Z-increment [mm]	Lack of fusion	Edge effect	Satellites	Height
316L HSi	H-11	1300	15	20	16	0,6	x	x	x	
316L HSi	H-18	1800	15	20	16	0,55		x	x	
316L	L-19	1300	12	20	14	0,85	x	x		
316L	L-20	1600	15	20	20	0,92				x
316L	L-22	1600	12	20	16	0,79	x		x	
316L	L-21	1600	12	20	14	0,94				
316L HSi	H-24	2000	15	20	16	0,6				
1530-CE	CE-11	1600	12	20	14	0,85				

5.3.1 Process quality



Figure 5.12: Side view of 20 deposited layers of 316L using a laser power of 1600 W, scanning speed of 12 mm/s and powder feed rate of 20 g/min. Scan direction is left to right (sample code L-21).

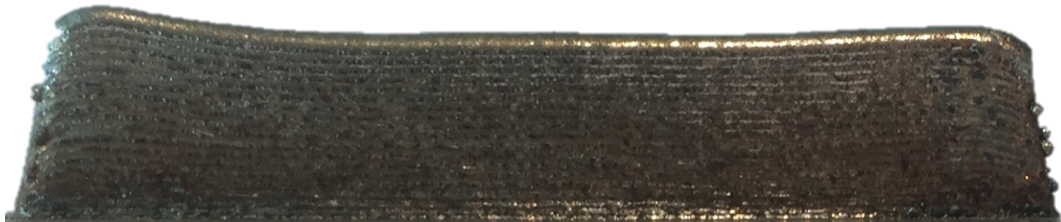


Figure 5.13: Side view of 20 deposited layers of 316L HSi using a laser power of 2000 W, scanning speed of 15 mm/s and powder feed rate of 20 g/min. Scan direction is left to right (sample code H-24).

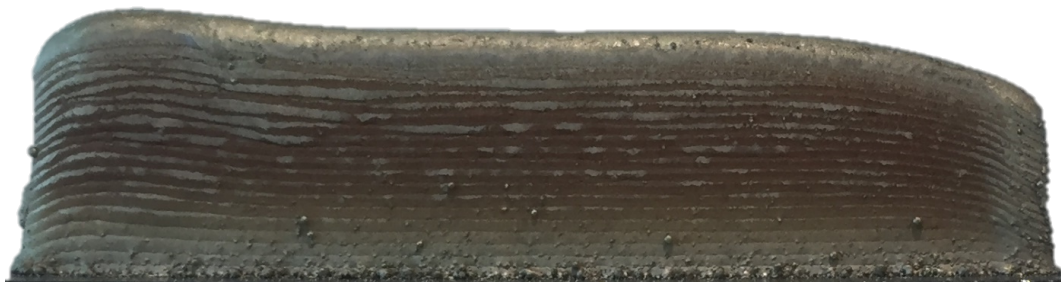


Figure 5.14: Side view of 20 deposited layers of 1530-CE using a laser power of 1600 W, scanning speed of 15 mm/s and powder feed rate of 20 g/min. Scan direction is left to right (sample code CE-11).

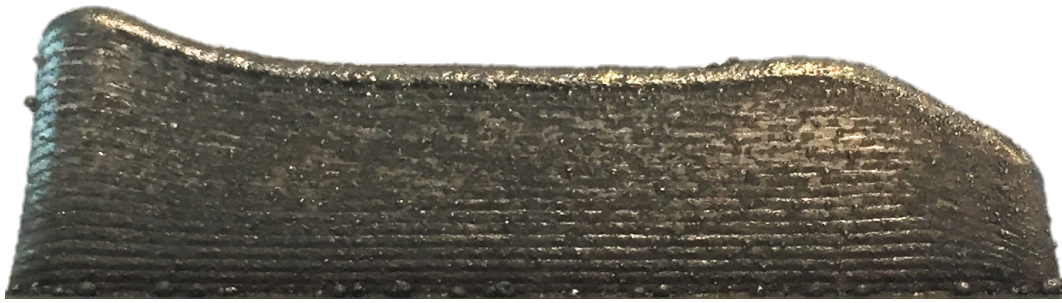


Figure 5.15: Side view of 20 deposited layers of 316L using a laser power of 1600 W, scanning speed of 12 mm/s and powder feed rate of 20 g/min. Scan direction is left to right (sample code L-22) This sample shows a defect called; edge effect. You have a peak at the start of the deposit (left) and a valley at the end of the deposit (right).



Figure 5.16: Side view of 20 deposited layers of 316L HSi using a laser power of 1300 W, scanning speed of 15 mm/s and powder feed rate of 20 g/min. Scan direction is left to right (sample code H-11) This sample shows a defect called; lack of fusion. The deposited material does not fuse to the substrate or to the previous layer.

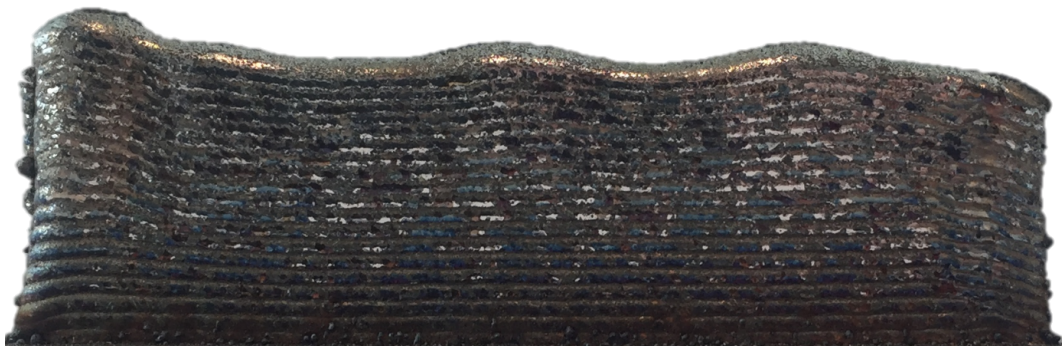


Figure 5.17: Side view of 20 deposited layers of 316L using a laser power of 1600 W, scanning speed of 12 mm/s and powder feed rate of 20 g/min. Scan direction is left to right (sample code L-20) This sample shows a defect called; waviness. The layers are wavy.

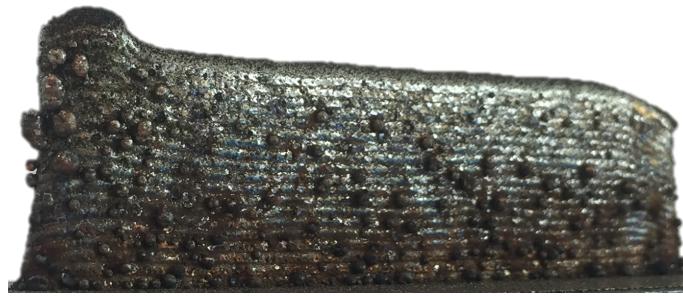


Figure 5.18: Side view of 20 deposited layers of 316L HSi using a laser power of 1800 W, scanning speed of 15 mm/s and powder federate of 20 g/min. Scan direction is left to right (sample code H-18) This sample shows a defect called; Satellites. Small round satellites are fused to either one side wall or both.



Figure 5.19: Side view 316L sample during deposition with DED (layer 10). Process parameters are the same as for sample code L-21. Snapshot of the build with the laser near the end of track #10. Temperature at the start of track #10 has dropped well below red-hot temperature due to heat conduction through previous layers.

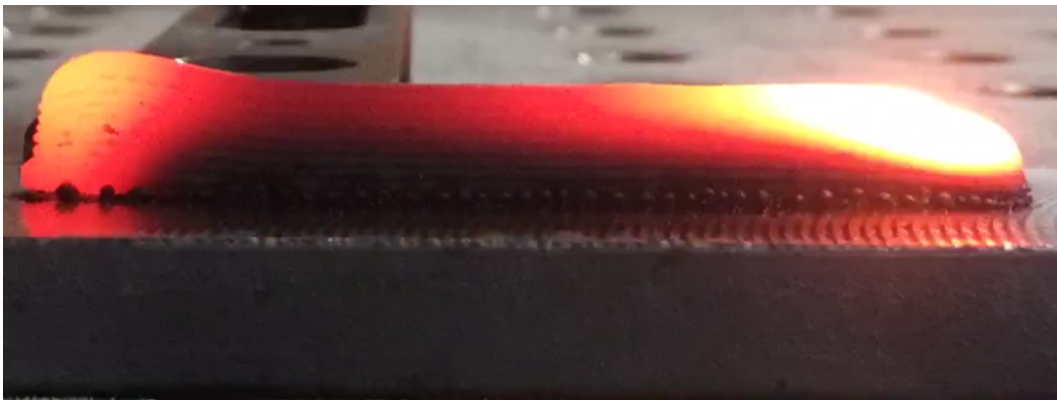


Figure 5.20: Side view 316L sample during deposition with DED (layer 10). Process parameters are the same as for sample code L-21. Snapshot of the build with the laser near the end of track #10. Temperature at the start of track #10 is still red-hot due to impaired heat conduction through the build. Thea heat conduction is interrupted by lack of fusion defect at the start of the build.

5.4 Metallography

This section shows process quality from the DED experiment section 4.3. Cross-sections of 316L, 316L HSi and 1530-CE samples can be seen in Figure 5.21. You can see that 316L HSi have barely no porosity, 316L has a few pores and 1530-CE some porosity. You can see each layer of 316L (Figure 5.21(a)). 316L HSi (Figure 5.21(b)) and 1530-CE (Figure 5.21(c)) have better surface roughness it is harder to see each layer. 316L have the same thickness all the way. 316L HSi is thick in the beginning but then it is straight. 1530-CE have a hourglass shape, it is thick on the bottom and top and thin in the middle. The height of 316L was measured to 18,1 mm, 316L HSi was measured to 12,5 mm and 1530-CE was measured to 17,6 mm. Measurements are shown in Appendix A in Figure A.1. Figures 5.22 to 5.24 shows etched cross-section of 316L, 316L HSi and 1530-CE. Figures in 5.22 to 5.24 to the left shows the overview image of the sample and to the right you see images at higher magnification at the top, middle and bottom of the samples.

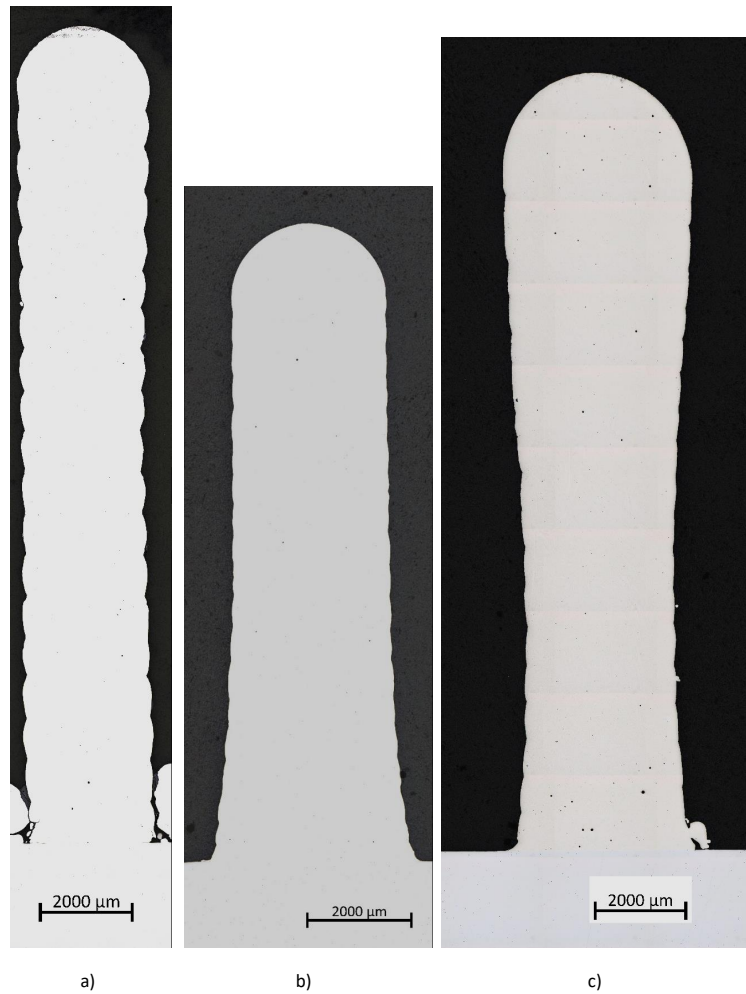


Figure 5.21: Light optical microscopy showing a cross-section in the polished condition. a) 316L (L-21), b) 316L HSi (H-24) and c) 1530-CE (CE-11).

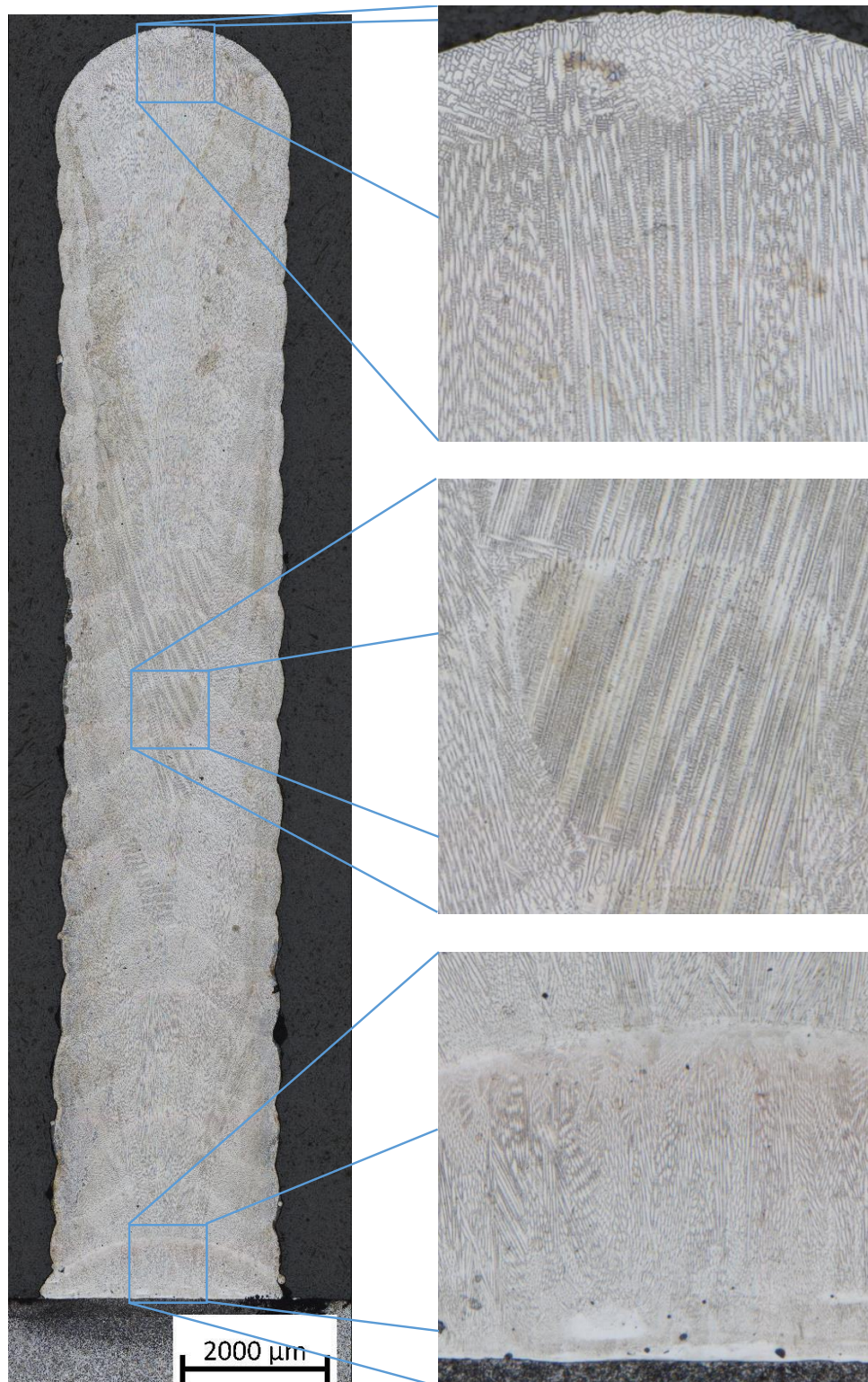


Figure 5.22: Light optical microscopy of etched cross-section of 316L (sample code L-21), to the left is the overview of the sample. To the right, images at higher magnification taken near the top, middle and bottom.

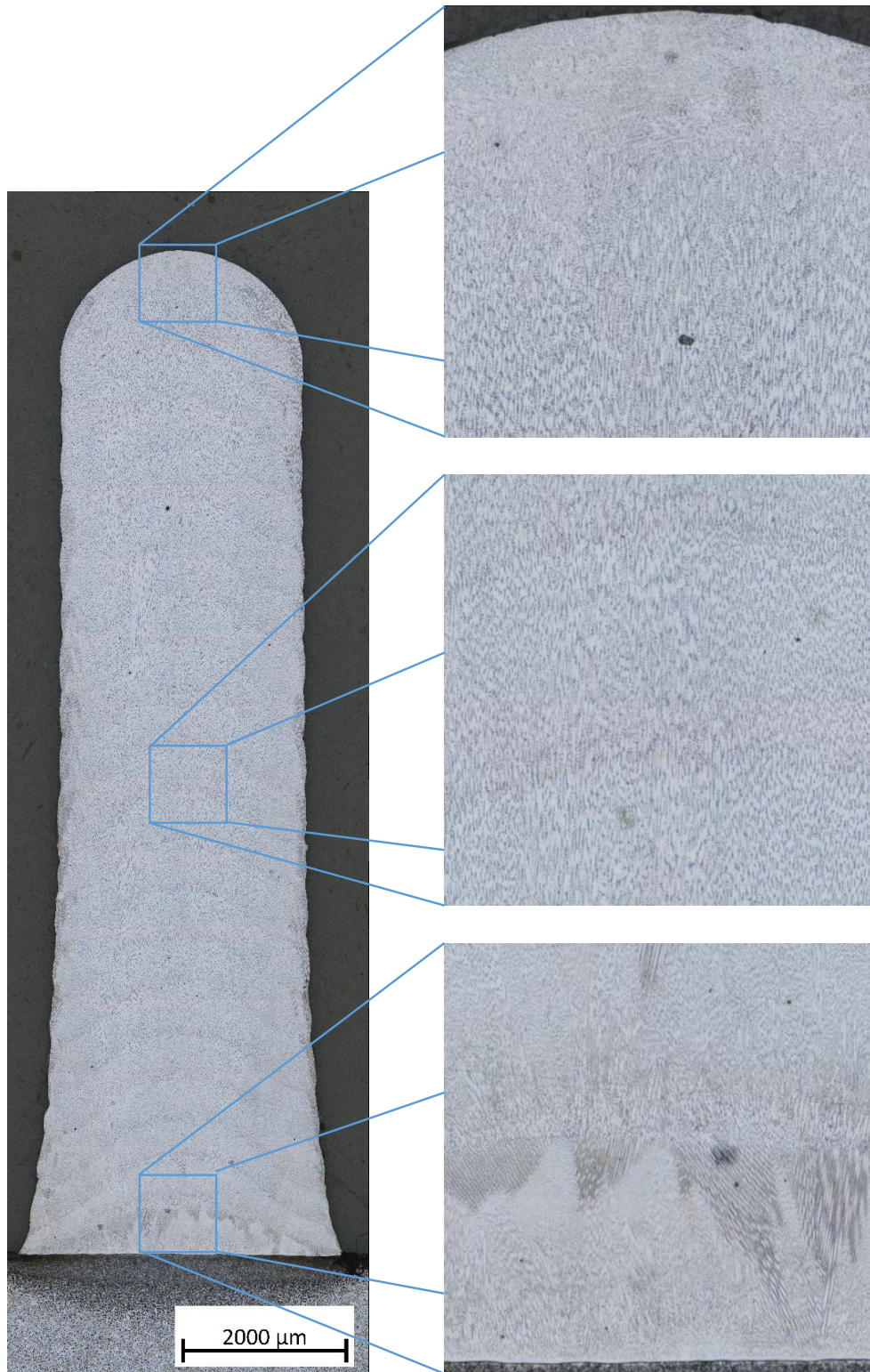


Figure 5.23: Light optical microscopy etched cross-section of 316L HSi (sample code H-24), to the left is the overview of the sample. To the right, images at higher magnification taken near the top, middle and bottom.

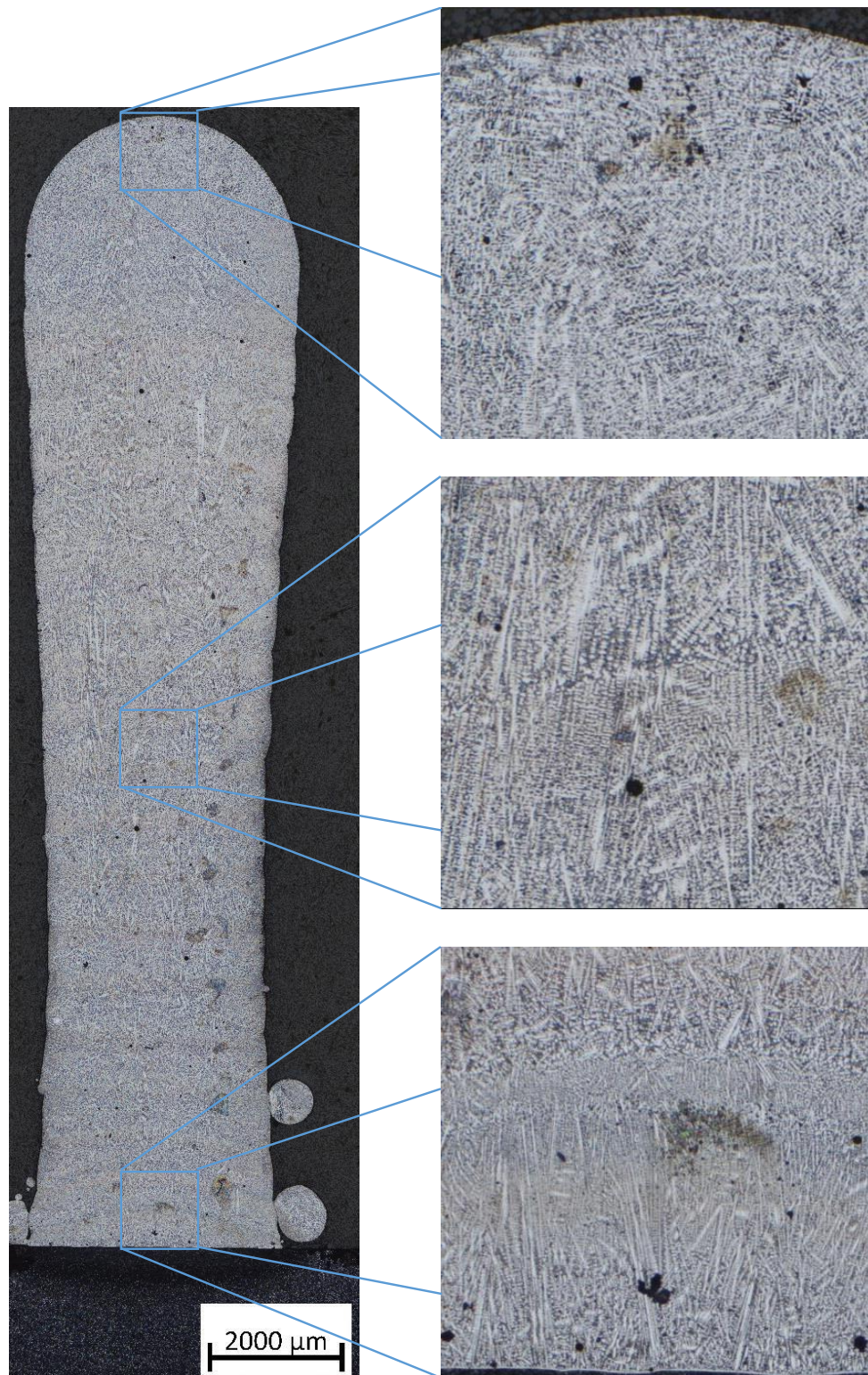


Figure 5.24: Light optical microscopy etched cross-section of 1530-CE (sample code CE-11), to the left is the overview of the sample. To the right, images at higher magnification taken near the top, middle and bottom.

5.5 EBSD

This section shows results from EBSD. Figures 5.25 to 5.27 shows (a) selected area for EBSD, (b) Euler figure from EBSD, (c) pole figure maps (d) Inverse pole figure. From Figures 5.25 and 5.27 (b,c,d) shows that the samples (316L 1600 W and 1530-CE 1600 W) have an anisotropic grain texture towards building direction. From Figure 5.26 (b,c,d) shows that the sample (316L 1300 W) have an homogeneous grain texture. The Table 5.2 shows phase fraction calculated from EBSD.

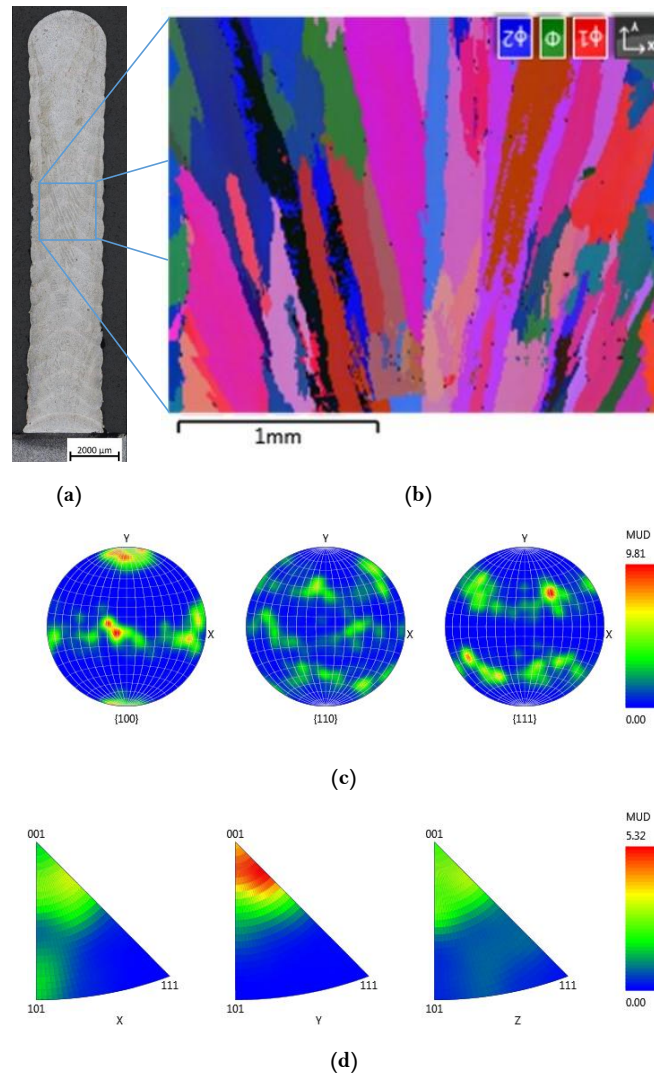


Figure 5.25: Electron backscatter diffraction pattern images of sample L-21, 316L using a laser power of 1600 W, scanning speed of 12 mm/s and powder feed rate of 20 g/min. (a) Light optical microscope overview image of area investigated (b) Euler figure from EBSD. Image is created by using the Euler angles to colour code the rgb-pixels, ϕ_1 is red intensity, ϕ is green intensity and ϕ_2 is blue intensity. (c) Pole figure maps (d) Inverse pole figure

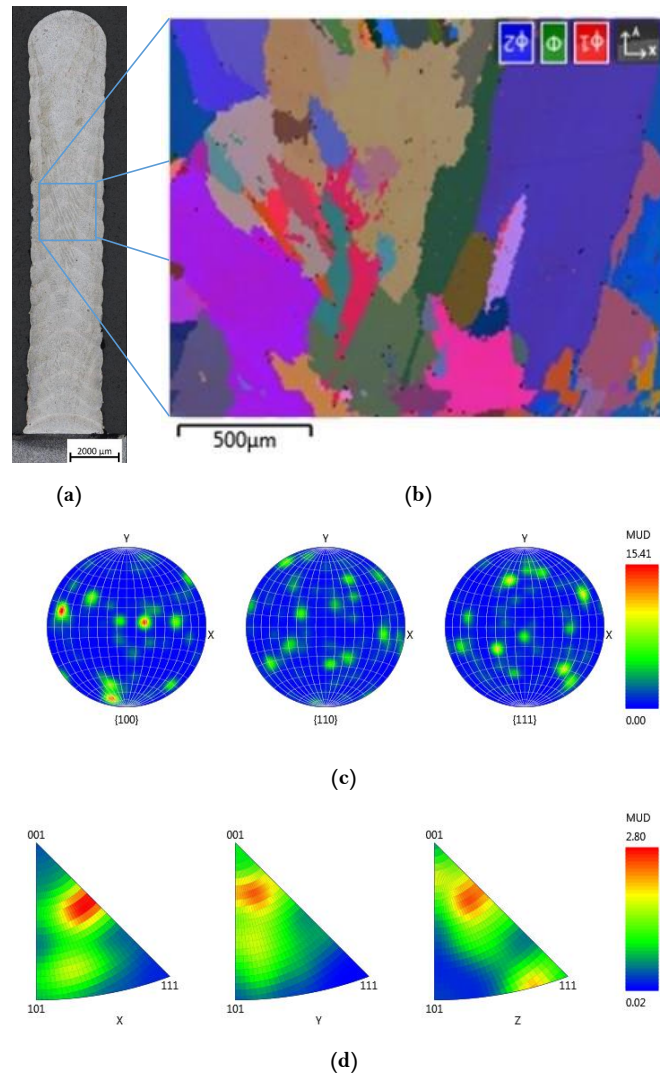


Figure 5.26: Electron backscatter diffraction pattern images of sample L-19, 316L using a laser power of 1300 W, scanning speed of 12 mm/s and powder feed rate of 20 g/min. (a) Light optical microscope overview image of area investigated. (b) Euler figure from EBSD. Image is created by using the Euler angles to colour code the rgb-pixels, ϕ_1 is red intensity, ϕ is green intensity and ϕ_2 is blue intensity. (c) pole figure maps (d) Inverse pole figure

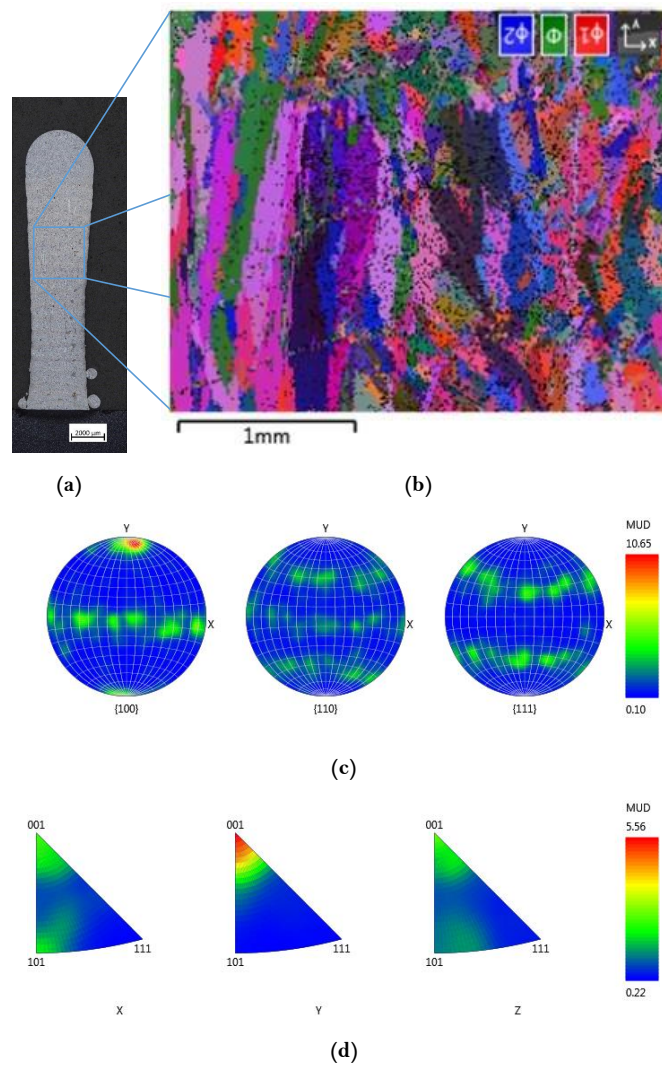


Figure 5.27: Electron backscatter diffraction pattern images of sample CE-11, 1530-CE using a laser power of 1600 W, scanning speed of 12 mm/s and powder feed rate of 20 g/min. (a) Light optical microscope overview image of area investigated. (b) Euler figure from EBSD. Image is created by using the Euler angles to colour code the rgb-pixels, ϕ_1 is red intensity, ϕ is green intensity and ϕ_2 is blue intensity. (c) Pole figure maps (d) Inverse pole figure

Table 5.2: Phase fraction calculated from EBSD

Phase name	316L 1300 w			316L 1600 w			1530-CE 1600 W	
	fcc	δ -bcc	other	fcc	δ -bcc	other	fcc	other
Phase Fraction %	99.40	0.4	0.2	99.37	0.27	0.36	89.96	10.04

6

Discussion

6.1 Material selection

Resistance from oxidation is an important feature of a metal that is used for DED, due to the fact that oxidation impairs on the wetting of the material. Oxidation will affect other factors too, such as microstructure and laser absorption. Figure 5.2 shows metallic materials in the iron, nickel, cobalt-chromium and titanium family with acceptable or excellent resistance to oxidation at 500 °C. All materials mentioned have been used in DED see Table 4.1. Selected list of some materials used for DED process can be located acceptable and excellent region. Acceptable means that the material may require additional protection and excellent means that no degradation in material performance expected after long-term exposure. It is important to note that it is at a temperature around 500 °C and the DED process achieves melting point temperatures and by melting most materials oxidize more or less. Therefore, it is important to use protective gas to prevent oxidation. But when the material is cooled down, it is not surrounded by protective gas and after a number of deposited layers, the temperature rises in the DED component and this may affect oxidation. Therefore, it is important to use oxide-resistant metals. One can see from Figure 5.2 that in the excellent region you can find materials like stainless steel, nickel alloys and cobalt-chromium alloys, these have been considered to be very suitable for the DED process. In the acceptable region you can find, low-alloy steel, tool steel, carbon steel and titanium. Many of these steels in has been considered difficult to process within DED. Titanium must be in a protective atmosphere to be processed. Therefore, small tents that surround DED are used to protect the titanium from oxidation.

It is known that weldable materials are easier to use in AM. In the Figure 5.3 it seen metallic materials in the iron, nickel, cobalt-chromium and titanium family and the material's relation to weldability. Here is a small spread, all the materials mentioned in the Table 4.1 can be found spread among poor, good and excellent weldability. Where poor means that the material can be welded, but the resulting joint may have undesirable properties. Welding is not usually used with this material unless other joining methods are not possible. Good means that the material can be welded and the joint has acceptable properties, but additional techniques or consumables may be needed, for example preheating. And excellent means that the material can be readily welded, and the welded joint can achieve comparable properties to the parent

material. No preheating is required. In poor you will find many tool steels like M4, S7, low alloy steels, some nickel alloys like Inconel 713, 738. In the Good category you will find maraging steels, some low alloy steels stainless steels like martensitic, ferritic, duplex and precipitation hardening steels. In the Excellent category you will find all austenitic stainless steels of 300 grade, some carbon steels and nickel alloys. Here you can see clearly that almost all austenitic steels are excellent to weld, and they are quite simple materials without any advanced phases transformations. Austenitic stainless steels usually have a small amount of δ -ferrite in an austenitic matrix. These materials do not go through large phase transformations. Therefore, these materials are suitable for AM.

To achieve as good thermal shock resistance according to the function $\sigma_f/E\alpha$, the material must be low in stiffness but must be strong and you want to minimize thermal expansion. The plot of thermal shock resistance vs thermal conductivity of metallic materials in the iron, nickel, titanium and cobalt-chromium family can be seen in Figure 5.4. Aluminum was removed from that chart due to that aluminum has too high thermal conductivity. And you want to have low thermal conductivity because you want a small and stable melt pool. Titanium alloys due to good strength they show a high thermal shock resistance and low thermal conductivity. After titanium alloys, we have nickel and iron alloys.

Nickel, cobalt-chromium and iron alloys have a large spread in the plot but nickel alloys have a thermal conductivity between 8-20 which is pretty low, Here we have many materials used in today's DED. Then we have quite a large spread on cobalt-chromium alloys, many steel alloys have a thermal conductivity between 50 and 60 which is quite high (see Figure 5.4). Therefore, they end up far back in the plot, but they have the same spread of thermal shock resistance. Between nickel and steel alloys, we have stainless steels. Even these have the same spread of thermal shock resistance, this is due to the fact that many variants of alloys in the same family group that have different strengths. In Figure 5.5 which focuses on stainless steel, one can see that they are clearly divided. At the bottom right, we have martensitic stainless steels with the highest thermal conductivity then comes ferric, duplex and precipitation hardening stainless steels. Far to the left is austenitic stainless steel which has the lowest thermal conductivity.

If you choose to only be interested in the material with excellent weldability and oxidation at 500 °C, 50 different materials pass all the requirements of 1831 materials counted in CES Selector. See Figure 5.6 of these 50 materials, we have austenitic stainless steels and nickel alloys, thereof 5 materials are used in today's DED, Inconel 625, Hastelloy X, 304L and 316L.

316L is common AM material and has proven itself printable with DED. And it is available with the right particle distribution for the DED process. Therefore, this was chosen as a base material for comparison. In order to not investigate too many variants, 316L HSi was chosen as second material because it has a very similar chemical composition as 316L but it contains a double amount of silicon. And silicon works as a wetting agent on stainless steel during welding. A cladding material 1530-CE was also chosen to see if there was any difference in the printing

behavior.

In Figures 5.7 to 5.11 thermodynamic calculations with JMatPro can be seen. Thermodynamic properties for 316L and 316L HSi are quite similar, they have almost the same solid-liquid region, for 316L it is between 1360 °C to 1450 °C and for 316L HSi it is between 1300 °C to 1440 °C. Average expansion coefficient and thermal conductivity are almost identical. Liquid viscosity and surface tension are different from each other. They should be different because extra amount of silicon in 316L HSi works as a wetting agent. Therefore the liquid viscosity is lower than 316L, but even the surface tension is higher than 316L.

6.2 Direct Energy Deposition

Different process parameters have been used to find the best process parameters for each of the materials (316L, 316L HSi and 1530-CE). Process parameters evaluated in this work which was free of defects can be seen in Table 5.1 these have the sample cod: H-24, L-21 and CE-11. These samples were selected because they did not show major defects during printing with DED. You can see the samples in Figures 5.12 to 5.14.

Common defects that occurred during printing were edge effect, lack of fusion, waviness and satellites. These examples can be seen in Figures 5.15 to 5.18 and their process parameters in Table 5.1. It was not possible to achieve a “flying start and stop” without the robot having to accelerate at start and retard at stop, during the project, due to difficulties in programming the laser and the robot. This also contributes to the quality at the beginning and end of the single-track wall as the edge effect. Edge effect occurred for all materials except for 316L HSi where it was quite rare that it occurred during printing. Edge effect had a height peak at the deposition start and a slope towards the end of the sample. This effect was quite difficult to eliminate for 316L and 1530-CE, but it decreased in generally by lowering the focus point by 2 mm below the substrate and by correct the movement in the z-direction. A good example can be seen when comparing sample L-21 and L-22, see Figures 5.12 and 5.15. Both had the same printing parameters except L-21 had another laser start focus where it was 2 mm below the deposition surface and had a bit higher step movement in the build the direction. Sample L-20 had a laser start focus where it was 2 mm over the deposition surface this caused instead a waviness defect see Figure 5.17. The substrate starts at a room temperature and heats up during the deposition. Therefore, it is not warmer and warmer for each layer, but it gets warmer even compared to the start of the deposit and the end of the same track (and single-track wall). This also contributes to residual stresses and affects lack of fusion. Lack of fusion (Figure 5.16) was caused by too low laser power. The deposited material did not want to fuse to the substrate at the start of the track. But it had no problem to fuse with previous layers. That the deposit material does not fuse with the substrate may be due that the substrate may be too cold, the substrate consists of Low alloy steel and has a melting point at 1700 °C which is higher than 316L, 316L HSi and 1530-CE and it needs more laser power to be melt.

Another defect that occurred during printing was satellites, it looks like small balls attached on both sides and sometimes one only side on the walls of the samples. This effect can be seen in Figure 5.18. Satellites occurred at low laser power for 316L (≤ 1500 W) and 1530-CE (≤ 1200 W), but for 316L HSi also occurred at higher laser powers (≤ 1900 W). These satellites probably have no major impact on the part, they were not fused hard on the samples and quite easy to brush off. These satellites probably occur because there is no sufficient laser power to melt all deposited powder, the powder feed may also be too high. When satellites occur on just one side of the walls this may be due to misalignment of laser and deposited powder.

From the Figures 5.19 and 5.20 you can clearly see it is important that it does not occur defect as lack of fusion because this will affect on how the heat will flow out from the component. At first layers, the heat will be carried away very fast, because it is close to the substrate. But after a couple of layers, the heat will only be able to flow through the single-track wall. Therefore, the heat will build up after a couple of layers, because it will be harder and harder for the heat to be removed. Figures 5.19 and 5.20 were produced with exactly the same parameters. The difference is just that substrate in sample in Figure 5.20 had oxides and this made that the first layer was not properly fused together and this caused lack of fusion, which prevents the heat from being carried away properly.

Cross-section examination of sample 316L, 316L HSi and 1530-CE showed no view of defects like cracks see Figure 5.21. Defects such as porosity can be found in all three materials. 1530-CE turned out to have an hourglass shape see Figure 5.21(c). This effect was almost impossible to detect earlier than at LOM. This form is probably due to that 1530-CE has a much lower melting point than 316L and 316L HSi, due to temperature history it gets warmer after each layer. The viscosity is temperature dependent and therefore the material probably flows more after couple layers when it's warmer. Or it is z-increment that is not optimal. Unfortunately, JMatPro had some trouble simulating 1530-CE because you cannot compare the viscosity of the material. Therefore, it is somewhat difficult to estimate the viscosity of 1530-CE.

Etched samples highlighted the microstructure and melt pools. You can see a clear dendritic structure on all three samples (H-24, L-21 and CE-11) see Figures 5.22 to 5.24. The CE-11 shows a much more eutectic microstructure. You can also see each layer of L-21 and H-24 but much less for CE-11. You can see that the dendrites grow against the building direction. You can see between two layers that the dendrites become thicker. You can see enlarged image of overlap of two layers in Figures 5.22 to 5.24 in center to the right. Sometimes dendrites become shorter as well, and sometimes the dendrites continue to grow through two, three layers.

EBSID shows the texture of the materials, L-21 shows a view of an anisotropic microstructure, the grains are about 1 mm and also shows grain growth in the building direction, see Figure 5.25(b to d). Same material (316L) but which was processed with a lower laser power (1300 W) shows a more homogeneous microstructure, the grains are thicker to their length, you can see that this sample have no grain growth in a specific direction see Figure 5.26(b to d). The CE-11 shows a similar texture to

L-21 with grain growth in the building direction but with smaller grain, see Figure 5.27(b to d).

EBSD shows that you can achieve different microstructures depending on the laser power you use during printing. From EBSD one can see clearly that the texture changes depending on the laser power. It should also take into account that the samples do not reflect an optimal building process with DED. The samples are small and you are building the next layer fairly quickly. This causes the temperature to rise quite quickly after a couple of layers. Therefore, having been more optimally to wait a while until the first layer will cool down before the next layer is built.

7

Conclusions

1. Single-track walls with minimum defects could be built with 316L, 316L HSi and 1530-CE. These materials are ranked from best to worst regarding wetting, thermal conductivity, surface oxides:
 - **Wetting** (good–low wetting angle): 1530-CE $\rightarrow$ 316L HSi $\rightarrow$ 316L
 - **Thermal conductivity** (good–low thermal conductivity): 1530-CE $\rightarrow$ 316L / 316L HSi
 - **Surface oxides** (good–few and thin oxides): 1530-CE $\rightarrow$ 316L HSi $\rightarrow$ 316L
2. Laser movement could not be optimized (start and stop). This causes the defects at the beginning and end of the samples.
3. The DED process is sensitive to cooling.
 - An anisotropic and homogeneous microstructure was achieved.

8

Recommendations

There is a lot that can be researched in this area of additive manufacturing. Below are three recommendations to understand the DED process better and to understand how materials behave.

1. The DED process is sensitive to cooling. The single-track walls which were manufactured in this work was short and it was a short waiting period between each layer, this will not be an optimum process to produce the large component that this process is more suitable for. A longer waiting time between the layers can be used to simulate production of a large component.
2. This work tests quite simple materials that do not have major phase transformations. When testing materials with more advanced phase transformations, temperature control will be something important in this process. This can be achieved by measuring temperature in certain layers or with an infrared camera to know if you are within a certain temperature range so no undesired phase transformations or segregations in the material occur during DED.
3. Computer simulation of the process will, in turn, improve the understanding of how the material will behave during DED. Appropriate simulations can be, to simulate the melt pool to find out what it has for shape, which is affected by laser power, scanning speed and powder feed rate. How the heat flows from the component during the process. How different deposition strategies affect the DED process. In that way, expensive and time-consuming experiments will be saved. This will also lead to a better understanding of how materials behave and that means you can design new materials according to the process in the future.

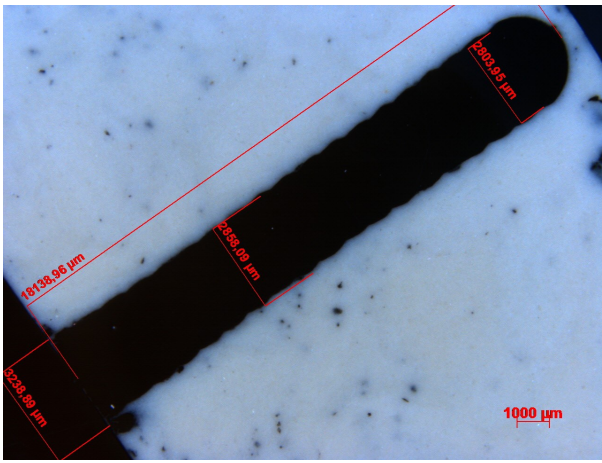
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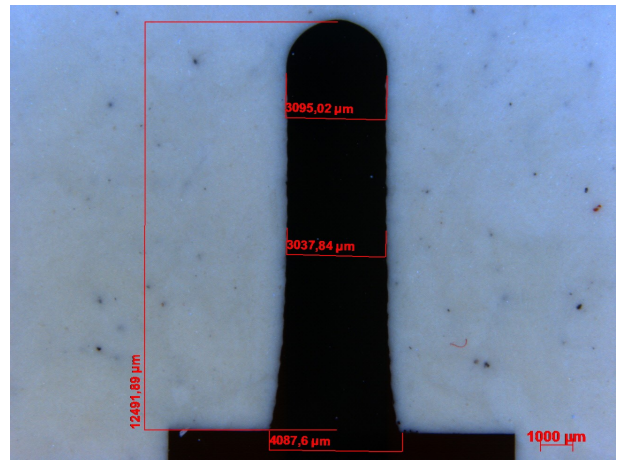
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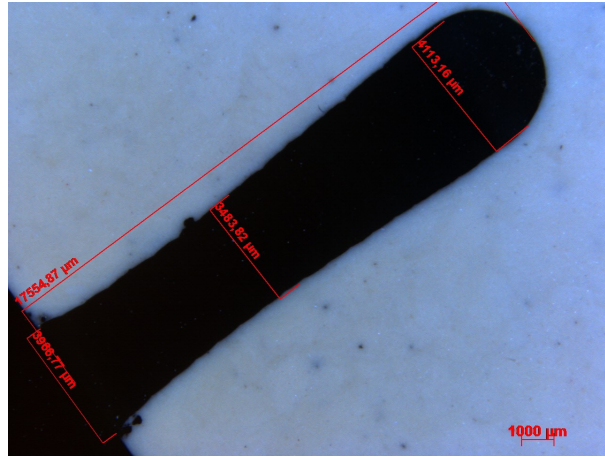
Appendix 1



(a) 316L (code L-20)



(b) 316L HSi (code H-24)



(c) 1530-CE (code CE-11)

Figure A.1: Measurements of the height and width of the Single-track walls.