nature portfolio

Peer Review File

Compositional Criteria to Predict Columnar to Equiaxed Transitions in Metal Additive Manufacturing

Corresponding Author: Professor Mark Easton

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
This paper provides a thoughtful and systematic approach to addressing the critical challenge of predicting and controlling the columnar-to-equiaxed transition (CET) in additively manufactured alloys. By evaluating three key parameters: ΔTs, Q, and P across a range of Ti alloys, the authors make a significant contribution to understanding the factors governing microstructural evolution particularly grain microstructure in AM processes. The experimental verification of the constitutional supercooling parameter (P) as the most reliable predictor for alloy design is a notable advancement, offering practical guidance for tailoring alloy compositions to achieve equiaxed grain microstructures and mitigate mechanical anisotropy in AMed engineering alloys. Furthermore, the integration of numerical CET models provides a robust theoretical framework, linking P to dendrite tip undercooling under high growth velocities characteristic of AM. This is continuous research following the authors' previous work, which advances the understanding of CET and grain refinement in additively manufactured alloys. It can be considered for publication if the following major concerns can be addressed in the revision.
The study focuses on Ti alloys, and while the results for the constitutional supercooling parameter are promising, it remains unclear how universally applicable this parameter is across different alloy series, e.g., stainless steels, Ni-based superalloys, Al alloys, etc. The experimental verification results for at least another class of alloys should be provided in this work.
The influence of process parameters on CET and grain refinement is mentioned and discussed a bit, mainly laser power in this work. Recently, Tan et al. (https://www.nature.com/articles/s41467-024-47257-w) reported that powder size distribution can also induce CET and grain refinement in fusion-based AM processes, where all the existing methods for triggering CET and grain refinement are inclusively reviewed. The introduction part of this manuscript should be more updated with the latest development in the community.
Given the complexity of AM processes, including but not limited to versatile process parameters, dynamic laser-mater interactions, melt pool far-from-equilibrium solidification, and so on, additional work might be needed to discuss and quantify these effects separately. In particular, it seems that the significance of
Experimental verification of P is highlighted, but there may be challenges in isolating the effects of P from other influencing factors, such as thermal gradients and solidification rate in melt pool solidification, which are inherently coupled in AM processes.
It is noted that 99.9% pure elemental powders used in the AM deposition experiments. What are the impurities in the powders and how do these impurities affect the constitutional supercooling?

Reviewer #2

(Remarks to the Author)
This work compares the effect of key solidification parameters on achieved grain refinement in DED-AM custom titanium alloys and others found in the literature. It is very useful for the AM titanium community to know that constitutional supercooling appears to be the most effective parameter for predicting whether a CET can be achieved for a particular alloy, especially since it seems common thermodynamic modelling software is capable of facilitating this, so I find this a valuable research contribution and worthy of publication.

Overall, the paper is well written and structured. I have some minor corrections/suggestions:
-Eq. 2 should be Q = Pk I believe.

-How was Fig. 1f collected? Backscatter electron SEM detector?
-(P6, L6-8) '...some incidence of partially melted Ti powder is present, however these do not appear to be the cause of the refinement.' I would tend to agree, but I feel this should be elaborated upon to make the argument.
-There are no details regarding the beta reconstruction in the experimental write up. These are not trivial and I feel these need to be added for experimental replicability.

Reviewer #3

(Remarks to the Author)
Generally the paper could benefit from some rework to more clearly demonstrate the work done by the authors, how these data were analyzed, and their meaning in the broader context. I found the paper difficult to follow, particularly in the discussion, which pulls in a lot of context from previous work, but did not sufficiently explain (for this reader at least), what the authors analysis actually entailed. There is also a lot of what appears to be relevant and needed data in supplementary info that makes following the results and discussion more difficult. Is it possible for the authors to pull more of this in to the main body of the manuscript? I believe a longer format manuscript may benefit the authors in getting their message across.

I feel as though the authors have some interesting data to present, but it was hard for me to understand their contribution clearly, and how this fits in to both the historical context of solidification theory with more recent additions by other communities such as those looking at AM processes. I believe reworking the manuscript to improve clarity in telling a linear, cohesive story will greatly benefit the reader and make the authors' results and impacts more clear, but lost the thread as they transitioned near the end of the results into the discussion section.

More detailed comments follow below.

Introduction

Do you think repeated remelting also has something to do with the highly directional nature of AM microstructures? Any equiaxed grains grown at the top of a layer will be remelted on subsequent layers, so you are preferentially favoring the epitaxial growth regime. May be worth adding a sentence or two here on this point, I believe some researchers at ORNL (Kirka, DeHoff, and others) found remelting can go as deep as 10 build layers in powder bed processes.
I see you are looking at DED, with a much smaller dilution zone, so most of the material is in fact only melted once or twice, but it might be interesting to consider your works applicability to other AM processes.

I may suggest relying less on the symbols in favor of the physical description of the parameter in the introduction. Different groups studying solidification have employed different symbols to describe the same parameters. For example, the repeated use of Q as shorthand in the intro for growth restriction factor may make it hard for non subject-matter experts to follow the text.

Results

Can you be sure the grains are in fact equiaxed without at least two perpendicular cross-sections? I would suggest making similar grains size measurements with an XY plane as well (within a build layer). Also what does the microstructure look like at the melt pool boundaries? These are quite small field of views that may be from the interior of the melt pool only.

You should be more clear that you are showing prior beta reconstructions and not as collected EBSD data, and it would be helpful to see some of the actual EBSD data of the as-deposited samples, which I assume are alpha titanium. You may also want to cite or explain how you are doing the prior beta analysis. It is quite interesting to see how varying growth restriction and freezing range affect the primary beta that forms, but how does this affect the final formed microstructures after the solid state transformation to alpha? Otherwise, I see this as a useful study to conduct on beta Ti alloys with changes to the alloy to control the actual microstructure that we observe after printing.

Materials and Methods

Where are your elemental powders from?

What is the rough wavelength and beam diameter of your loader. Is it a Ytterbium fiber or something else?

Can you provide the build settings for your samples, as well as what system you used to fabricate the parts?

Discussion

I am having trouble following the first part of your discussion surrounding Figure 4. The fact that so many parts of relevant data lie in supplementary material complicate this section. Is figure 4c-e from your micrographs only, or also others from literature? You spend a lot of time talking about work from Welk and Nartu, but appear to be using different data from Brooke in your figure.

Did you recalculate the "a" and "n" parameters for the Gaumann model? These are highly alloy dependent, as was shown in Gaumann's original extension of Hunt's model as well as in more recent work in the AM superalloy space that also used Gaumann's approach. You can do this calculation using CALPHAD techniques to get solidus and liquidus slopes for

multicomponent alloys.

Reviewer #4

(Remarks to the Author)
The authors present a study of the formation of equiaxed grains (as opposed to columnar ones) during the additive manufacture (AM) of metal alloys using Direct Energy Deposition (DED). This is a currently active field of research internationally, and criteria for the Columnar to Equiaxed Transition (CET), originally developed for casting and welding, are now being adapted for deployment in AM. The work here is original, and careful experimentation and analysis have been carried out by the authors. A surprising outcome – considering the highly non-equilibrium nature of solidification, due to very high cooling rates, in AM – is that a parameter (P) is the most reliable indicator; P is actually equal to the equilibrium freezing range of the alloy. The report is a useful contribution to the field. However, some improvements to the manuscript can be made, as outlined below.

DETAILED COMMENTS

ABSTRACT
The authors should explain a bit about their DED AM experiments here.
Line 20: “predicts” should read “predict”.

INTRODUCTION
A number of CET criteria have been reviewed from the literature. Consideration could also be given to the equiaxed index (ISIJ International, 45,(1), pp. 37-44, 2005) which has since proven to be quite a good indicator of CET. Other workers have managed to use theory and modelling to create equiaxed regions in metal AM by design (e.g. Additive Manufacturing, 46, 102092, 2021).
Equation (2): there is an error in how it relates to Eqn. (1).
The authors state that P is the constitutional supercooling (CS) parameter, but the latter, including the well-known CS criterion developed by Chalmers and his team in Toronto in the 1950s should also include the velocity (V) of the solid-liquid interface.
As P is proportional to (k-1) it is worth noting that k~1.0 will give very little CS, and departure of k from unity (k<<1.0 or k>>1.0) should therefore help promote CET.
p. 3, line 5: refer here to Table S1, to help the reader follow the flow of the report.

RESULTS
Bottom p. 6, top p.7: differences in melting of Ti vs. Mo powder particles may simply be due to the large difference in melting points.
Fig. 4: (a) and (b) captions are mixed up; (e): Brooke et al. is not ref. [23].
p. 8: 2nd full paragraph: what about the effects of alloy thermal conductivity on the thermal gradient (G)?
p. 8, last sentence: meaning is unclear. What is the relevance of “steady state CS”? AM is a highly transient process.
Fig 5: caption refers to Eqn. 2 but that is not relevant. The real problem is that there are two equations 2!
p. 9: line 28: re. thermal undercooling – recalescence is unlikely to occur on equiaxed growth in AM due to the very high rate of heat extraction from the system.
In rapid solidification (RS), such as what occurs in AM as the authors correctly point out, solute trapping occurs in the solid and its composition can approach Co (nominal alloy composition), thus reducing solute rejection into the liquid and decreasing the CS effect. Please explain how this physics relates back to the effect of parameter P on CET? We certainly depart from the equilibrium phase diagram.

MATERIALS AND METHODS
It may be a Nature house style, but normally one expects Materials and Methods before Results.
The equation numbering re-starts from 1 here (see above related problem).
The nucleation factors deltaTn and N0 are critical to the Hunt (G,V) diagrams – see Fig. 5(b). Changing these will change the positions of the CET curves – for both models – and could so be considered “adjustment/tuning parameters” for experimental point fitting purposes – please comment. Did the authors use the same values of deltaTn and N0 for both CET models? If not, their conclusions are not sound. The position of the alloy points in (G,V) space are of course independent of the CET model: the authors should make this point very clear to the readers.
Table S6: clarify that P = deltaT0.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The authors addressed most of the reviewers’ comments in the response letter. However, there are still some remaining concerns over this manuscript.
It is understood that the calculation or estimation of the non-equilibrium solidification range (ΔTs), the growth restriction factor (Q) and constitutional supercooling parameter (P) are critical to this work by using CALPHAD. The reviewer noted that the authors mainly used PANDAT for calculation, and JMatPro for the comparison of some calculation results. Why did the

authors not use the more reliable ThermoCalc for the calculations? Also, it is important to know and understand the difference that may occur by using the different CALPHAD software.
The authors define the rapid solidification as its cooling rates of 105-108 K/s, and they obtained from Rosenthal approximation that the cooling rate in their DED-LB process is at 1.1-1.6 x104 K/s. So they said they don't see solute trapping during the AM process. Firstly, the reference provided by the authors with regard to the cooling range of rapid solidification is not very authoritative and its saying is also confusing because in the same paper it's mentioned that "The process of rapid solidification involves the cooling of a liquid metal at high rates, typically in the range of 103 – 106 K/s. The authors are suggested to double check the generally accepted cooling rate range for rapid solidification. Secondly, how did the authors confirm that no solute trapping in the DED process? It is unclear if and how the solute trapping occurs in melt pool rapid solidification influence the calculation of P value. If no solute trapping in the particular DED process, then the title of this manuscript on metal additive manufacturing is not valid and this work might not be representative in the field.

Reviewer #2

(Remarks to the Author)

Reviewer #4

(Remarks to the Author)
The authors have responded well to the reviewers' comments and the manuscript is much improved.

I just have a couple of minor suggestions.

The authors conclude that P is strongly related to CET formation in AM, where P is the equilibrium freezing range of the alloy. They also include some data from Al-Cu alloys (Table S6) which shows that P increases with the level of solute (Cu) in the alloy. Research which first introduces the equiaxed index (ISIJ International, 45,(1), pp. 37-44, 2005) was also developed with Al-Cu as the demonstrator alloy and also shows (that paper's Fig. 9 and Table 4) that this index also increases significantly as the alloy concentration (and so P; Fig. R1 from current authors) increases. So this supports the current contribution. The authors note that the ISIJ paper covers solidification conditions; in fact it also treats alloy composition as a key variable.

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The images or other third party material in this Peer Review File are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain

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We appreciate the time and effort the reviewers have dedicated to the consideration of our work.

Please see below a point-by-point response (coloured in blue). The authors have also amended the manuscript accordingly with the changes highlighted in the revised manuscript.

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

This paper provides a thoughtful and systematic approach to addressing the critical challenge of predicting and controlling the columnar-to-equiaxed transition (CET) in additively manufactured alloys. By evaluating three key parameters: ΔTs, Q, and P across a range of Ti alloys, the authors make a significant contribution to understanding the factors governing microstructural evolution particularly grain microstructure in AM processes. The experimental verification of the constitutional supercooling parameter (P) as the most reliable predictor for alloy design is a notable advancement, offering practical guidance for tailoring alloy compositions to achieve equiaxed grain microstructures and mitigate mechanical anisotropy in AMed engineering alloys. Furthermore, the integration of numerical CET models provides a robust theoretical framework, linking P to dendrite tip undercooling under high growth velocities characteristic of AM. This is continuous research following the authors' previous work, which advances the understanding of CET and grain refinement in additively manufactured alloys. It can be considered for publication if the following major concerns can be addressed in the revision.

Thank you for your careful review. Each comment has been addressed and has made the manuscript of higher quality.

The study focuses on Ti alloys, and while the results for the constitutional supercooling parameter are promising, it remains unclear how universally applicable this parameter is across different alloy series, e.g., stainless steels, Ni-based superalloys, Al alloys, etc. The experimental verification results for at least another class of alloys should be provided in this work.

Additional alloy systems and AM methods have also been considered and included. Several PBF-LB Al alloys (where k<1) show the increasing solute content leads to CET and grain refinement in particular the Al-Cu, Al-Ni and Al-Si systems (Figs R1-R3).

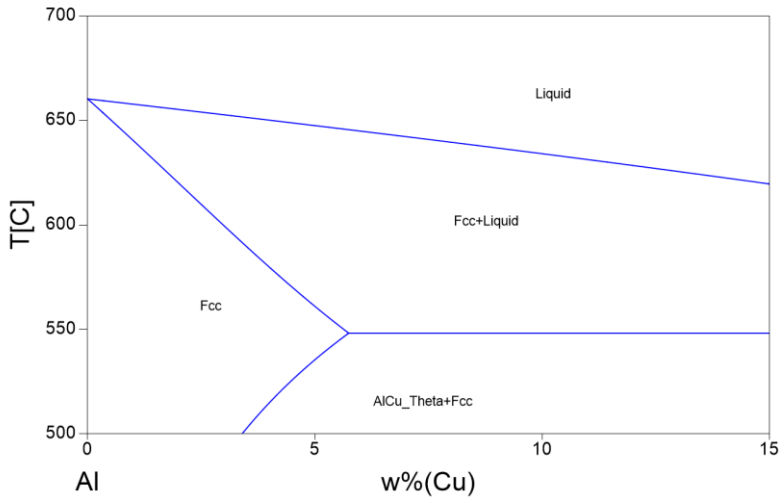


Fig R1: Al-xCu binary phase diagram

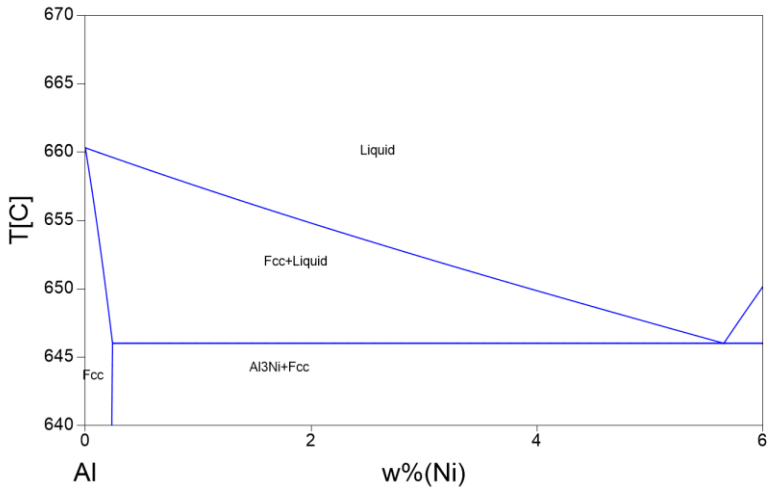


Fig R2: Al-xNi binary phase diagram

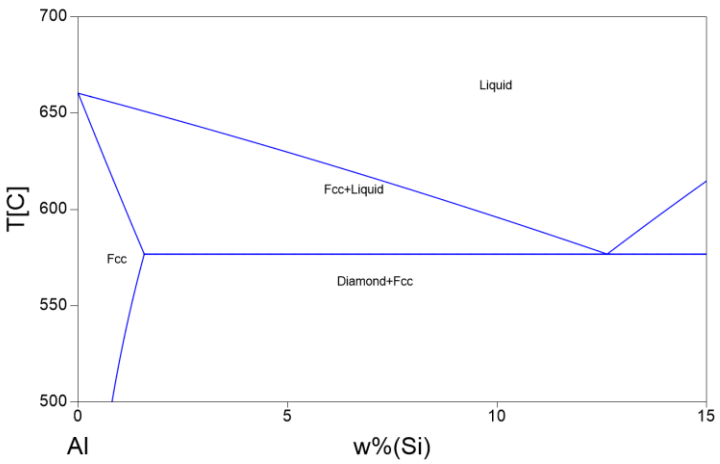


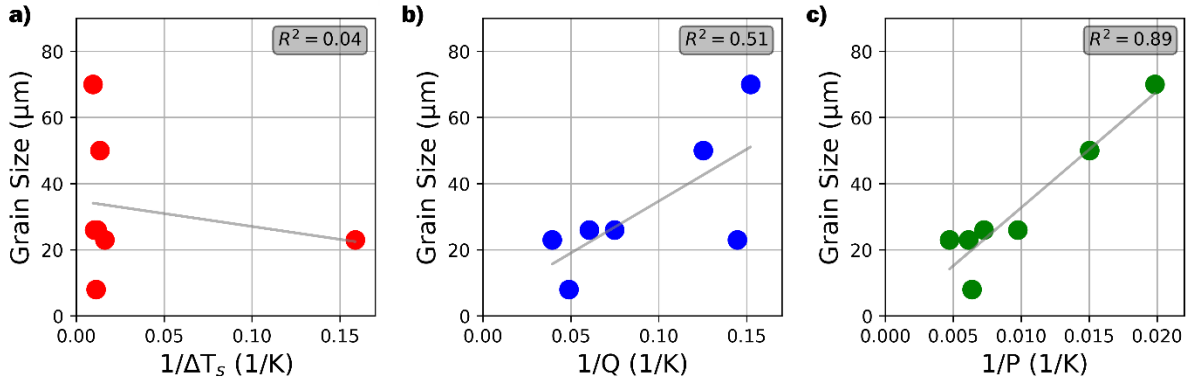
Fig R3: Al-xSi binary phase diagram

From <https://doi.org/10.1016/j.addma.2021.102516> (reference [35] in manuscript) and the produced phase diagrams (Figs R1, R2 and R3) we can assess the correlation between ΔT_s, Q and P and the resulting grain size.

This data has been included in the supplementary data as Table S5.

Composition	ΔT_s (K)	Q (K)	P (K)	Manufacturing Method	Average Grain Size (um)	Grain morphology (C- columnar; E-equiaxed)	Reference
Al	0	0	0	PBF-LB	~78	C	[35]
Al-1.5Si	74.6	8	66.5	PBF-LB	~50	C	[35]
Al-3Cu	104.5	6.6	50.4	PBF-LB	~70	C	[35]
Al-3Ni	6.3	6.9	163.3	PBF-LB	~23	C+E	[35]
Al-3Si	84.5	16.5	137.7	PBF-LB	~26	C+E	[35]
Al-6Cu	96.7	13.4	102.5	PBF-LB	~26	C+E	[35]
Al-4.5Si	61.5	25.4	211.5	PBF-LB	~23	C+E	[35]
Al-9Cu	88.6	20.5	156.9	PBF-LB	~8	E	[35]
Cu-30Ni	155.5	57.9	47.4	WAAM	~257-385	C	[38]

The relationship to grain size for Al alloys is graphically illustrated below and provided in the supplementary data as Fig. S5



Additionally, a WAAM Cu-30Ni alloy is considered, as this alloy shows a similar CALPHAD simulation to Ti-12Mo. With a relatively high Q, but low P, i.e. k>1, this alloy when produced via WAAM shows a columnar grain morphology. <https://doi.org/10.3390/ma17040876> but is equiaxed when solidified via casting < https://doi.org/10.1007/s10853-010-5189-6>.

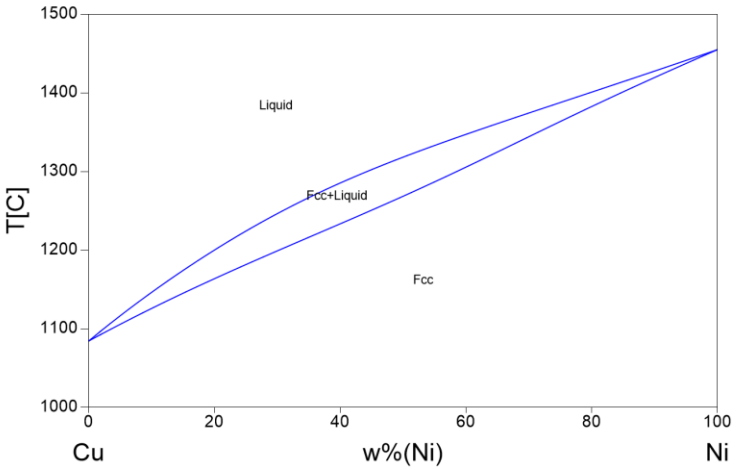


Fig R5: Cu-xNi binary phase diagram

This discussion regarding additional alloy systems and AM manufacturing methods is included in the manuscript:
P8L38-47 "A reanalysis of the data of PBF-LB Al-Si, Al-Cu and Al-Ni alloys [35], also shows P as a better indicator for CET during AM (see Fig. S5 and Table S5). As the thermal gradients during PBF-LB are greater than that of DED-LB [36] it would be likely the threshold P for a CET would be higher using this manufacturing method. Wire-arc additive manufacturing (WAAM) is generally associated with lower thermal gradients [37] therefore less constitutional supercooling is required to overcome the critical undercooling for nucleation to produce a CET. A Cu-30Ni alloy produced via WAAM [38] produced a columnar grain morphology as the overall constitutional supercooling (P) is low (see Table S5). Cu-30Ni is a similar case to that of Ti-12Mo (i.e. k>1), which have a high rate of development of CS (Q) but low overall CS (P), leading to columnar grains during AM. Like Ti-Mo, cast Cu-30Ni can be produced with an equiaxed grain morphology [39]."

The influence of process parameters on CET and grain refinement is mentioned and discussed a bit, mainly laser power in this work. Recently, Tan et al. (https://www.nature.com/articles/s41467-024-47257-w) reported that powder size distribution can also induce CET and grain refinement in fusion-based AM processes, where all the existing methods for triggering CET and grain refinement are inclusively reviewed. The introduction part of this manuscript should be more updated with the latest development in the community.

Yes, thank you, this study is useful to mention and therefore has been included into the introduction and more emphasis has been made into the aim of the study, i.e. investigating the compositional effects on CET.

P2L40-P3L2: 'As the implemented process parameters influence grain refinement [26], these were initially kept constant to isolate compositional effects. It is also worth noting that the powder size distribution can additionally influence the solidification conditions [27], therefore the feedstock powder distribution was kept constant.'

Given the complexity of AM processes, including but not limited to versatile process parameters, dynamic laser-mater interactions, melt pool far-from-equilibrium solidification, and so on, additional work might be needed to discuss and quantify these effects separately. In

particular, it seems that the significance of (this comment seemed to be cutoff)
We agree that the complexity of AM makes the prediction more difficult. This is the motivation of looking at the compositional effects solely at higher solidification velocity (as present in AM). We believe these findings are an important step forward in understanding compositional effects on CET. However, future work on implementing a compositional parameter + solidification condition component would be extremely useful and should be the focus of additional research.

Experimental verification of P is highlighted, but there may be challenges in isolating the effects of P from other influencing factors, such as thermal gradients and solidification rate in melt pool solidification, which are inherently coupled in AM processes.
Yes, we agree, and this is the motivation for comparison of alloys produced on the same system with the same energy density was used for these verifications. Under these conditions, the supercooling parameter, P, produces the strongest correlation with the grain aspect ratio in Figure 4e. This implication can also be applied broadly to AM, i.e., when designing alloys for AM, increasing the supercooling parameter P will increase the likelihood for a CET. However, a threshold value of P for a CET would be dependent on the process conditions.

It is noted that 99.9% pure elemental powders used in the AM deposition experiments. What are the impurities in the powders and how do these impurities affect the constitutional supercooling?
Powders were all delivered by Eckart TLS. The main impurities include 0.1 wt% oxygen and 0.03 w% nitrogen. The segregating power of oxygen and nitrogen is much lower than the added solutes, i.e., Fe, Cu, etc. So, these impurities have negligible effect on the constitutional supercooling, and hence their contribution to $P/Q/\Delta Ts$, was not included in the current study. Detail on the powder manufacture was included into the method P10L28-29 'The nominal compositions were created by mixing 99.9 % pure elemental powders (from ECHKART TLS)'. The impurities have a negligible effect on the CS.

Reviewer #2 (Remarks to the Author):

This work compares the effect of key solidification parameters on achieved grain refinement in DED-AM custom titanium alloys and others found in the literature. It is very useful for the AM titanium community to know that constitutional supercooling appears to be the most effective parameter for predicting whether a CET can be achieved for a particular alloy, especially since it seems common thermodynamic modelling software is capable of facilitating this, so I find this a valuable research contribution and worthy of publication.

We appreciate your comments and suggestions, each have been carefully considered and addressed.

Overall, the paper is well written and structured. I have some minor corrections/suggestions:
-Eq. 2 should be Q = Pk I believe.
Yes, thank you. This has been corrected P2L13
-How was Fig. 1f collected? Backscatter electron SEM detector?
Fig. 1f was collected under a BSE mode and the prior-beta grain boundaries were traced upon hyper eutectoid Ti_2Cu sitting along the grain boundaries, as also can be seen from

supplementary document Fig. S3. The caption was amended to highlight this as follows.
P4L2-4 'Figure 1: Ti-Fe (a and b) and Ti-Cu-Fe (c and d) and Ti-Cu (e and f) alloys produced at a corresponding Q of ~42 and ~93K. (a-e) depict the reconstructed parent β-grains from EBSD data. (f) depicts the traced parent β-grains marked by hyper eutectoid Ti_2Cu from BSE-SEM, note the increased magnification of Ti-12.6Cu (f)'
-(P6, L6-8) '...some incidence of partially melted Ti powder is present, however these do not appear to be the cause of the refinement.' I would tend to agree, but I feel this should be elaborated upon to make the argument.
Yes, thank you, this has been elaborated on P6L6-9 'In the 600 W Ti-4Fe sample (Figure 3a), some incidence of partially melted Ti powder is present, however these do not appear to be the source of refinement, as the equiaxed grains are throughout the bulk and not wholly concentrated near these particles. This has similarly been shown in additional Ti alloys [26].'
-There are no details regarding the beta reconstruction in the experimental write up. These are not trivial and I feel these need to be added for experimental replicability.
We agree with the reviewer's comment and more detail has been added to the methodology for EBSD reconstruction for clarity as follows.
P10L37-44 'Electron backscatter diffraction (EBSD) was collected at 20 kV and at a step size of 2.5 μm for the Ti-Fe and Ti-Cu-Fe samples. Finer step sizes of 1μm and 0.5μm were required for the Ti-6Cu and Ti12.6Cu samples, respectively. Parent grain reconstruction was undertaken using Aztec Crystal software which implements a version of the method described by Huang et al. [38] using the burgers orientation relationship of the child (α) and parent (β) phases [39]. A grain boundary threshold angle of 5° was used and the parent grains were additionally verified using an overlay of fitted ellipses. Grains were generally easily identified by the presence of grain boundary α-phase. Only the reconstructed β-grains were measured for the calculation of the area weighted average grain size.'

Reviewer #3 (Remarks to the Author):

Generally the paper could benefit from some rework to more clearly demonstrate the work done by the authors, how these data were analyzed, and their meaning in the broader context. I found the paper difficult to follow, particularly in the discussion, which pulls in a lot of context from previous work, but did not sufficiently explain (for this reader at least), what the authors analysis actually entailed. There is also a lot of what appears to be relevant and needed data in supplementary info that makes following the results and discussion more difficult. Is it possible for the authors to pull more of this in to the main body of the manuscript? I believe a longer format manuscript may benefit the authors in getting their message across.

I feel as though the authors have some interesting data to present, but it was hard for me to understand their contribution clearly, and how this fits in to both the historical context of solidification theory with more recent additions by other communities such as those looking at AM processes. I believe reworking the manuscript to improve clarity in telling a linear, cohesive story will greatly benefit the reader and make the authors' results and impacts more clear, but lost the thread as they transitioned near the end of the results into the discussion section.

We appreciate the comments and guidance to make the manuscript clearer and of higher quality. The manuscript has been updated within the bounds of the Nature Communications journal style. We have rigorously addressed each comment as below.

More detailed comments follow below.

Introduction

Do you think repeated remelting also has something to do with the highly directional nature of AM microstructures? Any equiaxed grains grown at the top of a layer will be remelted on subsequent layers, so you are preferentially favoring the epitaxial growth regime. May be worth adding a sentence or two here on this point, I believe some researchers at ORNL (Kirka, DeHoff, and others) found remelting can go as deep as 10 build layers in powder bed processes.
I see you are looking at DED, with a much smaller dilution zone, so most of the material is in fact only melted once or twice, but it might be interesting to consider your works applicability to other AM processes.
Yes, thanks, this would be of additionally consideration especially during PBF-L. The directional nature is most often considered due to the direction of heat extraction. Much like in castings where the columnar grains grow away from the mould walls in the opposite direction to heat flow, as in AM they grow away from the substrate, leading to the columnar grains.
This research is specifically considering how solutes and their effect on the constitutional supercooling characteristics effect the as solidified microstructure. By comparing samples produced on the same machine with the same input energy density, we can draw conclusions on the effect of the different solutes and their corresponding compositional parameters (ΔT_s, Q and P). When the process changes and therefore the solidification conditions, the same conclusions are applicable, but not the necessarily same 'threshold-values'. This is due to the changes in the thermal gradient and solidification velocities. Further alloy systems and examples have been added for WAAM and LPBF to show the greater applicability, which are displayed in response to Reviwer 1.

I may suggest relying less on the symbols in favor of the physical description of the parameter in the introduction. Different groups studying solidification have employed different symbols to describe the same parameters. For example, the repeated use of Q as shorthand in the intro for growth restriction factor may make it hard for non subject-matter experts to follow the text.
Thank you, we have updated the introduction and figure captions. Parameters are now presented as the shorthand and the descriptor for the first half of the Introductions and should be easily referable.
P1 L36-37 'the constitutional supercooling (CS) parameter (P), the growth restriction factor (Q) and the non-equilibrium (Scheil) freezing range (ΔTs).'
P1 L38 'P is the constitutional supercooling available during steady-state solidification'
P2 L1-2 'In a binary system the supercooling parameter P is calculated as:'
P2 L6 'In a binary system the supercooling parameter P is calculated as:'
P2 L12 'The growth restriction factor Q is calculated by:'
P2 L30 'ΔTs is the freezing range calculated from CALPHAD software.'
Additionally, these descriptors have been added to Figures 1-4 for further reference points.

Results

Can you be sure the grains are in fact equiaxed without at least two perpendicular cross-sections? I would suggest making similar grains size measurements with an XY plane as well (within a build layer). Also what does the microstructure look like at the melt pool boundaries? These are quite small field of views that may be from the interior of the melt pool only.
We are confident that these are the representative grain morphologies. During AM the grains

generally tend to grow along the build direction (Z direction). It is common practice to study the grain morphology and grain size in the build direction plane, i.e. XZ plane, because the cross section along XY plane always show 'equiaxed' morphology regardless of columnar grains or truly equiaxed grains. In addition, the layer height was 250 µm, and fields are 1.16mm in the Z direction. Therefore, EBSD fields are around 4.6 layers. Thus, we sampled multiple melt pool boundaries, and the fields are not just the melt pool interiors.

You should be more clear that you are showing prior beta reconstructions and not as collected EBSD data, and it would be helpful to see some of the actual EBSD data of the as-deposited samples, which I assume are alpha titanium. You may also want to cite or explain how you are doing the prior beta analysis. It is quite interesting to see how varying growth restriction and freezing range affect the primary beta that forms, but how does this affect the final formed microstructures after the solid state transformation to alpha? Otherwise, I see this as a useful study to conduct on beta Ti alloys with changes to the alloy to control the actual microstructure that we observe after printing.

Thank you, more clarity has been added. The prior-β grains of AM Ti is of interest due to their contribution to the mechanical anisotropy. Due to the limited orientation relationships between α and β phase, once crystallographic texture forms due to the columnar grains, the α variants are also textured. Therefore, the interest is in forming equiaxed grains in the parent phase to reduce the overall mechanical anisotropy after the allotropic transformation. This is the same methodology taken by Nartu et al. [7], Welk et al [32], for example. Additionally, this temperature region between the solidus and liquidus is where the solute driven undercooling will occur.

The fact these are reconstructed grains is further highlighted in the revised manuscript as follows:

P3L13 'corresponding parent β-grain morphology,'

P4L3 ' depict the reconstructed parent β-grains from EBSD data'

P5L1 ', parent β-grain analysis indicates'

P5L4 'with parent grain reconstruction'

P5L7 '. Clear parent β-grain boundaries'

P5L13 'with parent grain reconstruction'

The methodology was also updated as:

P10L39-44 'Parent grain reconstruction was undertaken using Aztec Crystal software, which implements a version of the method described by Huang et al. [38] using the burgers orientation relationship of the child (α) and parent (β) phases [39]. A grain boundary threshold angle of 5° was used and grains were verified using an overlay of fitted ellipses. Grains were generally easily identified by grain boundary α-phase. Only the reconstructed β-grains were measured for the calculation of the area weighted average grain size.'

Materials and Methods

Where are your elemental powders from?

ECKART TLS.

This was added to the methodology

P10L22-23 'from ECHKART TLS

What is the rough wavelength and beam diameter of your loader. Is it a Ytterbium fiber or something else?

This was updated in the methodology P10L30-32'The TruDisk solid state laser (Yb:YAG Disc

Laser) with a wavelength of 1030 nm and a Gaussian beam profile was operated under the continuous laser setting.'
Yb:YAG is ytterbium:yttrium aluminum garnet

Can you provide the build settings for your samples, as well as what system you used to fabricate the parts?
Yes, this is in the methodology and included for further clarity.
P10L29-35 'manufactured using direct energy deposition on the Trumpf Trulaser cell 7020. The TruDisk solid state laser with a Gaussian beam profile was operated under the continuous laser setting. 20x10x10 mm samples were produced using laser power of 900 W, scan speed of 900 mm/min and spot size of 1.5 mm. The layer height was 0.25 mm, powder feed rate ~1.8 g/min, track overlap of 0.45 mm and an interlayer dwell time of 20 secs. Ti-4Fe and Ti-12Mo were additionally produced at laser powers of 600 W and 1200 W.'

Discussion

I am having trouble following the first part of your discussion surrounding Figure 4. The fact that so many parts of relevant data lie in supplementary material complicate this section. Is figure 4c-e from your micrographs only, or also others from literature? You spend a lot of time talking about work from Welk and Nartu, but appear to be using different data from Brooke in your figure.
Thank you, we have endeavoured to make this clearer and easier to follow. We discussed Welk and Nartu's work as an example of the general trends in increasing P leading to a CET and grain refinement. However, as we have attempted to point this out, varying the process does influence the CET. These papers all used a different AM system and process parameters. In contrast, when keeping the process constant and only varying the composition (and the resulting compositional parameters), a much more significant relationship is found. We have made this clearer as follows.

P8L23-27 'It has been shown that manufacturing with vastly different process parameters can change the observed microstructure drastically for DED-LB Ti alloys. Additionally, the grain refinement produced in Ti-Cu binary alloys is also dramatically different to other Ti alloys. Therefore, in Figures 4c, 4d and 4e, Ti alloys other than Ti-Cu binary alloys produced with similar process conditions are considered (Alloys from Brooke et al. [25] and this research (Table S1 and S2)), to obtain greater insight into the various parameters (ΔTs, Q or P).'

In fact, the general trend is still obvious – that favours P - even if the data from various processing conditions are included as shown in the figure below. However, we have decided not to include this in the manuscript as the compositional effect.is the focus of this study.

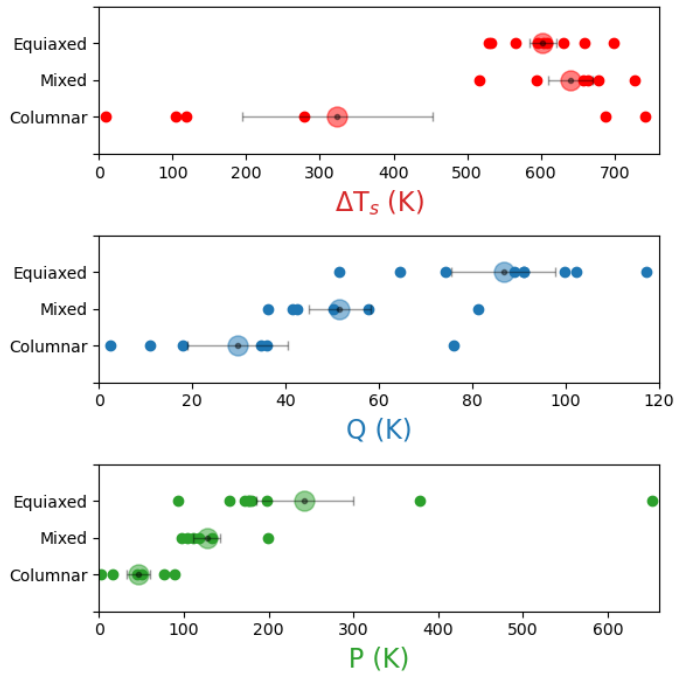


Fig R6: Calculated ΔT_s, Q and P and their corresponding grain morphology (columnar, C+E (mixed) or Equiaxed) from this research and additional data from Brooke et al., Welk et al. and Nartu et al. Ti-Cu alloys are excluded due to the grain refinement from the highly active eutectoid. The average is the black point and error bar depicts the standard error. Data included from Table S1, S2, S3 and table R1.

Table R1: Additional data for Fig R6.

	ΔTs	Q	P	Grain morphology	Ref.
Ti-20V	9.8	2.5	2.3	C	[7] Nartu et al.

Did you recalculate the "a" and "n" parameters for the Gaumann model? These are highly alloy dependent, as was shown in Gaumann's original extension of Hunt's model as well as in more recent work in the AM superalloy space that also used Gaumann's approach. You can do this calculation using CALPHAD techniques to get solidus and liquidus slopes for multicomponent alloys.

We did originally, however opted to instead use the direct solutions from the numerical model. Rather than adding a further step and associated introduced error by curve fitting, it is more accurate to use the numerical solutions from the model.

Reviewer #4 (Remarks to the Author):

The authors present a study of the formation of equiaxed grains (as opposed to columnar ones) during the additive manufacture (AM) of metal alloys using Direct Energy Deposition (DED). This is a currently active field of research internationally, and criteria for the Columnar to Equiaxed Transition (CET), originally developed for casting and welding, are now being adapted for deployment in AM. The work here is original, and careful experimentation and analysis have been carried out by the authors. A surprising outcome – considering the highly non-equilibrium nature of solidification, due to very high cooling rates, in AM – is that a parameter (P) is the most reliable indicator; P is actually equal to the equilibrium freezing range of the alloy. The report is a

useful contribution to the field. However, some improvements to the manuscript can be made, as outlined below.

Thank you for your useful comments and suggestions, we have considered each carefully and have made changes as below.

DETAILED COMMENTS

ABSTRACT
The authors should explain a bit about their DED AM experiments here.
Thank you, we have updated the abstract to include this 'Predicting the columnar to equiaxed transition (CET) and grain refinement for additively manufactured alloys from thermodynamic databases has been a long-standing challenge and an ongoing source of discussion. Efforts are focused on designing alloy compositions to achieve fully equiaxed microstructures, thereby eliminating the mechanical anisotropy commonly associated with the large columnar grains of additively manufactured alloys. Here, three compositional parameters proposed in the literature are evaluated across a range of Ti alloys: the non-equilibrium solidification range (ΔTs), the growth restriction factor (Q) and constitutional supercooling parameter (P). DED-LB produced Ti-Fe, Ti-Cu, Ti-Cu-Fe and Ti-Mo alloys experimentally verified that P is the most reliable parameter to guide the selection of alloying elements for additively manufactured (AM) alloys. Similar verification was found in additional alloy systems and AM methods. The numerical CET models also predict that P is closely related to dendrite tip undercooling at high growth velocities as found in AM.'

Line 20: "predicts" should read "predict".
Corrected. Thank you.

INTRODUCTION
A number of CET criteria have been reviewed from the literature. Consideration could also be given to the equiaxed index (ISIJ International, 45,(1), pp. 37-44, 2005) which has since proven to be quite a good indicator of CET. Other workers have managed to use theory and modelling to create equiaxed regions in metal AM by design (e.g. Additive Manufacturing, 46, 102092, 2021).
Research by Browne < https://www.jstage.jst.go.jp/article/isijinternational/45/1/45_1_37/_pdf> and Plotkowski et al.< https://doi.org/10.1016/j.addma.2021.102092> focuses more on the solidification condition effect and are a fantastic example of the variation in solidification condition causing a CET. An update on P6L1-2 was made to highlight this 'Research in DED-LB [26] and electron beam powder bed fusion [30] illustrate the influence that solidification conditions have on CET and grain refinement.' This research focuses on the compositional related effect on CET for the use in alloy design.

Equation (2): there is an error in how it relates to Eqn. (1).
Thank you, this was corrected.

The authors state that P is the constitutional supercooling (CS) parameter, but the latter, including the well-known CS criterion developed by Chalmers and his team in Toronto in the 1950s should also include the velocity (V) of the solid-liquid interface.
Thank you for the suggestion. We consider the compositional effect on CS and how this is measured (ΔTs, Q or P). While increasing P corresponds to CET for AM, further investigation

using the KGT model (at the increased Velocity of AM) shows that at the solidification velocity of DED, the tip undercooling trends towards P. As Chalmers suggests CS is dependent on the solidification velocity V. This has been highlighted in P10L4-7 'These findings correlated well with historic models of the CET based on dendrite tip undercoolings. The solute driven constitutional supercooling is dependent on the solidification velocity. At high solidification velocities the dendrite tip undercooling correlated more closely with P, in contrast to low solidification velocities which correlated more closely with Q'

As P is proportional to (k-1) it is worth noting that k~1.0 will give very little CS, and departure of k from unity (k<<1.0 or k>>1.0) should therefore help promote CET.
Thank you, this prompted the analysis and graphs below in Fig R7. Q is proportional to (k-1) and the liquidus gradient (ml). P is proportional to (k-1)/k and the liquidus gradient (ml). If k is very small, Q or P should be high, however is also dependent on ml.

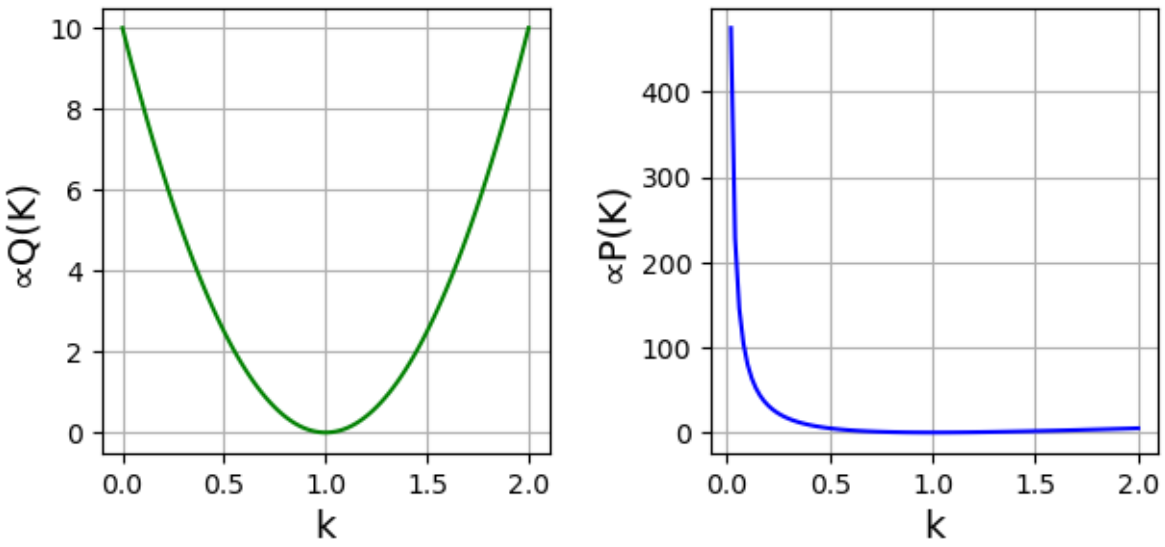


Fig R7: The proportional effect of k on Q and P.

p. 3, line 5: refer here to Table S1, to help the reader follow the flow of the report.
Thank you, this was added.

RESULTS
Bottom p. 6, top p.7: differences in melting of Ti vs. Mo powder particles may simply be due to the large difference in melting points.
Yes, thank you, this was made clearer. P6L20 'AM of Ti-Mo requires higher energies (as Mo has a higher melting temperature than Ti)'

Fig. 4: (a) and (b) captions are mixed up; €: Brooke et al. is not ref. [23].
Yes, thank you, this has been corrected.

p. 8: 2nd full paragraph: what about the effects of alloy thermal conductivity on the thermal gradient (G)?
Yes, this effect is approximated by Rosenthal in Fig 5b, where Ti-Mo has greater thermal gradient than Ti-Fe due to the increased thermal conductivity. The values used are shown in table S7.

This is discussed P9L30-32 'Furthermore, the approximation of the G and V values from the Rosenthal equation [42] (Eq. 8-11) indicate that the alloy chemistry of Ti-12Mo actually increases the thermal gradient'.

p. 8, last sentence: meaning is unclear. What is the relevance of "steady state CS"? AM is a highly transient process.
Thank you, this was not as clear as could be. The intention was to point out the CS available during the pseudo-steady state that occurs during directional solidification, which occurs during DED-LB. As the thermal gradient and solidification velocity remains similar during the bulk build. This however was confusingly phrased and has been removed. Instead, the following has been included P9L21-23 'At the solidification velocities associated with AM the overall CS (P) is a better indicator of the CS available to overcome the high thermal gradients of AM.'

Fig 5: caption refers to Eqn. 2 but that is not relevant. The real problem is that there are two equations 2!
Yes, thank you, these have been corrected.

p. 9: line 28: re. thermal undercooling – recalescence is unlikely to occur on equiaxed growth in AM due to the very high rate of heat extraction from the system.
Thank you, this was removed.

In rapid solidification (RS), such as what occurs in AM as the authors correctly point out, solute trapping occurs in the solid and its composition can approach Co (nominal alloy composition), thus reducing solute rejection into the liquid and decreasing the CS effect. Please explain how this physics relates back to the effect of parameter P on CET? We certainly depart from the equilibrium phase diagram.

Solute trapping has been considered, but has not been seen in this or any of our previous research on DED-LB. Rapid solidification is considered to occur at cooling rates around 10^5-10^8 K/s <https://doi.org/10.1051/e3sconf/202450501020>

According to our Rosenthal approximation, our cooling rates are lower at 1.1-1.6 x10^4 K/s. Hence, we do not see solute trapping during our DED-LB process.

Additionally, quantitative analysis on the solute trapping effect shows negligible changes (as shown in the Table R1) to the partition coefficient (the modified partition coefficient k_v) using <https://doi.org/10.1063/1.329867>:

$$k_v = \frac{(k+\frac{a_o v}{D_i})}{(1+\frac{a_o v}{D_i})}$$

where k is the equilibrium partition coefficient, a_o the atomic jump radius, v the laser scanning speed and D_i the solute diffusion.

Table R1: The calculation of the modified partition coefficient for Ti alloys used in the experimentation.

	Ti-xFe	Ti-xMo	Ti-xCu
a_o	0.289×10^{-9} m	0.289×10^{-9} m	0.289×10^{-9} m
D_i	1.2×10^{-8} m^2/s	1.2×10^{-8} m^2/s	1.2×10^{-8} m^2/s
v	0.015 m/s	0.015 m/s	0.015 m/s

k	0.36	1.67	0.39
kv	0.3602	1.668	0.392

Simulation by Ren et al. <https://doi.org/10.1038/s41467-023-43563-x> suggests only very small regions of solute segregation during PBF-L, however this is at much higher cooling rates than the current experimentation. At the very high cooling rates of some PBF-LB processes, solute trapping may require greater consideration.

During our process we depart from equilibrium solidification, however not to an extent to reach rapid solidification. This study has cooling rates between the two, however the KGT model was designed for laser remelting, which is even closer to rapid solidification, but remains applicable to AM processes.

MATERIALS AND METHODS

It may be a Nature house style, but normally one expects Materials and Methods before Results.

Yes, this is to follow Nature Comm style.

The equation numbering re-starts from 1 here (see above related problem).

Thank you, the equation numbering was corrected.

The nucleation factors deltaTn and N0 are critical to the Hunt (G,V) diagrams – see Fig. 5(b). Changing these will change the positions of the CET curves – for both models – and could so be considered "adjustment/tuning parameters" for experimental point fitting purposes – please comment. Did the authors use the same values of deltaTn and N0 for both CET models? If not, their conclusions are not sound. The position of the alloy points in (G,V) space are of course independent of the CET model: the authors should make this point very clear to the readers.

ΔT_N and N_0 are the same for both models. Yes, we agree these are 'tuned parameters' and this is included in the methodology P11L13-15 'The true values for ΔT_N and N_0 are difficult to determine but were rationally chosen to fit the approximated solidification velocities and thermal gradient (see table S6).'

Further clarity was added to the caption of Figure 5 P9L8 'The CET lines are tuned to the Rosenthal approximation.'

Table S6: clarify that P = deltaT0.

Yes this is correct and has been updated, thanks.

Thank you for you careful review again. We have responded to each comment in blue.

The authors addressed most of the reviewers' comments in the response letter. However, there are still some remaining concerns over this manuscript.
It is understood that the calculation or estimation of the non-equilibrium solidification range (ΔTs), the growth restriction factor (Q) and constitutional supercooling parameter (P) are critical to this work by using CALPHAD. The reviewer noted that the authors mainly used PANDAT for calculation, and JMatPro for the comparison of some calculation results. Why did the authors not use the more reliable ThermoCalc for the calculations? Also, it is important to know and understand the difference that may occur by using the different CALPHAD software.

Thank you for the comment and review, we note that Pandat software uses the CALPHAD approach similarly with ThermoCalc software. The accuracy of the results relies on the accuracy of the databases used.
Pandat PanTi and PanAl databases (2022) are fully assessed for Ti-Cu, Ti-Fe, Ti-Mo, Ti-Ni, Al-Si, Al-Ni, Al-Cu and Cu-Ni over the full composition ranges and with the highest reliability rating (10). This can be seen in the database manuals at https://computherm.com/databases
The methodology has been updated to highlight databases accuracy.

P10L12-14: 'Databases have fully assessed binary systems for Ti-Cu, Ti-Fe, Ti-Mo, Ti-Ni, Al-Si, Al-Ni, Al-Cu and Cu-Ni with the highest reliability rating by PANDAT™'

The authors define the rapid solidification as its cooling rates of 105-108 K/s, and they obtained from Rosenthal approximation that the cooling rate in their DED-LB process is at 1.1-1.6 x104 K/s. So they said they don't see solute trapping during the AM process. Firstly, the reference provided by the authors with regard to the cooling range of rapid solidification is not very authoritative and its saying is also confusing because in the same paper it's mentioned that "The process of rapid solidification involves the cooling of a liquid metal at high rates, typically in the range of 103 – 106 K/s. The authors are suggested to double check the generally accepted cooling rate range for rapid solidification. Secondly, how did the authors confirm that no solute trapping in the DED process? It is unclear if and how the solute trapping occurs in melt pool rapid solidification influence the calculation of P value. If no solute trapping in the particular DED process, then the title of this manuscript on metal additive manufacturing is not valid and this work might not be representative in the field.

Thank you for the comments. The best indicator for the influence of rapid cooling rates and solidification velocities on solute trapping is in calculating the change to the solute distribution coefficient, *k*.

The cooling rates that rapid solidification and any significant solute trapping occurs is dependent on the alloy system, as k_v is a function of the solute diffusion coefficient D_i as well as the atomic jump radius a_0, i.e. $k_v = \frac{\left(k+\frac{a_0 v}{D_i}\right)}{\left(1+\frac{a_0 v}{D_i}\right)}$. (1)

Glicksman states the solute distribution coefficient (*k)* at sufficiently high interface speed can in principle reach 1 [1], leading to full solute trapping. Using Eqn 1, we calculated negligible change in the solute distribution coefficients *(k_v)* for DED-LB Ti alloys. For the PBF-LB of Al alloys, a small change in k_v is observed.

With common alloying elements (depending on their diffusivity) the change in k_v is small, as observed by the microsegregated microstructures. This is a topic of another paper that we currently have under review, which explains the extended solubility sometimes observed in AM in another way.

We have added some analysis on this in the discussion, included an extended Figure for the Al Alloys (Figure 7). Table 1 and 2 also correspond to this analysis. Additionally, the Method for this analysis has been included in the Methods section. This is all highlighted in the updated manuscript.

Although only minor solute trapping may be occurring, the increased solidification velocities do affect the overall tip undercooling, as shown by the analysis using the KGT numerical model which is what is considered in the current paper.

[1] M. Glicksman, *Principles Of Solidification*. Springer, 2011.

Updated discussion P10L8-19: 'Consideration of the effect on solidification rate on the solute partitioning by calculating the modified partition coefficient (kv) [38] (Eq. 4) shows negligible solute trapping effect on the DED-LB Ti alloys as shown in Table 1.

A reanalysis of the data of powder bed fusion-laser beam (PBF-LB) Al-Si, Al-Cu and Al-Ni alloys [37], also shows *P* is a better indicator for CET and grain refinement during AM as shown in Figures 7a-c. However, at the increased speeds occurring during PBF-LB, the modelling suggests there is some minor effect on the partition coefficient caused by solute trapping. *Q* and *P* were recalculated using the modified partition coefficient, k_v shown in Table 1, as Q_v and P_v which are listed in Table 2. Solute trapping may require consideration when designing alloys for PBF-LB, however, again P_v is best correlated to a CET and grain refinement as shown in Figures 7d-e. Solute trapping causes less solute rejection, reducing overall CS, therefore designing for higher *P* and therefore P_v will promote a CET and grain refinement.'

Reviewer #4 (Remarks to the Author):

The authors have responded well to the reviewers' comments and the manuscript is much improved.

I just have a couple of minor suggestions.

The authors conclude that P is strongly related to CET formation in AM, where P is the equilibrium freezing range of the alloy. They also include some data from Al-Cu alloys

(Table S6) which shows that P increases with the level of solute (Cu) in the alloy. Research which first introduces the equiaxed index (ISIJ International, 45,(1), pp. 37-44, 2005) was also developed with Al-Cu as the demonstrator alloy and also shows (that paper's Fig. 9 and Table 4) that this index also increases significantly as the alloy concentration (and so P; Fig. R1 from current authors) increases. So this supports the current contribution. The authors note that the ISIJ paper covers solidification conditions; in fact it also treats alloy composition as a key variable.

Thank you for the comment and review.