Stabilizing nanocrystals via higher entropy interfaces

Zhaoping Lu (✉ luzp@ustb.edu.cn)

University of Science and Technology Beijing <https://orcid.org/0000-0003-1463-8948>

Yuan Yuan

University of Science and Technology Beijing

Yuan Wu

University of Science and Technology Beijing

Honghui Wu

University of Science and Technology Beijing

Hui Wang

University of Science and Technology Beijing, State Key Laboratory for Advanced Metals and Materials

<https://orcid.org/0000-0002-9089-628X>

Xiongjun Liu

University of Science and Technology Beijing <https://orcid.org/0000-0002-1663-4636>

S. H. Jiang

University of Science and Technology Beijing

Zhi Yang

University of Science and Technology Beijing <https://orcid.org/0000-0002-1297-7981>

Xiaoyuan Yuan

University of Science and Technology Beijing

Huihui Zhu

University of Science and Technology Beijing

Terence G. Langdon

University of Southampton

Yi Huang

University of Southampton

Lin Gu

Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China <https://orcid.org/0000-0002-7504-031X>

Qinghua Zhang

Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

Baptiste Gault

Max Planck Institute for Iron Research <https://orcid.org/0000-0002-4934-0458>

Dierk Raabe

Max-Planck-Institut für Eisenforschung <https://orcid.org/0000-0003-0194-6124>

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Abstract

Nanocrystalline (NC) metals are attractive due to their outstanding mechanical, physical and chemical properties. However, they are generally metastable and prone to undergo grain coarsening, which severely impedes their engineering application, particularly at elevated temperatures. A strategy to counteract this phenomenon lies in decreasing the energetic driving force for grain growth, through grain boundary segregation according to the Gibbs adsorption isotherm. The natural thought of ‘more segregation is better’, which was exercised over decades to solve this problem, however, does not work because interfaces themselves are thermodynamic entities, with only limited solute decoration tolerance. Herein, we propose to solve this long-standing problem via introducing multi-component co-segregated interfaces. This concept allows us to maximize the solute decoration of interfaces and minimize their energy, without triggering formation of new phases. This is enabled by extending the high entropy alloy (HEA) concept from the bulk to interfaces, a strategy we refer to as interfaces with higher entropy. This design concept is not transferred one-to-one but constrained by a few rules that reflect the nature of interfaces: use of several co-segregating elements with high mixing entropy; segregation remains in the dilute limit; and use of elements with high segregation coefficient. The latter criterion marks an important difference to the HEA concept as a high segregation coefficient guarantees that alloying elements are deposited only to those locations where they are needed, namely, to the interfaces, thus drastically reducing alloying costs. We applied this new design approach to NC-Nb and show that we can increase its stability from 873 to 1023 K with as little alloying as only 1 at.% of Ti, Ni, Co and Hf with equal fractions. The material maintains its nanocrystalline structure even after 2200 h at 973 K. This work thus offers a new paradigm for designing stable dilute NC materials for advanced engineering application.

Full Text

Nanocrystalline (NC) metals with a large interface density resulting from their nanometer-sized grains have shown unique combinations of mechanical, chemical as well as physical properties¹⁻⁵. However, their small grains experience a high capillary driving force exerted through the interface energy which triggers competitive coarsening. The effect scales inversely with the average grain size, an effect described by the Gibbs-Thompson capillary effect^{6,7}. For some NC metals, grain coarsening thus occurs even at moderate temperatures⁸⁻¹⁰. Such capillary-driven coarsening is an “Achilles’ heel” of NC metals, severely hindering their fabrication and application.

One approach to addressing this problem is a classical kinetic strategy, including solute drag and the Zener pinning from second-phase particles to slow down grain growth. Another approach is genuine thermodynamic stabilization, i.e., reducing their interface energy to lower the cause which drives the capillary pressure. This effect was discovered more than 100 years ago by Gibbs¹¹. It states that reshuffling of solute elements from the grain interior onto the interfaces (i.e. segregation) linearly reduces their energy, thus decreasing the driving force for coarsening^{11,12}. As a result, the idea of ‘more segregation is better’ has been applied over decades to stabilize NC metals¹³⁻¹⁹. However, the solute

decoration capacity of grain boundaries (GBs) is limited, and is determined by the thermodynamic properties of the interfaces themselves. When reaching a certain decoration level, the elements that decorate the interfaces start to decompose and form particles, namely, when their segregation content exceeds the local dilute limit of the GBs. This effect imposes a strict thermodynamic limit to this approach and thus also to the stabilization of NC metals. Therefore, novel approaches which exploit the maximal reduction of the interfacial energy by segregation for stabilizing NC metals in the dilute limit are urgently required so that their application range as engineering materials can be extended.

Inspired by the concept of high-entropy alloys (HEAs)²⁰⁻²⁴, here we apply the high-entropy concept to interfaces, with the aim to improve the thermal stability of NC metals by depositing multiple alloying elements only to those locations where they are needed, i.e., to the GBs²⁵. On the one hand, the interface energy can be thermodynamically reduced significantly via GB decoration by multiple elements, promoted by the mixing entropy^{26,27}. On the other hand, considering the sluggish diffusion in massive solid-solutions, GB migration rates can also be reduced by the solute drag force exerted by the different solutes²⁸⁻³⁰.

Herein, we therefore transfer the high-entropy concept from the bulk to its internal interfaces, a concept we refer to as interfaces with higher entropy. This approach enables a substantial reduction in alloying cost, as these elements are needed only at the interfaces at not in the bulk material where they do not contribute to the stabilization of the GBs. This concept allows us to maximize the solute decoration of interfaces in the dilute limit, which leads to strong GB energy reduction, thus reducing competitive capillary coarsening.

As a demonstrator of drastically enhanced thermal stability, we selected Nb as our model NC-metal, and alloyed it with a total amount of 1, 2, 5 and 10 at.% of Ti, Ni, Co and Hf (each of them with equal atomic fraction). For reference, a binary Nb-Ni alloy with 1 at.% Ni was also prepared. For simplicity, these five alloys are hereafter referred to as 1HEA, 2HEA, 5HEA, 10HEA and 1Ni alloys, respectively. All alloys were processed by high-pressure torsion (HPT) deformation under the same conditions (see Methods). The average grain size of all these materials are below 100 nm. The initial grain size of the as-HPT samples slightly decreases with increasing solute content, e.g., from an average grain size of 79 ± 4 nm for 1HEA to 41 ± 2 nm for 10HEA, whilst the benchmark 1Ni alloy has a similar average grain size as 1HEA. The alloys' thermal stability is evidenced in **Figs. 1a** and **b** that show the dependence of the average grain size and the corresponding hardness as a function of annealing temperature and time for all HPT-processed alloys. For comparison, the data for an unalloyed pure NC-Nb are also included.

Annealing at increasing temperatures for 2h demonstrates that the onset temperature for grain growth, seen in **Fig. 1a**, varies significantly with alloying. Pure Nb with an initial grain size of 80 ± 4 nm starts to grow at 873 K, accompanied with a loss in hardness³¹. Both the 1Ni and 10HEA alloys show a similar onset growth temperature around 873K with a hardness drop, indicating that the addition of 1 at.% Ni or a mixture of 10 at.% HEA (i.e., 2.5 at.% each of Ti, Ni, Co and Hf) do not substantially alter thermal stability. Strikingly, the 1HEA alloy shows the highest onset growth temperature of 1023 K, 150 K higher than that

of pure NC-Nb. This indicates that minor addition of 0.25 at.% with the dopants Ti, Ni, Co and Hf already dramatically enhances the stability of NC-Nb. The hardness of 1HEA remained almost unchanged when annealing below 1023 K. Once the grain coarsening commences, the growth rate is inversely proportional to the concentration of alloying elements, i.e., a reduced slope of the coarsening kinetics, caused by an increasing alloying content, indicates an enhanced kinetic pinning effect from solutes at elevated temperatures. The thermal stability of these NC alloys is further demonstrated by isothermal annealing at 973 K for up to 2200 h.

The corresponding grain size and hardness evolution for all alloys are plotted in **Fig. 1b**, thereby confirming the exceptional stability of 1HEA. The comparison of grain growth rates in the same temperature range $\sim 0.3-0.4 T_m$ (T_m : melting point) is plotted as a function of the total alloying concentration in **Fig. 1c** for traditional NC alloys and our proposed new alloys. The 1HEA shows not only the slowest grain growth rate but also the lowest total alloying content, demonstrating the compositional efficiency of our new stabilization approach.

Fig. 2 illustrates the microstructure evolution from as-HPT-processed up to 2200 h annealing at 973 K for 1Ni, 1HEA and 10HEA obtained from electron microscopy. The grains in NC-Nb coarsened quickly to micrometer sizes, and its hardness dropped from 2.88 ± 0.22 to 1.50 ± 0.06 GPa after 2 h annealing (**Fig. 1b**). A similar trend was observed for 1Ni. In contrast, 1HEA shows no change in grain size and morphology after 1000 h annealing (89 ± 7 nm), and only minute increase after 2200 h annealing (103 ± 6 nm), as shown in **Fig. 2b**. As expected, the hardness remained almost unchanged ($\sim 3.64 \pm 0.05$, 3.86 ± 0.17 and 3.65 ± 0.18 GPa for the as-HPT-processed, 1000 and 2200 h annealed samples, respectively) (**Fig. 1b**). Further, no detectable grain coarsening was observed in 1HEA after annealing at 1023 K for 100 h (**Extended Data Fig. 1**), and the hardness remained stable. However, obvious coarsening occurred in 10HEA, i.e., its grain size gradually increases to about 133 ± 8 nm for 2 h and 447 ± 26 nm for 1000 h annealing (**Fig. 2c**), with a dramatic hardness decrease from 4.79 ± 0.51 GPa to 2.61 ± 0.18 GPa.

Second phase drag forces, e.g. such as exerted by Zener particle pinning can also retard grain growth of NC metals and alloys³²⁻³⁵. One or more second phases precipitated in some of the NC alloys, enabled by the increase in alloying content and extended heat treatment. As shown in **Fig. 2b**, no precipitates were observed in 1HEA, annealed at 973 K for 2200 h. At the same temperature and for annealing time beyond 100 h, precipitates and grain coarsening are visible in 2HEA (**Extended Data Fig. 2a-b**). Increasing the alloying content leads to more precipitates, mostly distributed along GBs and triple lines (indicated by red arrows in **Fig. 2c**) in 5HEA and 10HEA (**Extended Data Fig. 2c**) after only 2 h annealing at 973 K.

As the annealing temperature was raised to 1023 K, precipitates were not formed in NC 1HEA (**Extended Data Fig. 1a**), but started to appear in NC 2HEA annealed for 2 h (**Extended Data Fig. 2d**). We note that once precipitates were formed, substantial grain growth subsequently occurred in these NC-Nb alloys, associated with a drop in hardness, as shown in **Extended Data Figs. 2 and 3**. Therefore, the dramatically enhanced thermal stability of 1HEA cannot be attributed to Zener pinning from precipitates on GBs.

To reveal the underlying mechanism enabling the high thermal stability of 1HEA, phase constitution, elemental distribution and atomic structure of the material and particularly of the interfaces were characterized by advanced techniques including synchrotron high-energy X-ray diffraction (XRD), atom probe tomography (APT), energy dispersive spectroscopy (EDS) analysis and aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). As shown in **Fig. 3a**, only diffraction peaks pertaining to a single *bcc* (body-centered cubic) phase are present in the XRD patterns of NC 1HEA alloy before and after annealing at 973 K for 1000 h, revealing that no formation of extra phases or precipitates with a XRD detectable volume fraction. However, for the 10HEA alloy, the XRD pattern shown in **Extended Data Fig. 4a** reveals additional weak peaks identified as B2 in the as-HPT sample, and after 2 h annealing at 973 K, these peaks become more obvious, suggesting that a significant amount of B2 (~10%) has precipitated during annealing, consistent with the TEM observation shown in **Fig. 2**.

Reconstructions of APT datasets obtained around GB regions of the NC 1HEA alloys are shown in **Fig. 3b**. In the as-HPT-processed sample, Ti, Ni and Co are enriched at GBs, with peak concentrations of 0.83, 2.06 and 1.96 at.% respectively. Such nonequilibrium segregation of solute elements on GBs has also been found in electrodeposited binary NC alloys^{33,36-39}. After annealing at 973 K for 1000 and 2200 h, the Hf segregation becomes obvious with the peak concentration increasing to 1.41 and 2.63 at.%, respectively, and the segregation of each element clearly increases at the GB with increasing annealing time at 973 K, as shown in **Fig. 3c**. The peak concentration of Ti, Ni, Co and Hf increases gradually from about 1.60, 2.04, 1.51 and 0.89 at.% in the sample annealed for 2 h, to 1.76, 3.25, 1.89 and 1.49 at.% in the 1000 h annealed sample, and further to 1.98, 4.75, 3.78 and 2.63 at.% in the 2200 h annealed sample, respectively, manifesting a sluggish segregating process and thus contributing to a retarded precipitation process.

For the 10HEA material, annealed at 973 K for 2 h, both EDS analysis and 3D-APT results reveal that numerous precipitates enriched with Ti, Ni, Co and Hf but depleted with Nb were formed (**Extended Data Fig. 4b-c**). Also, the segregation of four elements Ti, Ni, Co and Hf on the GB was observed in the APT reconstruction, with a higher concentration (Ti 1.69 at.%, Ni 1.74 at.%, Co 1.83 at.%, Hf 0.81 at.%), as compared with that found in the 1HEA alloy for the same annealing time and temperature (**Extended Data Fig. 5a**). The XRD and compositional analysis for the second phase precipitate (**Extended Data Fig. 5b**) show that these nanoparticles also have B2 structure, with near equal atomic ratio of Nb, Ti, Ni, Co and Hf. Therefore, a high doping content and very high segregation to GBs is not helpful for controlling grain size when the segregating elements start to decompose and form particles⁴⁰. In other words, co-segregation with a higher entropy on GBs in the dilute limit seems to be more efficient and effective in reducing the GB energy and at the same time reducing the trend for early GB precipitation.

Neither the HAADF-STEM, **Fig. 4a**, nor high-resolution TEM images, **Extended Data Fig. 6**, reveal any noticeable structural change upon annealing, as evidenced by the presence of lattice fringes at the GB highlighted by yellow line. The corresponding EDS maps reveal the enrichment of solute atoms at GBs and provide further evidence of solutes-enriched clusters in the 1HEA alloy annealed at 973 K for 1000 h.

Further in-plane composition analysis of GBs by APT revealed inhomogeneous distribution of the solutes and solutes-enriched clusters in the 1HEA after 1000 h annealing (**Fig. 4b**), which is consistent with the EDS mapping results shown in **Fig. 4a**. The composition of these clusters varies, as illustrated in **Fig. 4c**. As the annealing proceeds, both the number density and size of solute-enriched clusters on the GBs keep increasing with annealing (**Fig. 4d**). The number of solute-enriched clusters seemingly reaches the maximum after annealing for 1300 h. Subsequently, these clusters start to coarsen slowly and reach 5-10 nm when the annealing time approaches 2200 h.

Following the Gibbs' absorption isotherm, both linear and planar defects are thermodynamically susceptible to attract solutes from the grain interior. The amount of segregated atoms gradually increases and linearly reduces the interfacial free energy¹⁴. For yielding a maximum energy reduction effect the segregated atoms should remain in the dilute limit, otherwise the system will be driven out of the solid solution, undergoing for instance spinodal decomposition or particle formation²⁵, resulting in faster grain growth. In 1HEA, during annealing, solutes of Ti, Ni, Co and Hf co-segregate to GBs, and their respective concentrations continuously increase over time, but without formation of any second phases. The synergistic thermodynamic and kinetic effect of multi-elemental co-segregation and the formation of solute-enriched clusters leads to an enhanced thermal stability of GBs in 1HEA.

The segregation of multiple solutes changes the GB state and energy in a specific manner, as the multiple elements at a GB may mutually affect each other, changing the enthalpy of segregation. This means that one solute element can increase the segregation tendency of another, and thus increase the effective enthalpy of segregation, $\Delta H^{seg-eff}$. This phenomenon has been referred to as synergistic co-segregation, and it competes with site competition³⁴. In the current system, Co and Ni form one group of solutes, while Ti and Hf form another, due to their respective similar chemical properties and zero enthalpy of mixing. Thus, 1HEA can be approximated as a pseudo-ternary Nb-(Co, Ni)(Ti, Hf) system. The effective segregation enthalpy of (Ti, Hf) in Nb-(Co, Ni) and (Co, Ni) in Nb-(Ti, Hf) can be calculated as 19.1 and 135.8 kJ/mol, respectively, according to the method proposed by Xing et al⁴¹. The latter value is substantially higher than those of the individual quasi-binary systems (Ti, Hf) in Nb (19.03kJ/mol) and (Co, Ni) in Nb (84.79kJ/mol). This shows that the co-decoration in the current system indeed [introduces a synergistic](#) co-segregation effect, which translates into a corresponding reduction in GB energy.

Moreover, ideally, it is the free energy of segregation ΔG^{seg} that should be computed, $\Delta G^{seg} = \Delta E^{seg} - P\Delta V - T\Delta S_{seg}^{XS}$, where P is the pressure, ΔV is the change in volume and ΔS_{seg}^{XS} is the excess entropy of segregation. In McLean's isotherm with its implicit assumption of ideal mixing and the corresponding entropy contribution, the excess entropy ΔS_{seg}^{XS} and the term $P\Delta V$ are assumed to be negligible, and ΔG^{seg} is thus approximated by the internal energy ΔE^{seg} ⁴². However, the ΔS_{seg}^{XS} values of Ti, Ni, Co, Hf were calculated to be 1.1R,

13.6R, 11.7R and 0.3R (where R is Boltzmann's constant), respectively, as elaborated in the **Extended Data Discussion**⁴³. Therefore, the contribution of ΔS_{seg}^{XS} cannot be neglected in the current case, which would further decrease the free energy of segregation and further stabilize the GBs.

Besides these thermodynamic considerations, the GBs are also kinetically affected, due to the joint solute-drag effect of Ti, Ni, Co and Hf acting on their motion^{26,27}. Depending on the velocity regime, this imposes a linear or non-linear back-driving force²⁸⁻³⁰. The solute-enriched clusters on GBs are also capable of strongly pinning GBs due to the Zener drag effect, preventing their migration and thus hindering grain growth, which is similar to the effect observed for Ta nanoclusters in a binary Cu-Ta NC alloy⁴⁴. Therefore, the occurrence of co-segregation of multiple solutes significantly stabilizes nanograin boundaries through both, thermodynamic and kinetic effects in the 1HEA material. With an excessive addition of solutes, beyond the GB solubility limit, such as e.g. in alloys 2HEA, 5HEA and 10HEA, GB precipitation occurred. This effect limits GB solute segregation, as these GB precipitates absorb the adjacent GB solute content, due to local partitioning, and lead to a reduced GB decoration content⁴⁵. This translates to a lower reduction in GB energy and thus lower GB stability.

Our approach is different from the binary NC alloy such as the 1Ni alloy and the over-doped alloys such as 10 HEA alloy. Although Ni segregation was also observed in the annealed binary 1Ni (**Extended Data Fig. 7**) alloy, the segregation only of Ni without co-segregation and solute-rich clusters on the GBs seems insufficient to effectively suppress GB migration. In the 10HEA alloy, the loss of GB stability is associated with the precipitation of a secondary phase. In contrast, the high stability of the 1HEA alloy originates from the interplay of multicomponent solute segregation and solute clusters. This unique stabilization strategy of an entropy-enhanced massive decoration of GBs is achieved by alloying multiple solute elements with a preference to segregate at GBs and a high tendency for the formation of clusters. **Fig. 5** schematically shows the development of this synergistic co-segregation and of the clusters with annealing. The solute atoms represented by full circles with different colors progressively segregate to GBs (**Fig. 5a-b**), and the segregation degree of multiple solutes increases with annealing, reducing the GB energy thermodynamically. As the annealing time/temperature increases, solutes start to form clusters (**Fig. 5c**). As annealing continues, the clusters become aggregated and coarsened with further reduction of Nb in the clusters (**Fig. 5d**), which stabilizes the GBs both thermodynamically and kinetically, as outlined above.

In conclusion, we transferred some of the ideas from the high-entropy alloying concept from the bulk to the interface, by depositing the alloying elements only to those locations where they are needed, i.e., to the GBs in the current case. The stability of the GBs in such NC solute solution materials was substantially enhanced by equipping the GBs with higher entropy, thus enhancing the effect of solute decoration of interfaces which reduces their energy. By doping the material with several solutes that tend to decorate GBs, not only synergistic GB co-segregation of multicomponent elements was found, but also solute-rich clusters at the GBs were formed. This creates a joint stabilization mechanism which includes

(a) a reduced GB energy from multicomponent co-segregation according to the adsorption isotherm and thus a reduced driving force for grain growth and (b) reduced GB motion from solute drag and Zener drag from the solute-rich clusters. This novel multicomponent GB design strategy is not limited to Nb-based NC alloys, but it is also applicable to a wide range of other metallic alloys.

Methods

1. Materials.

Ingots of six Nb-(TiNiCoHf) alloys, i.e. unalloyed Nb, Nb₉₉(TiNiCoHf)₁, Nb₉₈(TiNiCoHf)₂, Nb₉₅(TiNiCoHf)₅, Nb₉₀(TiNiCoHf)₁₀ and one binary Nb₉₉Ni₁ alloy were synthesized by arc-melting a mixture of constituent ingredients with a purity above 99.9 % in a Ti-gettered high-purity argon atmosphere. All cast ingots were re-melted at least six times, to ensure chemical homogeneity of the blocks. Afterwards the materials were subjected to high-pressure torsion (HPT) for grain refinement. For the HPT process, disks with a diameter of 10 mm and an initial thickness of 0.8 mm were cut directly from the ingots and then polished. The HPT process was conducted at room temperature at a nominal pressure of 6 GPa and a rotational rate of 1 rotation per minute for altogether 5 rotations under quasi-constrained conditions⁴⁶.

2. Thermal annealing treatment.

It is reported that the microhardness in the HPT-processed pure Nb, exposed to 6 GPa for 5 rotations, begins to saturate at a radius of about 1.5 mm from the center and extends towards the outer rim of the HPT disk, due to microstructural inhomogeneity⁴⁷. In the current study specimens for heat treatment were taken from the same radial location across the HPT disks of above 1.5 mm from the center.

a) Isochronal annealing. The HPT-processed NC pure Nb, 1HEA, 2HEA, 5HEA, 10HEA and binary 1Ni samples were placed into a vacuum quartz tube and then annealed at temperatures of 673, 773, 873, 973, 1023, 1073, 1123 and 1173 K for 2 h, respectively. The NC 10HEA sample was additionally further annealed at 1273 K for 2 h, to study the material's grain growth response.

b) Isothermal annealing. The HPT-processed NC unalloyed Nb samples were placed into a vacuum quartz tube and then annealed at 973 K for 2, 10, 40 and 100 h, respectively. The binary NC 1Ni samples were isothermal annealed at 973 K for 2 and 100 h and the NC 1HEA, 2HEA, 5HEA and 10HEA samples were annealed at this temperature for 2 and 100 h and even longer time to 600 and 1000 h. Specifically, the NC 1HEA, and 10HEA alloys were annealed at 973 K for 10, 20 and 40 h. The NC 1HEA was also annealed at 973 K for longer time for 1300 and 2200 h. In addition, the NC 1HEA samples were also isothermal annealed at higher temperature of 1023 K for 100h.

3. Nano-hardness measurement

Nano-hardness tests of samples before and after annealing were performed using a MTS DCM nanoindentation system equipped with a triangular-pyramid indenter. Experiments were conducted at a

constant strain rate of 0.05 s^{-1} to a total indentation depth of 2000 nm. Nano-hardness values were averaged with at least 5 indentations. The spacing between two neighboring indents was above 50 μm to avoid any overlapping effect.

4. Microstructural characterization and grain boundary structure

Structural characterization was conducted using synchrotron XRD probing on the 11-ID-C beam line of the Advanced Photo Source at Argonne National Laboratory, USA. The wavelength of the X-ray was 0.1173 Å. Microstructure and morphology were characterized by a Zeiss Supra 55 field emission scanning electron microscope which was equipped with a backscatter electron (BSE) detector and an AZtecHKL electron back-scatter diffraction analysis system. The scanning electron microscope specimens were polished with 5000-grit SiC paper. Subsequently they were mechanically polished using 0.04 μm silica suspensions. The electron back-scattering diffraction specimens were initially polished with 2,000-grit SiC paper and subsequently electrochemically polished using 12 g anhydrous magnesium perchlorate per 100 ml methanol at a direct voltage of 60-70 V at 228-243 K. Bright-field images were taken in the Tecnai F30 transmission electron microscope (TEM) operated at 300 kV, as well as high-resolution TEM images. STEM-HAADF images were taken in an aberration-corrected JEOL-ARM200F TEM operated at 200 kV and a FEI Titan G260-300kV S/TEM equipped with an aberration corrector. Energy-dispersive spectroscopy (EDS) was used to construct the elemental map. The TEM specimens were prepared using a focused ion beam (FIB, FEI Helios Nanolab 600i). Both SEM and TEM were used to photograph grains. The average grain size was calculated using Image J software. The distribution of GB planes was computed by the collected EBSD mapping data.

5. Grain boundary segregation and composition analysis

Atom probe tomography (APT) was employed to investigate the distribution of elements in the HPT-processed and annealed samples, placing attention on the GB decoration. Specimens with a sharp tip of about 50-60 nm for APT probing were fabricated by focused-ion-beam (FIB) milling using a FEI Helios Nanolab 600i instrument. APT experiments were then performed on a Cameca LEAP 5000XR local electrode instrument with magnetically enhanced flight path for highest mass-to-charge resolution at a specimen temperature of 70 K, under pulsing UV laser exposure using a laser energy of 80 pJ. The pulse repetition rate was 200 kHz at an ion collection rate of 3 ions per 1000 laser pulses. APT data three-dimensional (3D) atomic reconstruction and quantitative analysis were carried out using the CAMECA IVAS version 3.8.2 software.

Declarations

Extended Data

Extended Data is available Online.

Acknowledgements

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Author contributions

Z. Lu and Y. Wu designed the study. Y. Yuan, H Wu, H. Wang, X Liu, S Jiang and Z Yang carried out the main experiment. Y. Yuan, Y. Wu, Z. Lu and D. Raabe analysed the data and wrote the main draft of the paper. X. Yuan conducted the 3D-APT characterization. L. Gu and Q. Zhang conducted the TEM characterization. All authors contributed to the discussion of the results, and commented on the manuscript.

Data availability

The data that support the findings of this study are available from the corresponding authors on reasonable request.

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Figures

Figure 1

Thermal stability. (a) Variation of average grain size and nanohardness of the NC 1HEA, 10HEA, and binary 1Ni alloys and the unalloyed Nb reference material as a function of annealing temperature for a fixed annealing time of 2 h. (b) Average grain sizes and nanohardness of the NC 1HEA, 10HEA, 1Ni and unalloyed Nb samples annealed at 973 K as a function of annealing duration. Only a subtle change was observed in the NC 1HEA even after long-term annealing of 2200 h at 973 K and after 2 h annealing at 1023 K, demonstrating the high thermal stability of this specific NC alloy. (c) The average grain growth rate, i.e. the grain size increment induced by annealing time ($\Delta d / \Delta t$) on a logarithmic scale with different alloying additions for the alloyed NC Nb alloys, in comparison with other nano-grained materials at the temperature range of $\sim 0.3-0.4 T_m$ (T_m : melting point). The error bars are 95% confidence interval of the mean.

Figure 2

Pre- and post-annealing structures. (a) TEM image of the 1Ni alloy after HPT and backscattering SEM images of the NC 1Ni alloy after annealing at 973 K for 2 and 100 h. (b) TEM image of the 1HEA after HPT and annealing at 973K for 1000 and 2200 h. (c) show TEM image of the 10HEA after HPT and annealing at 973K for 2 and 1000 h. The insets in (c) are the corresponding backscattering SEM images. Substantial grain growth occurred in the annealed NC 1Ni while massive precipitation was observed in

the 10HEA, together with obvious grain growth in the sample annealed for 1000 h. Notably, a retained NC structure with no precipitates in the annealed NC 1HEA was observed even after 2200 h annealing.

Figure 3

Synchrotron XRD patterns and APT analysis of the NC 1HEA before and after annealing at 973 K for different time durations. (a) Synchrotron XRD patterns of the HPT-processed and the annealed 1HEA. (b) 3D-APT reconstructions of the 1HEA alloy annealed at 973 K for 2, 1000 and 2200 h. (c) 1D compositional profiles with increasing annealing time along the cylinders perpendicular to the grain boundary.

Figure 4

Annealing-induced GB clustering in the NC 1HEA alloy annealed at 973 K. (a-c) Microstructure characterization of the NC 1HEA alloy after annealing at 973 K for 1000 h: (a) HAADF-STEM image and the corresponding EDS maps showing the atomic structure and the compositional distribution of GBs; (b) Distribution of Ti, Ni, Co and Hf solute atoms within the GB plane and 2D in-plane compositional analysis of the identical sample in **Fig. 3**. The threshold of the iso-composition surface for GB identification is 1.2 at.% Ni, encompassing regions of the entire GB. The image in the lower left corner shows a close-up of one solute-enriched cluster circled by red line within the GB and (c) 4 at.% Hf iso-composition surfaces with Co and Hf atoms in the reconstruction and the corresponding 1D compositional profiles of two solute-enriched clusters along the direction indicated by the pink cylinder and green arrow. (d) Evolution of solute distribution within the GB plane with increasing annealing time.

Figure 5

Schematic diagram illustrating stabilization strategy of entropy-induced heterogeneity in a NC metal. The atoms in the centers of the crystals are indicated by open circles. The atoms in the GB regions are represented as full circles with different colors, respectively. The clusters are circled by black lines.

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