Improvement of densification and microstructure of ASTM A131 EH36 steel samples additively manufactured via selective laser melting with varying laser scanning speed and hatch spacing

Wang, Jingjing; Wu, Wen Jin; Jing, Wei; Tan, Xipeng; Bi, Gui Jun; Tor, Shu Beng; Leong, Kah Fai; Chua, Chee Kai; Liu, Erjia

2019

Wang, J., Wu, W. J., Jing, W., Tan, X., Bi, G. J., Tor, S. B., . . . Liu, E. (2019). Improvement of densification and microstructure of ASTM A131 EH36 steel samples additively manufactured via selective laser melting with varying laser scanning speed and hatch spacing. *Materials Science and Engineering: A*, 746, 300-313.
doi:10.1016/j.msea.2019.01.019

<https://hdl.handle.net/10356/140649>

<https://doi.org/10.1016/j.msea.2019.01.019>

© 2019 Elsevier B.V. All rights reserved. This paper was published in *Materials Science and Engineering: A* and is made available with permission of Elsevier B.V.

Downloaded on 26 Apr 2023 20:06:35 SGT

Improvement of densification and microstructure of ASTM A131 EH36 steel samples additively manufactured via selective laser melting with varying laser scanning speed and hatch spacing

Jingjing Wang^a, Wen Jin Wu^a, Wei Jing, Xipeng Tan^a, Gui Jun Bi^b, Erjia Liu^{c*}, Shu Beng Tor^c, Kah Fai Leong^c, Chee Kai Chua^c

a. Singapore Centre for 3D Printing, Nanyang Technological University, 50 Nanyang Avenue, Singapore

b. Singapore Institute of Manufacturing Technology, 73 Nanyang Drive, Singapore

c. School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore

* Corresponding author: Tel: +65-67905504, Email: mejliu@ntu.edu.sg

Abstract

ASTM A131 (EH36 grade) steel samples with a high density (>99.5%) were additively manufactured (AM) through a selected laser melting (SLM) process. The AM process parameters were optimized through tuning scanning speed from 100 to 300 mm/s and hatch spacing from 0.08 to 0.13 mm with a layer thickness of about 50 μm using a laser power of 175 W under a chess board scanning strategy. By varying heat input mainly via lowering scanning speed, a near full density of the samples could be achieved. And, the processing at lower scanning speed was broadened to a larger window of hatch spacing, which improved the density

of the printed samples well above 99%. The microstructure of the samples under different scan speeds was subsequently studied and compared. Cellular-dendritic grains with a diameter of around $1 \pm 0.5 \mu\text{m}$ were observed. Regions with acicular grains of up to $2\text{-}3 \mu\text{m}$ were also observed at different locations. A large plate-like martensite structure was found in coarse columnar grains (up to $20 \mu\text{m}$). With lower scanning speed, the grains were coarser and more like a cellular structure. With higher scanning speed the grains were finer and more like a cellular-dendritic structure. However, different morphologies of martensite grains were found mainly in cellular, columnar and lath shapes, which probably resulted from different transformation mechanisms and were controlled by cooling rate. Electron back scattered diffraction analysis showed that the prior elongated columnar grains with the martensitic plate-like structure inside them delineated the columnar grain boundaries. The micro-hardness and tensile properties of the selected samples were correlated to their microstructures. The resultant mechanical properties were attributed to a combined effect of martensitic structure and possible precipitation, solid solution and dislocation strengthening for the EH36 steel samples built via SLM. The fractured surfaces, examined with scanning electron microscopy, showed mostly a dimple type of failure but with a low elongation of 5 to 6%. The microsegregation behavior of the samples was believed to accompany this rapid solidification process and the degree of element escaping from the lattice was believed to be dependent on the cooling rate.

Keywords: ASTM A131 (EH36) steel, selective laser melting, densification, microstructure, microhardness, tensile strength

1. Introduction

As a low carbon, high strength structural steel, ASTM A131 (EH36 grade) possesses both high strength and good toughness. In Marine and Offshore industry building a large scale structure is usually a lengthy and labor intensive process. Instead, additive manufacturing, known as a one-step near-net-shape manufacturing, can largely reduce production cycles. It is a building process through a computer controlled layer-by-layer technology with almost no design boundary. A large heat affected zone (HAZ) is usually induced in a welded part, which can be effectively reduced if the part is additively manufactured. Meanwhile, the good weldability of EH36 steel makes this grade of steel ready to be printed using AM processes. There are many types of metal that have been developed successfully through various AM processes like selective laser melting (SLM), direct metal deposition (DMD), electron beam melting (EBM), etc. [1-6]. Functional parts fabricated through AM processes with certified properties have been applied in various industries [5, 7, 8].

However, there have been limited studies on AMed A131 EH36 steel. In addition, a previous research on EH36 steel materials printed via SLM reported a relative low densification (~97%). Thus, improvement of densification for AMed EH36 steel is necessary [9]. It is good for a structural steel to possess both good strength and toughness that depend on the density of the structures made from it [10]. To achieve a high density of AMed materials, process optimization is needed. An orthogonal method by incorporating a few key process parameters can help optimize the process parameters that will contribute to varying heat input that is believed to be crucial to densification. Usually, energy density (ED) and densification is in a positive proportional relationship [2, 11-15]. Two most crucial parameters for ED are laser power (P) and scanning speed (v) as depicted by the formula, $ED = P/(hvt)$, where h is the hatch spacing and t is the layer thickness [10]. Some others parameters such as scanning strategy, preheating

temperature, etc. also affect heat input in different aspects. For example, an optimized volumetric energy density of 125 J/mm^3 in an SLM built 316L material has been reported by Wang et al. [16], which can increase the primary dendritic spacing while the microstructure can be refined by increasing scanning speed. Yadroitsev et al. have studied the effect of energy input mainly through controlling scanning speed and preheating of SLM processed 316L samples and suggested that scanning speed be a more effective factor to tailor the process and while preheating is only pronounced when temperature is above $0.5 T_m$ of the 316L material, where the risk of track instability and balling is the highest [17]. The general criteria would be, if energy density is some too high, burning and sputtering that will happen and cause balling or satellites thus preventing proper bonding and high build density. On the other hand if energy density is not enough, incomplete melting of the powder will lead to poor wetting that will also cause balling effect [17, 18].

The relationships between the mechanical properties and microstructure of various AM built metals have been reported [19-23], which have discussed various defects like lack of fusion that often acts as the crack initiation point. The orientation related mechanical properties are related to defects distribution as well as anisotropic microstructure with the elongated cellular sub-grains resulting from a high cooling rate [3, 10, 24-29].

This work aimed to improve the densification of SLM printed EH36 samples through controlling laser scan speed and hatch spacing in the printing process as it was believed that more consistent tensile properties would benefit from the high density of the printed samples. Different types of martensitic structures were observed under TEM and microsegregation was found accompanying the rapid solidification process when the in-process cooling rate was not high enough to suppress element segregation.

2. Experimental details

2.1. Materials and sample preparation

An ASTM A131 powder (EH36 grade, gas atomized) with particle size in the range of 20-53 μm was provided by Sandvik Osprey (UK) with the chemical composition listed in Table 1 and the surface morphology of the powder shown in Figure 1. 18 cubic samples (10 mm x 10 mm x 10 mm) and several rectangular blocks (60 mm x 12 mm x 10 mm, to be machined to tensile test specimens) were built with an SLM250 machine in an Argon gas environment. The SLM process and the printing layout of rectangular blocks are schematically shown in Figure 2[30]. All the rectangular specimens were printed along the horizontal plane (x-y plane), with laser power of 175 W, layer thickness of 50 μm , laser scanning speed from 100 to 300 mm/s and hatch spacing from 0.8 to 0.13 mm. Three scanning speeds were studied, i.e., 200 mm/s (denoted as S200, with hatch spacing at 0.1 mm), 250 mm/s (denoted as S250, with hatch spacing at 0.12 mm) and 300 mm/s (denoted as S300, with hatch spacing at 0.12 mm). Scanning speed at 100 mm/s was not selected due to a surface burn mark indicating that a certain degree of oxidation happened during printing. A preheating temperature of 100 °C was used to relieve residual stress and prevent the samples from cracking.

Table 1 Chemical composition of EH36 powder (wt%)

C	Si	Mn	P	S	Cr	Mo	Ni	V	Cu	Nb	Ti	Fe
0.18	0.1-0.5	0.9-1.6	0.035	0.035	0.2	0.08	0.4	0.05-0.1	0.35	0.02-0.05	0.02	Balance

Figure 1 SEM micrographs showing (a) overview and (b) surface morphology of EH36 powder stock

Figure 2 Schematic of SLM process[31] with printing layout of rectangular blocks

Metallographic preparation was done following the standard procedures. The cross-section examination to the vertical build direction was conducted by cutting through the middle of the samples using electrical discharge machining (EDM) followed by grinding and polishing until using 1 μm diamond paste. The freshly prepared surfaces were then etched by a saturated picric acid or 2% nital for a few to tens of seconds using an immersion method. The etched samples were then immediately washed thoroughly with purified water and then ethanol.

Tensile test coupons were machined from the rectangular blocks with the dimensions shown in Figure 3 with all the dimensions in mm. At least 2 - 3 pieces of tensile coupons were tested to get average values of tensile properties.

Figure 3 Drawing of tensile test coupon with all dimensions in mm

TEM samples were prepared with the following procedure: A slice was sectioned off from each printed block and thinned down to a thickness of about 100 μm by sand paper. A disk of 3 mm in diameter was formed by blanking and mounted for further dimple grinding (Gatan Model 656) to a thickness of about 10 μm using 1 μm diamond paste. Finally, ion milling (Gatan Model 691) was used to make the disk even thinner until perforated. The ion milling operation was run at a large angle of 8° for 30 min followed by a small angle milling at 4° and 2° , respectively, until the

sample was perforated. The sample was taken out and checked under optical microscope every 15 min to prevent from over milling and damage.

2.2. Characterization

The microstructure and surface morphology of the samples were characterized using optical microscopy (Zeiss and Olympus), scanning electron microscopy (JEOL JSM-5600LV), FE-SEM (JEOL JSM-7600F) and transmission electron microscopy (JEM 2010). X-ray Diffraction (Philips) was used for phase determination. Elemental analysis was analyzed by using energy dispersive X-ray spectroscopy (FE-SEM, JEOL JSM-7600F). The hardness of the samples was measured by Vickers microindenter (FM-300e) under a fixed load of 50 g for 10 s per measurement. A universal testing machine was used for tensile testing with a maximum loading of 50 kN (Instron 5569).

The density of the printed samples was measured by using an Archimedes method with ethanol at room temperature (~23 °C). The average density of a sample was calculated from at least 3 repeated measurements.

3. Results and discussion

3.1 Phase determination

A basic BCC structure is confirmed by the XRD spectra shown in Figure 4 where all three samples S300, S250 and S200 demonstrate similar diffraction patterns with five characteristic peaks indicated in the spectra by solid circles, which are attributed to a martensitic structure [32]. A few minor peaks are detected as well, which belong to either retained austenite (solid diamond) or iron carbide (solid triangle) as indicated in the XRD spectra.

The resulted mixed mode of phases can be related to the EH36 steel composition and SLM process parameters. The formation of the main phase martensite is explained as follows: Firstly, high martensite start (M_s) and finish (M_f) temperatures make a near complete martensitic transformation possible. The M_s of over 400 °C is estimated from the equation: $M_s (K) = 731 - 227(C+N) - 17.6Ni - 22.5Mn - 17.3Cr - 16.2Mo$ [33]. For this low carbon steel, M_f shall fall at around 300 °C. With the preheating temperature lowered to 100 °C, a temperature difference of about 200 °C makes a full martensitic transformation possible. Secondly, the cooling rate for the martensitic transformation to happen is satisfied by SLM process (above 10^3 K/s). From the CCT diagrams of steels a high enough cooling rate is needed for a martensitic transformation to take place and a high cooling rate is usually achieved by a quenching process. Here, the SLM process can achieve a very high cooling rate up to 10^8 K/s, which is realized through directed heat dissipation where the substrate acts as the heat sink. These two are believed to be the main factors that lead to the near full martensite structure in the SLM printed EH36 steel samples.

Figure 4 XRD spectra of selected EH36 samples identified as martensite, retained austenite and iron carbide

Excess retained austenite could result from a very high cooling rate. As known a higher cooling rate renders higher undercooling[34] and reduced M_s (due to finer grain structure, etc.)[35] compared with conventional water/oil quenching process, where martensite transformation can be suppressed. The higher RA content is evidenced by the small FCC peak detected in sample S300 that incurred with highest cooling rate among the three samples with highest scanning speed. There is similar report claiming higher amount of retained austenite in AM processed steels where a set of reasons were stated mainly factors that can 1) suppress $\gamma \rightarrow \alpha'$ transformation (strain at high-angle grain boundaries, γ stabilizing elements, environment of powder & part manufacturing) 2) reduce M_s temperature (finer grain structure, higher dislocation density) [25].

Higher retained austenite have been reported in SLM processed 17-4PH stainless steel compared with wrought grade [25]. This is believed attributed to a core-shell dendritic structure with α' phase in core and γ phase at shell (based on Scheil-Gulliver non-equilibrium solidification simulation) with possible reasons stated as: Nitrogen absorption that stabilized austenite phase, lowered martensite starting temperature (M_s) due to fine submicron sizes of dendrite, microsegregation caused austenite stabilizers suppressing the martensitic transformation. Meanwhile the influence of residual stress was concluded based on as-built 4340 steel (DMD process) and stress relieved equivalent [19]. Results implied the existence of residual stress decreased M_s (measured through CCT experiment).

Small amount of iron carbide detected in sample S250 is believed to be formed either upon deposition or tempered out by applied heat source. The element segregation is believed to make precipitation thermal dynamically favorable. The heat comes from three main sources: laser

scanning, subsequent laser scanning, preheating. Those may play effect to the microstructure in the aspect of martensite self-tempering, tempering and aging, etc. The highest value of micro-hardness of sample S250 (present in the later section) could be due to the strengthening effect of the precipitates formed probably due to appropriate thermal cycles that happened under this scanning speed.

Moreover, due to very low local cooling rate and higher drop back temperature (above M_s), etc., some bainite or ferrite phases may also form. However, it is difficult to differentiate them from martensitic BCT (body centered tetragonal) crystal structure because of the low tetragonality of this low carbon steel. The martensite, retained austenite and possible iron carbide precipitates are further characterized using TEM and EBSD in the following part.

3.2 Macro-scale features

Melting pool, pores and inclusions, etc. characterize the macro-scale features of the SLM printed EH36 steel samples. Figure 5 displays the optical images of vertical cross sections for the etched samples S300 and S200. They are featured by melting pool and lack of fusion. The overall color of sample S200 is darker than S300 and with larger size of lack of fusion that can range up to a few hundred microns. The average melting pool depths for the samples S300 and S200 are about 70 - 90 μm and 100 μm respectively. A re-melting layer of 20 - 40 μm in depth is estimated from the average melting pool depth compared with the top-most layer using the sample S300. This ensures an enough penetration depth for a thorough melting of a 50 μm powder layer and metallurgical bonding with the previous solidified layers. Process parameters can influence melting pool behavior that may result in different grain structures subsequently being formed as well as features like lack of fusion and inclusions, etc. Here the two samples built with different

scanning speeds demonstrate different macro-features that can in turn determine their mechanical behavior.

The average melting pool depth of sample S200 is larger than that of sample S300 which is due to higher energy input induced by lower scanning speed. This is consistent with the findings on SLM processed 316L that higher the energy input deeper of the melting pool obtained[22]. Meanwhile the maximum void size suggesting lack of fusion, in sample S200 is larger than that in sample S300. This is most probably due to more irregular melting pool morphology that deteriorated the surface roughness and hence the interlayer bonding. The melting pool irregularity was most probably generated from higher energy input as a result of lower scanning speed[36]. Small round pores in micron scale shown in Figure 5 are mainly due to trapped gas which can't escape from molten metal. More small pores in S200 are probably resulted from more vigorous evaporation at higher energy input.

Figure 5 Optical images of vertical cross sections for etched samples: (a) S300 and (b) S200

Lack of fusion zone is usually coexisting with unmelted powder and inclusions. Those unmelted powders are present at lack of fusion region where there is non-enough energy penetrating through and melt the layer below. Certain degree of melt pool surface oxidation results in metal

oxide which left at inter-bonding layer, in the size of tens of microns. The kinetics of oxide forming is explained by Thijs et al. in the SLM processed maraging steel[37]. And void or crack could be formed along with it [20]. In most AM printed metals the lack of fusion and unmelted powder is regarded as unpreventable [38]. Pores together with unmelted powder could possibly initiate crack as often observed in the fractured surface of AM built metals [19, 20]. And it could also deteriorate ductility, modulus, toughness and fatigue properties due to its stress concentration effect[19]. And sometime the lack of fusion can promote synergistic oxidation which may deteriorate mechanical properties from large aspect[19]. Obviously the quantity of those kinds of unmelted or partially melted powder is less found in sample S200 due to its higher energy input from lower scanning speed.

3.3 Micro-scale features

Micro-scale features cover cellular-dendritic grains with their forming mechanism and evolution together with possible microsegregation-precipitation behaviors accompanied this rapid solidification process. Aside the cellular-dendritic grains the rapid solidification process induces various shapes of grains including acicular and coarsened columnar grains that will be discussed together with the possible martensitic transformation mechanism within the columnar grains.

As seen from Figure 6(a) the optical image of the etched vertical cross section of sample S300 shows the cellular-dendritic grains within the melting pool and some equiaxed grains ($5 - 6 \mu\text{m}$) near the centre of it. The average diameter of the cellular-dendritic grains is around $1 \pm 0.5 \mu\text{m}$.

The acicular shape of grains with the size of $1-2 \mu\text{m}$ characterized by smaller aspect ratios is observed within the same melting pool. The elongated cellular-dendritic grains with large aspect ratios grow from the bottom of the crescent-like melting pool to its center along the heat dissipation direction. However, the optical image of the etched vertical cross section of the

sample S200 in Figure 6(b) shows indistinct cellular grains with darker intercellular regions. The structure is dominated by a more cellular-like shape and the grains are obviously coarsened. The size of the cellular grains can reach about 2 μm . In some regions short and wide acicular shaped grains with the size of 2 -3 μm are observed. For the both samples a near fusion white band distinguishes melting pool boundaries.

In sample S300, a grain evolution from planar (enclosed region with dotted line) to cellular and cellular dendritic morphology (with dendrite arm) is observed as shown in the SEM image in Figure 6(c). Cross section of etched sample shows that S300 has a mixture of cellular and dendritic grains. The dendritic grains dominate which in many cases defined as cellular-dendritic grains [23, 39]. However cross section of etched sample shows that S200 has indistinct cellular grains. No obvious evolution phenomena being observed and cellular boundaries are rather vague. There are some acicular shapes of grains with boundaries decorated by tiny precipitates as shown in Figure 6(d). The tiny precipitate is analyzed by EDS for its chemical composition (see section Microsegregation/precipitation).

Figure 6 (a & b) Optical images of etched vertical cross sections showing: (a) S300 with cellular-dendritic grains within melting pool and some equiaxed grains near the centre of it, (b) S200 with indistinct cellular grains within melting pool and darker intercellular regions, and (c & d) SEM images of etched vertical cross sections showing: (c) S300 with cellular grains with a planar zone (enclosed region with dotted line) and some polygonal grains below it, and (d) S200 with indistinct cellular grains and some acicular shapes with sharp grain boundaries decorated by tiny precipitates

The metastable grains and their evolution rules are believed to be related to G/R ratio, where G is temperature gradient and R is solidification rate. At melting pool boundary, high G/R ratio (high G and low R) favors formation of planar crystal. Moving into the melting pool centre, with gradually decreased G and increased R , grains may evolve into cellular, cellular-dendritic, dendritic or even to equiaxed. Equiaxed grains are most probably found in the center near the surface of the melting pool probably due to isotropic heat dissipation [40, 41]. The equiaxed grains found in the middle of the melting pool is believed to form according to this mechanism. It is also reported in SLM processed 300 maraging steel that equiaxed grains are formed at the surface of the melting pool due to isotropic heat dissipation[42]. Because the R equals scanning speed at the center of the melting pool, a higher G/R ratio in the slower scanning speed case that favors cellular grain formation as observed by more cellular like grains in sample S200[23, 39]. And lower G/R ratio favors cellular-dendritic grain as observed in sample S300.

The microstructure formation can usually be explained by theory of solidification [43, 44]. According to this theory the rapid solidification is caused by constitutional undercooling. Constitutional undercooling is believed coupled with solute redistribution that helps to achieve necessary undercooling in front of the solidification front (below liquidus temperature), where constitutional supercooling is determined by G/R ratio. The morphology of liquid/solid interface is determined by the constitutional undercooling that is this G/R ratio. However this constitutional supercooling theory based on solute redistribution is challenged by a recent study[45], which claimed no micro-/nano-segregation that can be found at intercellular grain boundaries of SLM processed 316L. The author believed that it was possibly due to largely suppressed element movement due to high cooling rate of about 1.7×10^6 K/s that was achieved by pulsed laser at high scanning speed of 5000 mm/s. This put forward a need for a new theory to explain the rapid solidification behavior.

Grains formed during SLM process are again related to materials thermo-physical properties and process parameters that are related to G x R value. Based on solidification theory cooling rate is governed by G x R value. With increased G x R value, cooling rate increases. This explains the microstructure characteristic of the two samples printed at different scanning speed. With higher scanning speed, the cooling rate could be higher resulting in finer grains. With lower cooling rate the grains are coarser in due as observed in S200. Similar findings were reported by other researchers including fine cellular or cellular-dendritic subgrains with size of $1 \pm 0.5 \mu\text{m}$ in many alloys [22, 45] e.g. SLM processed 316L[40] and maraging steel[10] that is resulted from the rapid solidification process[46, 47]. The effect of slower scanning speed has been reported to lead to the lower cooling rate due to its higher energy input[22] and microstructure coarsening can happen in due. Meanwhile higher energy input could influence the microstructure in the way

of phase transformation, precipitation and release of residual stress through larger heat input from subsequent laser scanning resulting in more vague intercellular grain as reported[42, 48, 49]. Here in SLM processed EH36 steel the darker color in sample S200 is probably due to large amount of tiny precipitates being etched. The enlarged black holes are due to over-etching. The microsegregation/precipitation behavior is discussed as following.

As seen from Figure 6 the optical images of the etched vertical cross sections show that the sample S200 has darker intercellular boundaries compared to the relatively white intercellular/dendritic interface of S300. The SEM image in Figure 7(a) shows the sample S200 with possible tiny particles distributed along its indistinct cellular or acicular grain boundaries. The EDS spectrum of the tiny particles in Figure 7(b) illustrates mainly Fe and C and a small amount of Si, where the percentages may not be stoichiometric owing to the small size of the particles.

Figure 7 (a) SEM image showing indistinct cellular grains with particles distributed along intercellular region in sample S200, and (b) EDS spectrum of the tiny particles in (a)

The observation and EDS analysis confirmed there was precipitation behavior at lower scanning speed 200 mm/s. The mechanism of precipitation is believed related to microsegregation that accompanied the rapid solidification process that makes precipitation energetically favorable.

For sample S200 longer retaining time at high temperature is believed prompting higher degree of element migration to the intercellular region during this lower cooling rate scenario. The relatively white intercellular/dendritic interface of sample S300 seems indicating absence of microsegregation or there could be in such a level that is much lesser amount. A greater degree of suppression of element redistribution was believed due to higher cooling rate that incurred in sample S300. And those proved that the microsegregation/precipitation behavior is related to process parameters that coupled with different thermal cycles. Solidification mechanism could be different as stated above. More research is needed on this topic and work is undergoing to this SLM processed EH36 steel.

It has also been reported that the high cooling rate in AM process can enhance the limit of trapped solute in the crystal lattice, however a complete avoidance of microsegregation is not possible even up to 10^4 - 10^6 K/s[48]. The microsegregation phenomena was found in various AM metals such as SLM processed 316L of Mo segregation into intercellular grain boundaries[50], LMD processed maraging steel with Ti segregation into the intercellular grain boundaries[48], and SLM processed Inconel 738LC with precipitates being found at intercellular and interdendritic region[48], etc. As many authors dictated that the segregation or solute redistribution is a coupling behavior with the rapid solidification process and the microstructure forming mechanism is explained based on that[43]. However other solidification theory was brought forward by the new findings as stated above[45].

Sparsely found polygonal grains ($\sim 2 \mu\text{m}$) located right below the white band region are believed to be within a heat affected zone where the grains may have undergone recrystallization upon the laser scanning of next layer. Chemical segregation or carbide precipitation may occur within this

regime. The heat effect of the laser source is not only constrained to the heat affected zone. A higher amount of heat accumulation can be another consequence.

Coarsened columnar grains

As shown in Figure 8 for the both samples S300 and S200, the melting pools consisting of the coarse columnar grains were observed, where the columnar grain size can go up to 20 μm . Within the coarsened columnar grains are the differently oriented plate-like structures that delineate the columnar grain boundaries (as indicated by red arrows). Though the exact forming mechanism of those coarsened columnar grains is not clear yet, it is attributed to lower cooling rate. The lower cooling rate is probably caused by heat accumulation from adjacent track or layer as reported[42]. The plate-like structures are formed with the martensite grains, where the coarsened columnar grains are due to some prior phase (e.g. γ austenite) before the martensitic transformation takes place within it. The array pattern of differently oriented martensite grains constrained inside the bigger columnar grains seems to demonstrate a $\gamma \rightarrow \alpha'$ transformation and details will be discussed in the following phase transformation section.

In some scenarios metastable submicron-sized cellular grains can grow into bigger cellular grains upon excess heat influence that comes from adjacent or next layer laser scanning which is observed in other researcher's report whereas timing and temperature is crucial for this merging to happen[51, 52]. But from the optical microscopic images shown in Figure 8(a) one of the coarsened columnar grains was at topmost layer where there is no further building layers above. This assures its formation upon deposition.

Figure 8 (a & d) Optical micrographs showing coarse columnar grains with big plate-like martensite structure at different orientations inside of (a) S300 and (d) S200 (both etched with 2% nital) , and (b, c, e & f) SEM images showing coarse columnar grains and some finer regions with acicular shape of grains in etched samples of (b) S300 and (e) S200 with respective enlarged views in (c & f) showing plate-like martensite structure at different orientations inside coarse columnar grains from area A in (b) and area B in (e), respectively

Occasionally some stray grains are found in between the arrayed cellular/dendrite grains. This is most probably resulting from varied local heat flow as reported elsewhere[53]. And microstructure variation within one melting pool was observed in this SLM processed EH36 steel implying the complexity of its thermal cycles. And this complex heat and mass transfer within one melt pool is usually a consequence of rapid solidification. Meanwhile novel metastable structures and phases may form along with the non-equilibrium solidification process as reported [54]. All those phenomena can be linked to process settings which resulted in tailored microstructures [55, 56]. This is realized by the approach of process adjustment through scanning speed, laser power, etc. In SLM process this results in different heat input that can lead

to different thermal cycles which open a chance to be tailored for desired microstructure so as to desired mechanical properties.

3.4 Nano-scale features

Martensite grains are observed using TEM with multiple types of grain in different morphologies. As shown in Figure 9 the TEM images (a-d) of the sample 300 show the bright field and dark field microstructures disclosing lath, cellular and columnar shapes of grains and (e & f) of the sample S250 show the cellular and columnar shape of grains.

A SAED (selected area electron diffraction) pattern inserted shows each lath a single crystal in body centered cubic (BCC) phase. It confirmed as martensite lath with lath width about 100 to 200 nm that parallel-oriented in a band and retained austenite (the dark field image with SAED inserted showing a FCC phase) lying in between as shown in Figure 9(d). The size of cellular grains and columnar grains are 500 - 1000 nm and up to 300 nm respectively which located at different sites of the sample. The cellular grain seems slightly smaller than the cellular-dendritic grains that was observed using optical microscope and grow from bottom of the melting pool to center of it. The size of cellular grains and columnar grains in sample S250 is up to 1 μm and 500 nm respectively which are slightly coarser than that in sample S300. The SEAD pattern inserted confirmed a single BCC martensite crystal of each columnar shape grain. There is no lath martensite and retained austenite being found in current S250 sample. Reasons could be due to higher amount of retained austenite in sample S300 resulting from higher cooling rate. The dislocation density in cellular shape of martensite grains seems higher than that in columnar and lath shape for both samples S300 and S250.

As shown in Figure 9(b & e) with the TEM images, the cellular boundary of S250 is obviously vague that is in a contrast to the clear cellular boundary of S300. Inserted SEAD pattern (around

cellular grain boundary) confirmed its BCC martensite matrix with carbide precipitates. And EDS measurement in sample S250 shows higher concentration of Cr element around the intercellular region and a slightly higher concentration of Ni, C and Si element as well compared with inner grain region. The vague cellular grain boundaries are probably due to an increment of dislocation density resulted from microsegregation or nanoprecipitates to the boundaries.

From above observation, obviously the columnar shape of martensite grains in the size of a few hundred nm was transformed from some prior grains as shown in Figure 9(c). The TEM observation was consistent to above optical graphs (coarsened columnar grains partitioned by plate-like martensite structures). For the type of cellular shape of martensite grains the transformation mechanism is not that clear. It could be dictated that the cellular shape of martensite grains partitioned the prior austenite cellular grains (which is larger in size) upon solidification while both are in similar cellular shapes but differs in scale. It may follow conventional hierarchical transformation scheme as dictated in DMD built AISI 4340 low alloy steel that was reported as same as conventional heat treat process[19]. And they also disclosed for the first time in open literature a Kurdjumov-Sachs relationship between martensite and austenite in DMD processed 4340 steel and similar findings were published earlier in DMD processed tool alloy steel [57]. However the cooling rate of SLM process is higher than DMD process. In view of the microstructure forming mechanism, further study is needed.

Figure 9 TEM images of (a-d) sample S300 showing: (a) bright field microstructure, (b) dark field microstructure, (c) cellular grain structure, and (d) columnar grain structure, and (e & f) S250 showing (e) cellular grain structure and (f) columnar grain structure

However a direct precipitation of martensite grains with no prior austenite phase formation can't be ruled out. Such early precipitation of posterior phase was reported by Kadiri et al. in LENS built AISI 4140 low alloy steel showing a direct nucleation of primary lower bainite from prior δ ferrite grain boundaries which cross a few γ prisms where it is not following the claimed transformation mechanism of δ ferrite $\rightarrow$ γ austenite $\rightarrow$ bainite [54]. It could be also the scenario here for SLM processed EH36 steel that the very high cooling rate renders the high temperature phase has no time to form and the molten metal was directly solidified into martensite crystal. This is based on the sayings that the very high cooling rate promotes formation of novel and metastable structures and phases as well as a new transformation mechanism in due.

There is other saying that the martensite structures within SLM processed steel samples could be away from conventional packet/block/lath hierarchical structures with support by several findings, e.g. it has been reported that lath martensite can't be formed due to this high cooling rate in LMD processed maraging steel [58]. Jäggle et al. reported martensite blocks (boundaries with misorientation above 50°) confined to a single dendrite that belongs to same prior austenite grain with retained austenite between dendrites in LMD built maraging steel but saying it is not following the conventional hierarchical structure [58]. And they also claimed the stabilized austenite at interdendritic regions is due to solute segregation of Ti, Mo and Ni.

However the lath structure and smaller size of columnar martensite grains is indeed identified in other researcher's work in spite of their micro cellular-dendritic morphologies[42]. The martensite transformation mechanism in AM built metals remains largely unknown and the perspective is rather uncertain. However the variety in martensite grains and shapes are believed to be related to their individual thermal cycles that evidenced the complexity of melting pool behavior. This work mainly presents the morphologies investigation to martensite grains in SLM processed EH36 steel and firm conclusions with evidence will be needed for its transformation mechanism. The micro/nano-segregation and nano-precipitation behavior also needs more studies and work is ongoing. As usual practice there is two types of martensite in steels: lath martensite and needle-shaped martensite. Low carbon steel usually takes the shape of lath martensite that is less brittle. The high strength and fair toughness of lath martensite, that has been long believed characterized by high density of dislocation, makes direct application possible, however the high density of dislocations is only found in very low carbon steels [32]. A general rule may apply that higher the cooling rate finer the structures obtained hence for a better strength and ductility [59, 60].

Retained austenite (RA) is found in the sample S300 as shown in the TEM image in Figure 9(d). The retained austenite grains lie in between the martensite laths. These RA grains have no much difference from a conventionally quenched RA that usually coexists with the lath martensite grains and lies in between. However it has been reported that the position of RA in a laser metal deposited maraging steel mainly exists at intercellular grain boundaries [58]. Here, EBSD is used to further investigate the nano-scale features of the samples from a larger point of view including the various martensite grains, retained austenite and possible carbide precipitates within the matrix.

An EBSD image with an inverse pole figure (IPF) shown in Figure 10 again clearly depicts a region with the big plate-like martensite structures distributed within some band substructures as shown in the lower part of the image with the band size of about 7 - 20 μm . The boundaries of those bands are delineated by various colored plate-like or block martensite crystals that are consistent with optical microscope observation. The patches in different colors demonstrate different crystallographic orientations. Those clearly show that the plate-like or block shapes array in certain angles with the band boundaries and there are a few different colors within one band. This could be a sign of some prior phase of grains formed first during solidification before martensitic transformation taking place within them. The predominant phase is BCC structure and grain sizes measured mostly falls around 1 μm which is consistent with TEM and optical microscopic observation. Due to large step size (0.2 μm) used or the similar crystallographic orientation of martensite crystals the measured grain size could be reduced if smaller step size is used. In the upper part of the image, some acicular shapes dominate. From the image, there is no obvious preferred orientation of crystal growth observed.

Figure 10 EBSD image of sample S300 with IPF

A small amount of FCC phase was detected that shall belong to retained austenite with the grain size ranging from about 0.2 to 0.4 μm. Retained austenite grains are spread at different locations within or along grain boundaries. This again may be reduced further by using smaller step size such as 0.1 μm. Trace amount of Fe₃C phases are also detected by EBSD scanning where it scatters mainly along the grain boundaries. Microstructure evaluation through EBSD depicts elongated columnar shape of grains with the overall length up to a few tens of microns in accordance to melt pool size measured from optical microscope.

This is the first time in open literature that the detailed features of SLM produced EH36 steel samples were reported including martensite grain morphologies and a general orientation, retained austenite, and possible precipitates.

3.5 Mechanical Properties

As described above tuning of process for a higher densification can be done through adjusting energy density where some of the key process parameters are correlated into this single factor, $ED = P / (S * H)$, In this equation, laser power is at numerator and scan speed and hatch space is at denominator. The basic theory is that with different energy density or heat input, the amount of heat that enters into the scanning regime or laser spot region will be different so as their effect to the melting pool behavior and the cooling rate. In a result the densification and final microstructure could be tuned. In this work laser power is fixed at 175W and layer thickness is fixed at 50 μ m for all cubes built by a 3 x 6 matrix where varying scanning speed and hatch spacing is conducted to find the optimized parameters. The results of densification versus energy density are shown in Figure 11. And a general proportional trend is correlated between them: density increases with energy density. But when energy density is above certain level, densification starts to fluctuate and seems being maximized. As indicated in the greyish boxes the high density (>99%) appear only above 8 J/mm². Below that there is no such high densification obtained.

And all high densification does appear within a wide range of ED 8 J/mm² to 22 J/mm² (indicated by green arrow). This could be linked to the downside effect of smaller hatch spacing and scanning speed as well explained in the literature[15, 38]. It was dictated that too much energy input can turn melting pool into unstable resulting in more irregular shape where density could be deteriorated.

Figure 11 Densification versus energy density for EH36 samples

For the effect of scanning speed on densification separate plot is drawn. Figure 12 illustrates scanning speed effect. Some ideas can be drawn:

1. At hatch spacing of 0.08 mm, 0.09 mm and 0.13 mm, higher the energy input (that is slower the scanning speed) higher the density is obtained. The maximum densification always happens at scanning speed of 100 mm/s followed by 200 mm/s and 300 mm/s.
2. But at hatch spacing of 0.10 mm, 0.11 mm and 0.12 mm, the above rule doesn't apply exactly. And this trend is most distinct at hatch spacing of 0.11mm where highest densification of 99.5% is achieved at scanning speed of 200 mm/s instead of 100 mm/s and this is also the highest among all specimens being tested in this work. In a word near linear relationship could be correlated between densification and scanning speed that is, slower the speed, higher the density or in another word higher the energy density higher the densification.

Figure 12 Density of EH36 samples with respect to scanning speed

However this is not true between hatch spacing and densification. The general trend of densification versus hatch spacing is wavy and there seems existing optimal spacing at different scanning speeds. In medium to high scanning speed range from previous researcher's work, there is no such conclusion being drawn out. Only knowing that optimum hatch spacing in the sense of achieving highest density was 0.12 mm with scanning speed at 300 mm/s, but this seems not true for scanning at slower speed. Obviously the optimum point is shifted to a smaller hatch spacing that is from 0.12 mm to 0.11 mm. And the density at lower scanning speed, 200 mm/s and 100 mm/s is higher in overall than that of 300 mm/s. And there are more population of high densification ($> 99\%$) at slower scanning speeds as circled out in the graph. This seems to say that the process is optimized by using scanning speeds lower than 300 mm/s for this EH36 steel. Regarding the optimum hatching spacing, there existed some explanations [61] claiming that the deterioration at high energy input was due to voids formed from too much energy input caused spattering effect at either narrower scanning space or slower scanning speed. This theory can be applied to scanning speed at 300 mm/s in this paper, but seems not applied exactly for lower

scanning speed especially at 100 mm/s. The densification increment from 98.5% to 99.5% does happen when narrowing the hatch spacing to 0.11 mm from 0.12 mm. This may benefit from the slower scanning speed that takes supplementary effect with spattering and need further study on it.

This work has achieved some satisfactory results via developing the scanning speed from 300 mm/s to 100 mm/s with varying hatch spacing. And it can be used as a guideline for processing this EH36 material. However study under different regimes may give different results as previously mentioned the interaction of multiple process parameters is complex. For instance, if we use higher laser power, higher scanning speed should be used to accommodate powder melting behavior.

Microhardness is measured on the polished vertical cross section of the samples. The measuring interval between points is 0.05 mm. Microhardness readings of sample S300 and S200 which are recorded from the top downward along the vertical build direction are shown in Figure 13. The average microhardnesses for the sample S300 and S200 are $HV351_{0.05}$ and $HV354_{0.05}$, respectively. The sample S300 shows a larger degree of fluctuation with one data point falling below $300HV_{0.05}$. One of the highest hardness ($HV428_{0.05}$) incurred in sample S300. This is mostly probably due to its finer microstructure, that is finer the microstructure, higher the hardness. One of the lowest hardness ($HV274_{0.05}$) also incurred in sample S300. This is most probably due to higher content of retained austenite due to its higher cooling rate that was confirmed by the XRD spectrum. For the 1st point measured in the upmost layer, both samples hold high hardness value around $HV400_{0.05}$. That represents the fresh deposited layer hardness. After the 1st point, both tempering and aging factor in resulting in the variation of the hardness values. The hardness of sample S200 decreases obviously. This is a tempering effect applied

from the laser heat source through subsequent scanning. The overall hardness for sample S200 is less fluctuated which seems demonstrating a more homogeneous microstructure type. This homogenization could be linked to the indistinct cellular structures being observed from the optical micrograph which is resulting from the higher heat input. Among the three samples, the overall influence of tempering and aging is most prominent to sample S250 that shows the highest average microhardness of HV373_{0.05}. That was not shown in the figure. This could be due to a higher degree of strengthening effect to the microstructure of sample S250 due to precipitation. Other phases like ferrite may be formed as well due to very locally thermal cycles.

Figure 13 Micro-hardness profiles of samples S200 and S300 measured along vertical cross sections

Theoretical hardness of a full martensitic structure containing 0.18% of carbon is around 450 HV [62]. This is higher than the results obtained here. Possibly this is due to certain percentage of ferrite or retained austenite formed in the matrix. However the hardness value is higher than water quenched EH36 steel being reported as 311 HV quenched from 1000°C (above 90%

martensitic transformation) [63]. The difference is 14%, 20% and 13% compared with sample S200, S250 and S300. Given the hardness is mostly related to microstructures. And the morphology of the grains as examined in TEM is even larger than the conventional martensite lath/packet size. Meanwhile the low angle cellular grain boundaries may not block dislocation movement as good as the high angle martensite block or packet. The relatively higher hardness of AM samples is possibly a combined effect of solid solution strengthening and dislocation with possible highly dispersed precipitate strengthening that needs to be confirmed afterwards.

The range of tensile strength (UTS), yield strength (σ_y) and elongation was shown in Table 2 against quenched EH36 steel. The average UTSs of the samples S250 and S300 are 1040 MPa and 1028 MPa, respectively. The yield strengths are taken from the 0.2% offset and averaged at 943 MPa and 864 MPa, respectively. Their elongations are averaged at 5% and 6%, respectively. The sample S300 shows higher ranges (maximum – minimum) than the sample S200 for the UTS ($R = 114$ MPa vs 5 MPa), σ_y ($R = 174$ MPa vs 9 MPa) and with the range being used to illustrate fluctuation. The UTS results shown here are measured using sub-sized specimens which are in agreement with the reported results (1100 MPa) measured using standard tensile coupons under similar conditions[9]. The slight lower UTS values from this study could be due to the size effect. The SLM built EH36 steel samples with the near full martensitic structure possess slightly higher UTS and yield strength than water quenched EH36 steel equivalent by about 13 - 15% and about 15 - 19% respectively.

As said the high tensile and yield strength of AM built metals benefits from the finer subgrain structures resulted from high cooling rate along with the rapid solidification process [50]. For this high strength steel built through SLM process the high strength comes from martensitic structure with possible solid solution, dislocation and precipitation strengthening [59]. In view

of the martensite grain size either the cellular, columnar or lath shape found in this work was not smaller than conventional martensite lath structure (100 – 200 nm). However it is believed that it is the martensite packet size that determined the strength instead of lath size. And the elongated cellular martensite grains are believed as the downside effect to the strength. As explained above, the size of the cellular is around 1 μm with length in tens of microns which is larger than the conventional martensite lath or block/packet. And those low angle cellular grains are believed to be weaker in strength compared with the conventional martensite packet, block and lath hierarchical structures. So the higher strength could be a combined effect with solid solution strengthening, dislocation and precipitation strengthening where those may diversify SLM process with high cooling rate from conventional manufacturing process. And the low level of retained austenite may contribute to the mechanical properties from certain aspect including ductility. Even though elongation is low, a 5% elongation for martensitic steels is believed decent [59].

The yield strength for sample S250 is higher than sample S300, about 9%. This is consistent with the microhardness results: the hardness of sample S250 is higher than sample S300. However tensile strength of sample S250 is only slightly higher than sample S300, about 1%. The relatively lowered difference of the tensile strength of sample S250 could possibly be due to its higher yield strength that the plastic deformation or work hardening stage is reduced especially for the miniature tensile samples [5, 27, 64, 65]. Meanwhile the smaller grain size could possibly give higher work hardening exponent as demonstrated by sample S300 with achieved highest tensile strength at 1101 MPa but at a smaller elongation of 6%.

Table 2 Tensile properties of samples S300 and S250

Sample	UTS (MPa)	$\sigma_{y,0.2}$ (MPa)		Elongation (%)
S300	987-1101	763-937	931(calc)	3.5-6
S250	1037-1042	938-947	1004(calc)	4.5-7
Quenched EH36_1000°C	906	795		

Moreover the measured yield strength is away from theoretical values converted from microhardness using the following equation: $\sigma_s = 3.28 \times HV - 221$ [66, 67]. Based on the calculation, a local yield stress of 931 MPa ($HV_{0.05} = 351$) and 1004 MPa ($HV_{0.05} = 373$) shall be obtained for sample S300 and S250. However there is certain discrepancy between measured and calculated value. For sample S250 the measured value is about 7% lower than calculated. And for sample S300 the measured value is about 8% lower than calculated. This difference could be related to the local defects such as pores, microstructure variation and anisotropy (with high aspect ratio for cellular grain) which are resulting from the rapid solidification process that renders bulk data away from the calculated.

Again the detrimental effect of microstructure inhomogeneity was reflected from the more varied data for sample S300. The pores acted as stress riser can lead to premature failure. More consistent results in sample S250 benefit from higher densification containing lesser amount of detrimental pores. This could be verified by the fractured surface for both samples as discussed in the following. Higher density is helpful to rule out porosity deterioration effect. Tensile strength could be improved from its aspect, but it could be a trade-off from grain coarsening resulted from lower cooling rate accompanied with slower scanning speed etc. Since grain refinement is an important strengthening mechanism for steels it is always good to have a comprehensive understanding from process, densification to microstructures and their correlated mechanical properties for a real “optimal” process.

Fractured surface morphologies are examined using SEM for both samples. Large amount of shallow dimples and micro-voids are found on both of the fractured surfaces as shown in Figure 14 and Figure 15, together with defects. For sample S300, porosities, lack of fusion containing un-melted or partially melted powders (indicated in red arrows) are all observed. Large flat surfaces were shown in Figure 14(b) aside a big void of lack of fusion that was spread with shallow dimples on the surfaces. The dimple size is around 1 μm which is comparable with the cellular grain size. The large lack of fusion void with the size more than 100 μm possibly acted as a stress riser for crack to initiate from. There is also de-bonding of melting pool boundaries (MPB) identified in the sample as shown in Figure 14(e) demonstrating brittle fracture features. Moreover some equiaxed grains attached to the surface of the partially melted powders as shown in Figure 14(d) can be the growth promoted by unmelted powder in the melting pool that act as nucleation sites during solidification [49].

Figure 14 SEM images of fractured surface for sample S300: (a) overview of fractured surface with lack of fusion and unmelted powder as indicated with yellow arrows, (b) enlarged view of area A in (a) where a big flat surface is covered by shallow dimples spread on it, (c) surface

covered by a number of shallow dimples, (d) partially melted powder particles with equiaxed grains, (e) melting pool boundary de-bonded during tensile loading, and (f) detailed view of dimples shown in (c)

But for sample S250, the amount of defects observed are lesser while in the similar types mainly porosities, lack of fusion containing lesser amount of unmelted powders and inclusions, and debonding of melting pool boundaries shown in Figure 15(a, d & e) (indicated in red arrows). Intercellular debonding is also observed in sample S250 with shallow dimples (around 1 μm) spreading on its surface and dimples are possibly initiated from the intercellular precipitates as shown in Figure 15(f) (indicated by red arrow). Some small particles in the size of a few hundred nanometers dispersed along the de-bonded melting pool boundaries as shown in Figure 16(a). Elemental analysis by EDS confirms the main elements of Mn, O, Fe, C, Si and Cr for larger particles shown in Figure 16(b), and C and Fe for smaller particles shown in Figure 16(c). It is said that totally avoiding lack of fusion for SLM process is difficult. All those observations proved that scanning at speed of 250 mm/s seems able to melt the powders better than S300 mm/s does and resulted in a better densification.

Figure 15 SEM images of fractured surface for sample S250: (a) overview of fractured surface where lack of fusion and unmelted powders is indicated with yellow arrows, (b) enlarged view of area A in (a), which shows a number of dimples, (c) detailed view of dimples shown in (b), (d) inclusions, (e) melting pool boundary de-bonded during tensile loading, and (f) inter-cellular debonding with shallow dimples on the surface

The small particles are believed to form during powder melting/solidification or being tempered out by subsequent laser scanning which weakened the inter-cellular or melting pool boundaries. The trace amount of oxygen level inside building chamber may provide the oxygen source to form metal oxide. It was explained from literature that the metal oxide droplets later form spherical particles that are not compatible with metal melt and dispersed inside the matrix during cooling [68]. As disclosed in other report that oxide and impurities intends to stay at MPB that may affect interlayer bonding and form crack[69]. Those may act as stress riser to lead to premature failure. For carbide formation as mentioned above it may precipitate out upon deposition or when subjected to enough heat sources that probably come from adjacent or next layer laser scanning in which the areas near melting pool boundary or fusion line experienced

highest temperature became heat affected zone (HAZ) where precipitates could form. And precipitates intend to accumulate at intercellular grain boundaries and melting pool boundaries.

Figure 16 (a) SEM image showing melting pool boundary detached from fractured surface of sample S250, (b) EDS spectrum of particles measured at spot 1 in (a), which indicates a high level of oxygen and other elements, and (c) EDS spectrum measured at spot 2 in (a), which depicts high concentrations of carbon and iron

The fractured mechanism and modes for AM built parts have been elaborated from different aspects including intergranular fracture, transgranular fracture (ductile or brittle) and melting pool boundary fracture etc. [27, 50]. Those large defects like lack of fusion, holes or voids ranging up to few hundred microns could be the critical points for crack initiation. Interestingly here mainly ductile dimples are observed with a small fraction of brittle fracture and melting pool debonding which is weakened by small particles or second phase precipitates. The fracture is believed mainly in transgranular mode where large amount of small particles located at the bottom of the dimples could be one of the sites for ductile failure to nucleate from. And the sizes of the dimples are in submicron to micron level which is comparable to cellular/dendrite size. In

general the defects from SLM process don't deteriorate tensile properties from a large scale and it seems quite tolerant to defects at least for tensile properties for the studied samples possessing high densification.

4. Conclusions

The microstructure, densification and mechanical properties of EH36 steel samples additively manufactured through an SLM process were systematically studied by varying laser scanning speed and hatch spacing using a checker board scanning strategy:

A high density of above 99.5% in the printed samples was achieved at a lower scan speed of 200 mm/s and a smaller hatch spacing of 0.11 mm. The densification showed a nearly linear relationship with the scanning speed, i.e., the lower the scanning speed, the higher the densification was. An average melt pool size of 70 - 90 μm was observed from the sample S300 that had mainly cellular-dendritic grains. With a higher heat input corresponding to a lower scanning speed, a deeper and wider melt pool was formed for the sample S200 but the cellular structure became indistinct possibly due to phase transformation, precipitation or stress relief. Due to a large heat input there was a larger chance of chemical segregation or precipitation to happen at the intercellular grain boundaries. A lower scanning speed also led to coarser grains and lower microhardness between the samples. The highest hardness of the sample S250 was attributed to a combined strengthening effect contributed by refined grains, precipitation, solid solution and dislocations. A high cooling rate suppressed the martensitic transformation and the highest level of retained austenite was detected in sample S300 that experienced the highest cooling rate during printing.

Single crystal martensite grains in cellular, columnar and lath shapes were observed using TEM, which contained retained austenite grains and possible carbide precipitates as revealed through EBSD. The martensitic transformation mechanism possibly followed a conventional packet/block/lath hierarchical pattern, though it remained unclear. The variety of martensite grains dominated by elongated cellular or acicular features together with columnar and lath shapes demonstrated a complex local heat flow during a rapid cooling process.

The tensile properties of the samples were correlated to their microstructures such as grain size, precipitation, lack of fusion, void, etc. and hence they were printing process related. A high yield strength was believed to be the reason for the lowered difference in UTS of sample S250 at a lower scanning speed with reduced plastic deformation or work hardening. The instable tensile properties of sample S300 were due to the intrinsic defects like pores. The predicted yield strengths of the printed samples were about 10% higher than the measured values, which indicated that the specimens were quite tolerant to the detrimental effect of defects.

Acknowledgements

This work was supported by the Singapore Centre for 3D Printing, Nanyang Technological University, Singapore. This research was under the Medium-Sized Centre funding scheme financially supported by the National Research Foundation, Prime Minister's Office, Singapore.

References

- [1]. Rombouts, M., et al., *Fundamentals of Selective Laser Melting of alloyed steel powders*. CIRP Annals - Manufacturing Technology, 2006. **55**(1): p. 187-192.
- [2]. Kamath, C., et al., *Density of additively-manufactured, 316L SS parts using laser powder-bed fusion at powers up to 400 W*. The International Journal of Advanced Manufacturing Technology, 2014. **74**(1-4): p. 65-78.
- [3]. Wang, W. and S. Kelly, *A Metallurgical Evaluation of the Powder-Bed Laser Additive Manufactured 4140 Steel Material*. Jom, 2016. **68**(3): p. 869-875.
- [4]. Beal, V.E., et al., *Scanning strategies and spacing effect on laser fusion of H13 tool steel powder using high power Nd:YAG pulsed laser*. International Journal of Production Research, 2007. **46**(1): p. 217-232.
- [5]. Gu, D.D., et al., *Laser additive manufacturing of metallic components: materials, processes and mechanisms*. International Materials Reviews, 2012. **57**(3): p. 133-164.
- [6]. Zhang, K., W. Liu, and X. Shang, *Research on the processing experiments of laser metal deposition shaping*. Optics & Laser Technology, 2007. **39**(3): p. 549-557.
- [7]. P.R.Strutt, *A Comparative Study of Electron Beam and Laser Melting of M2 Tool Steel*. Materials Science and Engineering, 1980. **44**: p. 239-250.
- [8]. Murr, L.E., et al., *Metal Fabrication by Additive Manufacturing Using Laser and Electron Beam Melting Technologies*. Journal of Materials Science & Technology, 2012. **28**(1): p. 1-14.
- [9]. Wu, W., et al., *Investigation on processing of ASTM A131 Eh36 high tensile strength steel using selective laser melting*. Virtual and Physical Prototyping, 2015. **10**(4): p. 187-193.
- [10]. Casalino, G.C., S. L.;Contuzzi, N.;Ludovico, A. D., *Experimental investigation and statistical optimisation of the selective laser melting process of a maraging steel*. Optics & Laser Technology, 2015. **65**: p. 151-158.
- [11]. Thompson, S.M., et al., *An overview of Direct Laser Deposition for additive manufacturing; Part I: Transport phenomena, modeling and diagnostics*. Additive Manufacturing, 2015. **8**: p. 36-62.

- [12]. Shamsaei, N., et al., *An overview of Direct Laser Deposition for additive manufacturing; Part II: Mechanical behavior, process parameter optimization and control*. Additive Manufacturing, 2015. **8**: p. 12-35.
- [13]. Gusarov, A.V., et al., *Heat transfer modelling and stability analysis of selective laser melting*. Applied Surface Science, 2007. **254**(4): p. 975-979.
- [14]. Tsopanos, S., et al., *The Influence of Processing Parameters on the Mechanical Properties of Selectively Laser Melted Stainless Steel Microlattice Structures*. Journal of Manufacturing Science and Engineering, 2010. **132**(4): p. 041011.
- [15]. Yadroitsev, I., et al., *Single track formation in selective laser melting of metal powders*. Journal of Materials Processing Technology, 2010. **210**(12): p. 1624-1631.
- [16]. Wang, D., et al., *Investigation of crystal growth mechanism during selective laser melting and mechanical property characterization of 316L stainless steel parts*. Materials & Design, 2016. **100**: p. 291-299.
- [17]. Yadroitsev, I., et al., *Energy input effect on morphology and microstructure of selective laser melting single track from metallic powder*. Journal of Materials Processing Technology, 2013. **213**(4): p. 606-613.
- [18]. Garibaldi, M., et al., *Metallurgy of high-silicon steel parts produced using Selective Laser Melting*. Acta Materialia, 2016. **110**: p. 207-216.
- [19]. Sun, G., et al., *Evaluation of defect density, microstructure, residual stress, elastic modulus, hardness and strength of laser-deposited AISI 4340 steel*. Acta Materialia, 2015. **84**: p. 172-189.
- [20]. Kim, H., et al., *Tensile Fracture Behavior and Failure Mechanism of Additively-Manufactured AISI 4140 Low Alloy Steel by Laser Engineered Net Shaping*. Materials (Basel), 2017. **10**(11).
- [21]. Xue, Y., et al., *Microporosity effects on cyclic plasticity and fatigue of LENS^{TM}-processed steel*. Acta Materialia, 2010. **58**(11): p. 4029-4038.
- [22]. Ma, M., Z. Wang, and X. Zeng, *A comparison on metallurgical behaviors of 316L stainless steel by selective laser melting and laser cladding deposition*. Materials Science and Engineering: A, 2017. **685**: p. 265-273.

- [23]. Deckers, J.P.K.E.Y.J., *Experimental investigation of Laser Surface Re-melting for the Improvement of Selective Laser Melting Process*. 14e Assises Européennes du prototypage rapide 24-25 Juin 2009.
- [24]. Amano, R.S. and P.K. Rohatgi, *Laser engineered net shaping process for SAE 4140 low alloy steel*. Materials Science and Engineering: A, 2011. **528**(22-23): p. 6680-6693.
- [25]. Cheruvathur, S., E.A. Lass, and C.E. Campbell, *Additive Manufacturing of 17-4 PH Stainless Steel: Post-processing Heat Treatment to Achieve Uniform Reproducible Microstructure*. Jom, 2015. **68**(3): p. 930-942.
- [26]. Zhang, K., et al., *Characterization of stainless steel parts by Laser Metal Deposition Shaping*. Materials & Design, 2014. **55**: p. 104-119.
- [27]. Shifeng, W., et al., *Effect of molten pool boundaries on the mechanical properties of selective laser melting parts*. Journal of Materials Processing Technology, 2014. **214**(11): p. 2660-2667.
- [28]. Chlebus, E., et al., *Effect of heat treatment on the microstructure and mechanical properties of Inconel 718 processed by selective laser melting*. Materials Science and Engineering: A, 2015. **639**: p. 647-655.
- [29]. Smith, D.H., et al., *Microstructure and mechanical behavior of direct metal laser sintered Inconel alloy 718*. Materials Characterization, 2016. **113**: p. 1-9.
- [30]. J.-P. Kruth, M.B., E.Yasa, J. Deckers¹, L. Thijs, J. Van Humbeeck, *Parts and material properties in selective laser melting of metals*. 16th International Symposium on Electromachining (ISEM XVI), 2010.
- [31]. LEONG, S.S., *Selective Laser Melting of Novel Titanium-Tantalum Alloy as Orthopaedic Biomaterial*. PhD thesis, School of Mechanical and Aerospace Engineering, Nanyang Technological University, 2016.
- [32]. Zhang, P., et al., *Twin structure of the lath martensite in low carbon steel*. Progress in Natural Science: Materials International, 2016. **26**(2): p. 169-172.
- [33]. D.Qixun, *Iron steel* 1995. **30**: p. 52-58.
- [34]. Xu, J., et al., *Relation of cooling rate, undercooling and structure for rapid solidification of iron melt*. Computational Materials Science, 2017. **128**: p. 98-102.
- [35]. Garcia-Junceda, A.C., C; Caballero, FG; de Andres, CG, *Dependence of martensite start temperature on fine austenite grain size*. Scripta Materialia, Jan 2008. **58** (2): p. 134-137

- [36]. Mumtaz, K.A.a.H., N., *Top surface and side roughness of Inconel 625 parts processed using selective laser melting*. Rapid Prototyping Journal, 15 (2). ISSN 1355-2546, 2009: p. 96-103.
- [37]. Thijs, L.V.H., J.; Kempen, K.; Yasa, E.; Kruth, J.P., *Investigation on the Inclusions in Maraging Steel Produced by Selective laser melting*. 5th International Conference on Advanced Research and Rapid Prototyping, Polytechn Inst Leiria, Sch Technol & Management, Leiria, PORTUGAL, SEP 28-OCT 01, 2011
- [38]. Yadroitsev, I. and I. Smurov, *Surface Morphology in Selective Laser Melting of Metal Powders*. Physics Procedia, 2011. **12**: p. 264-270.
- [39]. A.Pinkerton; Z.Liub; I.Mannac; L.Lia, J.D.M., *Microstructure characterisation and process optimization of laser assisted rapid fabrication of 316L stainless steel*. Applied Surface Science, 15 July 2005. **247**(1-4): p. 320-327.
- [40]. Saeidi, K., *Stainless steels fabricated by laser melting - scaled-down structural hierarchies and microstructural heterogeneities*. PhD thesis, Stockholm University, 2016.
- [41]. ANTONYSAMY, A.A., *Microstructure, Texture and Mechanical property evolution during additive manufacturing of Ti6Al4V alloy for aerospace applications*. PhD thesis, University of Manchester, 2012.
- [42]. Tan, C., et al., *Microstructural evolution, nanoprecipitation behavior and mechanical properties of selective laser melted high-performance grade 300 maraging steel*. Materials & Design, 2017. **134**: p. 23-34.
- [43]. Yan, F., W. Xiong, and E. Faierson, *Grain Structure Control of Additively Manufactured Metallic Materials*. Materials, 2017. **10**(11).
- [44]. Lee, Y., et al., *Effect of Fluid Convection on Dendrite Arm Spacing in Laser Deposition*. Metallurgical and Materials Transactions B, 2014. **45**(4): p. 1520-1529.
- [45]. Qiu, C., et al., *A comprehensive study on microstructure and tensile behaviour of a selectively laser melted stainless steel*. Sci Rep, 2018. **8**(1): p. 7785.
- [46]. Ye, R., et al., *Numerical modeling of the thermal behavior during the LENS® process*. Materials Science and Engineering: A, 2006. **428**(1-2): p. 47-53.
- [47]. Saeidi, K., et al., *Hardened austenite steel with columnar sub-grain structure formed by laser melting*. Materials Science and Engineering: A, 2015. **625**: p. 221-229.

- [48]. Jäggle, E.A., et al., *Precipitation Reactions in Age-Hardenable Alloys During Laser Additive Manufacturing*. Jom, 2016. **68**(3): p. 943-949.
- [49]. Q.m., Z., et al., *Grain morphology control and texture characterization of laser solid formed Ti6Al2Sn2Zr3Mo1.5Cr2Nb titanium alloy*. Journal of Materials Processing Technology, 2016. **238**: p. 202-211.
- [50]. Zhong, Y., et al., *Intragranular cellular segregation network structure strengthening 316L stainless steel prepared by selective laser melting*. Journal of Nuclear Materials, 2016. **470**: p. 170-178.
- [51]. Pace, M.L., et al., *3D additive manufactured 316L components microstructural features and changes induced by working life cycles*. Applied Surface Science, 2017. **418**: p. 437-445.
- [52]. Saeidi, K., et al., *Transformation of austenite to duplex austenite-ferrite assembly in annealed stainless steel 316L consolidated by laser melting*. Journal of Alloys and Compounds, 2015. **633**: p. 463-469.
- [53]. Hu, G.W.J.L.Y.Z.T.J.X.S.Z., *Prediction of Dendrite Orientation and Stray Grain Distribution in Laser Surface-melted Single Crystal Superalloy*. Journal of materials science & technology, May 2017. **33**(5): p. 499-506.
- [54]. El Kadiri, H., et al., *Phase transformations in low-alloy steel laser deposits*. Materials Science and Engineering: A, 2008. **494**(1-2): p. 10-20.
- [55]. Amrei, M.M., et al., *Microstructure characterization and hardness distribution of 13Cr4Ni multipass weld metal*. Materials Characterization, 2016. **111**: p. 128-136.
- [56]. Carter, L.N., et al., *The influence of the laser scan strategy on grain structure and cracking behaviour in SLM powder-bed fabricated nickel superalloy*. Journal of Alloys and Compounds, 2014. **615**: p. 338-347.
- [57]. Sun, G.F., et al., *Influence of processing parameters on lattice parameters in laser deposited tool alloy steel*. Materials Science and Engineering: A, 2011. **528**(15): p. 5141-5145.
- [58]. Jäggle, E.A., et al., *Comparison of Maraging Steel Micro- and Nanostructure Produced Conventionally and by Laser Additive Manufacturing*. Materials (Basel), 2016. **10**(1).
- [59]. Krauss, G., *Martensite in steel: strength and structure*. Materials Science and Engineering, 1999. **A273-275**: p. 40-57.

- [60]. Morito, S., et al., *Effect of block size on the strength of lath martensite in low carbon steels*. Materials Science and Engineering: A, 2006. **438-440**: p. 237-240.
- [61]. Bai, Y., et al., *Influence mechanism of parameters process and mechanical properties evolution mechanism of maraging steel 300 by selective laser melting*. Materials Science and Engineering: A, 2017. **703**: p. 116-123.
- [62]. Tohru Arai, G.M.B., Charles E. Bates, Bruce A. Becherer etc., *ASM Handbook -Heat Treating*. 1991. **4**.
- [63]. Zhaoyong, L.P.B.Y.L.Z.F., *Study on Quenching Process of EH36 Hull Steel*. Material & Heat Treatment, Recieved on 24 Nov 2011.
- [64]. Delgado, J., J. Ciurana, and C.A. Rodríguez, *Influence of process parameters on part quality and mechanical properties for DMLS and SLM with iron-based materials*. The International Journal of Advanced Manufacturing Technology, 2011. **60**(5-8): p. 601-610.
- [65]. Rafi, H.K., T.L. Starr, and B.E. Stucker, *A comparison of the tensile, fatigue, and fracture behavior of Ti-6Al-4V and 15-5 PH stainless steel parts made by selective laser melting*. The International Journal of Advanced Manufacturing Technology, 2013. **69**(5-8): p. 1299-1309.
- [66]. Y.M. Li, B.X.Y.X.H.C.G.C.J.J.S., *Hardness control for base material and welded joints of 9-12% martensite steel*. Therm. Power. Gener., 2010(39): p. 57-60.
- [67]. Wang, X.-N., et al., *Microstructure formation and precipitation in laser welding of microalloyed C-Mn steel*. Journal of Materials Processing Technology, 2015. **226**: p. 106-114.
- [68]. Meng, Z., et al., *Fatigue and fracture behaviour of laser powder bed fusion stainless steel 316L: Influence of processing parameters*. Materials Science and Engineering: A, 2017. **703**: p. 251-261.
- [69]. Kruth, L.T.J.V.H.K.K.E.Y.J.P., *Investigation on the inclusions in maraging steel produced by selective laser melting*.