Grain refinement of additively manufactured stainless steel by ultrasound

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Abstract
Metallic alloys fabricated by fusion-based additive manufacturing (AM) or 3D printing undergo complex dynamics of melting and solidification, presenting challenges to the effective control of grain structure. Herein, we report on the application of high-intensity ultrasound that controls the solidification process during AM of 316L stainless steel. We find that the application of ultrasound favours the columnar-to-equiaxed transition, which can promote the formation of fine equiaxed grains with random crystallographic texture. The grain number density increases from 305 mm⁻² to 2748 mm⁻² by using ultrasound despite an associated decrease in cooling rate and temperature
gradient in the melt pool during AM. Our assessment of the relationship between grain size and cooling rate indicates that the formation of crystallites during AM is enhanced by ultrasound. Furthermore, ultrasound enables increased constitutional supercooling by lowering the temperature gradient in the bulk of the melt, thus creating a solidification environment that favours grain nucleation, growth and survival. This new understanding provides opportunities to better exploit ultrasound for the control of grain structure in AM-fabricated metallic materials.

**Keywords:** Additive manufacturing, 3D printing, Grain refinement, Ultrasound, Ultrasonic treatment, Steel.

1. **Introduction**

Metal additive manufacturing (AM), or 3D printing, enables the ability to create complex structural parts that can be mass customised [1-3]. However, the strong structural anisotropy of many AM-fabricated commercial alloys and the existence of defects have hindered their qualification and certification for broader implementation [4, 5]. Promoting the columnar-to-equiaxed transition (CET) in AM-fabricated alloys can optimize combinations of strength, ductility and toughness [6]. However, the low temperature gradients (G) required for the formation of equiaxed grains in many alloys is often difficult to achieve during AM based on established solidification maps [7-9]. Hence, further advances in metal AM systems are required to ensure high-quality microstructure and performance of the printed parts. In that regard, metal AM processes are deemed to continue their evolution in all fronts. For example, Todaro *et al.* [10]
have recently demonstrated the use of high-intensity ultrasound to control the grain structures of AM-fabricated Ti-6Al-4V and Inconel 625. The process can enable clear CET leading to fine and equiaxed grains. As a result, the attendant microstructure showed substantially reduced anisotropy with noticeably improved tensile strengths [10].

During ultrasound-assisted laser AM, a scanning laser beam fuses metal powder into subsequently solidified layers on a vibrating ultrasound sonotrode. At the same time, high-intensity ultrasound irradiates the melt pool, which remains molten for only about 0.01-0.1 s before solidifying, driving physicochemical effects. The primary effect associated with ultrasound is acoustic cavitation, namely, the formation, growth and collapse of bubbles in a liquid medium [11], which occurs instantly in molten metallic alloys (~0.00003 s), concluded by in situ synchrotron X-ray imaging studies [12]. Acoustic cavitation creates profound energy-matter interactions, with hot spots inside bubbles up to ~5000 °C, pressures up to ~10^5 kPa and heating and cooling rates at ~10^{10} °C s^{-1} [13]. Such effects are essential for grain refinement by ultrasound [14-16], through facilitating phase fragmentation [12, 17] and/or enhancing phase nucleation [18, 19]. Up till now, the alloy systems fabricated by ultrasound-assisted laser AM include Ti-6Al-4V [10], Inconel 625 [10], Al-12Si [20], and Ti-TiB composites [21]. In the last case [21], ultrasound was used to reduce porosity and improve distribution of reinforcement but resulted in refinement of grain structure at the same time.
In this research, we focus on control of grain structure during metal AM by extending the ultrasound-assisted laser AM process to 316L stainless steel, which is widely used in various sectors due to its excellent corrosion resistance, formability and affordability. AM-fabricated 316L stainless steel is typically composed of columnar grains, leading to anisotropic mechanical performance [22, 23]. The addition of sufficient foreign nucleating agents, such as oxides, sulphides or nitrides [24], can realize CET for improved mechanical properties. However, the nucleants risk facilitating pitting corrosion in stainless steels [25, 26]. Moreover, such nucleants could agglomerate to form clusters, which can entail degradation in the damage tolerance of parts in critical applications. We show that ultrasound-assisted laser AM can avoid these latent issues and therefore holds promise to produce fine-grained 316L stainless steel for improved mechanical performance without compromising its corrosion performance.

2. Experimental

Gas-atomized 316L stainless steel powder (45-90 μm) was used to produce cuboid samples with dimensions of 10 mm × 10 mm × 8 mm (length × width × height) by laser-directed energy deposition (L-DED; Trumpf, TruLaser Cell 7020). The sample without using ultrasound was printed on a stainless steel 4140 plate with the laser power of 300 W, laser spot size of 0.61 mm, scan velocity of 10 mm s⁻¹ and overlap ratio of 70%. For the sample with ultrasound, an ultrasound processor (Sonic Systems, L500; 20 kHz, 500 W consumed power) together with a 4140 stainless steel ultrasound sonotrode (25 mm diameter, 30 μm amplitude of vibration) was used to introduce ultrasound into the melt pool (Fig. 1). The sample was directly printed on the vibrating sonotrode using the same
parameters specified above but with a reduced laser power, since the ultrasound provides additional input power to the melt in the form of acoustic energy. We first calculated the extra power transmitted to the melt by ultrasound, which gives ~125 W (~25% of consumed power [15]). Then we compared with experimental studies and finalized a reduced laser power of 200 W for AM of near-defect-free 316L stainless steel. Samples were printed using linear bi-directional scans with a rotation of 0 and 90° for subsequent layers.

![Ultrasound during metal AM](image)

**Fig. 1** Ultrasound during metal AM. Schematic of metal AM by L-DED onto an ultrasound sonotrode vibrated at 20 kHz. Adapted from Ref. [10] under the terms of the Creative Commons Attribution 4.0 International (CC BY 4.0) license.

As-printed samples were sectioned along the build direction and prepared for microstructural characterization by standard techniques with final polishing by 0.04 μm colloidal silica suspension. Detailed optical microscopy (Leica, DM2500) was performed at the magnification of 1.25× to detect porosity and cracks on the polished
sections of the samples. Microstructural characterization was conducted using a scanning electron microscope (JEOL, JSM-7200F) equipped with an electron backscattered diffraction (EBSD) detector (Oxford Instruments, NordlysMax²). The operating parameters used in EBSD analyses were accelerating voltage of 20 kV, probe current of 16 nA, step sizes of 1.0 µm for the sample without ultrasound and 0.5 µm for the sample with ultrasound, working distance of 15 mm and sample-tilt angle of 70°. The EBSD data was interpreted using software Channel 5 (Oxford Instruments HKL, Abingdon, UK).

3. Results

3.1 Formation of defects

To evaluate the effect of ultrasound on the formation of defects in AM-fabricated 316L stainless steel, the samples fabricated without and with the assistance of ultrasound were examined by optical microscopy, as shown in Fig. 2. Both samples are nearly fully dense. The area fraction of porosity on the entire section approaches 0.01 area% for each sample based on measurements using thresholding of the optical microscopy images. Observations made from two other sections per sample are similar. In fact, excluding the sample peripheries, the ultrasound-assisted AM sample contains fewer small pores in the bulk of the sample (Fig. 2b), which tends to agree with Ref. [21] that applying ultrasound during laser AM can reduce porosity. As can be seen from Fig. 2, the as-fabricated 316L stainless steel sample shows more rugged side faces with ultrasound, consistent with our previous work on Ti-6Al-4V (see Fig. 2 in Ref. [10]). It is plausible that the application of ultrasound has altered the shape of the melt pool,
particularly at the periphery of the sample, which deserves further investigation. Nonetheless, these results indicate that the application of ultrasound did not introduce additional defects in the bulk of the AM-fabricated 316L stainless steel.

![Image](image.png)

**Fig. 2** Defects in the AM-fabricated 316L stainless steel without and with the assistance of ultrasound. *a, b* Optical microscopy images of the polished (unetched) sections of the samples without (*a*) and with (*b*) ultrasound.

### 3.2 Formation of grain structure

The distribution of grain orientation and grain size in 316L stainless steel samples fabricated without and with ultrasound by L-DED were characterized by EBSD. Fig. 3a shows the EBSD inverse pole figure (IPF) map of the sample without ultrasound, where the grains display irregular morphology, with slight elongation along the build direction. Dotted lines sketch the approximate melt pool envelopes in layers where the direction of the laser velocity ($\vec{V}_L$) is transverse (that is, the $y$-direction). The melt pool boundaries are determined by assuming that columnar grains usually grow nearly
perpendicularly from the bottom of each melt pool [27]. As revealed, many columnar grains of \(~50-80\ \mu m\) in width and \(~250\ \mu m\) in length are approximately normal to the fusion boundary at the bottom of each melt pool.

With ultrasound, the sample exhibits many fine (\(~15\ \mu m\)) nearly equiaxed grains (Fig. 3b). The melt pool is \(~260\ \mu m\) deep with ultrasound vs. \(~335\ \mu m\) deep without ultrasound, indicating that ultrasound has modified the geometry of the melt pool. We assessed the influence of ultrasound on grain refinement by examining the changes in number density of grains (number of grains per unit area), which is closely linked to nucleation [28]. The number density of grains based on the high-angle grain boundaries (Fig. 3c, d) is 305 \(\text{mm}^{-2}\) without ultrasound vs. 2748 \(\text{mm}^{-2}\) with ultrasound. Such a pronounced increase in number density indicates that ultrasound plays a key role in generating nuclei or crystallites during the solidification of 316L stainless steel when processed by L-DED.

The CET event may occur during solidification of a moving melt pool in AM processes, as observed both by experiment [29] and simulation [30]. A columnar zone can exist at the bottom of melt pools, which can transition into an equiaxed zone towards the top surface of the melt pool. We made measurements of the length of the columnar zone along the build direction in seven transverse melt pools per sample using EBSD IPF maps (see the dashed lines in Fig. 3a, b for examples of determining the CET event). The average length of the columnar zone is reduced from 202 \(\mu m\) (\(\pm 18\ \mu m\) standard
deviation) without ultrasound to 78 µm (±9 µm standard deviation) with ultrasound, indicating that ultrasound encourages the CET.
Fig. 3 Control of grain structure in AM-fabricated 316L stainless steel by ultrasound. 

**a, b** EBSD IPF maps along the build direction (z) showing the orientation of grains in samples without (a) and with (b) ultrasound. In layers where $\overrightarrow{V_L}$ is transverse (y-direction), the dotted and dashed lines indicate the approximate melt pool boundaries and CET event, respectively. **c, d** EBSD grain boundary maps showing HAGBs and low angle grain boundaries (LAGBs) in samples without (c) and with (d) ultrasound. HAGBs are coloured blue and LAGBs are coloured red.

### 3.3 Homogeneity of grain structure
To determine the influence of ultrasound on the homogeneity of grain structure, quantitative measurements of grain size \(d\) and grain aspect ratio \(\phi\) were carried out from EBSD area scans of 1.85 mm × 1.85 mm for each sample. The application of ultrasound to AM of 316L stainless steel reduces the grain size \(d\) from 52 ± 39 µm to 16 ± 12 µm and the aspect ratio \(\phi\) from 2.7 ± 1.6 to 2.0 ± 1.0, as shown in Fig. 4a, b. By defining equiaxed grains with \(\phi < 2.5\), near equiaxed grains with \(2.5 \leq \phi < 3.3\) and columnar grains with \(\phi \geq 3.3\) [31], after ultrasound, the frequency of equiaxed grains (defined as \(\phi < 2.5\)) increases by 21% while the frequency of columnar grains (defined as \(\phi \geq 3.3\)) decreases by 52%. Ultrasound-assisted AM clearly culminates in the replacement of many columnar grains with fine equiaxed grains. These observations confirm that the structural homogeneity in AM-fabricated 316L stainless steel improves by the application of ultrasound.

**Fig. 4** Quantitative measurement of grain structure in AM-fabricated 316L stainless steel samples without and with ultrasound. (a, b) Histograms of grain size (a) and grain aspect ratio (b) for samples with and without ultrasound measured using EBSD data. \(\mu\), mean; \(\sigma\), standard deviation.
For AM with ultrasound, the average grain size is ~16 µm for 316L stainless steel, ~9 µm for Inconel 625 [10] and ~117 µm for Ti-6Al-4V [10]. Alloy constitution is critically important to obtain fine equiaxed grains under a variety of solidification conditions, including ultrasonic [16, 32, 33] and AM [34-36] conditions. In particular, the generation of enough constitutional supercooling (CS) ahead of solid-liquid interface during solidification is essential to trigger effective grain refinement in metallic alloys. The amount of CS developed during the initial growth of grains is equal to the growth restriction factor ($Q$) [37]. We have established the value of $Q$ for 316L stainless steel, Inconel 625 and Ti-6Al-4V using the calculated phase diagram (CALPHAD) method [37]. $Q$ is ~134 K for stainless steel, ~184 K for Inconel 625 and ~6 K for Ti-6Al-4V. The resulting values provide insight into the mechanism by which 316L stainless steel and Inconel 625 have about an order of magnitude finer grain sizes than Ti-6Al-4V when additively manufactured with ultrasound.

### 3.4 Crystallographic texture

To assess the changes in crystallographic texture by ultrasound, we performed measurements of the EBSD pole figures with respect to {100}, {101} and {111} planes, and the results are shown in Fig. 5. The poles are given in multiples of uniform distribution (MUD), with a maximum MUD value of 1.0 representing a random texture. Without ultrasound, the material exhibits a clear crystallographic texture with a maximum MUD value of 3.9 (Fig. 5a). More specifically, each pole figure shows typical patterns of the preferred cube texture component {001}<100> (Fig. 5a), indicating that the <100> crystallographic directions of many of the grains are aligned with the
reference directions of the sample (x, y and z). With ultrasound, the maximum MUD value reduces from 3.9 to 1.7 and the cube texture component {001}<100> is avoided while no other texture component is found (Fig. 5b). The maximum MUD value of 1.7 obtained by the application of ultrasound is among the lowest values reported to date for as-printed AM-fabricated 316L stainless steel [27, 38, 39]. These results confirm that ultrasound mitigates preferred texture in AM-fabricated 316L stainless steel by producing grains in stochastic orientations, consistent with detailed texture analyses of Ti- and Ni-based alloys fabricated by ultrasound-assisted AM [10].
Fig. 5 Modification of texture in AM-fabricated 316L stainless steel by ultrasound. (a, b) The \{100\}, \{101\} and \{111\} contoured pole figures (in MUD) for the samples without (a) and with (b) ultrasound corresponding to the EBSD maps in Fig. 2. A preferred cube texture component \{001\}<100> develops without ultrasound, avoided with ultrasound.

4. Discussion

4.1 Solidification conditions

To estimate the local solidification conditions with and without ultrasound, we analysed the solidification microstructure of the AM-fabricated 316L stainless steel samples. Representative cellular structures of AM-fabricated 316L stainless steel without and with ultrasound are shown in Fig. 6a, b (perpendicular to the build direction). We made 125 measurements of the primary spacing of cells ($\lambda_c$) per sample by the line intercept
method from scanning electron microscopy (SEM) backscattered electron images. Fig. 6c compares the primary spacings in samples with and without ultrasound. The average value of primary spacing is 2.0 µm without ultrasound vs. 2.7 µm with ultrasound. The primary spacing of cells \( \lambda_c \) depends on the cooling rate (\( \dot{\lambda} \)) according to the relationship [40]:

\[
\lambda_c = K|\dot{\lambda}|^n
\]

(1)

where \( K \) and \( n \) are alloy dependent constants (unitless). For austenitic stainless steels, \( K \) is 80 and \( n \) is -0.33 according to experimental measurements [41]. Using Eq. 1 and the measurements of primary spacing in Fig. 6c, the average value of cooling rate \( \dot{\lambda} \) is estimated to be \( 7.2 \times 10^4 \) C s\(^{-1} \) (±0.7 \times 10^4 C s\(^{-1} \) standard error) without ultrasound and \( 2.9 \times 10^4 \) C s\(^{-1} \) (±0.3 \times 10^4 C s\(^{-1} \) standard error) with ultrasound. The average values of cooling rate reported here are of the same order of magnitude as those obtained by in situ pyrometry measurements during L-DED of stainless steel [42].
Fig. 6 Representative cellular structures of AM-fabricated 316L stainless steel without and with ultrasound (perpendicular to the build direction). (a, b) SEM backscattered electron images showing the typical cell microstructure of samples without (a) and with (b) ultrasound. (c) Histograms of cell spacing for samples with and without ultrasound. \( \mu \), mean; \( \sigma \), standard deviation.

The cooling rate \( \dot{T} \) at a solidifying interface under unidirectional heat flow conditions is given by [40]:

\[
\dot{T} = GV
\]  \hspace{1cm} (2)

where \( G \) is the temperature gradient and \( V \) is the growth rate. As schematically shown in Fig. 7, in a longitudinal section through the centreline of a laser track (that is, the \( x \)-direction), the growth rate \( V \) can be related to the laser velocity \( (V_L) \) by the relationship [43]:

\[
V = V_L \cos \theta
\]  \hspace{1cm} (3)

where \( \theta \) is the angle between \( V \) and \( V_L \). Since, at high temperature gradients, the grain structure orients itself nearly parallel to the heat flux, the angle \( \theta \) can be determined experimentally by measuring the orientation of grains with respect to the known laser scan direction [43]. Consequently, by assuming that the longitudinal laser traces in Fig.
7b, c (extracted from Fig. 3) are sectioned along their centrelines, \( \theta \) is \( \sim 34^\circ \) without ultrasound and \( \sim 48^\circ \) with ultrasound. We note that the grains are not perfectly aligned, possibly implying that the melt pools did not reach steady state. The laser velocity \( V_L \) is 10 mm s\(^{-1}\) for both samples. Eq. 3 then gives \( V = 8.3 \) mm s\(^{-1}\) without ultrasound and \( V = 6.8 \) mm s\(^{-1}\) with ultrasound. By Eq. 2, the temperature gradient is \( \sim 8.6 \times 10^3 \) °C mm\(^{-1}\) without ultrasound and \( \sim 4.3 \times 10^3 \) °C mm\(^{-1}\) with ultrasound. These results indicate that ultrasound reduces the temperature gradient ahead of the solid-liquid interface during solidification in AM by about 50%.

In addition to post-mortem analysis of the microstructure which suggests that ultrasound decreases the temperature gradient, recent modelling using finite element method coupled with fluid flow of heat transfer has shown that the acoustic streaming by ultrasound established a markedly lowered temperature gradient in a cast alloy Al-2Cu [44]. In this work, given the 0.61 mm laser spot size and the 10 mm s\(^{-1}\) scan velocity, the dwell time of the laser beam is 61 ms, which is much longer than the period of ultrasound (0.5 ms), allowing sufficient interactions between the ultrasound and the melt pool. Meanwhile, acoustic streaming is expected to develop immediately during ultrasound-assisted AM due to the small size of the melt pool \( (~260 \mu m) \). In this regard, it is reasonable that ultrasound could enhance convection to reduce the temperature gradient during AM. Besides, the heat generated by the ultrasonic energy may also decrease the cooling rate of the melt pool during solidification, as demonstrated by thermal analysis of bulk melts treated with ultrasound [45].
Fig. 7 Typical form of a melt pool during AM by L-DED. a A schematic of a longitudinal section of the solidification front at the centerline of a laser track. b, c EBSD IPF maps along the build direction (z) of a longitudinal cut across a single laser track without (b) and with (c) ultrasound.

Experimental data from the literature [46-54] and this work on grain size \( d \) and primary spacing of cells \( \lambda_c \) of AM-fabricated 316L stainless steel are compiled in Table 1. We used this data to plot how grain size \( d \) varies with cooling rate \( \dot{T} \) (calculated using Eq. 1), as shown in Fig. 8. A strong correlation is observed between the grain size \( d \) of samples without ultrasound (orange symbols) and the inverse square root of cooling rate \( \dot{T} \) of following the equation:

\[
d = 10.4 + \frac{1.2 \times 10^3}{\sqrt{\dot{T}}}, \quad R^2 = 0.91
\]  

(4)

Similarly, grain size \( d \) was previously demonstrated to be linearly related to the inverse square root of cooling rate \( \dot{T} \) in cast Al- [55] and Mg-based [56] alloys, suggesting that the linear relationship may be applicable to a range of alloy systems and solidification conditions.

A striking feature of the plot in Fig. 8 is that 316L stainless steel additively manufactured with ultrasound (blue symbol) does not follow the grain size-cooling rate
relationship revealed for without ultrasound (orange symbols). More specifically, the experimentally measured grain size with ultrasound is about five-times smaller than that predicted by Eq. 4 (15 µm vs. 83 µm, respectively). In that regard, ultrasound clearly provides favourable conditions for the generation of nuclei or crystallites during solidification, decreasing the grain size compared with no ultrasound.
Table 1 Comparison of the grain size and cell spacing of as-built AM-fabricated 316L stainless steel. The grain size is given as the grain width.

| AM process                                      | Grain size (µm) | Cell spacing (µm) | Ref.   |
|------------------------------------------------|-----------------|-------------------|--------|
| Laser-powder bed fusion                        | ~16             | ~0.5              | [46]   |
|                                                | ~18             | ~0.6              |        |
|                                                | ~19             | ~0.7              |        |
|                                                | ~21             | ~0.9              |        |
|                                                | ~22             | ~0.6              |        |
|                                                | ~25             | ~0.8              |        |
|                                                | ~24             | ~1.0              |        |
|                                                | ~27             | ~1.3              |        |
| Electron beam-powder bed fusion                | ~76             | ~2.6              | [47]   |
| Laser-powder bed fusion                        | ~12             | ~0.4              | [48]   |
| Laser-powder bed fusion                        | ~25             | ~1.25             | [49]   |
| Laser-powder bed fusion                        | ~15             | ~0.6              | [50]   |
| Laser-directed energy deposition                | ~45             | ~1.8              | [51]   |
| Laser-powder bed fusion                        | ~30             | ~0.67             | [52]   |
| Laser-powder bed fusion                        | ~15             | ~1.0              | [53]   |
| Laser powder bed fusion                         | ~21             | ~0.4              | [54]   |
| Laser directed energy deposition                | ~60             | ~2                 | This work |
| Laser directed energy deposition (with ultrasound) | ~15             | ~2.7              | This work |
Fig. 8 The dependence of grain size $d$ on cooling rate $\dot{T}$ in AM-fabricated 316L stainless steel. Grain size $d$ with the inverse square root of cooling rate $\dot{T}$ from the literature (open symbols) [46-54] and this work (solid symbols). The dashed line represents the line of best fit for the samples without ultrasound (orange symbols). The samples without ultrasound reveal a strong linear relationship ($R^2 = 0.91$) while the sample with ultrasound (blue symbol) deviates from this relationship.

4.2 Effect of ultrasound on solidification

CS largely controls the development of grain structure in metallic alloys solidified under a variety of conditions [57, 58], including under ultrasonic [16, 32, 33] and AM conditions [34-36]. In particular, the CET requires some growth of columnar grains to generate enough CS ($\Delta T_{CS}$) to trigger equiaxed grain nucleation on nucleants of potency $\Delta T_n$, i.e., requiring $\Delta T_{CS} \geq \Delta T_n$. This hypothesis has been verified by carefully designed
experimental studies in casting [59] and AM [34] technologies. In this work, the amount of columnar grain growth required for the CET reduced from 202 µm to 78 µm by the application of ultrasound, suggesting that ultrasound influences CS.

We schematically illustrate (Fig. 9) the development of the CS zone ahead of a growing grain during the printing of a layer with and without ultrasound. Without ultrasound (Fig. 9a), the first event occurs by epitaxial growth on the partially remelted previous layer at time $t_1$. The steep temperature gradient $G$ estimated to be $\sim 8.6 \times 10^3$ °C mm$^{-1}$ limits the $\Delta T_{CS}$ ahead of the growing grain (the yellow region, which is the difference between the equilibrium liquidus temperature, $T_E$, and the actual temperature in the melt, $T_A$), preventing activation of a potent nucleant present ahead of the solid-liquid interface and promoting columnar grain growth until time $t_3$. At time $t_3$, the columnar grain growth generates enough $\Delta T_{CS}$ to trigger activation of a potent nucleant, i.e., $\Delta T_{CS} \geq \Delta T_n$, driving nucleation and the CET event.

The solidification under high-intensity ultrasound irradiation is different (Fig. 9b). With ultrasound, the first event still occurs by epitaxial growth at time $t_1$. However, the reduced temperature gradient from $\sim 8.6 \times 10^3$ °C mm$^{-1}$ to $\sim 4.3 \times 10^3$ °C mm$^{-1}$ by ultrasound increases $\Delta T_{CS}$ (the yellow region). Consequently, the amount of columnar grain growth required to trigger the activation of a potent nucleant and the CET when $\Delta T_{CS} \geq \Delta T_n$ is significantly reduced, occurring earlier at time $t_2$. In addition, high-intensity ultrasound plays a key role to produce many initial crystallites near the solid-liquid interface, through cavitation-induced fragmentation [12, 17] and/or cavitation-
enhanced nucleation [18, 19] processes. This is corroborated by the observation that low-frequency mechanical vibrations (≤5000 Hz), where cavitation effects are absent, are only able to induce limited grain refinement during laser AM (cladding) [60]. The larger CS zone by ultrasound protects the cavitation-generated crystallites from readily re-melting as they move away from the solid-liquid interface. Thus, despite reducing the cooling rate (Fig. 8), ultrasound creates a solidification environment that favours the nucleation, growth and survival of grains, thus facilitating grain refinement and the CET. This concept can be used to explain the formation of a fine mostly equiaxed structure in the AM-fabricated 316L stainless steel sample with ultrasound.

We note that the discussion above assumes that the application of ultrasound has no or negligible effect on segregation of solute and the equilibrium liquidus temperature $T_E$. In experiments dedicated to testing the development of CS at the solid-liquid interface under a variety of ultrasound conditions, it was unexpectedly found that ultrasound showed little influence on solute redistribution up to an ultrasound intensity level of 1700 W cm$^{-2}$ [28]. In that regard, ultrasound may only influence the solute boundary layer to a limited extent over a short timescale and does not appreciably affect the short-range diffusion field of a developing CS zone, which should be verified in future studies.
Fig. 9 Schematic illustration of the development of the CS zone ahead of a growing grain during AM with and without ultrasound. **a** Without ultrasound, the formation of grain structure commences by epitaxial columnar growth from the prior layer at time $t_1$. At time $t_2$, the developing $\Delta T_{CS}$ (the difference between the equilibrium liquidus temperature, $T_E$, and the actual temperature in the melt, $T_A$) is less than the undercooling required for nucleation $\Delta T_n$ on a nucleant particle, then columnar grain growth continues. Columnar grain growth continues to time $t_3$, where $\Delta T_{CS} = \Delta T_n$, then equiaxed grain nucleation occurs and the CET is triggered. **b** With ultrasound, the CS zone is larger and longer due to the lowered temperature gradient from $\frac{dT_A}{dx}$ to $\frac{dT_A'}{dx}$, triggering nucleation of more grains at time $t_2$. Furthermore, acoustic cavitation generates many initial crystallites that can survive and grow in the CS zone. Hence, ultrasound facilitates nucleation, growth and survival of grains, creating conditions for the formation of a fine equiaxed grain structure.
Fine equiaxed grain structures can be obtained in AM by employing alloys with solute elements that generate high values of $Q$ to provide constitutional supercooling $\Delta T_{CS}$, as demonstrated in alloys Ti-Al-V-Fe [61] and Ti-Cu [35]. In addition, for AM-fabricated alloys with low values of $Q$, e.g., Ti-6Al-4V with $Q \approx 0$, the application of ultrasound can produce fine equiaxed grain structures [10]. 316L stainless steel has a moderate value of $Q$ equal to ~134 K. Meanwhile, thermal undercooling $\Delta T_{therm}$, which is always present in AM due to the high cooling rates, provides additional undercooling [62] (curvature undercooling can be neglected since it is generally insignificant across a variety of solidification conditions [63]). In this work, the total undercooling ($\Delta T_{total} = \Delta T_{CS} + \Delta T_{therm}$) is insufficient to promote significant nucleation for early CET in AM-fabricated 316L stainless steel without ultrasound with respect to the nucleating particles that naturally exist in the alloy melt. In contrast, the use of ultrasound generates new crystallites by enabling fragmentation [12, 17] or enhancing nucleation [18, 19] and fundamentally increases the region of $\Delta T_{CS}$ by reducing the temperature gradient (Fig. 9). These combined effects promote grain refinement and earlier CET in the sample with ultrasound.

5. Conclusions

In summary, 316L stainless steel was fabricated by laser additive manufacturing (AM) with and without ultrasound. Without ultrasound, the microstructure mostly consists of 250 $\mu$m long columnar grains with a preferred cube texture component \{001\}<100>. In contrast, with ultrasound, the columnar-to-equiaxed (CET) event occurs earlier and resultant microstructure shows predominantly fine (~15 $\mu$m) near equiaxed grains with
no preferred texture. Although ultrasound is associated with a decrease in cooling rate and temperature gradient in the melt pool, the number density of grains increases substantially from 305 mm$^{-2}$ to 2748 mm$^{-2}$ due to the application of ultrasound. In addition, the grain size of AM-fabricated 316L stainless steel with ultrasound deviates considerably from the grain size-cooling rate relationship revealed for conventional AM-fabricated 316L stainless steel. The increase in the number density of grains can be attributed to ultrasound generating many initial crystallites and facilitating the formation of a larger constitutional supercooling zone due to the lowered temperature gradient. Both these factors promote the CET and the formation of a fine equiaxed grain structure.

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Acknowledgements

This research work was supported by the Australian Research Council (ARC) Discovery Projects DP150104719 and DP140100702 and the ExoMet Project co-funded by the European Commission’s 7th Framework Programme (contract FP7-NMP3-LA-2012-280421), by the European Space Agency and by the individual partner organisations. M.A.E, D.Q. and D.H.S. further acknowledge the support of the ARC Discovery Project DP160100560. We thank both the Microscopy and Microanalysis Facility (RMMF) and the Advanced Manufacturing Precinct (AMP) at RMIT University for their facilities and technical assistance.