

Near-theoretical strength and deformation stabilization achieved via grain boundary segregation and nano-clustering of solutes

Corresponding Author: Professor En Ma

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 submitted manuscript "Near-theoretical strength and deformation stabilization achieved via grain boundary segregation and nano-clustering of solutes" by C. Liu et al. showed that a minor addition of Ni in a nanocrystalline TiZrNbHf refractory high entropy alloy could double the compressive strength. However, the experimental evidence provided by the current manuscript cannot fully support a couple of arguments made in the paper. A major revision is required for this manuscript to be considered for publication.

Major questions:

1. The strength and compressive ductility achieved in this study was not for bulk materials. A thorough discussion is needed to reflect on how this methodology can be transferred to the processing of bulk materials and how the strategy can affect the tensile ductility of the material.
2. Were there any microcantilever bending tests that could show increased fracture toughness in the material? Compressive ductility is inappropriate for showing the material's damage tolerance.
3. The evidence provided by the authors implies that all the dislocations observed were edge dislocations (subgrains and the HRTEM image shown in Fig. 4). It is well known that deformation in bulk TiZrNbHf-based alloys at room temperature is controlled by screw dislocations. Edge dislocation-controlled kink-band formation has also been observed, whereas the authors did not observe this phenomenon. In addition, the in-situ characterization of dislocations using atomic resolution STEM-HAADF cannot show dislocations clearly. The sample will be rotating out of the zone axis while loading and that is why Fig. 4b2 and 4b3 do not show proper atomic columns. The smeared contrast is prone to creating artifacts that show "fake dislocations" (especially when one tries to do FFT, masking, and IFFT). Furthermore, the Z-contrast fluctuation is tricky to interpret as purely originating from Ni clusters. First, the local thickness variation of the sample after deformation can cause this fluctuation. Second, a 3-nm cluster can hardly be seen after averaging through a 30-50 nm sample. Judging from Fig.4, the actual sample thickness seems to be above this value. A proper dislocation analysis postmortem is needed to justify the authors' arguments.
4. The experiments did not show how the addition of Ni stabilizes the NC structure. Comparative annealing tests of TiZrNbHf and (TiZrNbHf)Ni₂ are needed to show that grain growth in the latter is inhibited.

Minor issues:

1. Using the term "near-theoretical" to describe the high strength of the material can potentially be misleading because the theoretical strength of the material is calculated where there is no dislocation involved in the deformation of single crystals, which is not the case here. The reviewer will suggest a clarification early in the paper.
2. How do the authors account for the larger scatter of in-situ mechanical tests for small samples compared to that in bulk tensile and bending tests? How many tests were done for each sample?
3. How were the columnar grains aligned with the tensile and bending directions? Parallel or perpendicular, or both?

4. It is difficult to identify the 3-nm cluster in Fig. S5. What is the crystal structure of the cluster with Ni? Does the FFT of the cluster give the information? In addition, what is the thickness of the sample? A 3nm cluster will barely show any Z-contrast when averaged through a 30-50 nm sample.

Reviewer #2

(Remarks to the Author)

In the manuscript titled "Near-theoretical strength and deformation stabilization achieved via grain boundary segregation and nano-clustering of solutes", the authors Chang Liu, et al. have used electronic structure simulations and analytical models to identify potential alloying elements (not present in the alloy) that can enhance solute segregation to grain boundaries and will not form intermetallic phases in complex concentrated alloy consisting of Ti, Zr, Nb and Hf. Later, they synthesize an alloy with identified solute element, Ni, and demonstrate the superior mechanical properties obtained due to the inclusion of Ni. The manuscript is well structured, and the authors have performed a detailed experimental analysis to demonstrate the validity of their design strategy. Their results are noteworthy and if published would significantly advance this field. In the following I have listed a few comments.

Comments about the design strategy:

1. It seems from Fig. 1 (a) that atomic size of Ni is much smaller than the host atoms. Since the elastic strain energy depends on the atomic size mismatch, it is not clear why a smaller solute will necessarily decrease the elastic strain energy as mentioned in page 5.
2. The authors have used electronic structure calculations using density functional theory to verify if the identified solute element will lead to grain boundary segregation or not. It seems that they have not calculated the segregation energy. The formula provided in Eq. (2) was used to calculate grain boundary strengthening energy which is mentioned in Ref. [32] of the manuscript. The grain boundary segregation energy is different from the formula provided in Eq. (2). While in the method section, the authors state that "In present work, the segregation energy and strengthening energy are averaged over 5 independent samples", the caption associated with Fig. 1(c) mentions "Strengthening energy of the alloy's grain boundaries with Ni, obtained using DFT calculation."

Based on these observations, it is not clear how Ni was identified as the best candidate. Is normalized chemical potential (shown in Fig. 1(b)) then the best strategy to select potential alloying elements?

Comments about the use of solid solution strengthening model:

1. The solid solution strengthening model proposed in Ref. [33] was designed for bulk alloys in which the grain boundaries do not control/dominate the mechanical properties. On the other hand, as discussed in the manuscript, the strengthening mechanisms in nanocrystalline alloys are different. It will benefit the reader if the authors can provide some justification for the use of this model for their system.
2. Please include a table showing the values of quantities in Eqs. (3)-(4).

Reviewer #3

(Remarks to the Author)

This paper is interesting and some very detailed & difficult experimentation, but to my view the novelty & outcome (e.g. properties achieved) of the work does not meet the threshold of Nature Communications.

Alloy design via solute decoration at grain boundaries is a known concept, e.g. published in Nat Comms nearly 10 years ago - 10.1038/ncomms7858

Ductility would seem to be a key issue.

Yield strengths of 2GPa seem readily achievable in nanocrystalline alloys, key challenge would be to do it with ductility. Also further when testing the alloys micromechanically (size effect leads to higher strengths).

No real comparison of grain size and yield strength to state is exceptional, ~10nm grain size stated by authors, and even up to 10GPa micropillar strength reported in HEAs <https://doi.org/10.1038/ncomms8748>, compared to author's 30nm and 2.5GPa

Thermal stability not investigated – would the grains grow? Would intermetallics form?

Micropillar compression less impressive than macro-scale tensile when thinking about ductility.

In-situ TEM is impressive and the micromechanics, nice to see tied to the LCO and dislocations being distributed through the grains rather than excessive gb accumulation, however, this interesting finding would be most interested if tied to exceptional overall performance.

Nice to see the attempt to tie DFT and TEM together.

Alloy produced via thin-film, hard to see the scalability of the approach.

What is a targeted end application for such alloys to guide the design goals?

Ln66 assumption that exceeding the solubility limit in the host metal would lead to a brittle second-phase, is not always the case, can well be a solid solution, especially in relation to the paper topic of Ni within a bcc metal, or Cu etc, which could

form fcc phase at gbs. Or vice versa bcc as in Cantor/Yeh type HEAs.

Addition of Ni likely to promote intermetallics on thermal ageing

Stability of the grain size, and phases not demonstrated - 350 C for 1 hour not sufficient though may promote the fine-scale LCOs within grains, 600-800C for 100h might be more relevant to see grain coarsening / whether intermetallics form.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The submitted revision of "Near-theoretical strength and deformation stabilization achieved via grain boundary segregation and nano-clustering of solutes" by C. Liu et al. has added important experiments and clarifications and therefore addressed most of the reviewer's concerns. The reviewer will recommend the paper for publication if the following minor issues are resolved:

1. The reason why the addition of 2% Ni can increase the fracture toughness of the notched cantilever needs to be further explained in terms of GB cohesion, lattice distortion, and dislocation activity.
2. The reviewer will feel much more comfortable if more Ni-rich clusters can be identified through HRSTEM whose size distribution statistically matches the APT result. Mass-thickness fluctuation in HRSTEM's Z-contrast can also imply that any local thickness variation of the sample can result in islands that look just like Ni-clusters. Therefore, showing one instance of a lower-Z contrast cluster may not be sufficient.

Reviewer #2

(Remarks to the Author)

Dear Editor,

I have read the manuscript and the authors' response to comments by the reviewers. Overall this is a very nice piece of work, with lot of detailed experimental analysis performed to understand thermodynamic stability and mechanical properties. The authors have mostly addressed by concerns. I have a few minor comments:

1. Please include equations used to calculate the reduced chemical potential.
2. Designing an alloy with coherent LCO and stabilized GBs via segregation of solute atoms is appealing. Based on comments by the other referees, it seems proper measurement of ductility will significantly strengthen the manuscript. Perhaps the authors can include a comparison with values in Fig 1(b) of this paper: <https://www.nature.com/articles/s41586-023-06894-9>

Reviewer #3

(Remarks to the Author)

The manuscript outlines a high class thin film study, and demonstrates interesting ideas, however, there are fundamental limitations as to the translation of the approach, as well as an overstatement as to how revolutionary the properties achieved are.

Whilst the idea of gb solute strengthening is not new, the extension to refractory high entropy alloys is interesting and opens up new design ideas of value to the HEA community. It is good to see modelling used to try to instruct the design.

Why has CALPHAD not been employed here? It would seem easy to predict possible phases formation and select solute(s), e.g. using Thermocalc's TCHEA database, I would suspect Ni would promote intermetallics, which could form in thermally equilibrated samples. 600C is low for such alloys so is likely non-equilibrium, and the LCOs could predicate intermetallics formation – the caution is that gb intermetallics would embrittle.

The outcoming properties cannot be considered revolutionary, ~2.5 GPa modest for what can be seen in micropillars (e.g. 4.5 GPa possible at 1µm <https://doi.org/10.1126/sciadv.abc8288>), nor the fracture toughness of 4 to 6 MPa.m^{1/2} exceptional (4 to 6 MPa.m^{1/2} for Cr and NiAl, which are low toughness metals <https://doi.org/10.1002/adem.202101429>).

The discussion on how to transfer the desirable structure of the NC alloys to bulk materials is to me a bit weak, it's not easy to get NC by AM and certainly not by arc melting, and then not even with thermomechanical processing (10µm at best). This discussion also misses mechanical alloying, or severe plastic deformation.

The ability to translate the idea is not easy! Though is a worthy topic of its own onward new programmes of work.

Version 2:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

All the issues identified by the reviewer have been addressed in the current version of the manuscript. The reviewer thus recommends the paper be published in Nature Communications.

Reviewer #2

(Remarks to the Author)

In the revised version of the manuscript titled "Near-theoretical strength and deformation stabilization achieved via grain boundary segregation and nano-clustering of solutes", the authors have addressed my comments and I recommend this manuscript for publication.

Reviewer #3

(Remarks to the Author)

The authors have made substantial efforts to address the reviewer comments and revise the manuscript that is now of a high quality worthy of publishing.

I particularly look forward to seeing their onward scale up work being published (reasonable for it to be an article in its own right) "Our preliminary work obtained a conventional bulk alloy using arc melting following the alloy design strategy in the present work, which achieves a high yield strength of 1.25 GPa and tensile ductility of 25%."

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Response to the Reviewers' Report

Ms. No. NCOMMS-23-62916

Chang Liu, Jing Rao, Zhongji Sun, Wenjun Lu, James P. Best, Xuehan Li, Wenzhen

Xia, Yilun Gong, Ye Wei, Bozhao Zhang, Jun Ding, Ge Wu, En Ma

We would like to cordially thank the reviewers for the valuable suggestions and comments on our paper. Our response is structured as follows: The comments from the reviewers are copied below in black font. For each comment, we present a detailed response, a full description of the newly added experimental results, and the corresponding manuscript modifications (blue font: reply items). The amended manuscript is enclosed, and the changes we made to the revised version are shown in red font (change items).

Referee #1:

“The submitted manuscript “Near-theoretical strength and deformation stabilization achieved via grain boundary segregation and nano-clustering of solutes” by C. Liu et al. showed that a minor addition of Ni in a nanocrystalline TiZrNbHf refractory high entropy alloy could double the compressive strength. However, the experimental evidence provided by the current manuscript cannot fully support a couple of arguments made in the paper. A major revision is required for this manuscript to be considered for publication.”

Response: We thank the reviewer for recognizing that the interplay of the distinctly different species with the base elements in the CCA could drastically elevate strength. The resultant alloy achieves a high strength approaching theoretical limit and large deformability, demonstrating the effectiveness of the alloy design strategy.

To address the reviewer’s concerns on the experimental evidence, we have performed additional fracture toughness measurements and comparative annealing experiments. Also, we have thoroughly revised the manuscript, to unequivocally nail down the effect of Ni and the scalability of the approach, in full accordance to the reviewer’s comments.

“Major questions:

1. The strength and compressive ductility achieved in this study was not for bulk materials. A thorough discussion is needed to reflect on how this methodology can be transferred to the processing of bulk materials and how the strategy can affect the tensile ductility of the material.”

Response: We thank the reviewer for the comments. We have added thorough discussion about the scalability of the approach.

Modifications: On Pages 19 and 20 of the revised manuscript, the text has been revised to the following:

“The NC (TiZrNbHf)₉₈Ni₂ alloy achieves a yield strength of 2.5 GPa (σ_y) which corresponds to a τ_y (shear stress for the initiation of plastic flow)³⁷ of 1.25 GPa. The shear modulus (G) of the alloy is 39 GPa, calculated based on the elastic modulus measured using nanoindentation. The τ_y/G ratio of the NC (TiZrNbHf)₉₈Ni₂ alloy reaches 1/31, approaching the theoretical shear strength limit¹⁴. We anticipate numerous applications utilizing the alloy’s outstanding strength and deformability, for example as high wear-resistance coatings for cutting tools. Furthermore, the above-mentioned alloy design concept should guide the design of other materials. In the microcantilever bending tests (Fig. 2c, d) where the upper portion of the material withstands tensile loading, the (TiZrNbHf)₉₈Ni₂ alloy shows a higher deformability than that of the base alloy, and its upper portion withstands a tensile strain of 11% without cracking. This means, through utilizing the favorable interplay of the distinctly different species with the base elements in the CCA to promote intragrain LCOs and GB segregation (enhancing GB cohesion), the alloy’s strength and tensile ductility can be simultaneously improved.

The NC (TiZrNbHf)₉₈Ni₂ alloy in the present work was prepared using magnetron sputtering with a high cooling rate (above 10⁸ K/s)³⁸. In order to transfer the desirable structure of the NC alloys to bulk materials, additive manufacturing with a relatively high cooling rate can be considered as a good candidate for fabricating the bulk counterparts. The cooling rate can also be tuned through optimizing the printing

parameters, e.g., laser power and scanning speed. The high cooling rate ensures the solutioning of the distinctly different species with the matrix, and reduces the grain size of the alloy. For conventional bulk sample prepared using arc melting, the alloy needs to be fast quenched from a solid solutioning temperature to avoid the formation of intermetallics; and then annealed at an intermediate temperature to promote LCOs. The grain size of the alloys prepared using additive manufacturing or arc melting might not reach nanoscale. Nevertheless, the alloys designed using our strategy, with intragrain LCOs and GB segregation, are expected to achieve substantially improved strength and ductility than those of base alloys.”

“2. Were there any microcantilever bending tests that could show increased fracture toughness in the material? Compressive ductility is inappropriate for showing the material’s damage tolerance.”

Response: We have performed additional microcantilever bending tests using pre-notched cantilevers, in full accordance to the reviewer’s comments. The (TiZrNbHf)₉₈Ni₂ alloy is observed to have an increased fracture toughness compared with that of the base TiZrNbHf alloy.

Modifications: On Pages 9 and 10 of the revised manuscript, the text has been revised to the following:

“In a recent work, a Nb₄₅Ta₂₅Ti₁₅Hf₁₅ (at%) CCA²⁴ achieves an exceptionally high fracture toughness, surpassing most commercial alloys and fcc HEAs that are known for their high fracture toughness. The severe lattice distortion of bcc CCA results in retarded motion of nonscrew dislocations²⁵. The edge-character dislocations form kink bands, which prolong nonuniform strain and increase the characteristic distance between the voids ahead of the crack tip, leading to the high toughness of the Nb₄₅Ta₂₅Ti₁₅Hf₁₅ alloy²⁴. We performed microcantilever (pre-notched) bending tests on the NC (TiZrNbHf)₉₈Ni₂ alloy (Fig. S9). The result shows a fracture toughness of 6.0 MPa·m^{1/2}, compared with 4.3 MPa·m^{1/2} for the reference NC TiZrNbHf alloy. The fracture toughness previously measured for NC alloys^{26–28}, tested using such micro-

cantilever (pre-notched) tests, usually ranges from 1.5 – 3.5 MPa·m^{1/2}. The NC (TiZrNbHf)₉₈Ni₂ alloy clearly shows a high fracture toughness in the class of NC alloys.”

We have added the following references in the revised manuscript:

24. Cook, D. H. *et al.* Kink bands promote exceptional fracture resistance in a NbTaTiHf refractory medium-entropy alloy. *Science* **384**, 178–184 (2024).
25. Wang, F. *et al.* Multiplicity of dislocation pathways in a refractory multiprincipal element alloy. *Science* **370**, 95–101 (2020).
26. Wang, Y. Q. *et al.* Fracture behavior and deformation mechanisms in nanolaminated crystalline/amorphous micro-cantilevers. *Acta Mater.* **180**, 73–83 (2019).
27. Cao, W. *et al.* Correlations between microstructure, fracture morphology, and fracture toughness of nanocrystalline Ni-W alloys. *Scr. Mater.* **113**, 84–88 (2016).
28. Xiao, Y. *et al.* Nanostructured NbMoTaW high entropy alloy thin films: High strength and enhanced fracture toughness. *Scr. Mater.* **168**, 51–55 (2019).

We have added fracture toughness results in Supplementary Fig. 9 in the revised supplementary information:

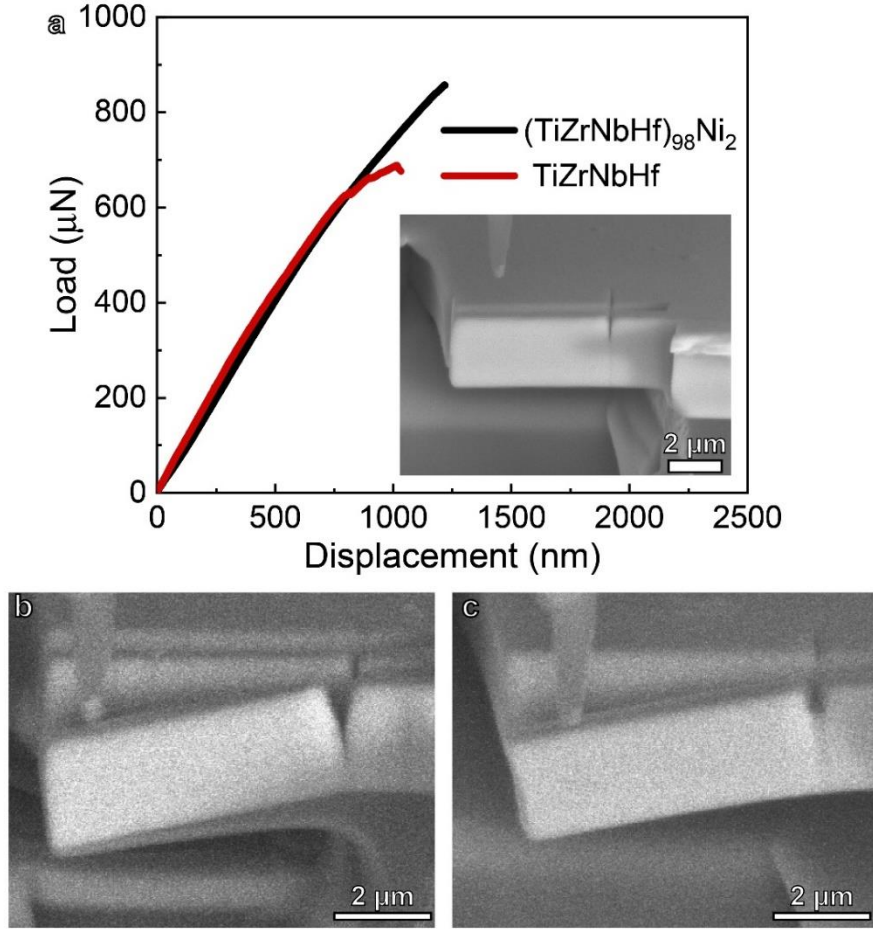


Figure S9. Fracture toughness of the NC (TiZrNbHf)₉₈Ni₂ and TiZrNbHf alloys.

(a) Load-displacement curves of the pre-notched microcantilevers prepared in the (TiZrNbHf)₉₈Ni₂ and TiZrNbHf alloys. The inset shows a notched (TiZrNbHf)₉₈Ni₂ microcantilever. (b, c) Snapshot SEM images of TiZrNbHf (b) and (TiZrNbHf)₉₈Ni₂ (c) microcantilevers with an identical beam deflection of 1.3 μm during testing, showing a much larger crack generated on the reference TiZrNbHf alloy compared with that on the (TiZrNbHf)₉₈Ni₂ alloy. The load-displacement curve of the TiZrNbHf alloy initially reveals a linear behavior, until it shows a deviation at a load of 630 μN, and reaches a maximum load of 686 μN. Due to the limited crack tip plasticity, linear elastic fracture mechanics is applicable^{s1}. The NC (TiZrNbHf)₉₈Ni₂ alloy requires a higher load for crack initiation, showing a maximum load of 857 μN. The fracture toughness is calculated using the equation described in Methods. The NC TiZrNbHf and (TiZrNbHf)₉₈Ni₂ alloy has a fracture toughness of 4.3 MPa·m^{1/2} and 6.0 MPa·m^{1/2}, respectively.

In the “Methods” section (Page 27) of the revised manuscript, we have added the following text:

“The in-situ SEM bending experiments for the evaluation of fracture toughness were performed using a PI85 PicoIndenter (Hysitron Inc.) with a diamond tip, under displacement-control mode and at a displacement rate of 5 nm/s. The loading direction in respect to the columnar grains were schematically depicted in Fig. S14. At least three samples were tested at each condition to ensure repeatability.”

“The pre-notched microcantilevers with length (L_0) of $\sim 8.0\ \mu\text{m}$, width (W) of $\sim 1.8\ \mu\text{m}$, thickness (B) of $\sim 1.5\ \mu\text{m}$ for fracture toughness evaluation were prepared using FIB. The cantilevers were notched at $2\ \mu\text{m}$ away from the cantilever beam support, with sharp notch tip radius of $\sim 50\ \text{nm}$ and notch depth (a) of $\sim 600\ \text{nm}$. We carefully controlled the a/W value to be 0.3, resulting in a dimensionless geometry factor⁴⁶ $f(a/W)$ of 6.6. The fracture toughness K_{IC} was calculated using the equation: $K_{IC} = \frac{F_{max} \cdot L}{B \cdot W^2} f(a/W)$, where the maximum load F_{max} was taken from the measured load during bending.”

We have added schematic illustration of the loading direction during fracture toughness measurement in Supplementary Fig. 14 in the revised supplementary information:

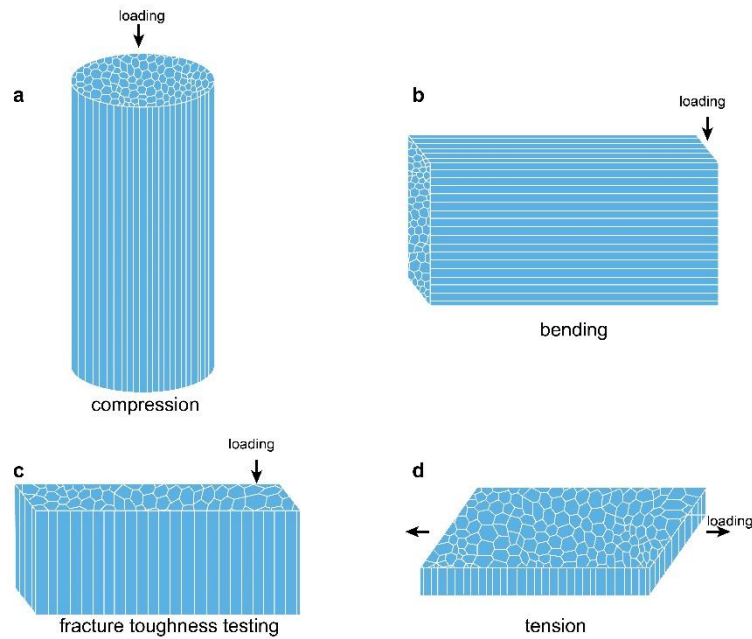


Figure S14. Schematic illustration of the loading directions during mechanical testing and their relation with respect to the columnar grains. Films often experience loading that is applied parallel with the columnar grains during application, we thus chose this loading direction for compression (a). In bending where the upper side of the cantilever experiences tension, the loading direction was selected so that the columnar grains withstand tensile loading (b). We further selected the loading direction that reflects more on grain boundary activities, for fracture toughness testing (c) and tension (d); in these tests, the sample needs to have high grain boundary cohesion to resist failure. The various mechanical testing, and the correspondingly various loading directions, enable a comprehensive evaluation of the properties of the $(\text{TiZrNbHf})_{98}\text{Ni}_2$ alloy.

“3. The evidence provided by the authors implies that all the dislocations observed were edge dislocations (subgrains and the HRTEM image shown in Fig. 4). It is well known that deformation in bulk TiZrNbHf-based alloys at room temperature is controlled by screw dislocations. Edge dislocation-controlled kink-band formation has also been observed, whereas the authors did not observe this phenomenon. In addition, the in-situ characterization of dislocations using atomic resolution STEM-HAADF cannot show dislocations clearly. The sample will be rotating out of the zone axis while loading and that is why Fig. 4b2 and 4b3 do not show proper atomic columns. The smeared contrast is prone to creating artifacts that show “fake dislocations” (especially when one tries to do FFT, masking, and IFFT).

Response: We have checked the BF-STEM image (added as Fig. S10 in the revised Supplementary Information) of the same region used for HAADF-STEM imaging in Fig. 4b2. The BF-STEM image clearly shows the presence of edge dislocations, although the sample is slightly tilted from the zone axis. Also, the BF-STEM image in Fig. 4b3 is the original image without masking or IFFT. We have added the BF-STEM image and the discussion to explain the presence of edge dislocation in the revised manuscript.

Modifications: On Page 12 of the revised manuscript, we have added the following text:

“The BF-STEM image of the region used for HAADF-STEM imaging in Fig. 4b2 was presented in Fig. S10, which clearly shows edge dislocations. The deformation in bulk TiZrNbHfTa alloy was found to be dominated by screw dislocations²⁹. It was later found that in a bcc TiNbMo CCA, the severe lattice distortion renders rugged atomic environment, which retards the motion of nonscrew dislocations²⁵. Recently, kink bands formed by edge-character dislocations promote exceptional fracture toughness in a Nb₄₅Ta₂₅Ti₁₅Hf₁₅ (at%) CCA²⁴. Dislocations with edge segments were also observed in a deformed bcc TiVNbHfAl₁₀ (at%) CCA with hierarchical chemical fluctuations³⁰. In the present (TiZrNbHf)₉₈Ni₂ alloy, the solute (Ni) is markedly different from the matrix elements, which greatly enhances the inhomogeneity and promotes lattice distortion of the alloy. It is thus reasonable to expect that, in addition to screw dislocations, edge-character dislocations also play an important role during deformation.”

We have added the BF-STEM image in Supplementary Fig. 10 in the revised supplementary information:

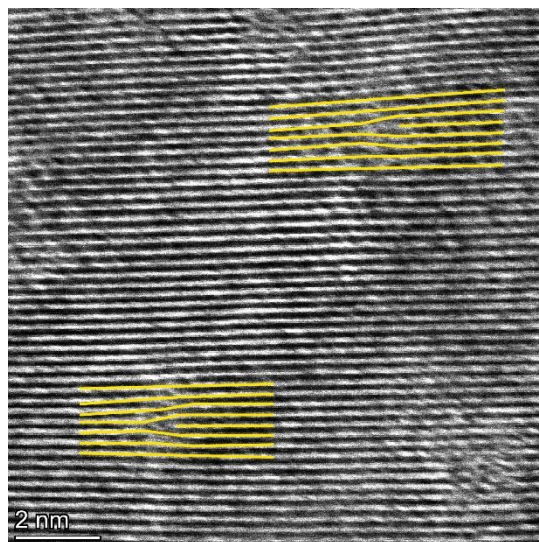


Figure S10. BF-STEM image of the deformed (TiZrNbHf)₉₈Ni₂. This is the same region as that for HAADF-STEM imaging in Fig. 4b2. Edge dislocations are highlighted using yellow lines.

The following references have been added in the revised manuscript:

24. Cook, D. H. *et al.* Kink bands promote exceptional fracture resistance in a NbTaTiHf refractory medium-entropy alloy. *Science* **384**, 178–184 (2024).
25. Wang, F. *et al.* Multiplicity of dislocation pathways in a refractory multiprincipal element alloy. *Science* **370**, 95–101 (2020).
29. Dirras, G. *et al.* Microstructural investigation of plastically deformed Ti₂₀Zr₂₀Hf₂₀Nb₂₀Ta₂₀ high entropy alloy by X-ray diffraction and transmission electron microscopy. *Mater. Charact.* **108**, 1–7 (2015).
30. An, Z. *et al.* Negative mixing enthalpy solid solutions deliver high strength and ductility. *Nature* **625**, 697–703 (2024).

Furthermore, the Z-contrast fluctuation is tricky to interpret as purely originating from Ni clusters. First, the local thickness variation of the sample after deformation can cause this fluctuation. Second, a 3-nm cluster can hardly be seen after averaging through a 30-50 nm sample. Judging from Fig.4, the actual sample thickness seems to be above this value. A proper dislocation analysis postmortem is needed to justify the authors' arguments."

Response: We have carefully controlled the FIB parameters when preparing the TEM sample. The undeformed sample used for STEM investigation (Fig. S5-S6) was thinned and cleaned until it was almost transparent in SEM at 2 kV, which indicates a thickness of <20 nm.

We fully agree that Z contrast fluctuation in HAADF-STEM image is not enough to reveal the presence and/degree of inhomogeneity. We have used STEM-EDS (Fig. S5), HAADF image (Fig. S6) and APT (Fig. 1d) results jointly to clarify the composition and structure of the Ni-enriched LCO. The HAADF-STEM image and EDS mapping in Fig. S5 reveal that the dark-contrast region in HAADF image corresponds to Ni-enriched LCOs. The APT results also confirm that ~3-nm-diameter Ni-enriched LCOs are uniformly dispersed within the nanograins.

We agree that a 3-nm cluster is often difficult to be observed after averaging through a 30-50 nm sample. Nevertheless, the TiZrNbHf base alloy has been known for its nanometer scale compositional fluctuation (Ref: *Mater. Today* 46 (2021) 28-34), and its inhomogeneity is greatly enhanced through Ni addition. The Ni-enriched LCO

has a composition markedly different from the matrix. The HAADF-STEM is highly sensitive to atomic mass, such that readily distinguishable contrast is seen in the HAADF image.

Also, we note that HAADF-STEM has been used in CCA to reveal the nanoclusters, presented in the image below (Ref: *Nature* 625 (2024) 697-703).

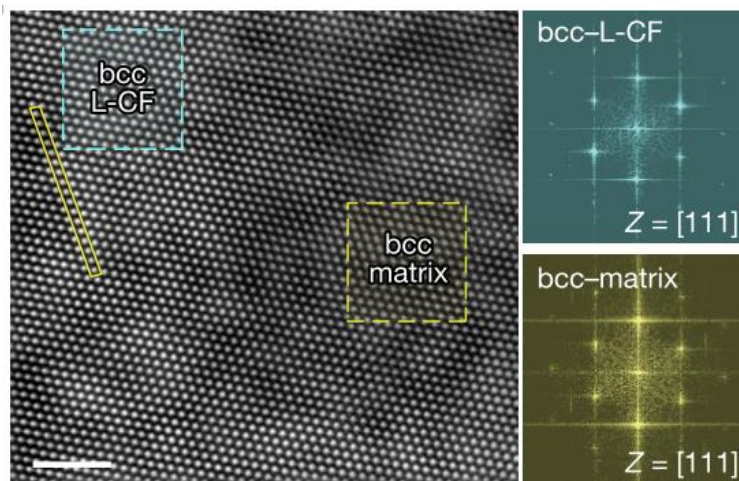


Figure R1. HAADF-STEM showing a nanocluster, termed as local chemical fluctuation (L-CF), embedded in the bcc matrix of a TiVNbHfAl₁₀ CCA. Scale bar, 2 nm.

“4. The experiments did not show how the addition of Ni stabilizes the NC structure. Comparative annealing tests of TiZrNbHf and (TiZrNbHf)Ni₂ are needed to show that grain growth in the latter is inhibited.”

Response: We have performed additional comparative annealing tests, which were also suggested by Reviewer #3. The results show that grain growth in the (TiZrNbHf)₉₈Ni₂ alloy has been suppressed, compared with that of the TiZrNbHf base alloy.

Modifications: On Page 13 of the revised manuscript, we have added the following text:

“We also evaluated the effect of Ni segregation on the thermal stability. The (TiZrNbHf)₉₈Ni₂ and TiZrNbHf alloys were annealed at 500 °C for 1 hour, and at 600 °C for 100 hours (Fig. S13). The base alloy experiences grain growth from the original 100 nm to over 200 nm, while the (TiZrNbHf)₉₈Ni₂ alloy shows unchanged grain size after annealing at 500 °C for 1 hour. With an increase of temperature to 600 °C and prolonged annealing time to 100 hours, the original columnar grains in the TiZrNbHf

alloy have become globular grains, while some of the columnar grains are maintained in the $(\text{TiZrNbHf})_{98}\text{Ni}_2$ alloy. The $(\text{TiZrNbHf})_{98}\text{Ni}_2$ alloy shows a much smaller grain size (~ 50 nm) compared to that of the TiZrNbHf base alloy (~ 150 nm).”

We have added comparative annealing results in Supplementary Fig. 13 in the revised supplementary information:

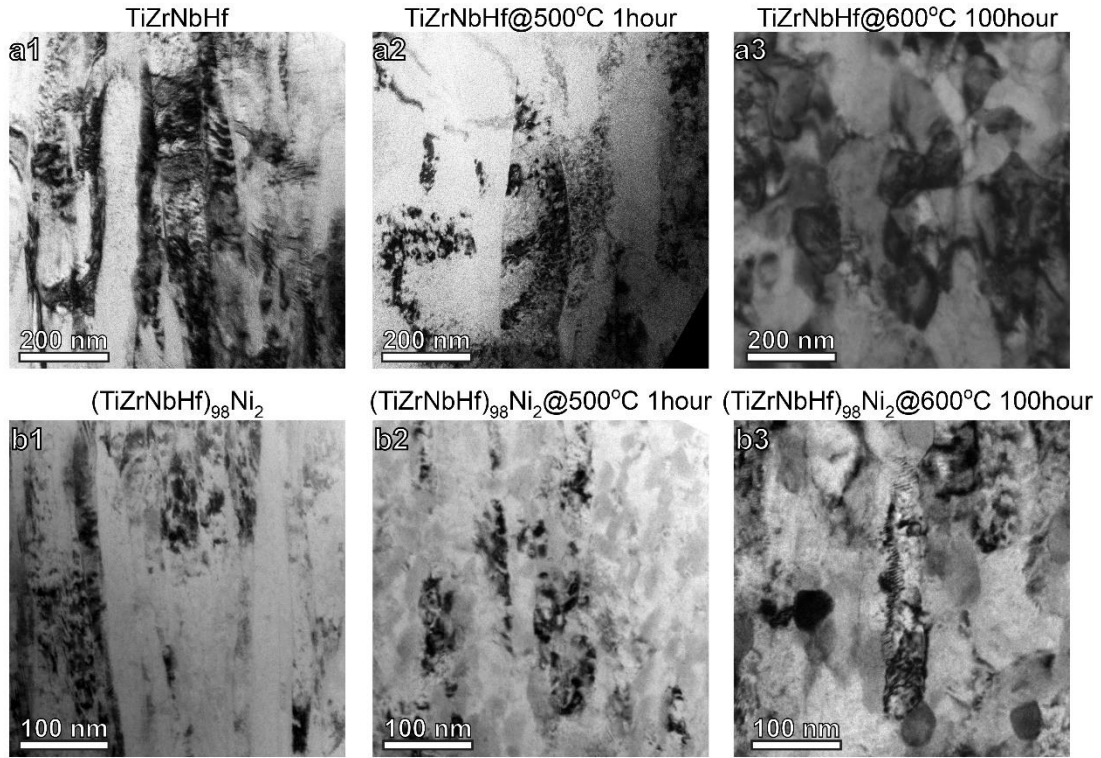


Figure S13. Grain structure of the TiZrNbHf and $(\text{TiZrNbHf})_{98}\text{Ni}_2$ alloy before and after annealing. The alloys subjected to annealing were encapsulated in quartz tubes, which were evacuated to $<10^{-4}$ Pa. **(a1-a3)**, Side-view TEM images of the TiZrNbHf alloy, showing that the columnar grain width is ~ 100 nm before annealing **(a1)**, which increases to over 200 nm after annealing at 500 °C for 1 hour **(a2)**. The original columnar grains of the TiZrNbHf alloy have become globular grains after annealing at 600 °C for 100 hours **(a3)**. **(b1-b3)**, Side-view TEM images of the $(\text{TiZrNbHf})_{98}\text{Ni}_2$ alloy, presenting that the columnar grain width is ~ 30 nm before **(b1)** and after **(b2)** annealing at 500 °C for 1 hour. The $(\text{TiZrNbHf})_{98}\text{Ni}_2$ alloy comprises both columnar and globular grains after annealing at 600 °C for 100 hours **(b3)**, and its grain size is markedly smaller than that of the reference TiZrNbHf alloy. The as-deposited $(\text{TiZrNbHf})_{98}\text{Ni}_2$ alloy has Ni-segregation stabilized grain boundaries, which

achieves higher stability upon both mechanical loading and annealing compared to the TiZrNbHf base alloy.

“Minor issues:

1. Using the term “near-theoretical” to describe the high strength of the material can potentially be misleading because the theoretical strength of the material is calculated where there is no dislocation involved in the deformation of single crystals, which is not the case here. The reviewer will suggest a clarification early in the paper.”

Response: We thank the reviewer for the comments, we fully comply and have clarified the term “near-theoretical” in the revised manuscript.

Modifications: On Page 4 of the revised manuscript, we have added the following text:

“The theoretical shear strength limit of around $G/10$ (G is the shear modulus) was proposed by Frenkel nearly a century ago¹⁵, and was achieved in nanowiskers¹⁶ and two-dimensional materials (e.g. graphene)¹⁷ that are free from dislocations and grain boundaries.”

On Page 19 of the revised manuscript, we have revised the following text:

“The NC (TiZrNbHf)₉₈Ni₂ alloy achieves a yield strength of 2.5 GPa (σ_y) which corresponds to a τ_y (shear stress for the initiation of plastic flow)³⁷ of 1.25 GPa. The shear modulus (G) of the alloy is 39 GPa, calculated based on the elastic modulus measured using nanoindentation. The τ_y/G ratio of the NC (TiZrNbHf)₉₈Ni₂ alloy reaches 1/31, approaching the theoretical shear strength limit¹⁴.”

“2. How do the authors account for the larger scatter of in-situ mechanical tests for small samples compared to that in bulk tensile and bending tests? How many tests were done for each sample?”

Response: We thank the reviewer for the comment. At least three samples were tested for each condition to ensure repeatability.

Modifications: On Page 9 of the revised manuscript, we have added the following text:

“Three stress-strain curves of the alloy are presented in Fig. S7, demonstrating the repeatability of the measured properties.”

On Page 27 of the revised manuscript, we have added the following text:

“At least three samples were tested at each condition to ensure repeatability.”

We have added repetitive stress-strain curves in Supplementary Fig. 7 in the revised supplementary information:

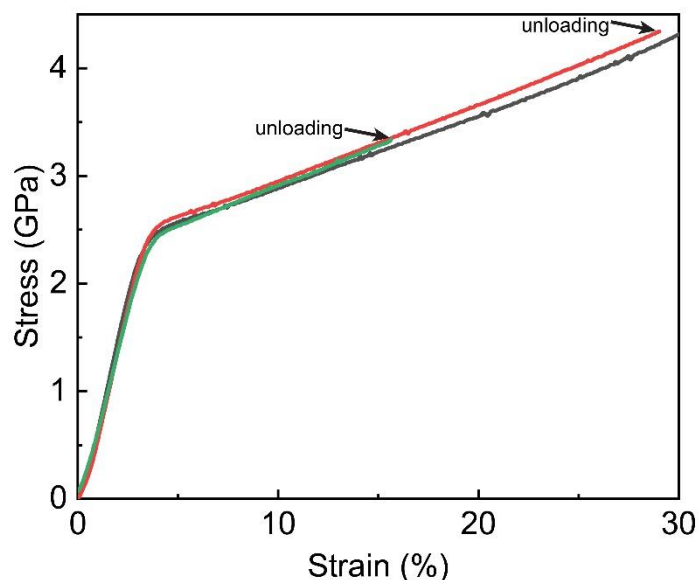


Figure S7. Stress-strain curves of the (TiZrNbHf)₉₈Ni₂ alloy measured in micro-pillar compression, demonstrating the repeatability of the measured properties.

“3. How were the columnar grains aligned with the tensile and bending directions? Parallel or perpendicular, or both?”

Response: We have added schematic illustration of the loading direction during mechanical testing as Supplementary Fig. 14 in the revised supplementary information. The figure and revised texts have been pasted in the above response to the comment “2. Were there any microcantilever bending tests that could show increased fracture toughness in the material?”.

“4. It is difficult to identify the 3-nm cluster in Fig. S5. What is the crystal structure of the cluster with Ni? Does the FFT of the cluster give the information? In addition, what is the thickness of the sample? A 3nm cluster will barely show any Z-contrast when averaged through a 30-50 nm sample.”

Response: The FFT pattern indicates that the Ni-enriched LCO adopts bcc structure that is fully coherent with the matrix. We have added the FFT results in Supplementary Fig. 6 in the revised supplementary information.

We have carefully controlled the FIB parameters when preparing the TEM sample. The undeformed sample used for STEM investigation (Fig. S5-S6) was thinned and cleaned until it was almost transparent in SEM at 2 kV, which indicates a thickness of <20 nm.

As presented in the response to the Comment 3 earlier, we have used STEM-EDS (Fig. S5), HAADF image (Fig. S6) and APT (Fig. 1d) results jointly to clarify the composition and structure of the Ni-enriched LCO. We agree that a 3-nm cluster is often difficult to be observed after averaging through a 30-50 nm sample. Nevertheless, the TiZrNbHf base alloy has been known for its nanometer scale compositional fluctuation (Ref: Mater. Today 46 (2021) 28-34), and its inhomogeneity is greatly enhanced through Ni addition. The Ni-enriched LCO reveals markedly different composition compared with the matrix, and the contrast in HAADF-STEM is highly sensitive to atomic mass, which result in the readily distinguishable contrast in HAADF image. Also, we note that HAADF-STEM has also been used in CCA to reveal the nanoclusters, as presented above in Figure R1 (Ref: *Nature* 625 (2024) 697-703).

Modifications: On Page 7 of the revised manuscript, we have revised the following text:

“Atom-resolved HAADF-STEM imaging reveals that the ~3-nm-sized intragrain LCO is fully coherent with the bcc matrix, and fast Fourier transformation (FFT) pattern suggests an absence of second phase (Fig. S6). These bcc LCOs are, like Guinier-Preston zones, an early stage of precipitation. That is, the Ni-enriched LCOs with bcc structure are formed after annealing at 350 °C for 1 hour.”

We have added the FFT pattern in Supplementary Fig. 6 in the revised supplementary information:

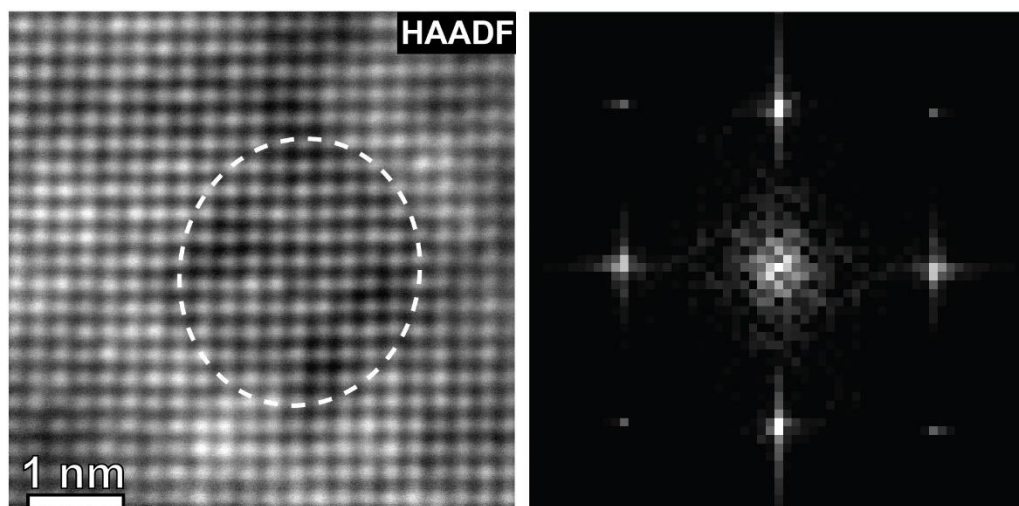


Figure S6. HAADF-STEM image (a) and the corresponding fast Fourier transformation (FFT) pattern (b) of the $(\text{TiZrNbHf})_{98}\text{Ni}_2$ alloy. a, The STEM image shows that the ~ 3 -nm-sized cluster in the nanograin is coherent with the matrix. The white dashed curve highlights the cluster. **b,** FFT pattern suggests that the alloy adopts a single-phase bcc structure.

Referee #2:

“In the manuscript titled “Near-theoretical strength and deformation stabilization achieved via grain boundary segregation and nano-clustering of solutes”, the authors Chang Liu, et al. have used electronic structure simulations and analytical models to identify potential alloying elements (not present in the alloy) that can enhance solute segregation to grain boundaries and will not form intermetallic phases in complex concentrated alloy consisting of Ti, Zr, Nb and Hf. Later, they synthesize an alloy with identified solute element, Ni, and demonstrate the superior mechanical properties obtained due to the inclusion of Ni. The manuscript is well structured, and the authors have performed a detailed experimental analysis to demonstrate the validity of their design strategy. Their results are noteworthy and if published would significantly advance this field.”

Response: We are very grateful to the reviewer for the supportive comments and for the recognition of the novelty and significance of our work. We have carefully revised the manuscript, in full accordance to the reviewer’s comments.

“In the following I have listed a few comments.

Comments about the design strategy:

1. It seems from Fig. 1(a) that atomic size of Ni is much smaller than the host atoms. Since the elastic strain energy depends on the atomic size mismatch, it is not clear why a smaller solute will necessarily decrease the elastic strain energy as mentioned in page 5.”

Response: We agree that it’s not appropriate to emphasize only the elastic strain energy here, while other contribution, e.g., chemical affinity (correlating with the electronegativity difference), would also determine the segregation energy of solutes at the GBs. We have deleted the previous statement “a smaller atomic radius for a lower elastic strain energy penalty when the solutes are accommodated at the grain boundary” and revised the text. We used DFT (updated Fig. S2) to calculate the segregation energy of Ni at the GBs, which is -1.919 eV. The negative value suggests that Ni solutes prefer to segregate at the GBs.

Modifications: On Page 6 of the revised manuscript, we have revised the following text:

~~“We identified potentially suitable solutes (Ni, Co, Fe, Rh, Ru, Ir) that have a markedly different electronegativity, a smaller atomic radius for a lower elastic strain energy penalty when the solutes are accommodated at the grain boundary¹³, relative to the matrix elements in the equiatomic TiZrNbHf alloy, and thus could induce a high tendency for solute segregation to GBs (Fig. 1a).”~~

~~“Moreover, using density-functional-theory (DFT) calculation, the segregation energy of Ni at the GB was evaluated (see Methods for details). The corresponding average segregation energy is -1.919 eV, suggesting that Ni solutes prefer to segregate at the GBs (Fig. S1). Besides, the strengthening energy of the GB, using the energy penalty required for boundary cleavage as a metric, was also calculated in DFT modelling (Fig. S2). The negative value of -1.33 eV for average strengthening energy indicates that the Ni solutes will enhance the grain boundary cohesion (Fig. 1c).”~~

2. The authors have used electronic structure calculations using density functional theory to verify if the identified solute element will lead to grain boundary segregation or not. It seems that they have not calculated the segregation energy. The formula provided in Eq. (2) was used to calculate grain boundary strengthening energy which is mentioned in Ref. [32] of the manuscript. The grain boundary segregation energy is different from the formula provided in Eq. (2).

While in the method section, the authors state that “In present work, the segregation energy and strengthening energy are averaged over 5 independent samples”, the caption associated with Fig. 1(c) mentions “Strengthening energy of the alloy’s grain boundaries with Ni, obtained using DFT calculation.”

Response: We thank the reviewer for the comment. We have added a figure presenting the DFT calculated segregation energy as Supplementary Fig. 1.

In the revised manuscript, the updated Supplementary Fig. 1 shows segregation energy obtained from DFT calculation, and Fig. 1c presents strengthening energy by DFT calculation. We have revised the formula in Eq. (2) for the calculation of

segregation energy, and added more detailed numerical information in the revised manuscript. The texts in the Methods section have also been revised to clarify the calculation of segregation energy.

Modifications: On Page 6 of the revised manuscript, we have revised the following text:

“Moreover, using density-functional-theory (DFT) calculation, the segregation energy of Ni at the GB was evaluated (see Methods for details). The corresponding average segregation energy is -1.919 eV, suggesting that Ni solutes prefer to segregate at the GBs (Fig. S1). Besides, the strengthening energy of the GB, using the energy penalty required for boundary cleavage as a metric, was also calculated in DFT modelling (Fig. S2). The negative value of -1.33 eV for average strengthening energy indicates that the Ni solutes will enhance the grain boundary cohesion (Fig. 1c).”

In the “Methods” section (Page 24) of the revised manuscript, we have revised the following text:

“To capture the segregation tendency of Ni atoms towards GB region, the segregation energy E_{seg} was calculated⁴⁰:

$$E_{seg} = (E_{GB}^{Ni} - E_{GB}) - (E_{bulk}^{Ni} - E_{bulk}) \quad (2)$$

Here, E_{GB}^{Ni} and E_{GB} are the total energies of the simulated GB model with and without Ni atoms, respectively. E_{bulk}^{Ni} and E_{bulk} denote the total energies of the corresponding bulk model with and without Ni atoms, respectively. Note that a negative E_{seg} indicates that the Ni segregation at GB is energetically favorable.”

We have added DFT calculation results for the segregation energy in Supplementary Fig. 1 in the revised supplementary information:

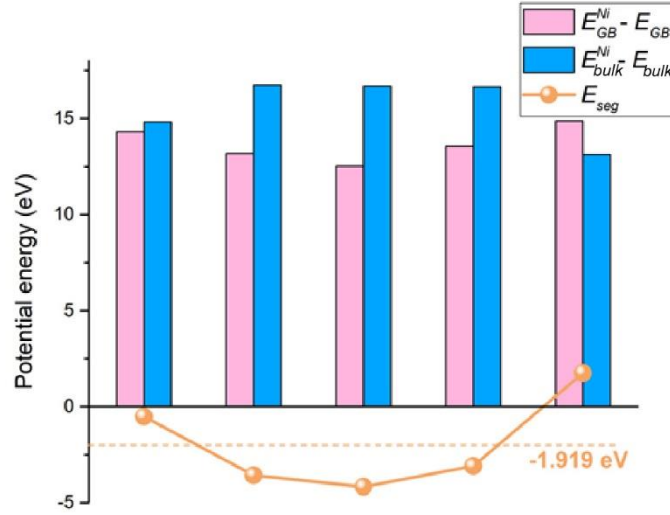


Figure S1. Density-functional-theory (DFT)-calculated segregation energy $E_{seg} = (E_{GB}^{Ni} - E_{GB}) - (E_{bulk}^{Ni} - E_{bulk})$ (according to Eq (2) in Methods) for five independent configurations. E_{GB}^{Ni} and E_{GB} are the total energies of the simulated grain boundary (GB) model with and without Ni atoms, respectively. E_{bulk}^{Ni} and E_{bulk} denote the total energies of the corresponding bulk model with and without Ni atoms, respectively. The average E_{seg} is -1.919 eV, suggesting that Ni solutes prefer to segregate at the GBs.

“Based on these observations, it is not clear how Ni was identified as the best candidate. Is normalized chemical potential (shown in Fig. 1(b)) then the best strategy to select potential alloying elements?”

Response: Ni was identified as the best candidate based on the following steps:

- (1) A selection of solutes with markedly different electronegativity relative to the matrix elements in the equiatomic TiZrNbHf alloy. Such solutes are expected to show a high tendency for segregation to grain boundaries. In this step, Ni, Co, Fe, Rh, Ru, Ir were identified (Fig. 1a);
- (2) Selection of the solute that reduces the chemical potential of the base alloy, and Ni was identified in this step (Fig. 1b).

We further used DFT calculation of the segregation energy and strengthening energy to verify that Ni would segregate to the grain boundaries and enhance the grain boundary cohesion of the alloy.

“Comments about the use of solid solution strengthening model:

1. The solid solution strengthening model proposed in Ref. [33] was designed for bulk alloys in which the grain boundaries do not control/dominate the mechanical properties. On the other hand, as discussed in the manuscript, the strengthening mechanisms in nanocrystalline alloys are different. It will benefit the reader if the authors can provide some justification for the use of this model for their system.”

Response: As correctly pointed out by the reviewer, the solid solution strengthening model was designed for micrometer-grained alloys in which the GBs do not dominate the mechanical properties. In NC alloys, the strengthening mechanisms are different and GBs play a crucial role.

Using the strengthening model, we predict the solid solution strengthening due to the misfit of 2% Ni solutes would add at most 200 MPa, while the actual yield strength increased from 1.3 to 2.5 GPa. The pronounced hardening (by 1.2 GPa) is not mainly contributed by the solid solution strengthening. That’s the main reason of using this theoretical model, which covers two additional contributors: grain size difference and elevation in Hall-Petch coefficient due to grain boundary segregation.

Modifications: On Page 18 of the revised manuscript, we have revised the following text:

“For micrometer-grained alloys, solid solution strengthening is highly effective in enhancing the strength. Solid solution strengthening also contributes to NC alloys, yet it is far from enough to elevate the strength to the observed level, as GBs also play a crucial role. The increase of strength (from 1.3 to 2.5 GPa, as shown in Fig. 2) is therefore from another two contributors, apart from solid solution. One is the grain size difference...The other factor is the elevation in K after the decoration of the GBs by the high-modulus Ni...”

“2. Please include a table showing the values of quantities in Eqs. (3)-(4).”

Response: We have added tables showing the values of the quantities in Eqs. (3)-(4).

Modifications: On Page 26 of the revised manuscript, we have added the Tables:

Table 1 Input parameters to the Curtin’s solid-solution strengthening model

Samples	$G(\text{GPa})$	ν	$a_0(\text{\AA})$
TiZrHfNb	24.9	0.393	3.428
(TiZrHfNb) ₉₈ Ni ₂	25.28	0.385	3.415

Table 2 Comparison of atomic misfit volume, ΔV_n , between (TiZrHfNb)₉₈Ni₂ and TiZrHfNb alloys

Samples	Ti	Zr	Hf	Nb	Ni
TiZrHfNb	-2.86	-2.26	+2.287	+2.789	/
(TiZrHfNb) ₉₈ Ni ₂	-0.565	+4.978	+4.396	-0.17	-8.88

Referee #3:

“This paper is interesting and some very detailed & difficult experimentation, but to my view the novelty & outcome (e.g. properties achieved) of the work does not meet the threshold of Nature Communications.

Alloy design via solute decoration at grain boundaries is a known concept, e.g. published in Nat Comms nearly 10 years ago - 10.1038/ncomms7858

Ductility would seem to be a key issue.

Yield strengths of 2GPa seem readily achievable in nanocrystalline alloys, key challenge would be to do it with ductility. Also further when testing the alloys micromechanically (size effect leads to higher strengths).”

Response: We thank the reviewer for the comments. Grain boundary engineering is one of the most important mechanisms for designing nanostructured alloys (Ref: Park, M. & Schuh C. *Nat. Commun.* 6 (2015) 6858). The resultant “nanocrystalline (NC) metals” can achieve high (such as ~ 2 GPa) yield strengths (σ_y) (Ref: Ma, E. & Zhu, T. *Mater. Today* 20 (2017) 323–331). As correctly pointed out by the reviewer, ductility is quite challenging for NC metals. This is because these materials generally lack the capacity for strain hardening, and the tiny grains are intrinsically unstable, such that they tend to grow during plastic deformation to large strains.

The present work advocates a new alloy design strategy to simultaneously achieve work hardening ability and stabilized grain structure against (deformation-assisted) grain growth for NC alloys. We have performed microcantilever bending test, in which the upper portion of the cantilever experiences tensile deformation. The (TiZrNbHf)₉₈Ni₂ alloy achieves an ultrahigh σ_{max} of 5.6 GPa, and crack generation is absent even at a large bending deflection of 640 nm (Fig. 2d). The upper portion of the (TiZrNbHf)₉₈Ni₂ cantilever withstands a tensile strain of 11% (measured as a reduction in the necking area). The bending tests reveal that the (TiZrNbHf)₉₈Ni₂ alloy achieves a higher ductility than that of the reference TiZrNbHf alloy.

Regarding to the sample size effect, the (TiZrNbHf)₉₈Ni₂ alloy in the present work has a grain size of ~ 30 nm (Fig. 1d, Fig. S4). This means a 1 μ m-diameter pillar contains

hundreds of columnar grains, and thus numerous defects such as grain boundaries and dislocations. Considering that the sample-size reduction induced strength increase mostly originates from a low density of defect or defect sources (Ref: *Science* 360, 300–302 (2018)), the sample size effect is unlikely to be important in the present study.

“No real comparison of grain size and yield strength to state is exceptional, ~10nm grain size stated by authors, and even up to 10GPa micropillar strength reported in HEAs <https://doi.org/10.1038/ncomms8748>, compared to author’s 30nm and 2.5GPa”

Response: The paper (<https://doi.org/10.1038/ncomms8748>) reports the mechanical properties of nanocrystalline (NC) NbMoTaW alloy in compression. The NC NbMoTaW alloy reveals a size-dependent strength, and the 10 GPa-strength is measured from a 70-nm-diameter NbMoTaW nanopillar, which is a result of size effect. Nanosized samples, e.g. nanowiskers (Ref: Banerjee, A. *et al. Science* 360, 300–302 (2018)), are known to reveal ultrahigh strength, sometimes even approaching the theoretical strength regime.

The (TiZrNbHf)₉₈Ni₂ alloy in the present work has a grain size of ~30 nm (Fig. 1d, Fig. S4). This means a 1 μm-diameter pillar contains hundreds of columnar grains, and thus abundant defects such as grain boundaries and dislocations. Considering that the sample-size reduction induced strength increase mostly originates from a low density of defect or defect sources, the sample size effect is thus not a relevant feature in the present study.

We would like to emphasize that the ultrahigh strength of the (TiZrNbHf)₉₈Ni₂ alloy results from the synergistic effects of grain boundary strengthening, LCO strengthening, and solid solution strengthening, instead of sample size effect. We also tested the NC TiZrNbHf alloy using the same pillar dimension and testing conditions. The marked difference of the strength for (TiZrNbHf)₉₈Ni₂ and TiZrNbHf alloy confirms this assertion.

“Thermal stability not investigated – would the grains grow? Would intermetallics form?”

Response: We have performed additional comparative annealing tests, showing that grain growth in the $(\text{TiZrNbHf})_{98}\text{Ni}_2$ alloy has been suppressed, compared to that of the TiZrNbHf base alloy.

Modifications: On Page 13 of the revised manuscript, we have added the following text:

“We also evaluated the effect of Ni segregation on the thermal stability. The $(\text{TiZrNbHf})_{98}\text{Ni}_2$ and TiZrNbHf alloys were annealed at 500 °C for 1 hour, and at 600 °C for 100 hours (Fig. S13). The base alloy experiences grain growth from the original 100 nm to over 200 nm, while the $(\text{TiZrNbHf})_{98}\text{Ni}_2$ alloy shows unchanged grain size after annealing at 500 °C for 1 hour. With an increase of temperature to 600 °C and prolonged annealing time to 100 hours, the original columnar grains in the TiZrNbHf alloy have become globular grains, while some of the columnar grains are maintained in the $(\text{TiZrNbHf})_{98}\text{Ni}_2$ alloy. The $(\text{TiZrNbHf})_{98}\text{Ni}_2$ alloy shows a much smaller grain size (~50 nm) compared to that of the TiZrNbHf base alloy (~150 nm).”

We have added comparative annealing results in Supplementary Fig. 13 in the revised supplementary information:

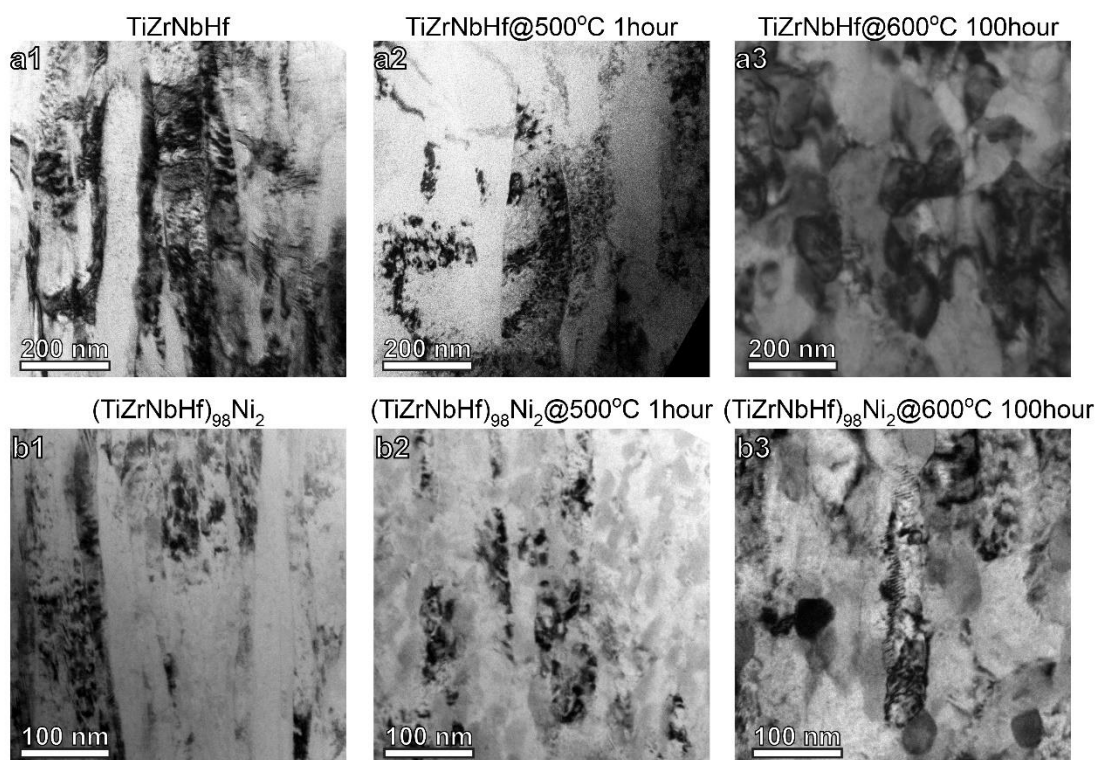


Figure S13. Grain structure of the TiZrNbHf and (TiZrNbHf)₉₈Ni₂ alloy before and after annealing. The alloys subjected to annealing were encapsulated in quartz tubes, which were evacuated to $<10^{-4}$ Pa. **(a1-a3)**, Side-view TEM images of the TiZrNbHf alloy, showing that the columnar grain width is ~ 100 nm before annealing **(a1)**, which increases to over 200 nm after annealing at 500 °C for 1 hour **(a2)**. The original columnar grains of the TiZrNbHf alloy have become globular grains after annealing at 600 °C for 100 hours **(a3)**. **(b1-b3)**, Side-view TEM images of the (TiZrNbHf)₉₈Ni₂ alloy, presenting that the columnar grain width is ~ 30 nm before **(b1)** and after **(b2)** annealing at 500 °C for 1 hour. The (TiZrNbHf)₉₈Ni₂ alloy comprises both columnar and globular grains after annealing at 600 °C for 100 hours **(b3)**, and its grain size is markedly smaller than that of the reference TiZrNbHf alloy. The as-deposited (TiZrNbHf)₉₈Ni₂ alloy has Ni-segregation stabilized grain boundaries, which achieves higher stability upon both mechanical loading and annealing compared to the TiZrNbHf base alloy.

“Micropillar compression less impressive than macro-scale tensile when thinking about ductility.”

Response: We agree that compressive deformability is not equivalent to tensile ductility, as high strain hardening rate is required for an alloy to achieve high tensile ductility, but not for achieving high compressive deformability (Ref: Ma, E. & Liu, C. *Prog. Mater. Sci.* 143, 101252 (2024)). To address this concern, we have performed bending test where the upper portion of the cantilever experiences tensile deformation (Fig. 2d). The NC TiZrNbHf base alloy shows a maximum flow stress (σ_{max}) of 3.6 GPa, and large cracks are initiated from the upper surfaces of the microcantilevers. The (TiZrNbHf)₉₈Ni₂ alloy, in comparison, achieves an ultrahigh σ_{max} of 5.6 GPa, and crack generation is absent even at a large bending deflection of 640 nm. The upper portion of the (TiZrNbHf)₉₈Ni₂ cantilever withstands a tensile strain of 11% (measured as a reduction in the necking area). The bending tests reveal that the upper portion of the (TiZrNbHf)₉₈Ni₂ cantilever achieves a high ductility under tensile stresses.

To answer the concern about the small sample size, we have added thorough discussion about the scalability of the approach.

Modifications: On Pages 19 and 20 of the revised manuscript, we have revised the following text:

“The NC (TiZrNbHf)₉₈Ni₂ alloy achieves a yield strength of 2.5 GPa (σ_y) which corresponds to a τ_y (shear stress for the initiation of plastic flow)³⁷ of 1.25 GPa. The shear modulus (G) of the alloy is 39 GPa, calculated based on the elastic modulus measured using nanoindentation. The τ_y/G ratio of the NC (TiZrNbHf)₉₈Ni₂ alloy reaches 1/31, approaching the theoretical shear strength limit¹⁴. We anticipate numerous applications related to the alloy’s outstanding strength and deformability, for example as high wear-resistance coatings for cutting tools. Furthermore, the above-mentioned alloy design concept should guide the design of other materials. In the microcantilever bending tests (Fig. 2c, d) where the upper portion of the material withstands tensile loading, the (TiZrNbHf)₉₈Ni₂ alloy shows a higher deformability than that of the base alloy, and its upper portion withstands a tensile strain of 11% without cracking. This means, through utilizing the favorable interplay of the distinctly different species with the base elements in the CCA, to promote intragrain LCOs and GB segregation (enhancing GB cohesion), the alloy’s strength and tensile ductility can be simultaneously improved.

The NC (TiZrNbHf)₉₈Ni₂ alloy in the present work was prepared using magnetron sputtering with a high cooling rate (above 10⁸ K/s)³⁸. In order to transfer the desirable structure of the NC alloys to bulk materials, additive manufacturing with a relatively high cooling rate can be considered as a good candidate for fabricating the bulk counterparts. The cooling rate can also be tuned through optimizing the printing parameters, e.g., laser power and scanning speed. The high cooling rate ensures the solutioning of the distinctly different species with the matrix, and reduces the grain size of the alloy. For conventional bulk sample prepared using arc melting, the alloy needs to be fast quenched from a solid solutioning temperature to avoid the formation of intermetallics; and then annealed at an intermediate temperature to promote LCOs. The grain size of the alloys prepared using additive manufacturing or arc melting might not

reach nanoscale. Nevertheless, the alloys designed using our strategy, with intragrain LCOs and GB segregation, are expected to achieve substantially improved strength and ductility than those of base alloys.”

“In-situ TEM is impressive and the micromechanics, nice to see tied to the LCO and dislocations being distributed through the grains rather than excessive gb accumulation, however, this interesting finding would be most interested if tied to exceptional overall performance.

Nice to see the attempt to tie DFT and TEM together.”

Response: We thank the reviewer for recognizing the in-depth strengthening and deformation mechanisms revealed by the in-situ TEM test, micromechanics, and DFT calculation used in the present work. The NC (TiZrNbHf)₉₈Ni₂ alloy achieves a yield strength of 2.5 GPa (σ_y) which corresponds to a τ_y (shear stress for the initiation of plastic flow) of 1.25 GPa. The shear modulus (G) of the alloy is 39 GPa. The τ_y/G ratio of the NC (TiZrNbHf)₉₈Ni₂ alloy reaches 1/31, reaching the near-theoretical shear strength regime. The marked difference of the strength for (TiZrNbHf)₉₈Ni₂ and TiZrNbHf alloy also confirms the effectiveness of our alloy design strategy.

“Alloy produced via thin-film, hard to see the scalability of the approach.”

Response: We thank the reviewer for the comments. We have added thorough discussion about the scalability of the approach.

The revised text has been pasted in the response earlier to the comment “Micropillar compression less impressive than macro-scale tensile when thinking about ductility”.

“What is a targeted end application for such alloys to guide the design goals?”

Response: We have added discussion about the targeted end application.

Modifications: On Page 19 of the revised manuscript, we have revised the following text:

“We anticipate numerous applications related to the alloy’s outstanding strength and deformability, for example as high wear-resistance coatings for cutting tools. Furthermore, the above-mentioned alloy design concept should guide the design of other materials. In the microcantilever bending tests (Fig. 2c, d) where the upper portion of the material withstands tensile loading, the $(\text{TiZrNbHf})_{98}\text{Ni}_2$ alloy shows a higher deformability than that of the base alloy, and its upper portion withstands a tensile strain of 11% without cracking. This means, through utilizing the favorable interplay of the distinctly different species with the base elements in the CCA, to promote intragrain LCOs and GB segregation (enhancing GB cohesion), the alloy’s strength and tensile ductility can be simultaneously improved.”

“Ln66 assumption that exceeding the solubility limit in the host metal would lead to a brittle second-phase, is not always the case, can well be a solid solution, especially in relation to the paper topic of Ni within a bcc metal, or Cu etc, which could form fcc phase at gbs. Or vice versa bcc as in Cantor/Yeh type HEAs.”

Response: We thank the reviewer for the comment, and we agree that when the solute concentration exceeds the solubility limit of the host metal, brittle second-phase intermetallics are not always formed. We have deleted this statement, and revised the main text accordingly.

Modifications: On Page 3 of the revised manuscript, we have revised the following text:

“The required solute concentration would exceed the solubility limit in the host metal such that a second phase forms.”

“Addition of Ni likely to promote intermetallics on thermal ageing
Stability of the grain size, and phases not demonstrated - 350 C for 1 hour not sufficient though may promote the fine-scale LCOs within grains, 600-800C for 100h might be more relevant to see grain coarsening / whether intermetallics form.”

Response: We have performed additional comparative annealing tests at 600 °C for 100 h. The results and revised texts have been pasted in the above response to the

comment “Thermal stability not investigated – would the grains grow? Would intermetallics form?”.

Response to the Reviewers' Report

Ms. No. NCOMMS-23-62916A

Chang Liu, Jing Rao, Zhongji Sun, Wenjun Lu, James P. Best, Xuehan Li, Wenzhen

Xia, Yilun Gong, Ye Wei, Bozhao Zhang, Jun Ding, Ge Wu, En Ma

We would like to cordially thank the reviewers for the valuable suggestions and comments on our paper. Our response is structured as follows: The comments from the reviewers are copied below in black font. For each comment, we present a detailed response, a full description of the newly added experimental results, and the corresponding manuscript modifications (blue font: reply items). The amended manuscript is enclosed, and the changes we made to the revised version are shown in red font (change items).

Referee #1:

The submitted revision of “Near-theoretical strength and deformation stabilization achieved via grain boundary segregation and nano-clustering of solutes” by C. Liu et al. has added important experiments and clarifications and therefore addressed most of the reviewer’s concerns. The reviewer will recommend the paper for publication if the following minor issues are resolved.

Response: We thank the reviewer for recognizing the improved quality of the revised manuscript. We have further revised the manuscript and resolved the issues raised by the reviewer.

1. The reason why the addition of 2% Ni can increase the fracture toughness of the notched cantilever needs to be further explained in terms of GB cohesion, lattice distortion, and dislocation activity.

Response: We have added the discussion about the mechanism for the increased fracture toughness in the revised manuscript.

Modifications: On Pages 12 of the revised manuscript, the text has been revised to the following:

“Fracture toughness is directly proportional to flow stress and strain to failure²⁴. In the (TiZrNbHf)₉₈Ni₂ alloy, the severe lattice distortion and LCOs retard dislocation motion, promoting a high yield strength. During plastic deformation, they promote the multiplication of dislocations in the nanograins, elevating the flow stress. Besides, GB cohesion is improved through Ni segregation (Fig. 1c), which impedes crack propagation and contributes to prolonged deformation, increasing the fracture strain. Consequently, the (TiZrNbHf)₉₈Ni₂ alloy achieves an enhanced fracture toughness relative to that of the base alloy.”

2. The reviewer will feel much more comfortable if more Ni-rich clusters can be identified through HRSTEM whose size distribution statistically matches the APT result. Mass-thickness fluctuation in HRSTEM's Z-contrast can also imply that any local thickness variation of the sample can result in islands that look just like Ni-clusters. Therefore, showing one instance of a lower-Z contrast cluster may not be sufficient.

Response: We have revised the supplementary Fig. 5 to show the distribution of the Ni-enriched LCOs, whose size distribution statistically matches the APT observation.

Modifications: HRSTEM image showing a high density of Ni-enriched LCOs, with a size distribution statistically matching the APT result, are presented as Supplementary Fig. 5 in the revised supplementary information:

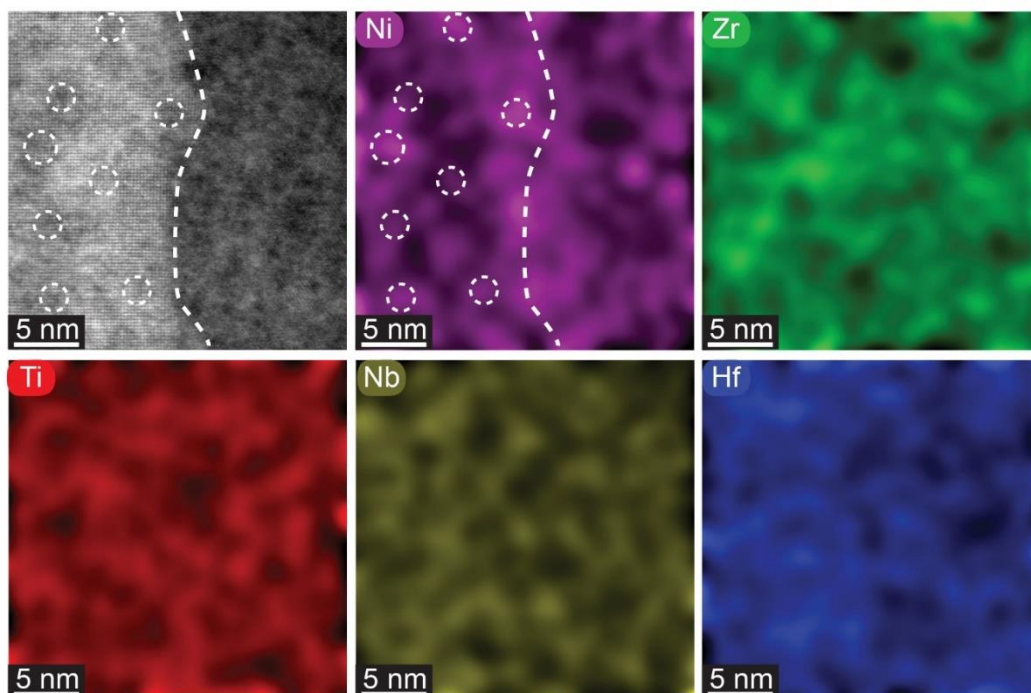


Figure S5. STEM imaging and EDS mapping of the $(\text{TiZrNbHf})_{98}\text{Ni}_2$ alloy. HAADF image of two adjoining grains, and corresponding maps for individual elements of Ni, Zr, Ti, Nb, and Hf. The grain boundary is indicated using white dashed line, and the Ni-enriched LCOs (~ 3 -nm-diameter) in the left-side grain are highlighted using white dashed circles.

On Pages 7 of the revised manuscript, the text has been revised to the following:

“Energy-dispersive X-ray spectroscopy (EDS) analysis further confirms the Ni-enrichment at the GBs and the presence of nanometer-scale Ni-enriched LCOs in the grain interior (Fig. S5). The HAADF-STEM and EDS images show that the size distribution of the LCOs matches that from the APT results.”

Referee #2:

Dear Editor,

I have read the manuscript and the authors' response to comments by the reviewers. Overall this is a very nice piece of work, with lot of detailed experimental analysis performed to understand thermodynamic stability and mechanical properties. The authors have mostly addressed by concerns. I have a few minor comments:

Response: We are grateful to the reviewer for recognizing the novelty and quality of our work. We have further revised the manuscript, in comply with the reviewer's comments.

1. Please include equations used to calculate the reduced chemical potential.

Response: We have added the equation and approaches used to calculate the chemical potential.

Modifications: On Pages 26 of the revised manuscript, the text has been revised to the following:

“Thermodynamic modeling. The thermodynamic calculations were carried out using the Thermo-Calc Software 2021a with the TCHEA3 database, which was specifically designed for high-entropy alloys. The stability of the bcc phase was evaluated by the change of the chemical potential (μ) after introducing the solute element.

Chemical potential (μ) is defined as the chemical energy (U_c) for 1 mol of substance, $\mu = \frac{U_c}{N}$, where N is the number of moles of the substance. Within the Calphad method, Gibbs free energy (G) is regarded to be equivalent to chemical energy (U_c), hence, $\mu = \frac{G}{N}$.

The underlying assumption is that for a simple system without the consideration of surface, electric, magnetic, and non-hydrostatic mechanical energy contributions, the total internal energy (U) is equal to the summation of thermal (U_t), mechanical (U_m), and chemical energies (U_c), $U = U_t + U_m + U_c$, where $U_t = T * S$, $U_m = -pV$, and $U_c = \mu N$. These are the fundamental equations of thermodynamics formulated by Gibbs, combining the first and second laws of thermodynamics. Hence, $G = U_c =$

$U - TS + pV$, the chemical potential $\mu = \frac{G}{N}$ is derived from the existing G information at the given composition within the commercial thermodynamic databases TCHEA3.”

2. Designing an alloy with coherent LCO and stabilized GBs via segregation of solute atoms is appealing. Based on comments by the other referees, it seems proper measurement of ductility will significantly strengthen the manuscript. Perhaps the authors can include a comparison with values in Fig 1(b) of this paper: <https://www.nature.com/articles/s41586-023-06894-9>

Response: We thank the reviewer for the suggestion. The $(\text{TiZrNbHf})_{98}\text{Ni}_2$ NC alloy in the present work has a thickness of several micrometer, making the direct measurement of ductility difficult. We have compared the yield strength and uniform strain with other HEAs, measured using micropillar compression at ambient temperature. The figure has been added in the revised supplementary information. We have also added the discussion about ductility in the revised manuscript.

Modifications: Comparison of mechanical properties with other HEAs, measured in micropillar compression at ambient temperature is presented as Supplementary Fig. 8 in the revised supplementary information:

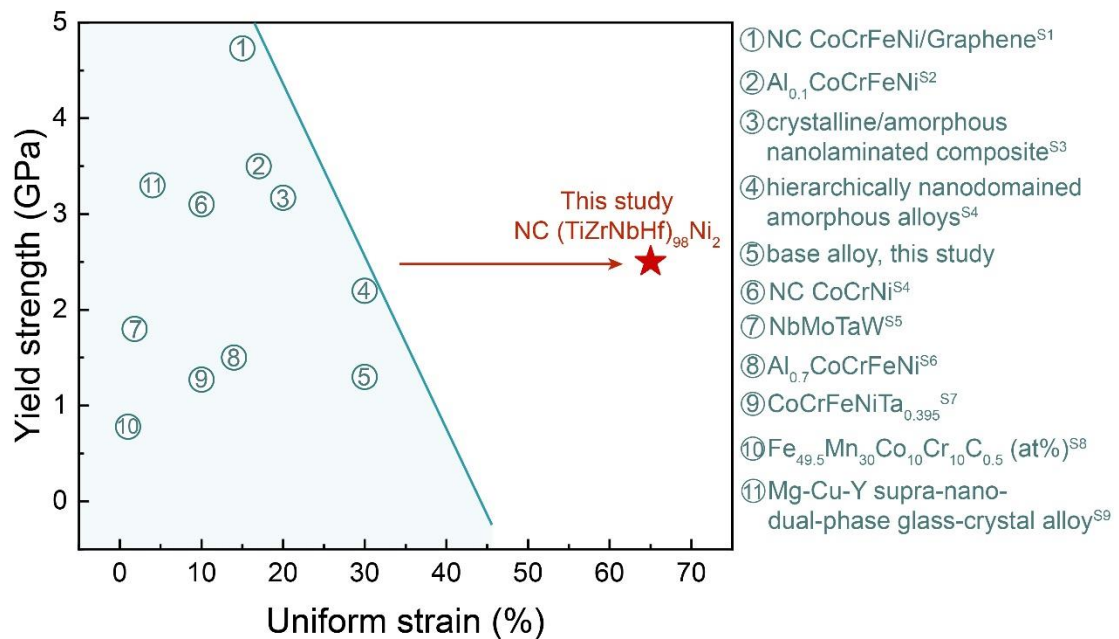


Figure S8. Yield strength vs. uniform strain of the (TiZrNbHf)₉₈Ni₂ alloy, in comparison with other HEAs^{S1–S8} and a supra-nano-dual-phase glass-crystal alloy^{S9} tested in micropillar compression at ambient temperature.

The following references have been added in the Supplementary Information:

- S1. Feng, X., Cao, K., Huang, X., Li, G. & Lu, Y. Nanolayered CoCrFeNi/Graphene Composites with High Strength and Crack Resistance. *Nanomaterials* **12**, 1–11 (2022).
- S2. Feng, X. *et al.* Ultrastrong Al_{0.1}CoCrFeNi high-entropy alloys at small scales: Effects of stacking faults: Vs. nanotwins. *Nanoscale* **10**, 13329–13334 (2018).
- S3. Wu, G. *et al.* Substantially enhanced homogeneous plastic flow in hierarchically nanodominated amorphous alloys. *Nat. Commun.* **14**, 3670 (2023).
- S4. Wu, G., Liu, C. & Yan, Y. Elemental partitioning-mediated crystalline- to-amorphous phase transformation under quasi-static deformation. *Nat. Commun.* **15**, 1223 (2024).
- S5. Zou, Y., Maiti, S., Steurer, W. & Spolenak, R. Size-dependent plasticity in an Nb₂₅Mo₂₅Ta₂₅W₂₅ refractory high-entropy alloy. *Acta Mater.* **65**, 85–97 (2014).
- S6. Giwa, A. M., Aitken, Z. H., Liaw, P. K., Zhang, Y. W. & Greer, J. R. Effect of temperature on small-scale deformation of individual face-centered-cubic and body-centered-cubic phases of an Al_{0.7}CoCrFeNi high-entropy alloy. *Mater. Des.* **191**, 108611 (2020).
- S7. Chen, Y. *et al.* Mechanical size effect of eutectic high entropy alloy: Effect of lamellar orientation. *J. Mater. Sci. Technol.* **82**, 10–20 (2021).
- S8. Zhang, W., Shen, J., Oliveira, J. P., Kooi, B. J. & Pei, Y. Crystallographic orientation-dependent deformation characteristics of additive manufactured interstitial-strengthened high entropy alloys. *Scr. Mater.* **222**, 115049 (2023).
- S9. Wu, G., Chan, K.-C., Zhu, L., Sun, L. & Lu, J. Dual-phase nanostructuring as a route to high-strength magnesium alloys. *Nature* **545**, 80–83 (2017).

On Page 9 of the revised manuscript, the text has been revised to the following:

“Fig. S8 shows improved mechanical properties of the (TiZrNbHf)₉₈Ni₂ alloy compared with that of other HEAs with similar sample dimensions.”

On Page 20 of the revised manuscript, the text has been revised to the following:

“Furthermore, the above-mentioned alloy design concept should guide the design of other materials. We note that a HfNbTiVAl₁₀ alloy with three-dimensional hierarchical chemical fluctuations (HCFs) achieves an outstanding strength and tensile ductility

synergy compared with the Al-free HfNbVTi alloy³⁰. The strong bonding among the atoms of different species with negative mixing enthalpy promotes a high strength. Besides, the HCFs retard dislocation motion, which increases the opportunities of dislocation entanglement and multiplication, enhancing strain hardening and tensile ductility. Hence, it is reasonable to expect that, through utilizing the favorable interplay of the distinctly different species with the base elements in the CCA, which promote intragrain LCOs and GB segregation (enhancing GB cohesion), the alloy's strength and tensile ductility can be simultaneously improved. This can be hinted from the microcantilever bending tests (Fig. 2c, d) where the (TiZrNbHf)₉₈Ni₂ cantilever shows a higher deformability than that of the TiZrNbHf base alloy.”

Referee #3:

The manuscript outlines a high class thin film study, and demonstrates interesting ideas, however, there are fundamental limitations as to the translation of the approach, as well as an overstatement as to how revolutionary the properties achieved are.

Response: We thank the reviewer for the comments. We have further revised the manuscript to clearly demonstrate the translation of the present alloy design strategy, and the mechanical properties of the (TiZrNbHf)₉₈Ni₂ alloy.

Whilst the idea of gb solute strengthening is not new, the extension to refractory high entropy alloys is interesting and opens up new design ideas of value to the HEA community. It is good to see modelling used to try to instruct the design.

Why has CALPHAD not been employed here? It would seem easy to predict possible phases formation and select solute(s), e.g. using Thermocalc's TCHEA database, I would suspect Ni would promote intermetallics, which could form in thermally equilibrated samples. 600C is low for such alloys so is likely non-equilibrium, and the LCOs could predicate intermetallics formation – the caution is that gb intermetallics would embrittle.

Response: We thank the reviewer for raising this question. We used CALPHAD method at the initial alloy composition formulation stage (Fig. 1b), but not for the prediction of GB strengthening for the reasons listed below. Using the commercial Thermocalc software, it is difficult to accurately describe the structure and chemistry of GBs. The GBs are decorated with high density of defects such as dislocations and vacancies, rendering their chemical potential formulations vastly different from those of matrix. There are formulations trying to describe GBs, like those proposed by J. W. Gibbs and Langmuir-McLean. Yet, most of these formulations were built based on several non-negligible assumptions and were mainly targeting materials in the equilibrium condition. For a rapid solidification processing route (solidification rate of $\sim 10^8$ K/s), the applicability of these models for GBs is further deteriorated. Thus, we use DFT modelling instead of CALPHAD calculation to predict the GB segregation tendency and GB cohesion.

At the initial alloy formulation stage, we evaluated the phase stability of the TiZrNbHf-X (X refers to the solute) alloys through CALPHAD modelling (Fig. 1b). The introduction of Ni into the TiZrNbHf reduces the chemical potential of the base alloy, predicting that the Ni addition would result in a bcc solid solution. Besides, it has been reported that a NC CrMnFeCoNi alloy experienced phase decomposition after annealing at 250 °C for 5 h or 300 °C for 1 h, having the same decomposed products as in its coarse-grained counterpart after annealing at 500 °C for 500 days (Ref: *Scripta Materialia* 183 (2020) 122–126). Thus, the annealing condition of 600 °C for 100 hours used in the present work should be enough to evaluate the structural stability for NC alloys. The (TiZrNbHf)₉₈Ni₂ alloy shows markedly smaller grain size than that of the TiZrNbHf base alloy after annealing at 600 °C for 100 hours, suggesting that Ni addition improves the structural stability of the alloy. Further, Ni segregation at the GB not only improves the stability of the alloy, but also enhances GB cohesion, which substantially improves the deformability.

The outcoming properties cannot be considered revolutionary, ~2.5 GPa modest for what can be seen in micropillars (e.g. 4.5 GPa possible at 1 μm <https://doi.org/10.1126/sciadv.abc8288>), nor the fracture toughness of 4 to 6 MPa.m^{1/2} exceptional (4 to 6 MPa.m^{1/2} for Cr and NiAl, which are low toughness metals <https://doi.org/10.1002/adem.202101429>).

Response: The Co₆₀Al₄₀ sample, as pointed out by the reviewer, adopts a structure of B2 intermetallic compound (Ref: *Sci. Adv.* 2021, 7, eabc8288). Intermetallics are known to have a mixture of metallic, ionic, and covalent bonds, stronger than pure metallic bonds. Therefore, it is not surprising that NC Co₆₀Al₄₀ micropillar presents a more impressive strength than our alloy.

As for toughness, NC metals are known to deliver rather low fracture toughness, ranging from 1.5 – 3.5 MPa·m^{1/2} in pre-notched microcantilever bending tests, far lower than their coarse-grained counterparts. We agree that the toughness value for our alloy is not exceptionally better, but is at least a factor of two higher than the normal range

for NC metals of similar grain size and specimen dimensions. The (TiZrNbHf)₉₈Ni₂ NC alloy has achieved markedly enhanced strength, deformability, and fracture toughness compared to the NC TiZrNbHf base alloy. The experimental results confirm that our alloy design strategy can substantially improve the mechanical properties of NC alloys.

The discussion on how to transfer the desirable structure of the NC alloys to bulk materials is to me a bit weak, it's not easy to get NC by AM and certainly not by arc melting, and then not even with thermomechanical processing (10μm at best). This discussion also misses mechanical alloying, or severe plastic deformation.

The ability to translate the idea is not easy! Though is a worthy topic of its own onward new programmes of work.

Response: We thank the reviewer for the comment. Additive manufacturing and arc melting were discussed because the intragrain LCOs and enhanced GB cohesion should also benefit micrometer-grained bulk alloys. Our preliminary work obtained a conventional bulk alloy using arc melting following the alloy design strategy in the present work, which achieves a high yield strength of 1.25 GPa and tensile ductility of 25%. This suggests that the present alloy design strategy have some relevance to bulk micrometer-grained samples, but this must await future investigation.

We have revised the discussion about the scalability of the present alloy design strategy. We have also added discussion about the approaches for realizing LCOs and GB segregation in bulk NC alloys prepared using mechanical alloy or severe plastic deformation.

Modifications: On Pages 21 of the revised manuscript, the text has been revised to the following:

“The (TiZrNbHf)₉₈Ni₂ alloy in the present work was prepared using magnetron sputtering with a cooling rate above 10⁸ K/s³⁸, and the high cooling rate promotes a NC structure. Mechanical alloying^{11,39} or severe plastic deformation^{4,40} are also known for preparing NC samples; in those approaches suitable solutes (with electronegativity markedly different from those of the matrix) can also be introduced with an amount that is sufficient to promote LCOs and GB segregation, while avoiding the formation of

second phases. The NC alloys can be annealed at an intermediate temperature to further promote the formation of LCOs. We would like to emphasize that the intragrain LCOs and enhanced GB cohesion may also benefit micrometer-grained bulk cast alloys, which requires future exploration.”