

Highly printable, strong, and ductile ordered intermetallic alloy

Corresponding Author: Professor Tao Yang

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)

The authors reported an innovative work on the 3D printing of chemically complex intermetallic alloy (CCIMA). By incorporating multi-principal elements, it is interesting to see that this novel CCIMA exhibits excellent printability, unique microstructures and unprecedented mechanical properties, which are rather different from most traditional metallic alloys. The underlying mechanisms have also been well clarified by using multiscale advanced techniques. In short, this paper would be of great interest and significance to both additive manufacturing and materials science communities. Given the excellent originality and innovation of this work, I recommend a major revision before the publication of this paper in Nature Communications.

1. Could the authors explain how this alloy composition was designed. Especially, it should provide some convincing evidences for the concept of intermetallic alloy for this type of alloy composition fabricated by laser 3d printing. Furthermore, the author should distinguish it from the well-known high entropy alloy, which can make a higher impact to the readers.

2. A scale bar should be given in Fig. 1b.

3. The 3D printed sample usually behaves different crystal orientations along different printing directions. The authors should indicate which plane was tested for the EBSD-IPF mapping in Fig. 2b. What's the grain size of as-printed sample in supplementary Fig. 2d? Both the IPF images of as-printed and heat-treated samples show a bimodal grain structure. Maybe, the grain size distribution can also be useful to understand the mechanical performance.

4. The deformation microstructures changed from APD, SISF, to L-C locks with the increase of strain, as shown in Fig. 4, what is the reason for this variation?

5. The actual chemical compositions in Fig. 2e seem to be not consistent with the element labels. Please correct it.

6. Different from the Ni₃Al intermetallic alloys with the same L12 type structure, the novel alloy composition exhibits an acceptable ductility around 5%, and an excellent improvement to 35%. The difference from the traditional Ni₃Al intermetallic alloys can be emphasized in detail.

Reviewer #2

(Remarks to the Author)

In this paper, the authors fabricated the L12-type chemically complex intermetallic alloy (CCIMA) through 3D printing techniques based on the laser powder bed fusion (LPBF). The microstructural characterization showed that these printed alloys have an ultralow porosity and excellent printability. Mechanical tests showed that these alloys exhibited ultrahigh strength and good ductility, surpassing previous 3D printed alloys. Further analyzes indicated that these excellent mechanical properties are attributed to presence of disordered interfacial nanolayer (DINL) and superlattice dislocation activities. Overall, the current manuscript is well-written and well-organized. The current study results provide a pathway to fabricate the intermetallic alloys with high performance through 3D printing techniques, which would have significant impact on the fabrication and design of strong and ductile intermetallic alloys. Therefore, the current manuscript can be recommended for publication. But the authors have to addressed the following issues to further improve the current

manuscript,

1. Figure 3 shows that there exists a DINL between grain boundary (GB) and grain interior. This layer structure plays an important role in toughening of CCIMA alloys. What is the volume fraction of DINL in alloy? What is the typical thickness of DINL? How did the DINL form? Did such layer structure form during 3D printing of alloys? Is formation of DINL related to dislocation evolution during 3D printing or thermal treatment? Such DINL has disordered structure and acts as a transition region from amorphous region (GB) to order structure (grain interior). Does there exist a mismatch strain between DINL and GB or between DINL and grain interior? Is such mismatch strain helpful for the stabilization of overall structure?
2. In the current study, the authors thought that high work hardening rate (WHR) is attributed to superlattice dislocation activities. The authors also mentioned the contribution of geometrically-necessary dislocations (GNDs). Does there exist the difference between superlattice dislocations and GNDs? Furthermore, on the lines 193-194, "the geometry necessary dislocation (GND)" should be "geometrically-necessary dislocation (GND)".
3. The authors mentioned that "apparent aggregations of GND were formed in the vicinity of grain boundaries". It means that GNDs accumulate and pile up against GBs. There should be an elastic interaction between DINL and dislocation. Does the DINL have influence on the accumulation and pile-up of GNDs? Did any GNDs locate in the DINL or pile up against DINL? Furthermore, recent references (Nature Reviews Materials, 5, 706-723, 2020, Scripta Materialia 186, 304-311, 2020, Matter, 5, 2430-2433, 2022) showed that when GNDs accumulate and pile up against GBs, the pile-up of GND leads to generation of back stress, which contributes to the work hardening. The authors are suggested to add the relevant discussion by referring to the above references.
4. The processing parameters (including laser power and scanning speed) of 3D printing has significant influence on the forming and mechanical properties of alloys. If possible, the authors are suggested to provide a window of processing parameters for forming of alloys with excellent mechanical properties.
5. Figure 1c shows the pore distribution of printed alloy. It looks unclear to visualize the volumes of pores. The authors should provide a high-resolution picture to show the volumes of pores or display a statistical distribution of pore size.

Reviewer #3

(Remarks to the Author)

This article reports a printable L12-type chemically complex intermetallic alloy (CCIMA). This alloy provides an extraordinary combination of ultrahigh tensile strength (~1.6 GPa) and large uniform elongation (~35%), which is remarkable. This alloy design is novel and can be scientifically significant. However, there are some concerns to be addressed if the manuscript is to be published. Please see detailed comments below.

1. Is this microstructure and superior tensile properties unique in additive manufactured material? Or it is also available in conventional ones with the same composition?
2. In the following two statements - 'The DINLs without anti-phase boundary (APB) barriers are more prone to dislocation multiplication and pile up.' and 'Dislocation slip is therefore easy to be activated in the DINL compared with the highly ordered grain interior', the authors emphasised the importance of dislocation behaviours in the DINL. However, no characterization results of dislocations in the DINL were presented. Hard to imagine the dislocations multiplication and pile up in DINL with a thickness of less than 5 nm.
3. The micro-CT result and optical microscopic images evidence that dense and crack-free CCIMA samples can be produced by LPBF process, which is remarkable in ordered intermetallic alloys. This novelty was emphasized by the 'excellent printability' in the abstract and 'highly printable' in the title and summary. However, the 'printability' has not been well-defined, and what 'high' means in 'highly printable' remains unclear. The authors may want to emphasize such novelty in a better way.
4. 'Unlike the conventional intermetallic alloys with extremely poor printability, the present CCIMA is highly printable and can be well manufactured by the LPBF method.' Following this statement, what is the difference between CCIMA and conventional intermetallic alloys, making this CCIMA more 'printable'?
5. The authors may want to briefly introduce the material science reason for unsatisfactory printability and mechanical properties of intermetallic alloys. And is there any effort made to improve their printability and mechanical properties?
6. Fig.1b shows some printed parts. Is that possible to print a 10mm*10mm*10mm crack-free bulk sample?
7. In Fig. 2a, please provide the lattice parameters. Is there a peak at ~71 degree? If yes, please index it.
8. Does the Fig. 2b show a heterogeneous microstructure? And is there any heterogeneous deformation induced strain hardening during the tension test?
9. In lines 131-132, what does the 'random' grain distribution mean? Texture? Size? If it refers to orientation distribution, please show the detailed texture information. If it refers to size distribution, please show the size distribution.
10. In the FFT of DINL inserted in Fig. 3c, please also explain unlabelled weak spots, which seem to be a pattern from other structures.
11. In Extended Data Fig. 1, please provide detailed printing parameters for all six conditions.
12. In the method of micro-CT, please provide sample size.
13. For XRD dislocation density calculation, there are a few questions:
 - a. Which kinds of dislocations were considered?
 - b. How were their q and $Ch00$ values calculated?
 - c. How was the average C value calculated? Based on the fraction of different types of dislocations?
 - d. Does the effect of stacking faults was considered? It can significantly impact the calculated dislocation density, especially when 'in stage III, the plastic deformation was dominated by high-density SISF networks'

Reviewer #4

(Remarks to the Author)

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Reviewer #5

(Remarks to the Author)

I recently reviewed an article titled, "Highly printable, ultra-strong, and ductile ordered intermetallic alloy" by Zhou et al. In this study, the authors produce an intermetallic alloy with the following composition, Ni_{58.48}Co_{18.9}Si_{11.6}Ti_{6.6}Al_{4.4}B_{0.02} and 3D print tensile bars using laser powder bed fusion. In the as-built state the alloy exhibited two intermetallic phases, γ' and G phase which impacted the tensile properties of the alloy. However, after heat treating the alloy the G phase was eliminated and the tensile properties were significantly improved. The heat-treated alloy appears to overcome the common strength-ductility-tradeoff by having both high tensile strengths (over 1600MPa) and ductility (>30%). The authors claim that this intermetallic alloy achieved this high ductility by incorporating disordered nanolayers near the grain boundaries. Though these results are quite interesting, I feel there are aspects to this material and the data presented in the study that need to be clarified. Below are a list of concerns that I would like to see addressed before the manuscript is published.

- 1.) My largest concern is that after reading the manuscript I still have questions pertaining to the microstructure of the heat-treated alloy. X-ray diffraction is the primary characterization the authors employ to determine phases in the alloy but I find their conclusion unsatisfactory since the 3 phases that would most likely arise in this composition are the G phase, L12, and γ phase. All of which have quite similar FCC crystal structures (Fm-3m). In particular, if the ductile γ phase exists it would help explain the improved ductility of the alloy but it would be quite difficult differentiating this phase from L12 in XRD. In fact, we already know this phase exists in this alloy because of the disordered FCC structure highlighted in Figure 3! Currently, the characterizations of the microstructure in the heat-treated alloy beyond EBSD are high magnifications using TEM or ATP. I would really like to see the type of characterization shown on the as-built alloy, as showcased in supplementary figure 2, for the heat-treated alloy. EDS scans of multiple grains will prove to the reader that the alloy is a homogenous L12 phase (except for the grain boundaries). It may also clarify if the gamma phase highlighted in Figure 3 is along all GBs or just a select few.
- 2.) In figure 1, the fracture surface shown in 1(d) is too high a magnification to prove that the alloy is ductile. A lower magnification image showing multiple grains will help show the reader how ductile the alloy is and what failure mechanisms may be present.
- 3.) In the introduction, the authors make note that what makes intermetallic alloys interesting are their anomalous yielding behavior (elevated temperature), excellent work hardening capability, and chemical resistance but none of these properties are highlighted in the paper. Though these room temperature properties are notable there are alloys that exhibit similar tensile properties at room temperature which are more economical (i.e. maraging steel). Can the authors test the alloy at elevated temperature or if not, can they discuss its possible thermal stability.
- 4.) Line 59 should be "layer-by-layer"
- 5.) I feel that the authors should discuss the disordered nanolayer at grain boundaries as " γ phase". It is a common phase for Ni-Co based alloys.
- 6.) It is not clear to the readers if the tensile tests were performed in the vertical or horizontal build directions. There may be significant tensile anisotropy based on these two orientations. Especially if the grains have not fully recrystallized after the heat treatment.
- 7.) Can the authors reference the G phase when it is first mentioned.
- 8.) I feel a single example of the γ phase at the grain boundary is not enough to claim it is the source of the ductility improvement. Can the authors discuss how prevalent this feature is in the alloy? SEM-EDS may be able to discern the Co segregation at grain boundaries as mentioned earlier.
- 9.) Figure 4(h) does not clearly show a single SISF in my opinion. Can the authors highlight the single atomic plane thick fault or change the description as a more generic stacking fault (SF)?
- 10.) In my opinion, the cracks highlighted in supplementary Figure 3(b) look to be solidification cracks from the printing process and not cracks from failure. Readers will be skeptical that this composition could be printed crack free. Can low resolution SEM images be provided to show that cracks do not exist in the as-built state?
- 11.) In supplementary Fig 3(c) the G phase is highlighted with clearly more dislocation content. Why would this intermetallic phase exhibit more dislocations over the L12 phase? Could it be γ phase?

Overall, I feel the study presents an interesting and notable alloy. However, I need to see more analysis over its microstructure to be convinced it truly is an intermetallic alloy before I would suggest the paper gets published in such a high impact journal.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors have well responded the reviewer's comment.

The manuscript quality has been improved. This work can provide more insight into the additive manufacturing of intermetallic alloys. It can also encourage the research to pay more attention to this field.

It is recommended to accept it now.

Reviewer #2

(Remarks to the Author)

According to all the reviewers' comments, the authors have revised the manuscript by adding more detailed analyses, characterization and discussions. I felt that the authors have addressed nearly all the concerns from the reviewers. The current study results provide a route to fabricate the high-performance intermetallic alloys through 3D printing techniques, which would have significant impact on design and fabrication of strong and ductile intermetallic alloys. Therefore, the current manuscript can be recommended for publication.

Reviewer #3

(Remarks to the Author)

The authors addressed some of my concerns. However, some further clarifications are still needed.

1. The reviewer agrees that this material can be printed with low porosity and appreciate the remarkable effort to develop new alloy for additive manufacturing. However, porosity is only one of the considerations in printability. As discussed in the reference cited by the authors [Mukherjee, T., Zuback, J.S., De, A. and DebRoy, T., 2016. Printability of alloys for additive manufacturing. Scientific reports, 6(1), p.19717.], to claim the high printability, the authors need to discuss at least the dimensional accuracy, composition change and standard features such as smallest rod/plate/holes etc, in addition to the porosity.
2. In Supplementary Fig. 3b and Supplementary Fig. 6d, the authors plotted the grain size distribution with varying bin size, which is unusual. These histogram with varying bin size is hard to support the near-Gaussian grain size distribution and the statement on heterogeneity. The authors may want to make further discussion on the heterogeneity. Please clarify what fraction means? Number fraction or area fraction? Please show both number fraction – grain size, and area fraction – grain size histogram with a fixed bin size.
3. Supplementary Fig. 4 shows the dislocations near the grain boundaries or near the DINL. However, the reviewer cannot see clear evidence to support 'dislocations accumulated at the DINL'. It would be interesting to see dislocations accumulating in a 5nm-thick DINL.
4. The calculation of q and $Ch00$ is not integrated in the ANIZC. You may calculate the C values for each hkl , then fit the $Chkl-H$ to obtain q and $Ch00$.

Reviewer #4

(Remarks to the Author)

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Reviewer #5

(Remarks to the Author)

I have reviewed the responses to my previous concerns and the revisions made to the manuscript and I feel that the author's adequately addressed all of my issues with the original draft. I feel the manuscript is now ready to be published.

Version 2:

Reviewer comments:

Reviewer #3

(Remarks to the Author)

The authors have address all the concerns and the reviewer is happy with the modified version for publication.

Reviewer #4

(Remarks to the Author)

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

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Response to Referees Letter

Journal: Nature Communications

Title: Highly printable, ultrastrong, and ductile ordered intermetallic alloy

Manuscript ID: NCOMMS-24-44404A

Dear Reviewers,

Thank you very much for your positive and constructive comments on our manuscript entitled “**Highly printable, ultrastrong, and ductile ordered intermetallic alloy**”, which helps us improve the quality and presentation of our work effectively. We have made modifications to the original manuscript carefully. The revised **manuscript** and **supplementary information** with the changes **highlighted in yellow** were uploaded to the paper submission system. Here below are our point-to-point responses (in blue color) to the comments received.

To Reviewer #1

The authors reported an innovative work on the 3D printing of chemically complex intermetallic alloy (CCIMA). By incorporating multi-principal elements, it is interesting to see that this novel CCIMA exhibits excellent printability, unique microstructures and unprecedented mechanical properties, which are rather different from most traditional metallic alloys. The underlying mechanisms have also been well clarified by using multiscale advanced techniques. In short, this paper would be of great interest and significance to both additive manufacturing and materials science communities. Given the excellent originality and innovation of this work, I recommend a major revision before the publication of this paper in

Nature Communications.

1. Could the authors explain how this alloy composition was designed. Especially, it should provide some convincing evidences for the concept of intermetallic alloy for this type of alloy composition fabricated by laser 3d printing. Furthermore, the author should distinguish it from the well-known high entropy alloy, which can make a higher impact to the readers.

Authors' response: Thanks for this useful comment. The CCIMA in this work was designed by incorporating multiple principal elements to Ni₃Al-type intermetallic alloy with an A₃B-type ordered structure. The Ni atoms in A site were partially replaced by Co, while the Al atoms in B site were partially replaced by elements Si and Ti. The detailed chemical composition was screened out based on the physical metallurgy principle of A₃B-type intermetallic compounds combined with the CALPHAD (CALculation of PHase Diagrams) technique and experimental verifications. Both the CCIMA and HEA are designed based on the multi-principal elements criterion. However, most HEAs focused on the random solid-solution structure with random site occupancies, while the elements in the CCIMA systems tend to occupy specific site positions with a long-range atomic ordering.

2. A scale bar should be given in Fig. 1b.

Authors' response: Thanks for your good suggestion. The scale bar was added to **Fig. 1b**, as shown below.

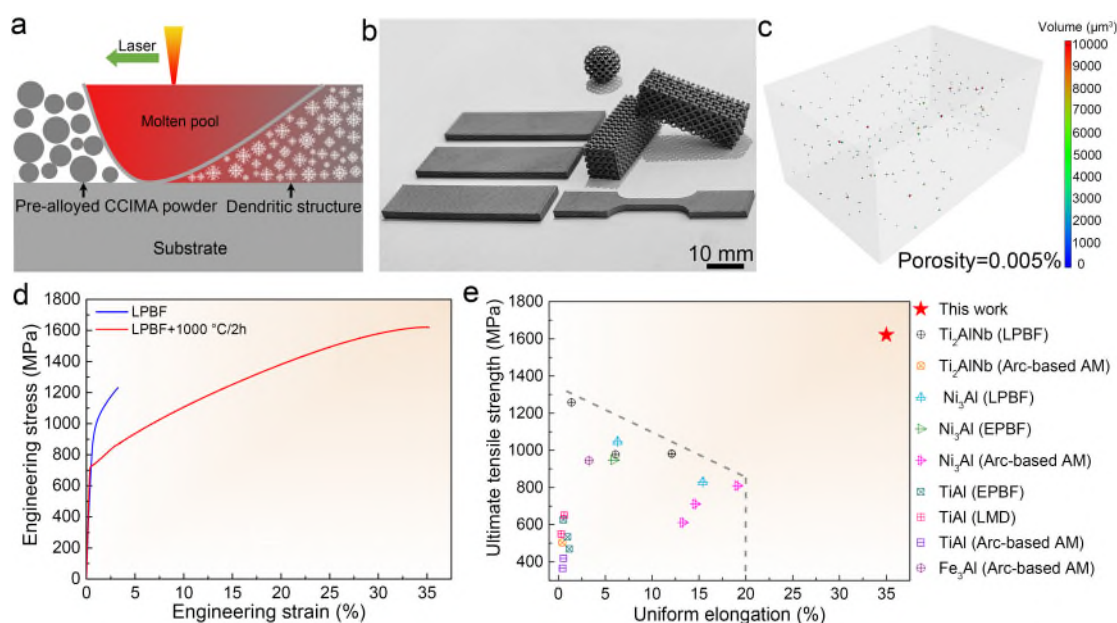


Fig. 1 Exceptional printability and tensile properties of the CCIMA. **a**, Schematic diagram showing the manufacturing of CCIMA by the LPBF technique. **b**, The solid samples and hollow samples with intricate lattice structures illustrating the excellent fabricability of the CCIMA. **c**, The pore defect distribution of the as-printed CCIMA measured by the micro-CT. **d**, Engineering tensile stress-strain curves of the as-printed and thermal-stabilized CCIMA samples. **e**, Comparison of ultimate tensile strength versus uniform elongation of the present CCIMA with conventional intermetallic alloys fabricated by various AM techniques.

3. The 3D printed sample usually behaves different crystal orientations along different printing directions. The authors should indicate which plane was tested for the EBSD-IPF mapping in Fig. 2b. What's the grain size of as-printed sample in supplementary Fig. 2d? Both the IPF images of as-printed and heat-treated samples show a bimodal grain structure. Maybe, the grain size distribution can also be useful to understand the mechanical performance.

Authors' response: Thanks for the good suggestions. The EBSD-IPF mapping in Fig. 2b is obtained by testing the plane perpendicular to the building direction (BD). The average grain

size of the as-printed sample is about 15.6 μm . The above-mentioned information has been provided in the **Methods** and **Supplementary Information** parts, respectively. Meanwhile, the grain size distributions of as-printed and thermal-stabilized samples are shown in the following **Figs. R1a and b**, respectively. No obvious bimodal grain structure was observed in both as-printed and thermal-stabilized samples, based on the grain distribution features.

Manuscript (Lines 387–388)

The EBSD-IPF mapping is obtained by testing the plane perpendicular to the building direction.

Supplementary Information (Lines 116–117)

The grain size distribution of the as-printed CCIMA shows a near-Gaussian distribution model with an average grain size of 15.6 μm (**Supplementary Fig. 6d**).

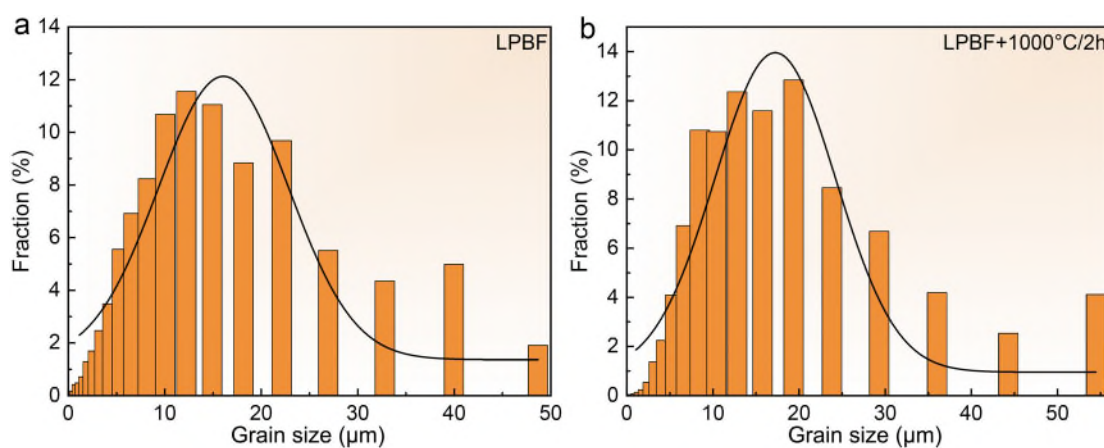
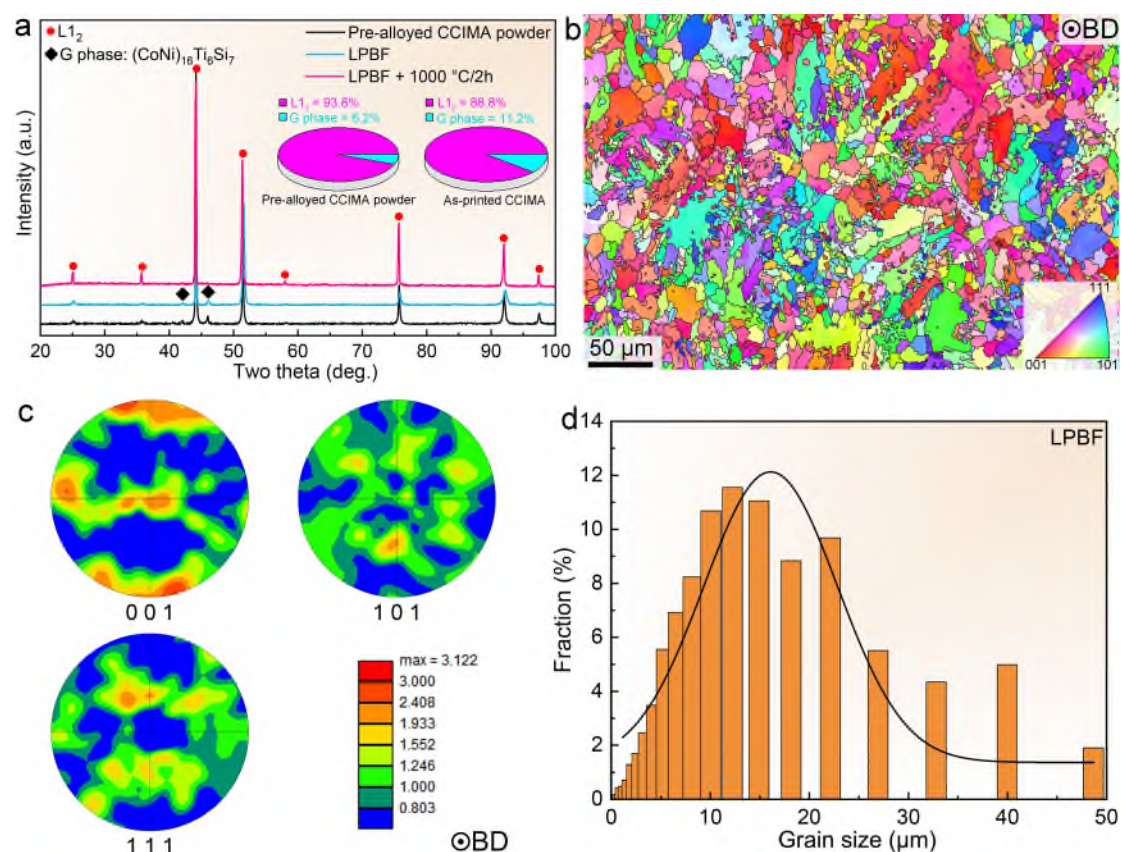


Fig. R1 Grain size distributions of the as-printed and thermal-stabilized CCIMA.



Supplementary Fig. 6 Phase structure and grain feature of the as-printed CCIMA. **a**, XRD spectra showing the phase constitutions of the pre-alloyed powder, as-printed, and thermal-stabilized CCIMA samples. **b**, EBSD-IPF maps revealing the random grain orientations. **c**, EBSD pole figure showing the texture intensity. **d**, Grain size distribution with a near-Gaussian distribution model.

4. The deformation microstructures changed from APD, SISF, to L-C locks with the increase of strain, as shown in Fig. 4, what is the reason for this variation?

Authors' response: Thanks for your insightful comment. The deformation modes are highly related to the planar fault energies of APB and SISF on the {111} slip planes. As illustrated in the **Extended Data Fig. 6**, the CCIMA meets the energy threshold for APB-type dissociation. Thus, at the initial stage of deformation, the sample tended to deform through the APB-type

dissociation. With the increase of deformation strain, the main deformation mechanism gradually changed from APB to SISF dissociation, once the flow stress exceeded the critical value for activating the SISF. With the deformation proceeded, the L-C locks were formed arising from the junction reactions of the SISFs on two intersecting $\{111\}$ planes, which are barriers for the approaching dislocations.

5. The actual chemical compositions in Fig. 2e seem to be not consistent with the element labels. Please correct it.

Authors' response: Thanks for your careful review of our work. **Fig. 2e** has been modified to maintain consistency between element labels and actual compositions. Detail is as follows.

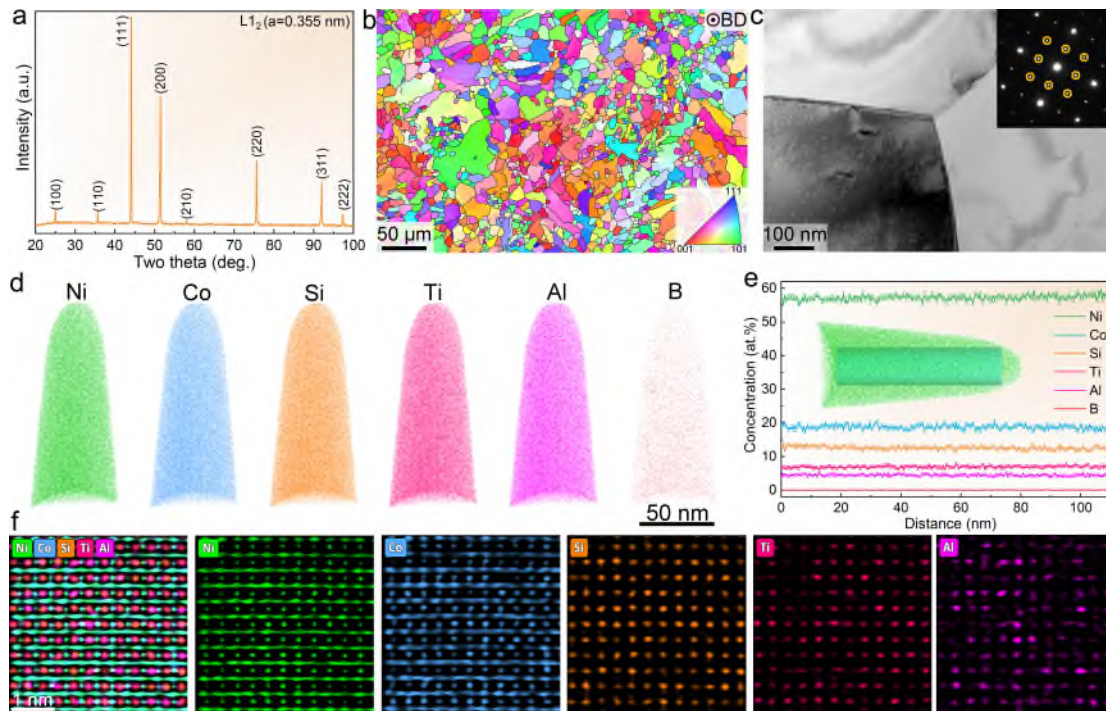


Fig. 2 Microstructural features of the thermal-stabilized CCIMA from microscopic to atomic scales. **a**, XRD spectrum illustrating an ordered L_{12} -type crystal structure. **b**, EBSD-IPF map showing the fine grain morphology perpendicular to the building direction (BD). **c**, TEM bright-field image showing the homogenous grain structure, the superlattice diffraction

spots highlighted by the yellow circles in the SAED pattern illustrating a highly ordered L1₂ structure of the grain interior (inset of Fig. 2b). d, 3D-APT results showing the homogeneous elements distribution within the grain interior. e, One-dimensional concentration profile showing the element distributions across the 3D-APT tip. f, Atomic EDS maps taken from the ordered grain interior along the [001] zone axis, showing the spatial occupations of each element.

6. Different from the Ni₃Al intermetallic alloys with the same L1₂ type structure, the novel alloy composition exhibits an acceptable ductility around 5%, and an excellent improvement to 35%. The difference from the traditional Ni₃Al intermetallic alloys can be emphasized in detail.

Authors' response: Thanks for this insightful comment. The Ni₃Al intermetallic alloys fabricated by LPBF usually suffer from serious cracks, leading to undesirable mechanical properties. In contrast, the CCIMA designed in this work shows excellent printability, enabling an achievement of high-dense samples without any cracks. After a simple heat treatment at 1000 °C for 2h, the CCIMA can sustain a high ductility of up to 35% even under a high tensile stress of 1600 MPa. The exceptional ductility of CCIMA can be attributed to the high printing quality (free of cracks), and unique microstructural features, i.e. the disordered interfacial nanolayer together with B segregations along the grain boundaries, which are hard to be achieved in the chemically simple Ni₃Al intermetallic alloy.

To Reviewer #2

In this paper, the authors fabricated the L12-type chemically complex intermetallic alloy (CCIMA) through 3D printing techniques based on the laser powder bed fusion (LPBF). The microstructural characterization showed that these printed alloys have an ultralow porosity and excellent printability. Mechanical tests showed that these alloys exhibited ultrahigh strength and good ductility, surpassing previous 3D printed alloys. Further analyzes indicated that these excellent mechanical properties are attributed to presence of disordered interfacial nanolayer (DINL) and superlattice dislocation activities. Overall, the current manuscript is well-written and well-organized. The current study results provide a pathway to fabricate the intermetallic alloys with high performance through 3D printing techniques, which would have significant impact on the fabrication and design of strong and ductile intermetallic alloys. Therefore, the current manuscript can be recommended for publication. But the authors have to addressed the following issues to further improve the current manuscript.

1. Figure 3 shows that there exists a DINL between grain boundary (GB) and grain interior. This layer structure plays an important role in toughening of CCIMA alloys. What is the volume fraction of DINL in alloy? What is the typical thickness of DINL? How did the DINL form? Did such layer structure form during 3D printing of alloys? Is formation of DINL related to dislocation evolution during 3D printing or thermal treatment? Such DINL has disordered structure and acts as a transition region from amorphous region (GB) to order structure (grain interior). Does there exist a mismatch strain between DINL and GB or between DINL and grain interior? Is such mismatch strain helpful for the stabilization of overall structure?

Authors' response: Thanks for your constructive comments. The thickness of DINL is about 5 nm based on the 3D-APT (**Fig. 3b**) and high-resolution HAADF-STEM images (**Fig. 3c**). The volume fraction of the DINL can be estimated by the equation of $f_{\text{DINL}} = 1 - (1 - t/d)^3$, where t is the thickness of DINL, d is the average grain size ($17.7 \mu\text{m}$)¹. Thus, the volume fraction of DINL is calculated to be 0.08%.

The DINL was formed by the segregation of Co along the grain boundaries during thermal treatment. Extra Co atoms in the DINL tend to substitute the Ni site and degrade the ordering energy, stabilizing the disordered FCC phase². Meanwhile, the Co segregation generates slightly covalent Ni-Co bonds, and hence weakens the covalency of Ni-Al bonds^{3,4}. Thus, the diffusion of Al via the vacancy diffusion mechanism becomes easier, promoting the anti-site occupation behavior (A-site atoms enter into B sites) and then destroys the long-range ordering of the L1₂ phase^{3,4}. Thus, a higher concentration of Co atoms will facilitate the order-to-disorder transition within the grain boundary regions.

The mismatch between the DINL and grain interior can be negligible due to the highly coherent interface. To quantify the lattice mismatch, we conducted the geometrical phase analysis (GPA) on the atomic structure in the high-resolution STEM image. As shown in **Fig. R2**, homogeneous lattice strain can be observed between the DINL and grain interior, indicating a rather small lattice mismatch, which is beneficial to the stability of DINL.

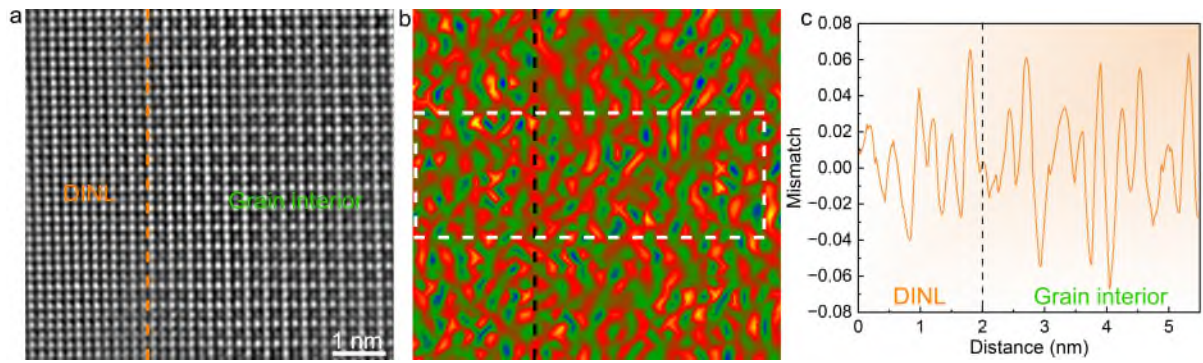


Fig. R2 Geometrical phase analysis across the DINL to grain interior. **a**, High-resolution STEM image showing the atomic structure between the DINL and grain interior. **b**, Strain map generated from the high-resolution STEM image in **Fig. R2a** showing negligible lattice mismatch. **c**, Average mismatch distribution along the white dash line in **Fig. R2b**.

Corresponding revisions were added to the Manuscript (Lines 174–177).

The thickness of this nanolayer is about 5 nm based on the 3D-APT (**Fig. 3b**) and high-resolution HAADF-STEM images (**Fig. 3c**). The volume fraction of the DINL can be estimated by the equation of $f_{\text{DINL}} = 1 - (1 - t/d)^3$, where t is the thickness of DINL, d is the average grain size ($17.7 \mu\text{m}$)¹. Thus, the volume fraction of DINL is calculated to be 0.08%.

References

- 1 Chookajorn T, Murdoch HA, Schuh CA. Design of stable nanocrystalline alloys. *Science* **337**, 951–954 (2012).
- 2 Chiba A, Hanada S, Watanabe S. Correlation between ductility and ordering energy of Ni₃Al. *Mater Trans, JIM* **31**, 824–827 (1990).
- 3 Gazda A, Rothova V, Cermak J. Interdiffusion in pseudobinary sections of Ni₃Al–Co ternary system. *Intermetallics* **10**, 859–864 (2002).

4 Zhao S, Osetsky Y. Structural and chemical disorder enhance point defect diffusion and atomic transport in Ni₃Al-based γ' phase. *Acta Mater* **207**, 116704 (2021).

2. In the current study, the authors thought that high work hardening rate (WHR) is attributed to superlattice dislocation activities. The authors also mentioned the contribution of geometrically-necessary dislocations (GNDs). Does there exists the difference between superlattice dislocations and GNDs? Furthermore, on the lines 193-194, “the geometry necessary dislocation (GND)” should be “geometrically-necessary dislocation (GND)”.

Authors’ response: Thanks for your insightful comments. “The geometry necessary dislocation (GND)” was revised as “geometrically-necessary dislocation (GND)”. The superlattice dislocation activities mainly occurred in the grain interior, such as dislocation multiplication, formation of K-W and L-C locks, contributing to the high WHR. While the GNDs were mainly formed near the grain boundaries to accommodate the strain incompatibility between grain interior and DINL. According to Li’s work, GNDs can pile up in the soft domains against their boundaries and act as obstacles to dislocation motion, which also contributes to the work hardening of the materials⁵.

Manuscript (Lines 202–204)

To reveal the crucial effect of the DINL in eliminating the intergranular embrittlement, geometrically-necessary dislocation (GND) distributions under different deformation strains were measured using the EBSD method.

Reference

- 5 Li X, Lu L, Li J, Zhang X, Gao H. Mechanical properties and deformation mechanisms of gradient nanostructured metals and alloys. *Nat Rev Mater* **5**, 706–723 (2020).

3. The authors mentioned that “apparent aggregations of GND were formed in the vicinity of grain boundaries”. It means that GNDs accumulates and piles up against GBs. There should be an elastic interaction between DINL and dislocation. Does the DINL have influence on the accumulation and pile-up of GNDs? Did any GNDs locate in the DINL or pile up against DINL? Furthermore, recent references (Nature Reviews Materials, 5, 706-723, 2020, Scripta Materialia 186, 304-311, 2020, Matter, 5, 2430-2433, 2022) showed that when GNDs accumulates and piles up against GBs, the pile-up of GND leads to generation of back stress, which contributes to the work hardening. The authors are suggested to add the relevant discussion by refereeing to the above references.

Authors’ response: Thanks for your constructive comments. As the reviewer suggested, there indeed exists an elastic interaction between DINL and dislocation. Compared with the highly ordered grain interior, the DINL without anti-phase boundary (APB) barriers is prone to dislocation generation and multiplication during deformation. To support this viewpoint, the dislocation behavior near the grain-boundary region of the deformed sample with a strain of 5% was further checked using STEM. As shown in **Supplementary Fig. 4**, dislocations accumulated at the DINL and piled up against GBs, indicating that the relatively soft DINL can sustain larger plastic strain prior to the hard L1₂ region. To coordinate this deformation inhomogeneity, GNDs were usually generated in the soft DINL first and then piled up against

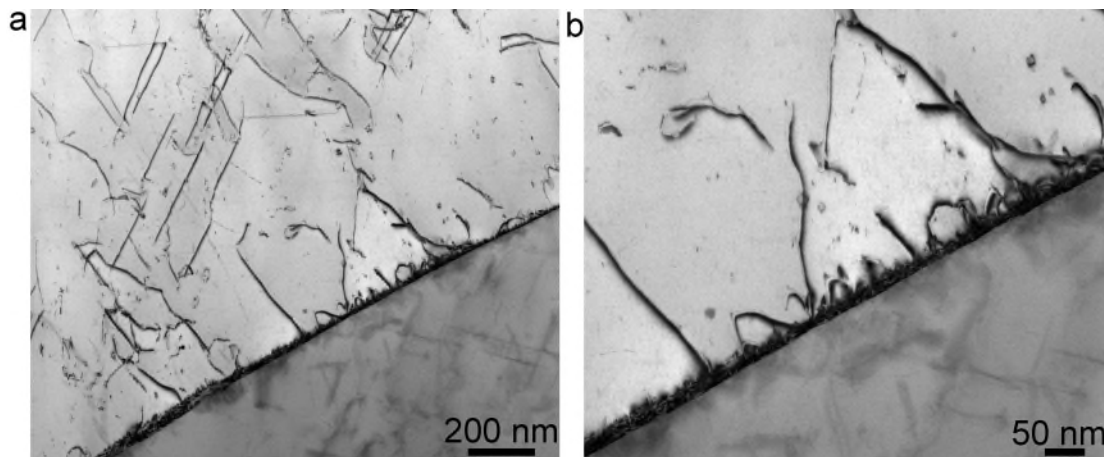
GBs. The pile-up of GNDs can act as obstacles to the dislocation motion and lead to generation of back stress, which in turn contributes to the work hardening of the CCIMA⁵⁻⁷.

Manuscript (Lines 215–219)

Dislocation slip is therefore easy to be activated in the DINL compared with the highly ordered grain interior. To support this viewpoint, the dislocation behavior near the grain-boundary region of the deformed sample with a strain of 5% was further checked using STEM. As shown in **Supplementary Fig. 4**, dislocations accumulated at the DINL and piled up against GBs, indicating that the relatively soft DINL can sustain larger plastic strain prior to the hard L1₂ region, which decreased the possibility of forming cracks and finally contributed to the exceptional ductility.

Manuscript (Lines 288–295)

Besides the superlattice dislocation behavior in the grain interior, the GNDs accumulated near the grain boundary also contributed to the work hardening capability. As shown in **Supplementary Fig. 4**, dislocations accumulated at the DINL and piled up against GBs, indicating that the relatively soft DINL can sustain larger plastic strain prior to the hard L1₂ region. To coordinate this deformation inhomogeneity, GNDs were usually generated in the soft DINL and piled up against GBs, which can act as obstacles to the dislocation motion and lead to generation of back stress, eventually contributing to the work hardening of the CCIMA⁵²⁻⁵⁴.



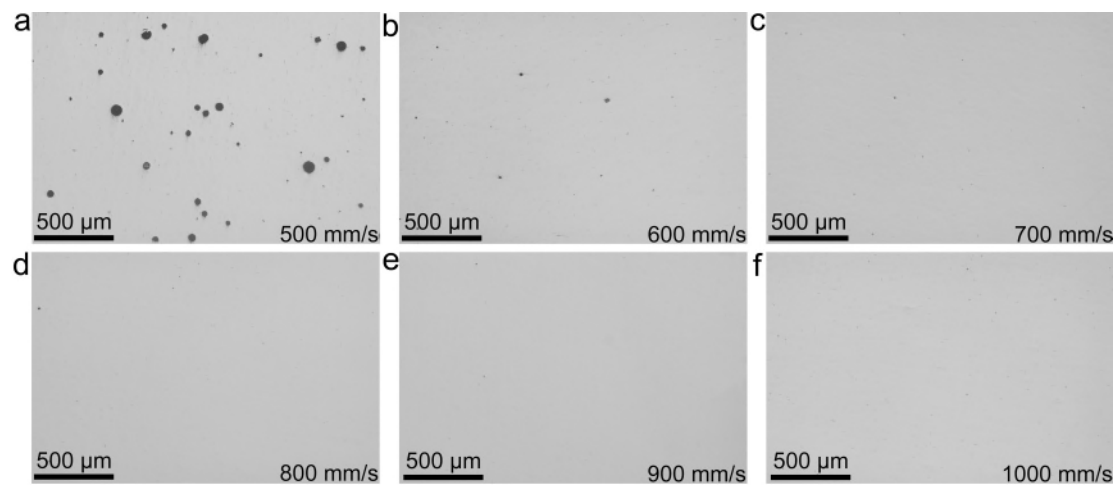
Supplementary Fig. 4 Deformation structure of thermal-stabilized CCIMA at a tensile strain of 5%. a, STEM-BF image showing the dislocation structures near the grain boundary and grain interior. b, Enlarged STEM-BF image revealing the entanglement of dislocations with DINL.

References

- 5 Li X, Lu L, Li J, Zhang X, Gao H. Mechanical properties and deformation mechanisms of gradient nanostructured metals and alloys. *Nat Rev Mater* **5**, 706–723 (2020).
- 6 Li J, Zhang Q, Huang R, Li X, Gao H. Towards understanding the structure-property relationships of heterogeneous-structured materials. *Scr Mater* **186**, 304–311 (2020).
- 7 Jiang J, Chen Z, Ma H, Xing H, Li X. Strength-ductility synergy in heterogeneous-structured metals and alloys. *Matter* **5**, 2430–2433 (2022).

4. The processing parameters (including laser power and scanning speed) of 3D printing has significant influence on the for forming and mechanical properties of alloys. If possible, the authors are suggested to provide a window of processing parameters for forming of alloys with excellent mechanical properties.

Authors' response: Thanks for your constructive suggestion. As the reviewer suggested, the SLM parameters, including laser power, scanning speed, hatch distance, and layer thickness have significant influence on the forming and mechanical properties of the as-printed materials. The hatch distance was determined to be 0.12 mm based on the laser spot diameter to guarantee a favorable overlapping rate. The layer thickness was set to be consistent with the average powder particle size to ensure sufficient melting for each layer. The laser power was set around half of the peak power to ensure its perfect Gaussian beam mode. Higher output laser power may cause mode instability⁸. Thus, in present work, we mainly probed the effects of scanning speed on the forming ability of the as-printed CCIMA. As shown in **Extended Data Fig. 1**, nearly fully dense samples were well obtained when the laser scanning speed varied from 600 to 1000 mm/s, indicating an excellent printability of this material.



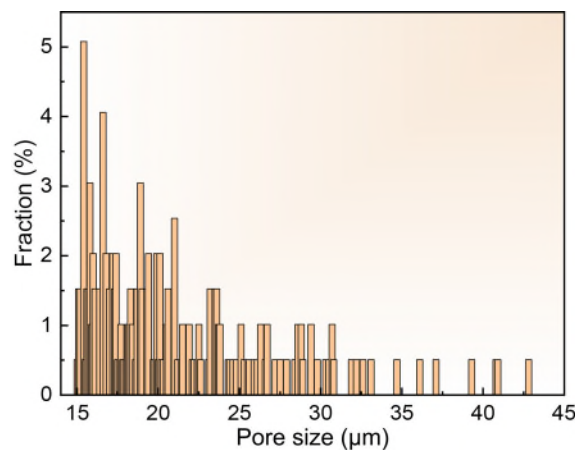
Extended Data Fig. 1 Defects distribution of the as-printed CCIMAs. a–f, Optical microscopy images showing the defects of the as-printed CCIMAs when the laser scanning speeds varied from 500 to 1000 mm/s. The pore defects are almost invisible from the optical microscopy images when the laser scanning speed exceeds 600 mm/s, illustrating the excellent printability of the present CCIMA.

Reference

- 8 Tao R, Zhou P, Xiao H, Wang X, Si L, Liu Z. Progress of study on mode instability in high power fiber amplifiers. *Laser Optoelectron Prog* **51**, 5–12 (2014).

5. Figure 1c shows the pore distribution of printed alloy. It looks unclear to visualize the volumes of pores. The authors should provide a high-resolution picture to show the volumes of pores or display a statistical distribution of pore size.

Authors' response: Thanks for your useful suggestion. The statistical distribution of pore size was provided in the **Supplementary Fig. 1**.



Supplementary Fig. 1 Pore size distribution of the sample printed at a laser power of 200 W and a scanning speed of 900 mm/s.

Manuscript (Lines 89–91)

The statistical distribution of pore size was provided in the **Supplementary Fig. 1**, showing an average pore diameter of 22.0 μm.

To Reviewer #3

This article reports a printable L12-type chemically complex intermetallic alloy (CCIMA). This alloy provides an extraordinary combination of ultrahigh tensile strength (~ 1.6 GPa) and large uniform elongation ($\sim 35\%$), which is remarkable. This alloy design is novel and can be scientifically significant. However, there are some concerns to be addressed if the manuscript is to be published. Please see detailed comments below.

1. Is this microstructure and superior tensile properties unique in additive manufactured material? Or it is also available in conventional ones with the same composition?

Authors' response: Thanks for the good comment. The special microstructure of CCIMA consists of L1₂-type ordered grains whose boundaries are decorated with disordered nanoscale FCC interfaces. This unique microstructure highly depends on compositional design, which can also be achieved through conventional thermal mechanical treatment, such as casting, multi-pass rolling and heat treatment. However, it is time-consuming and very costly to fabricate the CCIMA parts, especially for those with complex geometries. In contrast, additive manufacturing can quickly realize the preparation of geometrically complex CCIMA samples, providing great advantages for the potential applications in the advanced engineering fields like aerospace.

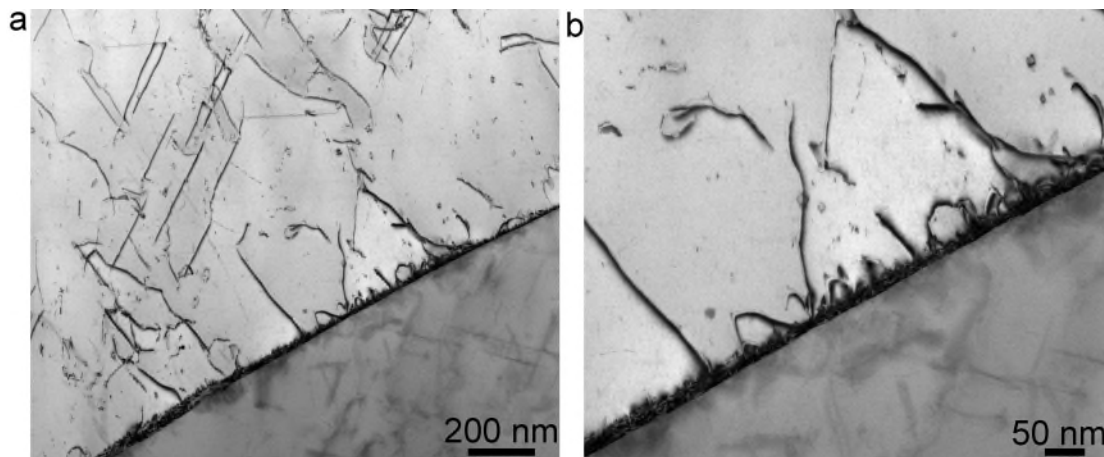
2. In the following two statements - 'The DINLs without anti-phase boundary (APB) barriers are more prone to dislocation multiplication and pile up.' and 'Dislocation slip is therefore easy to be activated in the DINL compared with the highly ordered grain interior', the authors

emphasised the importance of dislocation behaviours in the DINL. However, no characterization results of dislocations in the DINL were presented. Hard to imagine the dislocations multiplication and pile up in DINL with a thickness of less than 5 nm.

Authors' response: Thanks for your insightful comment. Compared with the highly ordered grain interior, the DINL without anti-phase boundary (APB) barriers are prone to dislocation generation and multiplication during deformation. To better support this viewpoint again, the dislocation behavior near the grain boundary region of the deformed sample with a strain of 5% was further checked using STEM. As shown in **Supplementary Fig. 4**, dislocations accumulated at the DINL and piled up against GBs, indicating that the relatively soft DINL can sustain larger plastic strain prior to the hard L₁₂ region, which decrease the possibility of forming cracks and finally contributes to the exceptional ductility.

Manuscript (Lines 215–219)

Dislocation slip is therefore easy to be activated in the DINL compared with the highly ordered grain interior. To support this viewpoint, the dislocation behavior near the grain-boundary region of the deformed sample with a strain of 5% was further checked using STEM. As shown in **Supplementary Fig. 4**, dislocations accumulated at the DINL and piled up against GBs, indicating that the relatively soft DINL can sustain larger plastic strain prior to the hard L₁₂ region, which decreased the possibility of forming cracks and finally contributed to the exceptional ductility.



Supplementary Fig. 4 Deformation structure of thermal-stabilized CCIMA at a tensile strain of 5%. a, STEM-BF image showing the dislocation structures near the grain boundary and grain interior. b, Enlarged STEM-BF image revealing the entanglement of dislocations with DINL.

3. The micro-CT result and optical microscopic images evidence that dense and crack-free CCIMA samples can be produced by LPBF process, which is remarkable in ordered intermetallic alloys. This novelty was emphasized by the ‘excellent printability’ in the abstract and ‘highly printable’ in the title and summary. However, the ‘printability’ has not been well-defined, and what ‘high’ means in ‘highly printable’ remains unclear. The authors may want to emphasize such novelty in a better way.

Authors’ response: Thanks for your good comment. The metallic parts produced by additive manufacturing are usually susceptible to forming undesired defects, especially the void and crack. The printability means the ability of an alloy to avoid these defects⁹. In this work, the as-printed CCIMA shows a very low porosity and is free of cracks, illustrating an excellent printability of this material. As a result, here we use “highly printable” to highlight this property, which has also been used in other published work^{10, 11}.

References

- 9 Mukherjee T, Zuback J, De A, DebRoy T. Printability of alloys for additive manufacturing. *Sci Rep* **6**, 19717 (2016).
- 10 Suntornnond R, Tan EYS, An J, Chua CK. A highly printable and biocompatible hydrogel composite for direct printing of soft and perfusable vasculature-like structures. *Sci Rep* **7**, 16902 (2017).
- 11 Chun K-Y, *et al.* Highly conductive, printable and stretchable composite films of carbon nanotubes and silver. *Nat Nanotechnol* **5**, 853–857 (2010).

4. ‘Unlike the conventional intermetallic alloys with extremely poor printability, the present CCIMA is highly printable and can be well manufactured by the LPBF method. Following this statement, what is the difference between CCIMA and conventional intermetallic alloys, making this CCIMA more ‘printable’?

Authors’ response: Thanks for the insightful comment. The printability of material is very sensitive to its chemical composition. The high hot-cracking susceptibility of conventional intermetallics, such as Ni₃Al, NiAl, TiAl alloys, is caused by their intrinsic brittleness, making them difficult to be manufactured via the processing methods, such as welding and additive manufacturing. However, in the CCIMA systems, such a brittleness problem can be significantly eliminated by elaborately incorporating multiple elements^{12–14}. Thus, the crack susceptibility was decreased in the CCIMA systems compared to the traditional intermetallic alloys. On the other hand, most studies attributed the cracking behavior of additive

manufactured intermetallic alloys to the low melting point eutectic liquid films at grain boundaries during solidification¹⁵. In contrast, it was reported that the segregation-induced phase transformation can reduce the detrimental effect of residual thermal strain and subsequently decrease the hot crack susceptibility^{16, 17}. Thus, the segregation-induced G phase formed along the grain boundaries (**Fig. R3**) may break up the continuous liquid film between the adjacent grains during solidification, which would in turn accelerate the bridging and prevent the hot cracking.

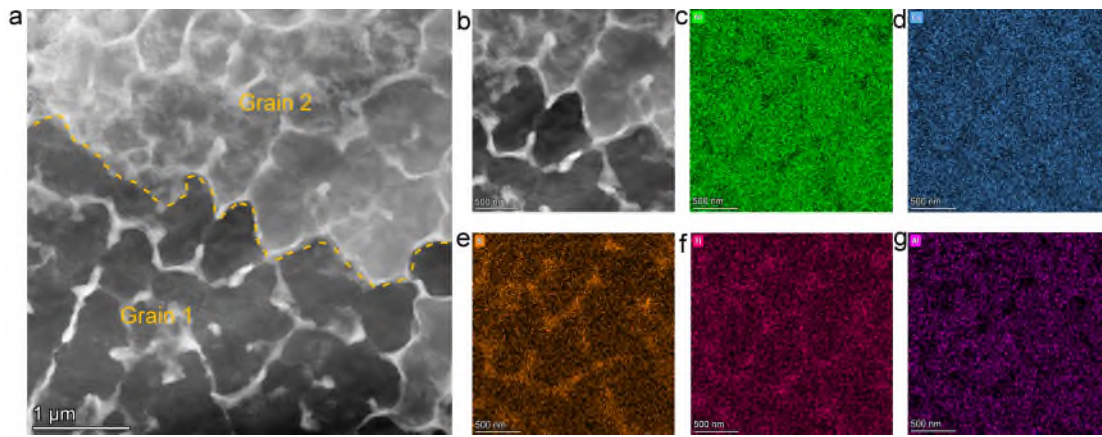


Fig. R3 Microstructural features of the as-printed CCIMA. a, STEM-HAADF image showing the microstructure within the adjacent grains, **b–g**, Enlarged STEM-HAADF image and corresponding EDS maps showing the element distribution across two grains.

References

- 12 Xiao, B. *et al.* Off-stoichiometry-guided design of high-strength chemically complex intermetallic-based alloys with outstanding ductility. *J. Mater. Sci. Technol.* **160**, 28–33 (2023).
- 13 Yang T, et al. Ultrahigh-strength and ductile superlattice alloys with nanoscale disordered interfaces. *Science* 369, 427–432 (2020).

- 14 Duan, F. *et al.* An order-disorder core-shell strategy for enhanced work-hardening capability and ductility in nanostructured alloys. *Nat. Commun.* **15**, 6832 (2024).
- 15 Chai, H. *et al.* Microstructure and cracking behavior of Ni₃Al-based IC21 alloy fabricated by selective laser melting. *Mater. Charact.* **196**, 112592 (2023).
- 16 Thapliyal, S. *et al.* Segregation engineering of grain boundaries of a metastable Fe-Mn-Co-Cr-Si high entropy alloy with laser-powder bed fusion additive manufacturing. *Acta. Mater.* **219**, 117271 (2021).
- 17 Sun, Z. *et al.* Reducing hot tearing by grain boundary segregation engineering in additive manufacturing: example of an Al_xCoCrFeNi high-entropy alloy. *Acta. Mater.* **204**, 116505 (2021).

5. The authors may want to briefly introduce the material science reason for unsatisfactory printability and mechanical properties of intermetallic alloys. And is there any effort made to improve their printability and mechanical properties?

Authors' response: Thanks for the insightful comment. The main problem for intermetallics is their severe brittleness, making the processing and application difficult or impossible. The intrinsic reasons for the brittleness of intermetallics can be attributed to the following factors.

First, intermetallics usually form part of covalent bonds, which are stronger and more rigid than the metallic bonds, making them quite brittle and more prone to cracking under stress¹⁸. The insufficient number of slip systems or dislocation mobility also decreases the deformation ability and increases the cracking probability¹⁷. More importantly, the weak grain boundary is

also one of the main reasons for the brittle nature of the intermetallics, which may be aggravated by the segregation of impurities¹⁸. These combined factors render most intermetallics very strong but quite brittle. Thus, so far, it is extremely difficult to fabricate such highly hot crack-susceptible materials via additive manufacturing techniques due to the severe residual stress generated during high-cooling rate.

During past years, many efforts have been made to improve the printability and mechanical properties of intermetallic alloys. However, from the perspective of the material itself, its printability is still hard to be improved once their chemical composition was determined¹⁹. Thus, optimizing the processing parameters, such as preheating the substrate, is widely used to reduce the cracking tendency during additive manufacturing processes²⁰. Nevertheless, until now, achieving good ductility in the conventional intermetallics is still highly challenging. Doping grain boundary strengthening elements such as B and Zr has been proved to be an effective way to inhibit the grain boundary embrittlement of Ni₃Al based intermetallics^{21–23}. However, this strategy is only effective under low stress level¹³. In conclusion, based on our findings here, developing the multicomponent intermetallic alloys with the chemical complex alloying would be an appreciate way to effectively overcome the strength-ductility trade-off.

References

- 13 Yang T, et al. Ultrahigh-strength and ductile superlattice alloys with nanoscale disordered interfaces. *Science* 369, 427–432 (2020).
- 18 Sauthoff, G. *Intermetallics*. (John Wiley & Sons, 2008).

- 19 Li, W. *et al.* Yttrium for the selective laser melting of Ti-45Al-8Nb intermetallic: Powder surface structure, laser absorptivity, and printability. *J. Alloys Compd.* **892**, 161970 (2022).
- 20 Gussone, J. *et al.* Microstructure of γ -titanium aluminide processed by selective laser melting at elevated temperatures. *Intermetallics* **66**, 133–140 (2015).
- 21 Liu, C. T., White, C. & Horton, J. Effect of boron on grain-boundaries in Ni₃Al. *Acta Metall.* **33**, 213–229 (1985).
- 22 Weihs, T., Zinoviev, V., Viens, D. & Schulson, E. The strength, hardness and ductility of Ni₃Al with and without boron. *Acta Metall.* **35**, 1109–1118 (1987).
- 23 Chiba, A., Hanada, S. & Watanabe, S. Ductility of recrystallized Zr-doped Ni₃Al alloys fabricated by isothermal hot-forging. *Mater. Trans., JIM* **35**, 286–290 (1994).

6. Fig.1b shows some printed parts. Is that possible to print a 10mm*10mm*10mm crack-free bulk sample?

Authors' response: Thanks for your good question. The bulk sample with a dimension of 10 mm×10 mm×13 mm can be well manufactured by LPBF using the optimized LPBF parameters of laser power of 200 W, and scanning speed of 900 mm/s (**Fig. R4a**). Meanwhile, no cracks can be observed in the as-printed bulk samples from the bottom to top regions (**Figs. R4b–d**), illustrating an excellent printability of the present CCIMA.

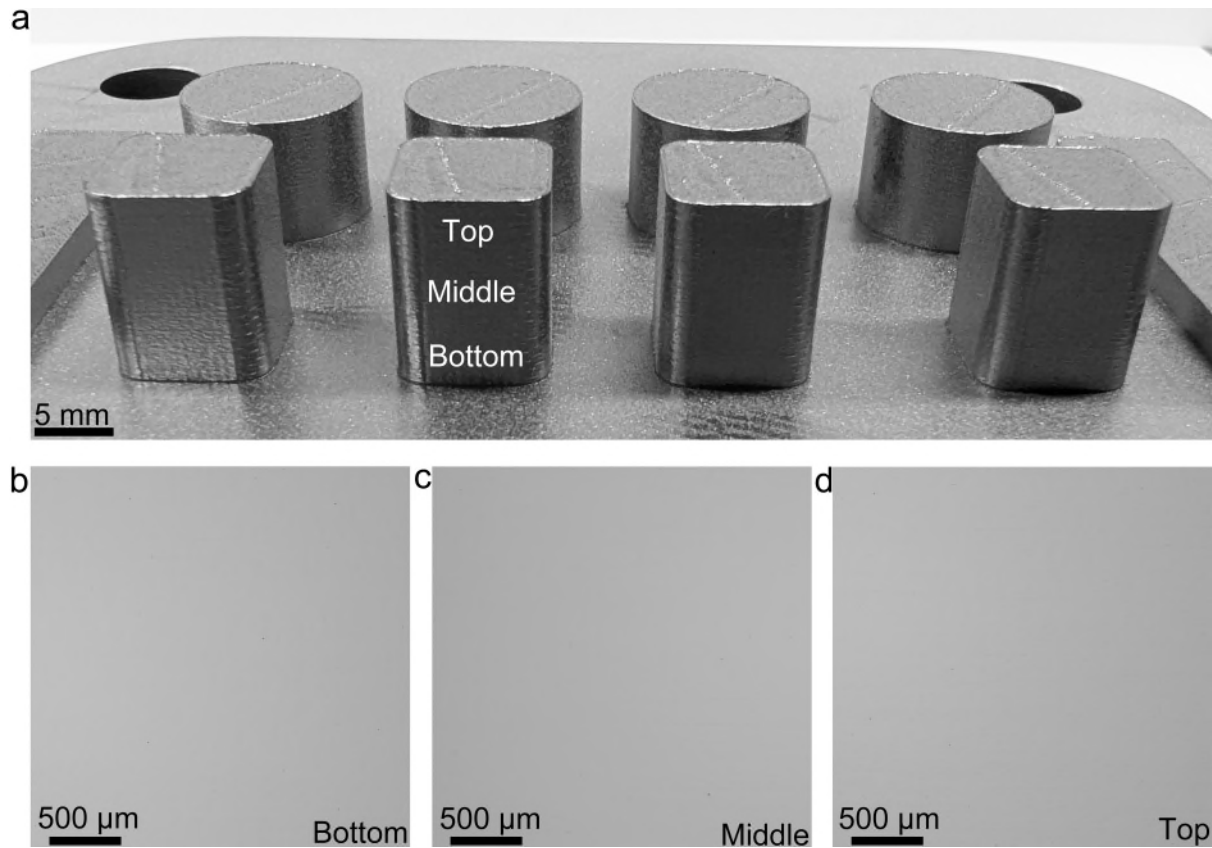


Fig. R4 Printability of the present CCIMA. **a**, Macroscopic image showing the bulk CCIMA samples fabricated by LPBF, **b–d**, Optical microscopy images illustrating no cracks formation in the as-printed CCIMA bulk samples from bottom to top regions.

7. In Fig. 2a, please provide the lattice parameters. Is there a peak at ~ 71 degree? If yes, please index it.

Authors' response: Thanks for this useful suggestion. The lattice parameters of the thermal-stabilized CCIMA were estimated to be 0.355 nm by fitting the XRD peaks. The weak peak at ~ 71 degree may be caused by the background noise of the XRD. So, we reconducted the XRD experiments three times using slow scanning speed to ensure its accuracy. As shown in **Fig. R5**, no weak peaks can be observed around 71 degree.

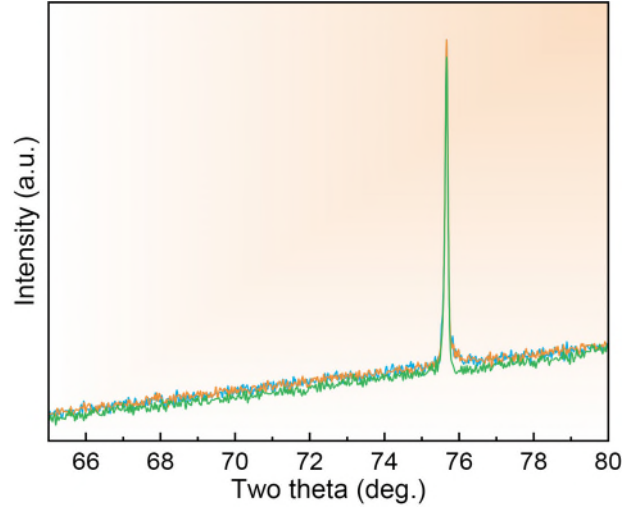


Fig. R5 XRD spectrum at a two theta range from 65 to 80° of the thermal-stabilized CCIMA.

Manuscript (Lines 155–165)

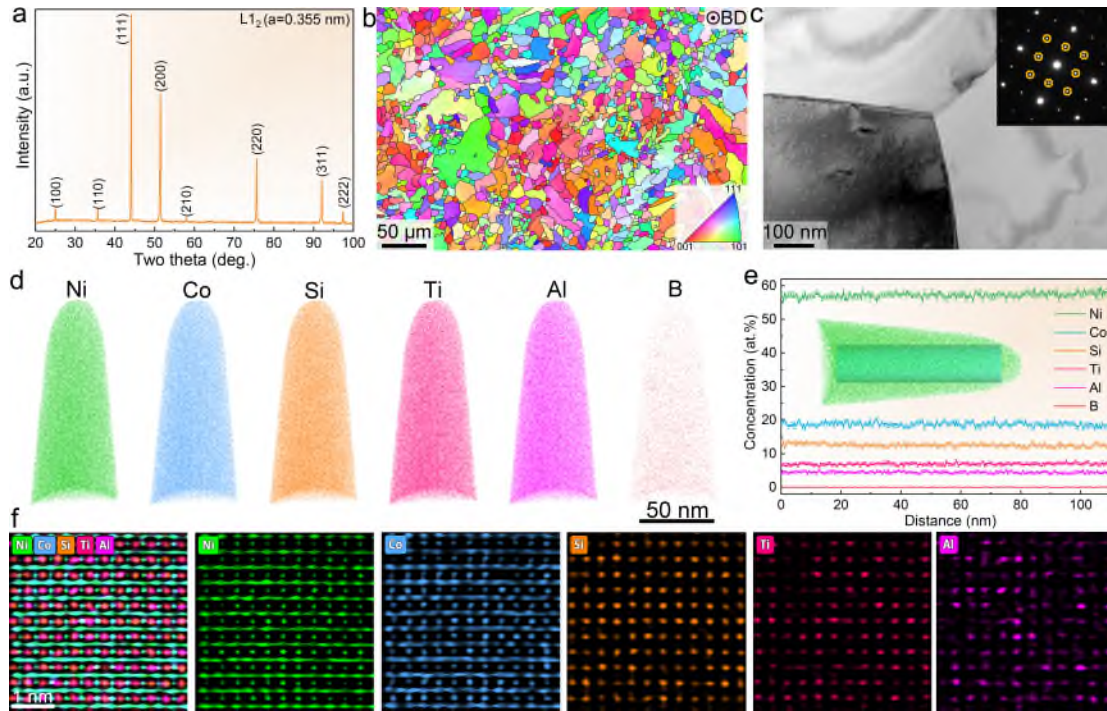
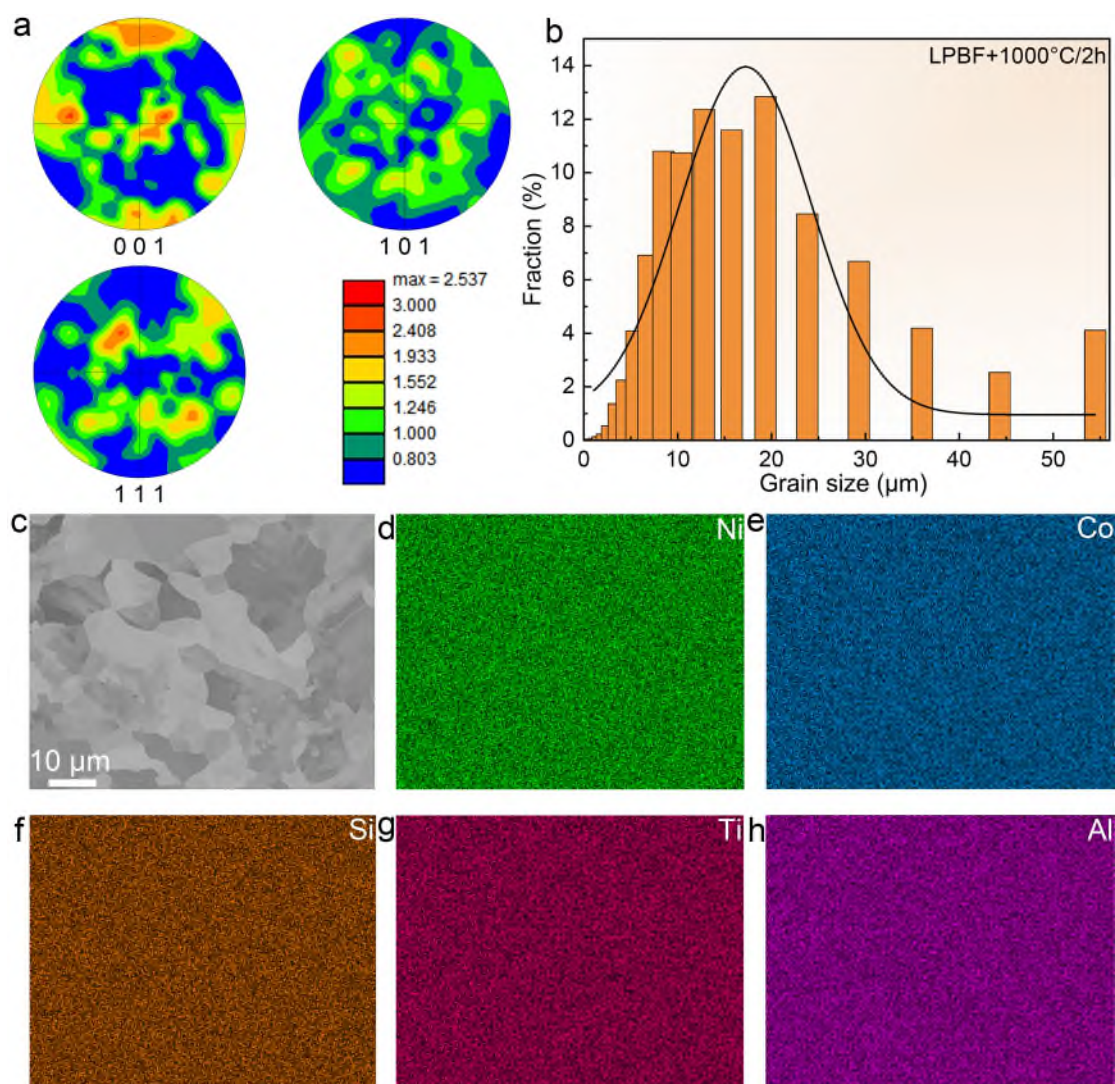


Fig. 2 Microstructural features of the thermal-stabilized CCIMA from microscopic to atomic scales. **a**, XRD spectrum illustrating an ordered $L1_2$ -type crystal structure. **b**, EBSD-IPF map showing the fine grain morphology perpendicular to the building direction (BD). **c**, TEM bright-field image showing the homogenous grain structure, the superlattice diffraction

spots highlighted by the yellow circles in the SAED pattern illustrating a highly ordered L1₂ structure of the grain interior (inset of **Fig. 2b**). **d**, 3D-APT results showing the homogeneous elements distribution within the grain interior. **e**, One-dimensional concentration profile showing the element distributions across the 3D-APT tip. **f**, Atomic EDS maps taken from the ordered grain interior along the [001] zone axis, showing the spatial occupations of each element.

8. Does the Fig. 2b show a heterogeneous microstructure? And is there any heterogeneous deformation induced strain hardening during the tension test?

Authors' response: Thanks for your good comment. To quantify the heterogeneity of the grain feature, we calculated the grain size distribution based on the EBSD method, which did not show obvious heterogeneous grain distribution, as proven in the **Supplementary Fig. 3b**. The work hardening response was mainly attributed to the special superlattice dislocation behaviors within the grain interior, such as cross-slip (K-W lock), L-C lock etc.



Supplementary Fig. 3 Microstructural features of the thermal-stabilized CCIMA. **a**, Pole figure showing the texture intensity of the plane perpendicular to the building direction, **b**, Grain size distribution, **c**, BSE image showing the equiaxed grains, **d–h**, EDS mapping showing the homogeneous elements distribution across multiple grains.

9. In lines 131-132, what does the ‘random’ grain distribution mean? Texture? Size? If it refers to orientation distribution, please show the detailed texture information. If it refers to size distribution, please show the size distribution.

Authors’ response: Thanks for your useful suggestion. The random grain distribution refers

to the orientation distribution. The texture information was revealed by EBSD pole figure. As shown in **Supplementary Fig. 3**, the maximum texture intensity is only about 2.5, indicating random grain orientations without serious texture preference.

Manuscript (Lines 133–137)

The electron backscatter diffraction (EBSD) inverse pole figure (IPF) mapping in **Fig. 2b** shows the random grain distribution with a maximum texture index of 2.5, as revealed by the pole figure in **Supplementary Fig. 3a**. The grain size distribution is shown in **Supplementary Fig. 3b**, revealing an average grain size of 17.7 μm .

10. In the FFT of DINL inserted in Fig. 3c, please also explain unlabelled weak spots, which seem to be a pattern from other structures.

Authors' response: Thanks a lot for your careful review of our work. The unlabeled weak spots were caused by the noise of FFT processing. Specifically, no other structures can be observed within the DINL and grain interior based on the SEM, high-resolution STEM HAADF and 3D-APT analyses. To avoid the possible confusion, the FFT image was optimized by using the FEI Velox software, and the new results were updated in **Fig. 3**.

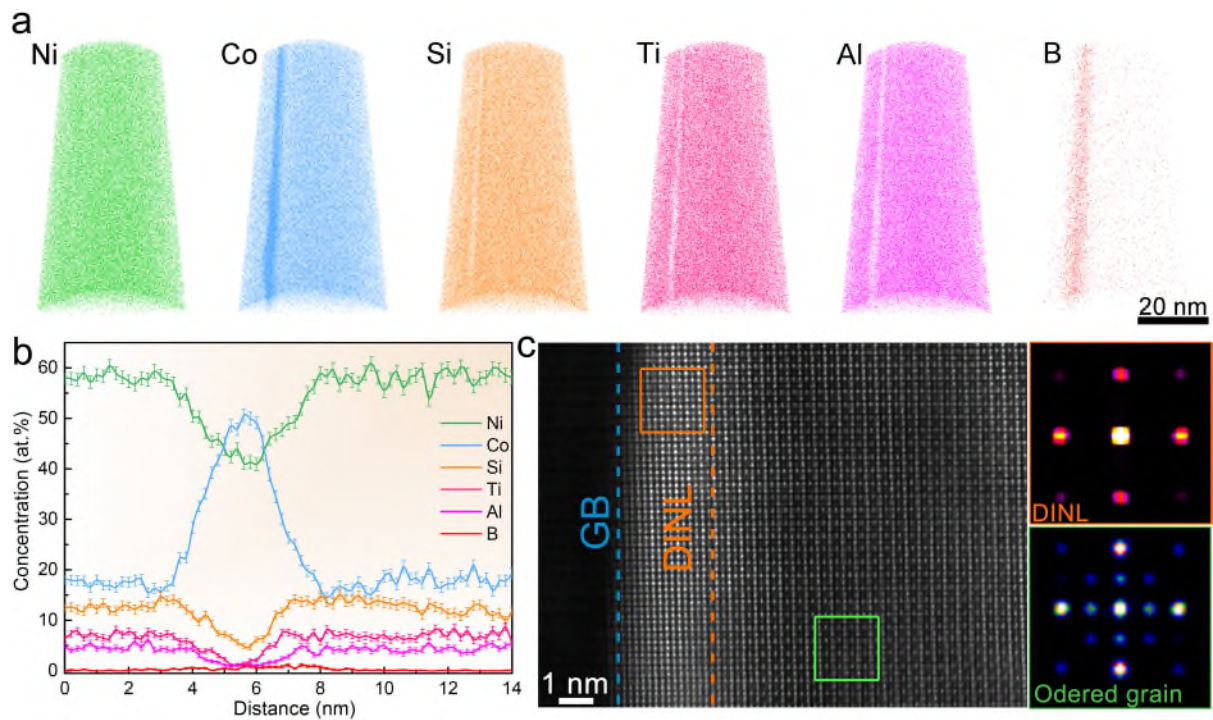


Fig. 3 Chemical and atomic structures of the DINL and ordered grain interior. **a**, 3D-APT maps showing the distribution of each element near the grain boundary. Elements Co and B co-segregated to the DINL while Ni, Al, Ti, and Al depleted accordingly. **b**, One-dimensional compositional profile revealing the elemental distributions across the grain interior and DINL. **c**, High-resolution HAADF-STEM image illustrating the atomic structures of the DINL and grain interior, the corresponding FFT images (insets in **Fig. 3c**) showing the disordered structure of the DINL and ordered structure of grain interior.

11. In Extended Data Fig. 1, please provide detailed printing parameters for all six conditions.

Authors' response: Thanks for your good suggestion. The detailed printing parameters for all six conditions are added in the **Methods** part. Details are as follows.

Manuscript (Lines 353–358)

To investigate the effects of scanning speed on the forming ability of the as-printed CCIMA, the scanning speeds varied from 500 to 1000 mm/s with a permanent increasement of 100 mm/s. The layer thickness of 0.03 mm, hatch distance of 0.12 mm, and a laser-beam rotation of 67° for the consecutive layers were fixed for all the samples. The tensile samples were directly printed using the optimized laser power of 200 W, and scanning speed of 900 mm/s.

12. In the method of micro-CT, please provide sample size.

Authors' response: Thanks for this good suggestion. The sample size for the micro-CT test was provided in the **Methods** part.

Manuscript (Lines 368–370)

The sample used for the micro-CT test with a dimension of $3.0 \times 2.0 \times 1.5 \text{ mm}^3$ was rotated from 0° to 360° with a step size of 0.2°.

13. For XRD dislocation density calculation, there are a few questions:

- a. Which kinds of dislocations were considered?
- b. How were their q and Ch00 values calculated?
- c. How was the average C value calculated? Based on the fraction of different types of dislocations?
- d. Does the effect of stacking faults was considered? It can significantly impact the calculated dislocation density, especially when ‘in stage III, the plastic deformation was dominated by high-density SISF networks’

Authors' response: Thanks for your constructive comment. We mainly considered the screw $\langle 110 \rangle$ type dislocation, which is the typical dislocation structure in the $L1_2$ type intermetallic alloys²⁴. The average orientation factor C is calculated by using the ANIZC program, which is available via the website (<http://metal.elte.hu/anizc/>). The calculations of q and C_{h00} are integrated in the ANIZC program.

The effect of stacking fault can be incorporated into the modified Williamson-Hall method by replacing the size term $(0.9/D)$ with an effective size expression, as developed by Warren²⁵:

here $\beta' = (1.5\alpha + \beta)/a$, where α and β are the stacking fault and twin boundary probabilities, a is the lattice constant; $W(g)$ is a constant that depends on the lattice plane, and its value for FCC structure can be found in the reference²⁵. α refers the probability of stacking fault occurrence between two consecutive atomic planes. The stacking fault probability α can be obtained by²⁶:

where ε is the lattice strain ($\Delta d/d_0$, $\Delta d = d - d_0$, d is the d -spacing, and d_0 is the initial d -spacing). which was estimated to be 0.355 nm by fitting the XRD data.

References

24 Fang J, Schulson E, Baker I. The dislocation structure in $L1_2$ ordered alloy Ni_3Ge .

- Philos Mag A 70, 1013–1025 (1994).
- 25 Warren B. X-ray studies of deformed metals. *Progr in Metal Phys* **8**, (1959).
- 26 Woo W, *et al.* Comparison of dislocation density, twin fault probability, and stacking fault energy between CrCoNi and CrCoNiFe medium entropy alloys deformed at 293 and 140K. *Mater Sci Eng, A* **781**, 139224 (2020).

Supplementary Note 3 Dislocation density calculation

To determine the dislocation multiplication of the thermal-stabilized CCIMA during tensile deformation, the dislocation density was calculated based on the modified Williamson-Hall (MWH) method by refining the XRD data¹⁰. The equation of the MWH method developed by Ungar et al. was written as¹⁰:

where θ , $\Delta\theta$, λ , and α are the diffraction angle, full width at half maximum (FWHM), and wavelength of the X-rays, respectively; α represents the FWHM caused by grain refinement; b is the Burgers vector; O is for higher order terms, which can be ignored; M is a constant related to the dislocation density and outer cut-off radius of dislocations R_e by $M = \frac{b}{R_e}$; M is estimated to be 2 for the materials with reasonable dislocation densities¹¹; C_{hkl} is the average dislocation contrast factor corresponding to (hkl) reflection, which can be expressed as:

where C_{h00} is the average contrast factor of (h00) reflection, depending on the elastic constants C_{11} , C_{12} , and C_{44} , which are determined to be 269.6, 161.9, 130.0 GPa respectively by the DFT

calculation, q is a parameter depending on the dislocation type and the elastic constants of the material, H represents the orientation factor given by:

The average orientation factor C is calculated using the ANIZC program, which is available via the website (<http://metal.elte.hu/anizc/>). The calculations of q and C_{h00} were integrated in the ANIZC program.

In the last stage of plastic deformation, the effect of stacking fault was incorporated into the modified Williamson-Hall method by replacing the size term $(0.9/D)$ with an effective size expression, as developed by Warren¹²:

$$\Delta d/d_0 = \frac{0.9}{D} + \frac{W(g)}{a} \left(1.5\alpha + \beta \right)$$

here $\beta' = (1.5\alpha + \beta)/a$, where α and β are the stacking fault and twin boundary probabilities, a is the lattice constant; $W(g)$ is a constant that depends on the lattice plane, and its value for FCC structure can be found in the reference¹². α refers to the probability of stacking fault occurrence between two consecutive atomic planes. The stacking fault probability α can be obtained by¹³:

$$\alpha = \frac{\Delta d/d_0 - \frac{0.9}{D}}{\frac{W(g)}{a}}$$

where ε is the lattice strain ($\Delta d/d_0$, $\Delta d = d - d_0$, d is the d -spacing, and d_0 is the initial d -spacing), which was estimated to be 0.355 nm by fitting the XRD data.

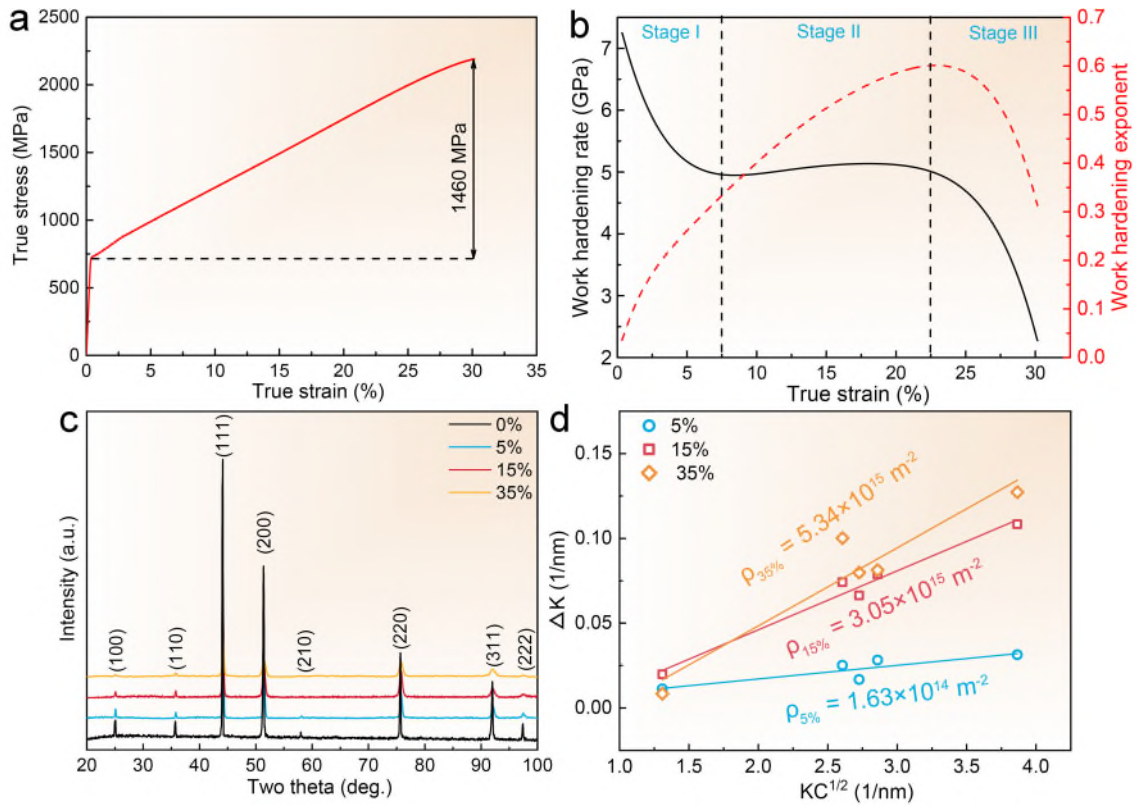
To eliminate the FWHM caused by the instrument, we chose the thermal-stabilized CCIMA as a base material, thus the dislocation multiplication under deformations strains of 5% and 15% can be calculated based on the **Eq. (4)**:

$$\rho = \frac{1}{b} \left(\frac{\Delta K}{K} \right) \quad (4)$$

Meanwhile, the dislocation multiplication under a deformations strain of 35% can be calculated by incorporating the stacking fault effect:

$$\rho = \frac{1}{b} \left(\frac{\Delta K}{K} \right) + \frac{1}{b} \left(\frac{\Delta K}{K} \right) \quad (5)$$

Thus, the dislocation multiplication densities at different deformation stages can be obtained by linear fitting versus $KC^{1/2}$ (for the case with deformation strain of 5% and 15%), and versus $KC^{1/2}$ (for the case with a deformation strain of 35%), as presented in (Extended Data Figs. 4c and d).



Extended Data Fig. 4 Deformation behavior of the thermal-stabilized CCIMA. **a**, The true tensile stress-strain curve of the CCIMA showing exceptional work hardening ability. **b**, Work hardening rate and exponent versus the true tensile strain curves. **c**, XRD data of the samples at different tensile strains showing the peak broadening caused by local strain indicating increases in dislocation densities. **d**, Calculated dislocation densities by refining the XRD data based on the modified Williamson-Hall method.

References in the Supplementary Information

- 10 Ungár T, Ott S, Sanders P, Borbély A, Weertman J. Dislocations, grain size and planar faults in nanostructured copper determined by high resolution X-ray diffraction and a new procedure of peak profile analysis. *Acta Mater* **46**, 3693–3699 (1998).
- 11 Ribárik G, Ungár T. Characterization of the microstructure in random and textured polycrystals and single crystals by diffraction line profile analysis. *Mater Sci Eng, A* **528**, 112–121 (2010).
- 12 Warren B. X-ray studies of deformed metals. *Progr in Metal Phys* **8**, (1959).
- 13 Woo W, *et al.* Comparison of dislocation density, twin fault probability, and stacking fault energy between CrCoNi and CrCoNiFe medium entropy alloys deformed at 293 and 140K. *Mater Sci Eng, A* **781**, 139224 (2020).

To Reviewer #4

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Authors' response: [Thanks for your valuable comments on our paper.](#)

To Reviewer #5

I recently reviewed an article titled, “Highly printable, ultra-strong, and ductile ordered intermetallic alloy” by Zhou et al. In this study, the authors produce an intermetallic alloy with the following composition, Ni_{58.48}Co_{18.9}Si_{11.6}Ti_{6.6}Al_{4.4}B_{0.02} and 3D print tensile bars using laser powder bed fusion. In the as-built state the alloy exhibited two intermetallic phases, γ' and G phase which impacted the tensile properties of the alloy. However, after heat treating the alloy the G phase was eliminated and the tensile properties were significantly improved. The heat-treated alloy appears to overcome the common strength-ductility-tradeoff by having both high tensile strengths (over 1600MPa) and ductility (>30%). The authors claim that this intermetallic alloy achieved this high ductility by incorporating disordered nanolayers near the grain boundaries. Though these results are quite interesting, I feel there are aspects to this material and the data presented in the study that need to be clarified. Below are a list of concerns that I would like to see addressed before the manuscript is published.

1.) My largest concern is that after reading the manuscript I still have questions pertaining to the microstructure of the heat-treated alloy. X-ray diffraction is the primary characterization the authors employ to determine phases in the alloy but I find their conclusion unsatisfactory since the 3 phases that would most likely arise in this composition are the G phase, L12, and γ phase. All of which have quite similar FCC crystal structures (Fm-3m). In particular, if the ductile γ phase exists it would help explain the improved ductility of the alloy but it would be quite difficult differentiating this phase from L12 in XRD. In fact, we already know this phase

exists in this alloy because of the disordered FCC structure highlighted in Figure 3! Currently, the characterizations of the microstructure in the heat-treated alloy beyond EBSD are high magnifications using TEM or ATP. I would really like to see the type of characterization shown on the as-built alloy, as showcased in supplementary figure 2, for the heat-treated alloy. EDS scans of multiple grains will prove to the reader that the alloy is a homogenous L12 phase (except for the grain boundaries). It may also clarify if the gamma phase highlighted in Figure 3 is along all GBs or just a select few.

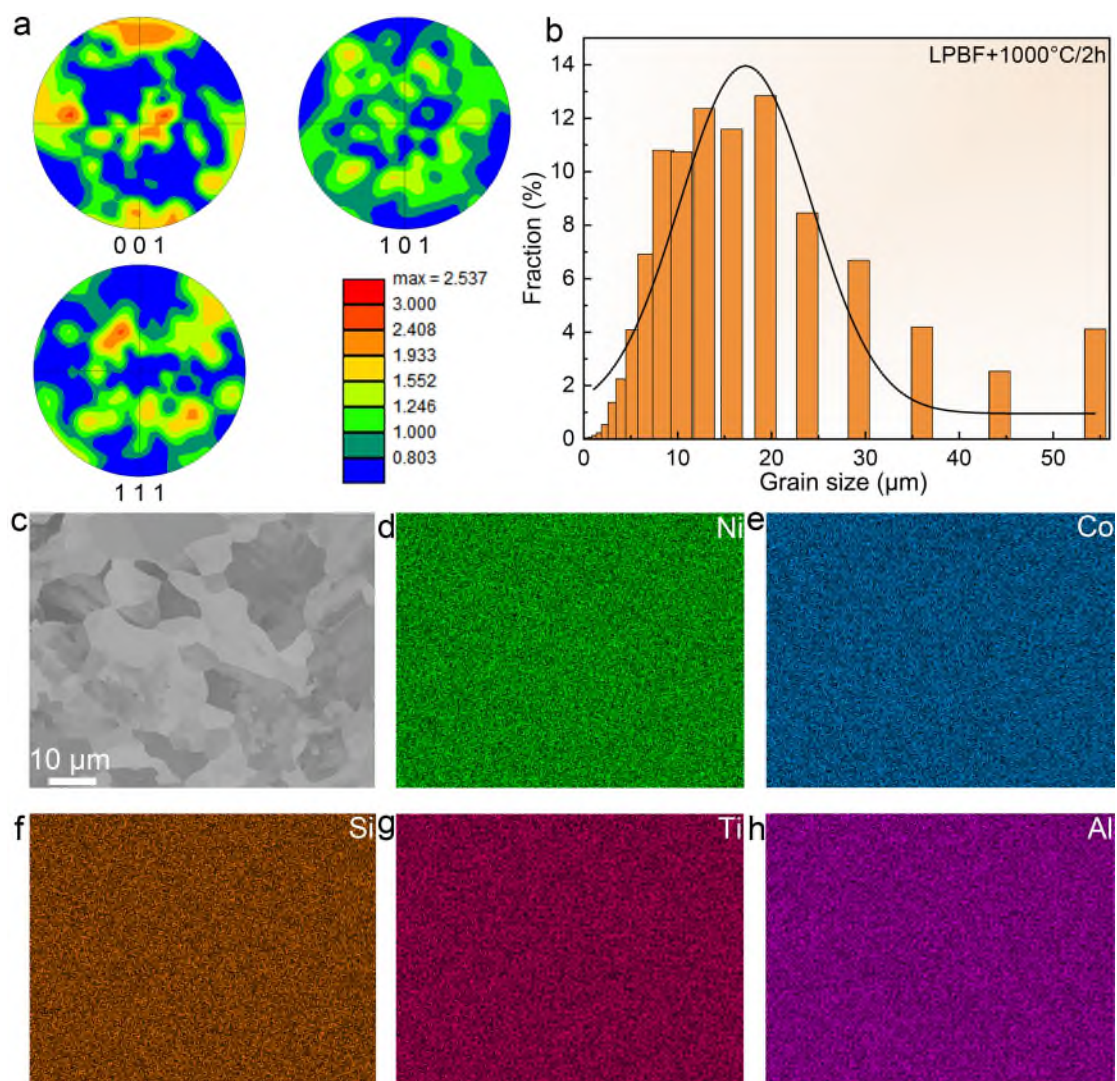
Authors' response: Thanks for the constructive comments. SEM and associated EDS experiments were performed to demonstrate the homogenous of L1₂ phase of the thermal-stabilized CCIMA. As shown in **Supplementary Fig. 3**, the thermal-stabilized CCIMA shows the equiaxed grain structure without detection of any other segregations or second phases in the grain interior. However, due to the limited accuracy of SEM-EDS method, the Co segregation along the grain boundaries cannot be detected. Thus, TEM-EDS experiment was carefully conducted across multiple grain boundaries. As revealed in **Fig. R6**, the Co-rich gamma phase layer exists at almost all the grain boundaries.

Manuscript (Lines 133–140)

The electron backscatter diffraction (EBSD) inverse pole figure (IPF) mapping in **Fig. 2b** shows the random grain distribution with a maximum texture index of 2.5, as revealed by the pole figure in **Supplementary Fig. 3a**. The grain size distribution is shown in **Supplementary Fig. 3b**, revealing an average grain size of 17.7 μm. The back scattered electron (BSE) image together with the EDS maps demonstrate fully equiaxed grains with a homogeneous elemental

distribution (**Supplementary Figs. 3c–h**). The overall chemical composition of the as-printed

CCIMA measured by SEM-EDS is $\text{Ni}_{58.0}\text{Co}_{19.5}\text{Si}_{11.3}\text{Ti}_{6.8}\text{Al}_{4.3}$ (at. %).



Supplementary Fig. 3 Microstructural features of the thermal-stabilized CCIMA. a, Pole figure showing the texture intensity of the plane perpendicular to the building direction, **b**, Grain size distribution, **c**, BSE image showing the equiaxed grains, **d–h**, EDS mapping showing the homogeneous elements distribution across multiple grains.

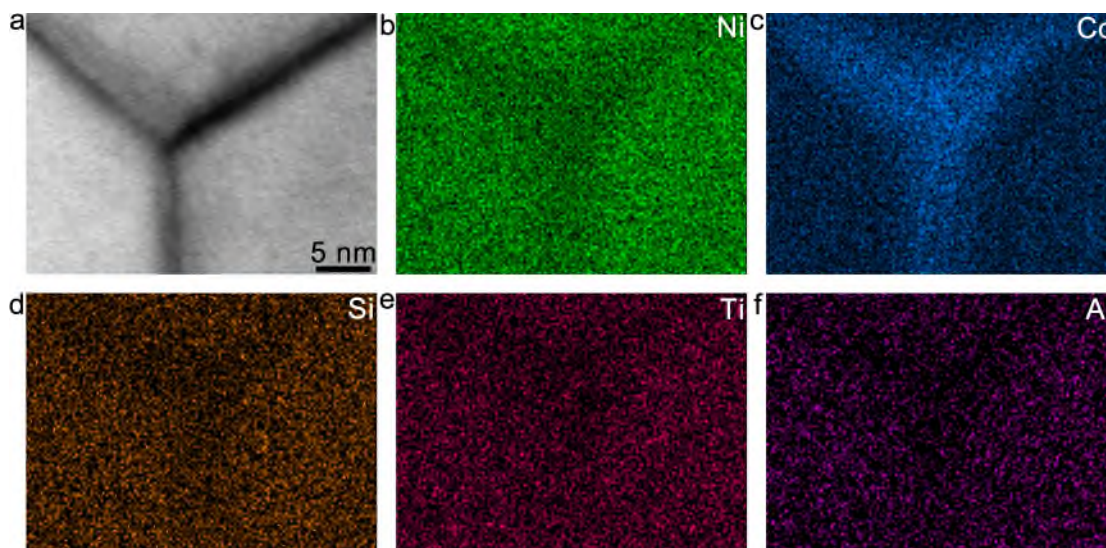


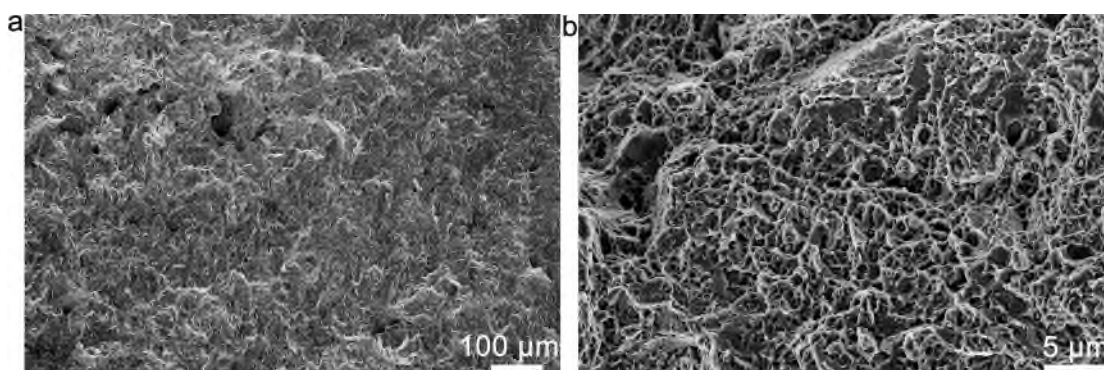
Fig. R6 STEM image and chemical composition across multiple grains. a, STEM image showing the trident grain boundaries. **b–f**, TEM-EDS maps showing the Co enrichment across the trident grain boundaries.

2.) In figure 1, the fracture surface shown in 1(d) is too high a magnification to prove that the alloy is ductile. A lower magnification image showing multiple grains will help show the reader how ductile the alloy is and what failure mechanisms may be present.

Authors' response: Thanks for the good suggestions. The fractured surface with a low magnification was provided in **Supplementary Fig. 2**. No grain-boundary dissociation can be observed, indicating a ductile transgranular fracture model.

Manuscript (Lines 110–114)

The fracture surface was first characterized by scanning electron microscopy (SEM). No grain-boundary dissociation can be identified on the overall fracture surface. (**Supplementary Fig. 2a**). Meanwhile, numerous micro-dimples are spread across the fracture surface (**Supplementary Fig. 2b**), indicating an intrinsic ductile feature of this alloy.



Supplementary Fig. 2 Fracture surface of the thermal-stabilized CCIMA. a, Low-magnification image showing the overall fracture surface, b, High-magnification image showing the ductile dimples.

3.) In the introduction, the authors make note that what makes intermetallic alloys interesting are their anomalous yielding behavior (elevated temperature), excellent work hardening capability, and chemical resistance but none of these properties are highlighted in the paper. Though these room temperature properties are notable there are alloys that exhibit similar tensile properties at room temperature which are more economical (i.e. maraging steel). Can the authors test the alloy at elevated temperature or if not, can they discuss its possible thermal stability.

Authors' response: Thanks for the insightful comments. The CCIMAs have high freedom of composition design. Their properties can be tailored over a wide range by optimizing the compositions. Currently, the CCIMA in this work is primarily designed for room-temperature applications under harsh working conditions of high stress and corrosion environments, etc. For instance, the maraging steels fabricated by LPBF possess excellent strength but suffer from poor ductility and corrosion resistance, making them impossible to be reliably used in the engineering fields with such aggressive environments^{27,28}. In contrast, our CCIMA behaves an

exceptional combination of strength and ductility. Moreover, we also further studied the corrosion behavior of the thermal-stabilized CCIMA samples under a 3.5% NaCl corrosive environment (**Fig. R7**). The corrosion current density, corrosion potential, and pitting potential, and impedance are 191.1 nA/cm^2 , -334.5 mV , 313.7 mV , and $2.61 \times 10^5 \text{ } \Omega \cdot \text{cm}^2$, which are superior to those of the maraging steel²⁸ and even comparable to 304L²⁹ and 316L³⁰ fabricated by LPBF. As for the high-temperature applications, we have also developed some other CCIMA systems by tailoring the chemical compositions and sublattice occupations³¹. 3D printing of them and associated deformation behaviors at elevated temperatures will be reported in another separate work in the near future.

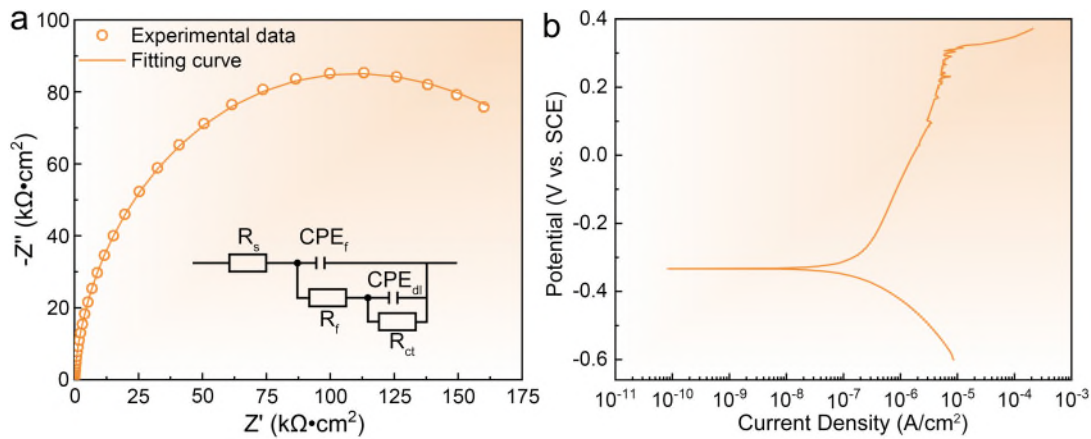


Fig. R7 Electrochemical behavior of thermal-stabilized CCIMA in 3.5 wt. % NaCl solution at room temperature. **a**, EIS Nyquist plot of the thermal-stabilized CCIMA with the inset showing an equivalent electrical circuit model used to fit the EIS data. The fitted curve is presented as solid line. **b**, Potentiodynamic polarization curves of thermal-stabilized CCIMA.

References

- 27 Mutua, J., Nakata, S., Onda, T. & Chen, Z.-C. Optimization of selective laser melting parameters and influence of post heat treatment on microstructure and mechanical

- properties of maraging steel. *Mater. Des.* **139**, 486–497 (2018).
- 28 Khan, H. *et al.* The impact of aging and drag-finishing on the surface integrity and corrosion behavior of the selective laser melted maraging steel samples. *Materialwiss. Werkstofftech.* **52**, 60–73 (2021).
 - 29 Yang, F. *et al.* Effect of heat treatment on the microstructure, mechanical properties and corrosion resistance of selective laser melted 304L stainless steel. *Acta Metallurgica Sinica (English Letters)* **35**, 1688–1702 (2022).
 - 30 Zhou, C. *et al.* Improvement of corrosion resistance of SS316L manufactured by selective laser melting through subcritical annealing. *Corros. Sci.* **164**, 108353 (2020).
 - 31 Xiao, B. *et al.* Ultrahigh intermediate-temperature strength and good tensile plasticity in chemically complex intermetallic alloys via lamellar architectures. *Acta. Mater.* **262**, 119459 (2024).

4.) Line 59 should be “layer-by-layer”

Authors’ response: Thanks for your kind reminder. The “layer by layer” in line 59 has been revised as “layer-by-layer.

Manuscript (Lines 58–59)

Remarkably, additive manufacturing (AM) or three-dimensional (3D) printing can flexibly design and fabricate components with customized complicated structures via a layer-by-layer way

5.) I feel that the authors should discuss the disordered nanolayer at grain boundaries as " γ phase". It is a common phase for Ni-Co based alloys.

Authors' response: Thanks for the constructive suggestions. The DINL and γ phase have the similar FCC structure. So, we also interpreted it as γ phase when it first appeared in the manuscript.

Manuscript (Lines 186–188)

As presented in **Fig. 3c**, a distinctive interfacial nanolayer can be observed near the grain boundary, which was identified as an FCC solid-solution structure (γ phase) based on the corresponding Fast Fourier Transform (FFT) image (**Fig. 3c**).

6.) It is not clear to the readers if the tensile tests were performed in the vertical or horizontal build directions. There may be significant tensile anisotropy based on these two orientations. Especially if the grains have not fully recrystallized after the heat treatment.

Authors' response: Thanks for the good comment. The tensile test was performed perpendicular to the building direction. Corresponding information has been added to the Methods part.

Manuscript (Lines 409–410)

At least four specimens were tested perpendicular to the building direction to guarantee the data reproducibility.

7.) Can the authors reference the G phase when it is first mentioned.

Authors' response: Thanks for your good suggestion. The G phase was referred to better understand its microstructural and mechanical properties. Details are as follows.

Manuscript (Lines 140–143)

The transmission electron microscopy-bright field (TEM-BF) image (Fig. 2c) further illustrates that the dendritic microstructure consisting of brittle G phase³⁶ existed in the as-printed CCIMA was effectively eliminated after the simple thermal treatment (Supplementary Note 2).

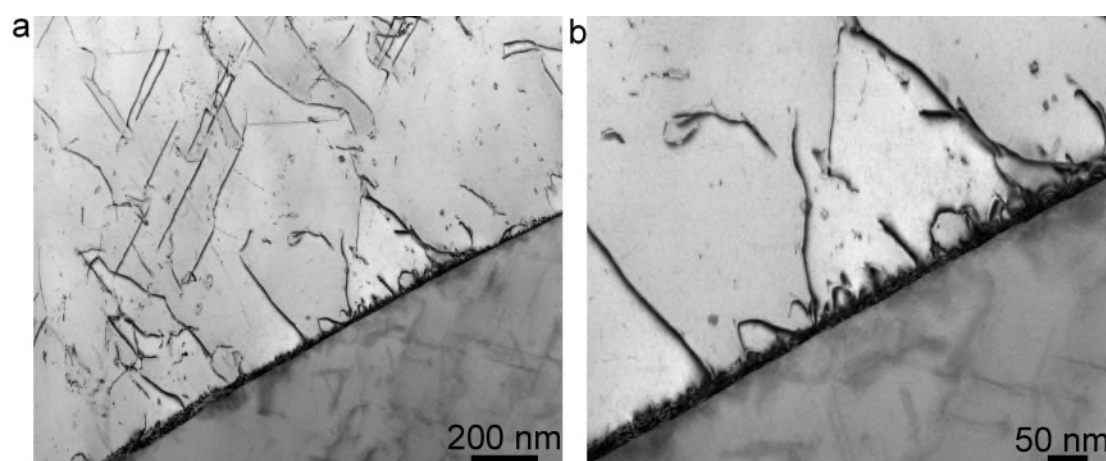
Reference in the manuscript.

36 Knowles, D., Thomas, C., Keen, D. & Chen, Q. In service embrittlement of cast 20Cr32Ni1Nb components used in steam reformer applications. Int. J. Press. Vessels Pip. 81, 499–506 (2004).

8.) I feel a single example of the γ phase at the grain boundary is not enough to claim it is the source of the ductility improvement. Can the authors discuss how prevalent this feature is in the alloy? SEM-EDS may be able to discern the Co segregation at grain boundaries as mentioned earlier.

Authors' response: Thanks for your insightful comments. Our previous works have shown that the CCIMAs behave serious brittleness without the formation of disorder γ phase at the grain boundary^{12–14}, indicating that the intergranular γ phase is indispensable for improving the ductility of CCIMAs by inhabiting the intergranular cracking. We further studied the

dislocation behavior near the grain boundary of the deformed sample at a strain of 5%. As shown in the **Supplementary Fig. 4**, dislocations accumulated within the disordered γ phase and piled up against GBs, indicating that the relatively soft γ phase can sustain larger plastic strain prior to the hard $L1_2$ region, reducing the probability of cracking along grain boundaries.



Supplementary Fig. 4 Deformation structure of thermal-stabilized CCIMA at a tensile strain of 5%. a, STEM-BF image showing the dislocation structures near the grain boundary and grain interior. **b**, Enlarged STEM-BF image revealing the entanglement of dislocations with DINL.

References

- 12 Xiao, B. *et al.* Off-stoichiometry-guided design of high-strength chemically complex intermetallic-based alloys with outstanding ductility. *J. Mater. Sci. Technol.* **160**, 28–33 (2023).
- 13 Yang T, et al. Ultrahigh-strength and ductile superlattice alloys with nanoscale disordered interfaces. *Science* 369, 427–432 (2020).
- 14 Duan, F. *et al.* An order-disorder core-shell strategy for enhanced work-hardening capability and ductility in nanostructured alloys. *Nat. Commun.* **15**, 6832 (2024).

9.) Figure 4(h) does not clearly show a single SISF in my opinion. Can the authors highlight the single atomic plane thick fault or change the description as a more generic stacking fault (SF)?

Authors' response: Thanks for your constructive comments. The stacking fault was generated in the superlattice $L1_2$ structure. So, the stacking fault was defined as superlattice stacking fault. Meanwhile, the atomic-resolution STEM-HAADF image in the revised **Fig. 4h** further confirms the stacking sequence of ABCBCABC, proving the formation of SISF.

Manuscript (Lines 299–302)

Once the applied stress exceeded the critical resolved shear stress for activating the superlattice stacking fault (SSF), SSF shearing will occur in this condition. Meanwhile, the atomic-resolution STEM-HAADF image in **Fig. 4h** confirms the stacking sequence of ABCBCABC, proving the formation of SISF.

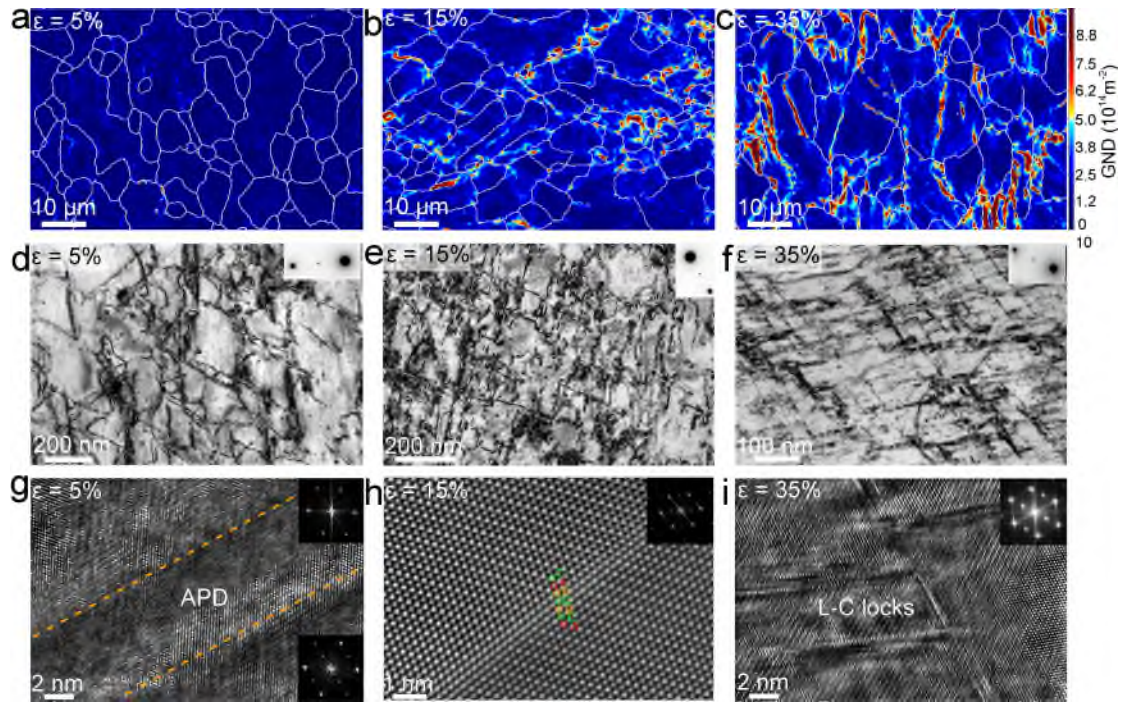


Fig. 4 Deformation mechanism of the CCIMA at different tensile strains. a–c, GND distribution maps revealing the varied stress concentrations near the grain boundaries with the increase of deformation strains from 5% to 35%. **d–f,** TEM bright field images taken along the (200) two-beam condition showing the morphologies of deformation substructures of the CCIMA at different strains. **g, and i,** High-resolution TEM and corresponding FFT images (insets) revealing the changes in the types of deformation substructures from APB-coupled superlattice dislocations (5%) to intersected SFs (35%). **h, Atomic-resolution STEM-HAADF image illustrating the existence of SISF at a strain of 15%.**

10.) In my opinion, the cracks highlighted in supplementary Figure 3(b) look to be solidification cracks from the printing process and not cracks from failure. Readers will be skeptical that this composition could be printed crack free. Can low resolution SEM images be provided to show that cracks do not exist in the as-built state?

Authors' response: Thanks for this useful comment. The optical microscopic images

(**Extended Data Fig. 1**), micro-CT result (**Fig. 1c**), and low-magnification SEM-BSE image (**Supplementary Fig. 7a**) all illustrate that dense and crack-free CCIMA samples can be produced by LPBF, as shown in the following **Fig. R8**. Based on these combined analyses, it is safe for us to conclude that the cracks highlighted in previous **Supplementary Fig. 3(b)** are generated during tensile test.

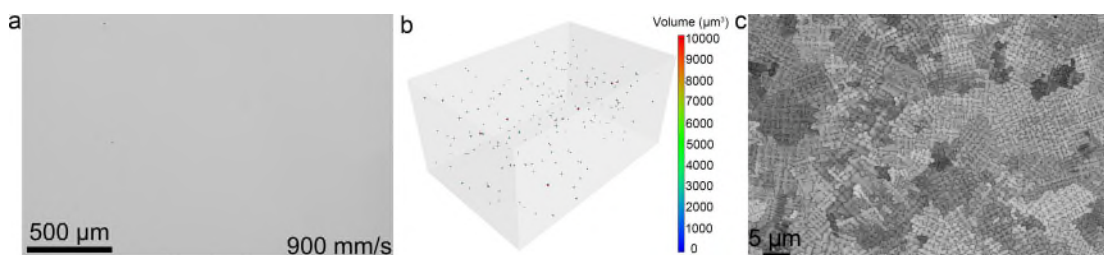
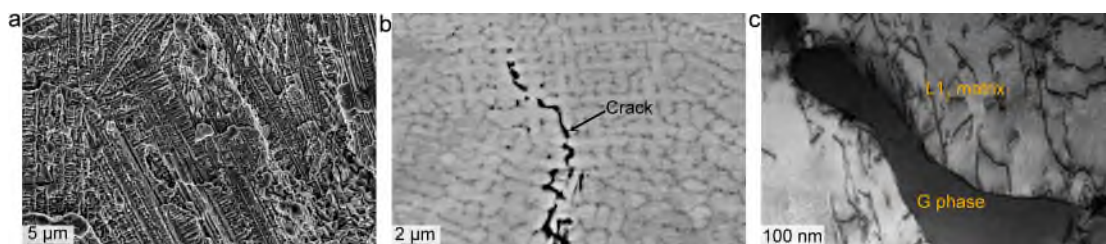


Fig. R8 **a**, Optical microscopy images showing the defects of the as-printed CCIMAs when the laser scanning speed is 900 mm/s. **b**, The pore defect distribution of the as-printed CCIMA measured by the micro-CT. **c**, SEM-BSE image showing the typical dendritic microstructure within the grains.

11.) In supplementary Fig 3(c) the G phase is highlighted with clearly more dislocation content. Why would this intermetallic phase exhibit more dislocations over the L12 phase? Could it be γ phase?

Authors' response: Thanks for the insightful comment. It seems difficult to judge the dislocation distribution feature in previous **Supplementary Fig 3c** due to the diffraction contrast of TEM. Thus, to avoid the possible confusion, we conducted the STEM experiment to further demonstrate the dislocation features in the fractured as-printed sample. As shown in the revised **Supplementary Fig 8c**, most of the dislocations were generated in the relatively soft L1₂ phases and piled up against L1₂/G phase boundaries to coordinate the deformation

compatibility. We also updated it in the newly revised manuscript.



Supplementary Fig. 8 Fracture mechanism of the as-printed CCIMA. **a**, SEM image showing the dendritic microstructure exfoliated from the fractured surface. **b**, Cross-section of the fractured sample showing the crack initiation along the G phase. **c**, STEM image revealing the dislocation pile up along the G phase, resulting in the localized stress concentration.

Overall, I feel the study presents an interesting and notable alloy. However, I need to see more analysis over its microstructure to be convinced it truly is an intermetallic alloy before I would suggest the paper gets published in such a high impact journal.

Authors' response: Many thanks for your positive and constructive comments. As mentioned above, more analyses on the microstructure of thermal-stabilized CCIMA have been provided. From the BSE image and corresponding EDS maps, it can be inferred that the thermal-stabilized CCIMA possesses the equiaxed grain structure with an average chemical composition of $\text{Ni}_{58.0}\text{Co}_{19.5}\text{Si}_{11.3}\text{Ti}_{6.8}\text{Al}_{4.3}$ (at. %). Meanwhile, based on the atomic EDS mapping in **Fig. 2f**, atoms Ni and Co mainly occupy the faced centers (A-type sublattice) of the L1_2 unit cell, while the vertices (B-type sublattice) are occupied by the atoms Si, Ti, and Al. Thus, the overall chemical composition meets the criterion of A_3B -type intermetallics. Furthermore, the superlattice diffraction peaks in XRD data (**Fig. 2a**) and superlattice

diffraction spots in SAED pattern (**Fig. 2c**) further confirm the highly ordered structure of thermal-stabilized CCIMA. Thanks again for your careful review of our research.

Response to Referees Letter

Journal: Nature Communications

Title: Highly printable, ultrastrong, and ductile ordered intermetallic alloy

Manuscript ID: NCOMMS-24-44404B

Dear Reviewer,

Thank you very much for your further positive and constructive comments on our manuscript entitled “**Highly printable, ultrastrong, and ductile ordered intermetallic alloy**”, which helps us improve the quality and presentation of our work effectively. We have made modifications to the original manuscript carefully. The revised **manuscript** and **supplementary information** with the changes **highlighted in yellow** were uploaded to the paper submission system. Here below are our point-to-point responses (in blue color) to the comments received.

To Reviewer #3

The authors addressed some of my concerns. However, some further clarifications are still needed.

1. The reviewer agrees that this material can be printed with low porosity and appreciate the remarkable effort to develop new alloy for additive manufacturing. However, porosity is only one of the considerations in printability. As discussed in the reference cited by the authors [Mukherjee, T., Zuback, J.S., De, A. and DebRoy, T., 2016. Printability of alloys for additive manufacturing. Scientific reports, 6(1), p.19717.], to claim the high printability, the authors need to discuss at least the dimensional accuracy, composition change and standard features such as smallest rod/plate/holes etc, in addition to the porosity.

Authors' response: Thanks for the constructive comment. As the reviewer suggested, printability is a multifaceted standard. Thus, we further discussed the dimensional accuracy, standard features, and composition change. As shown in the following **Fig. R1**, the holes and rods with different diameters can be well printed. To further quantify the dimensional accuracy, the diameter of each hole was determined by SEM method, while the diameter of each rod was measured by micrometer. The size limitation for hole and rod under our current printer is about 300 μm . The detailed dimensional information for holes and rods is summarized in **Table R1** and **R2**, respectively, revealing high dimensional accuracy of the LPBFed CCIMA.

Meanwhile, the composition of the thermal-stabilized CCIMA is almost unchanged compared to the pre-alloyed powder (**Table R3**), indicating a very small elemental change during printing and subsequent thermal treatment.

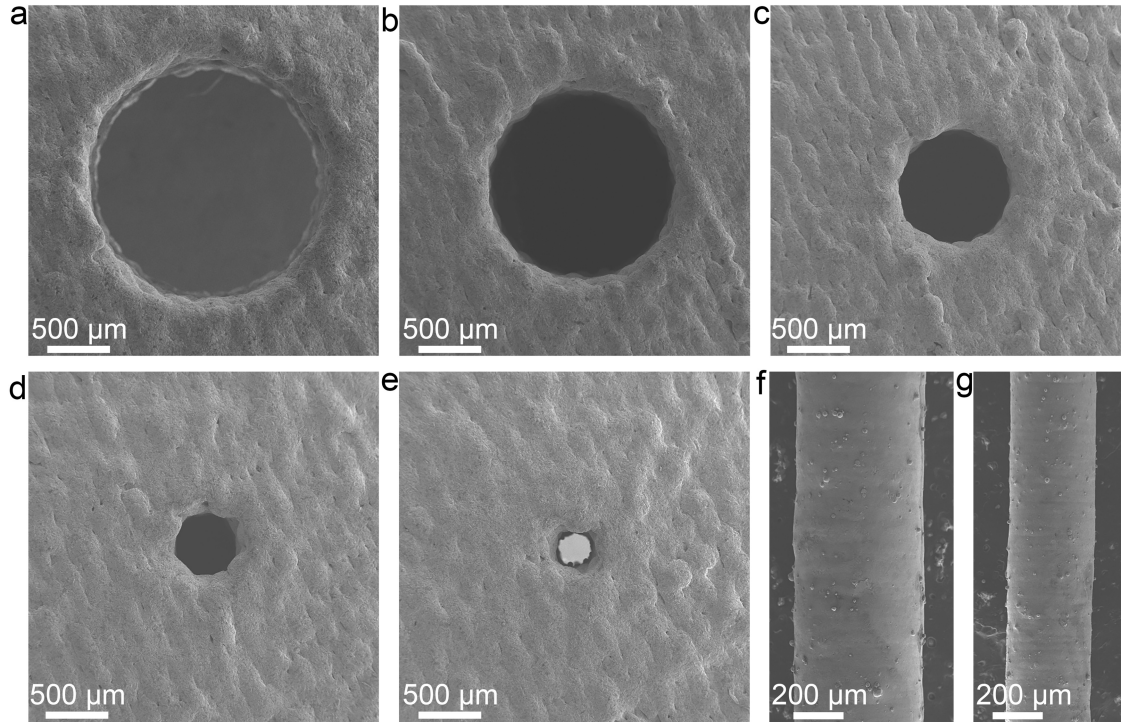


Fig. R1 The as-printed holes and rods with different diameters to explore the printing accuracy. **a–e**, SEM images showing the as-printed holes with theoretical diameters of 2, 1.5, 1, 0.5, 0.3 mm, respectively. **f–g**, SEM images showing the as-printed rods with theoretical diameters of 0.5 and 0.3 mm, respectively.

Table R1 The dimensional accuracy of holes with different diameters fabricated by LPBF

Theoretical value (mm)	2.0	1.5	1.0	0.5	0.3
Experimental value (mm)	1.987	1.505	1.005	0.502	0.299
Error (%)	0.65	0.33	0.50	0.40	0.33

Table R2 The dimensional accuracy of rods with different diameters fabricated by LPBF

Theoretical value (mm)	5.0	4.0	3.0	2.0	1.0	0.5	0.3
Experimental value (mm)	5.024	4.037	3.032	2.022	1.025	0.512	0.308
Error (%)	0.48	0.93	1.07	1.10	2.50	2.40	2.67

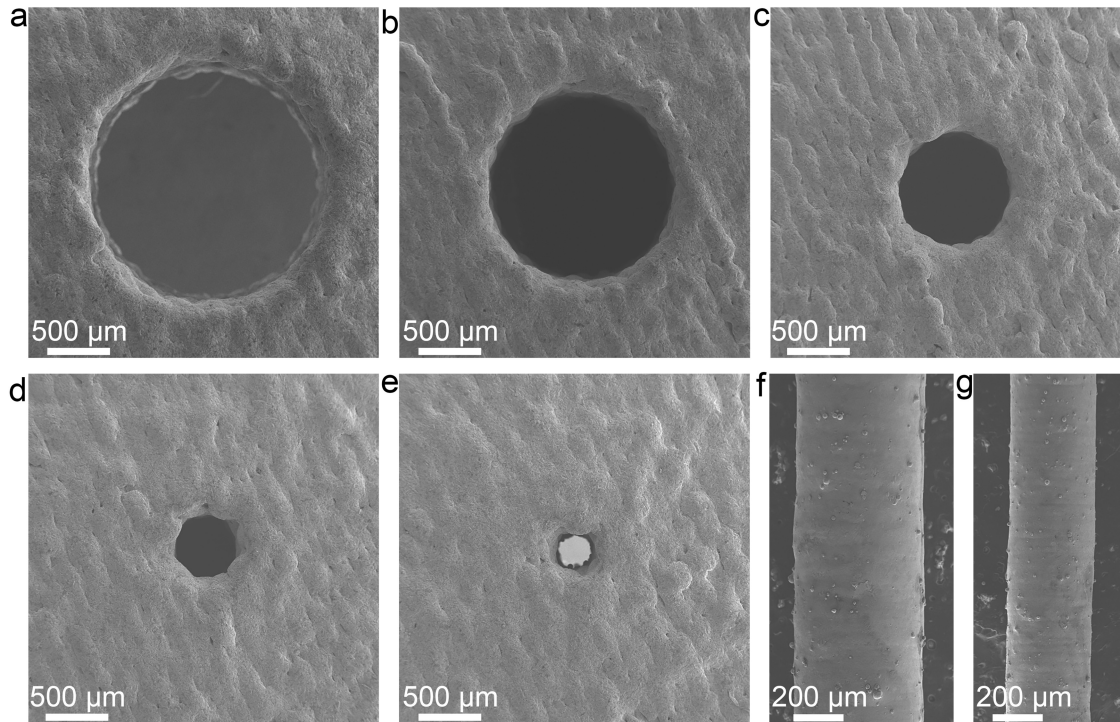
Table R3 The chemical composition of pre-alloyed powder and thermal-stabilized CCIMA (at. %)

Samples	Ni	Co	Si	Ti	Al
Pre-alloyed powder	58.48	18.9	11.6	6.6	4.4
Thermal-stabilized CCIMA	58.1	19.5	11.5	6.6	4.3
Error (%)	0.65	3.17	0.86	0	2.27

Corresponding discussion has been added to the **Manuscript** and **Supplementary Information**.

Manuscript (Page 5 Lines 102–106)

Besides the low porosity, we also printed some standard features such as holes and rods with different sizes to illustrate the dimensional accuracy of the as-printed CCIMA. As presented in **Supplementary Fig. 2 and Supplementary Tables 2 and 3**, the as-printed holes and rods show high dimensional accuracy with very small experimental errors, indicating a high printability of the CCIMA.



Supplementary Fig. 2 The as-printed holes and rods with different diameters to explore the printing accuracy. a–e, SEM images showing the as-printed holes with theoretical diameters of 2, 1.5, 1, 0.5, 0.3 mm, respectively. f–g, SEM images showing the as-printed rods with theoretical diameters of 0.5 and 0.3 mm, respectively.

Manuscript (Page 7 Lines 143–145)

The overall chemical composition of the thermal-stabilized CCIMA measured by SEM-EDS is $\text{Ni}_{58.1}\text{Co}_{19.5}\text{Si}_{11.5}\text{Ti}_{6.6}\text{Al}_{4.3}$ (at. %), showing a very small chemical change compared with the pre-alloyed powder.

2. In Supplementary Fig. 3b and Supplementary Fig. 6d, the authors plotted the grain size distribution with varying bin size, which is unusual. These histogram with varying bin size is hard to support the near-Gaussian grain size distribution and the statement on heterogeneity.

The authors may want to make further discussion on the heterogeneity. Please clarify what fraction means? Number fraction or area fraction? Please show both number fraction – grain size, and area fraction – grain size histogram with a fixed bin size.

Authors' response: Thanks for the good comment. The original **Supplementary Fig. 3b** and **Supplementary Fig. 6d** were revised with fixed bin size. The fraction means area fraction, which has been revised accordingly. Meanwhile, we also provided the grain size distribution histogram in terms of number fraction with a fixed bin size, as shown in the following **Fig. R2**. Based on the updated **Supplementary Fig. 4b** and **Supplementary Fig. 7d**, it can be concluded that the as-printed and thermal-stabilized CCIMAs do not show obvious heterogeneity in terms of grain size distribution and crystallographic orientation.

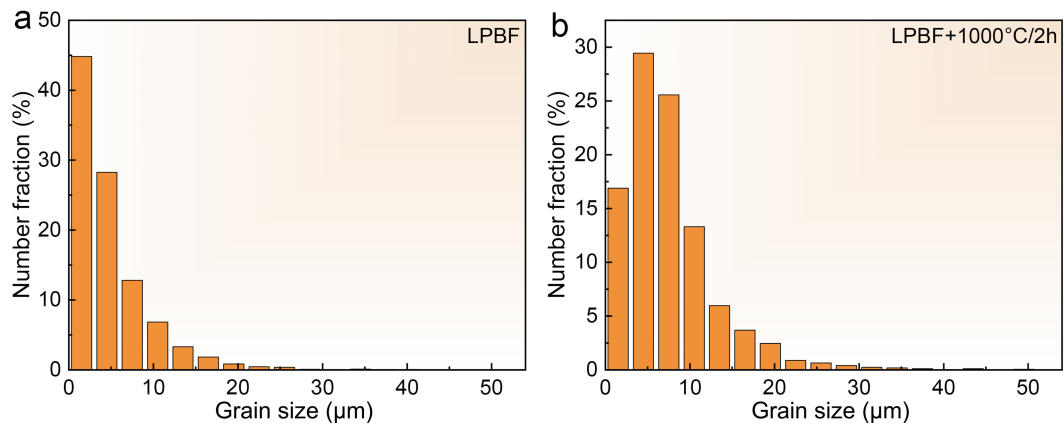
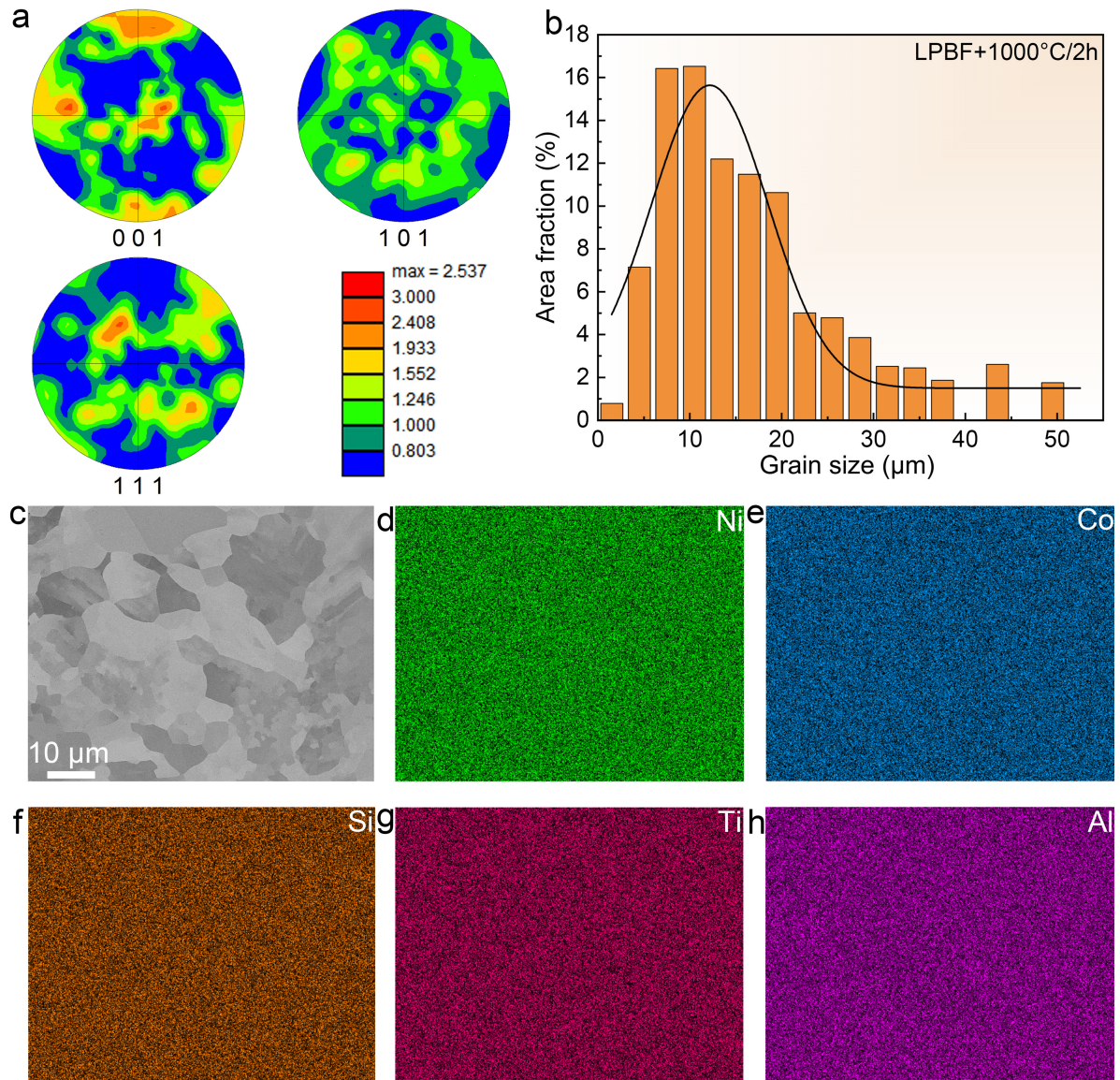
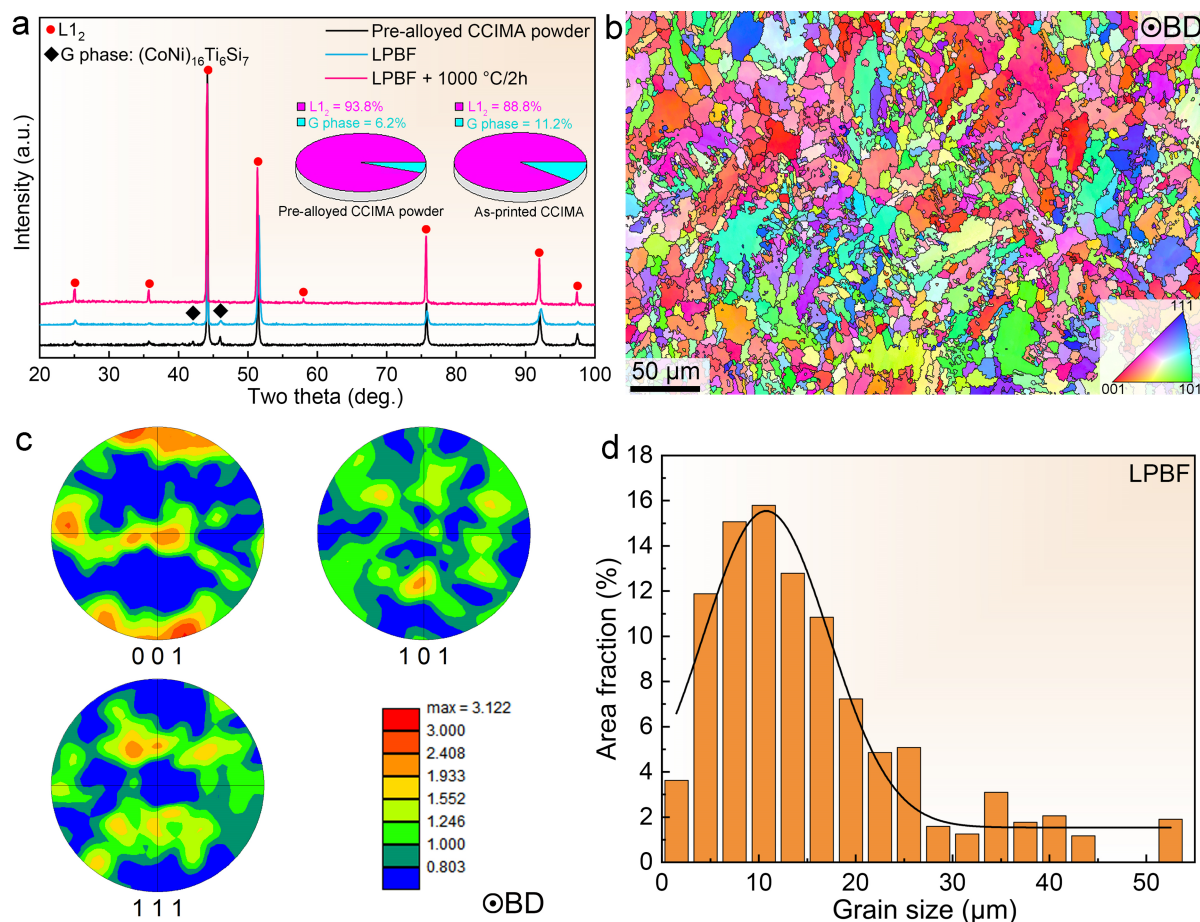


Fig. R2 Grain size distribution in terms of number fraction with a fixed bin size. a, the as-printed sample. **b,** the thermal-treated sample at 1000 °C for 2h.



Supplementary Fig. 4 Microstructural features of the thermal-stabilized CCIMA. **a**, Pole figure showing the texture intensity of the plane perpendicular to the building direction, **b**, Grain size distribution, **c**, BSE image showing the equiaxed grains, **d–h**, EDS mapping showing the homogeneous elements distribution across multiple grains.



Supplementary Fig. 7 Phase structure and grain feature of the as-printed CCIMA. **a**, XRD spectra showing the phase constitutions of the pre-alloyed powder, as-printed, and thermal-stabilized CCIMA samples. **b**, EBSD-IPF maps revealing the random grain orientations. **c**, EBSD pole figure showing the texture intensity. **d**, Grain size distribution with a near-Gaussian distribution model.

3. Supplementary Fig. 4 shows the dislocations near the grain boundaries or near the DINL. However, the reviewer cannot see clear evidence to support ‘dislocations accumulated at the DINL’. It would be interesting to see dislocations accumulating in a 5nm-thick DINL.

Authors’ response: Thanks for your insightful comment. The dislocation accumulated in the DINL was further characterized by STEM. As shown in Fig. R3, dislocation lines within the

DINL can be clearly observed, which can act as effective obstacles for the coming dislocations.

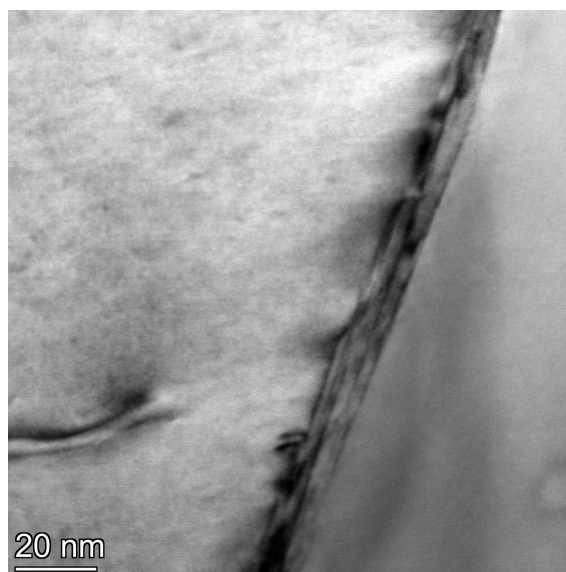


Fig. R3 Dislocation structure within the DINL.

4. The calculation of q and Ch_{00} is not integrated in the ANIZC. You may calculate the C values for each hkl , then fit the Ch_{kl} - H to obtain q and Ch_{00} .

Authors' response: Thanks for your careful review on our manuscript. As the reviewer suggested, the values for q and Ch_{00} can be obtained by fitting the Ch_{kl} - H for each hkl . Corresponding revision has been updated to the **Supplementary Information**.

Supplementary Information (Pages 187-189)

The average orientation factor C is calculated using the ANIZC program, which is available via the website (<http://metal.elte.hu/anizc/>). Then, the values for q and $\bar{C}_{h00}$ can be obtained by fitting the $\bar{C}_{hkl}$ - H for each hkl .