

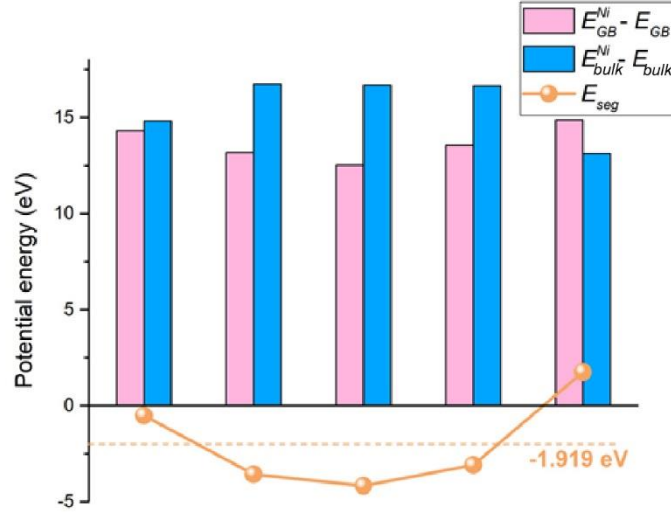
Supplementary Information for

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

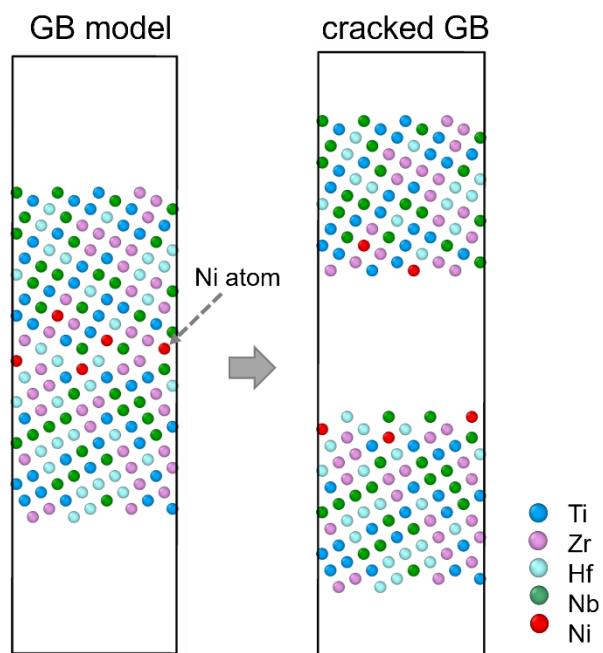
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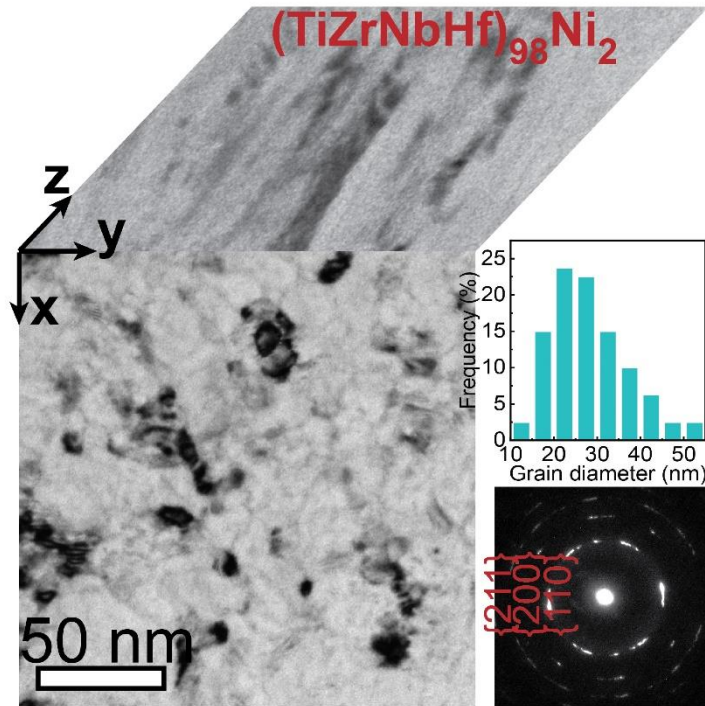
Supplementary Figure 1. Density-functional-theory (DFT)-calculated segregation energy $E_{seg} = (E_{GB}^{Ni} - E_{GB}) - (E_{bulk}^{Ni} - E_{bulk})$ (according to Eq (1) in Methods) for five independent configurations. E_{GB}^{Ni} and E_{GB} are the total energies of the simulated grain boundary (GB) 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.



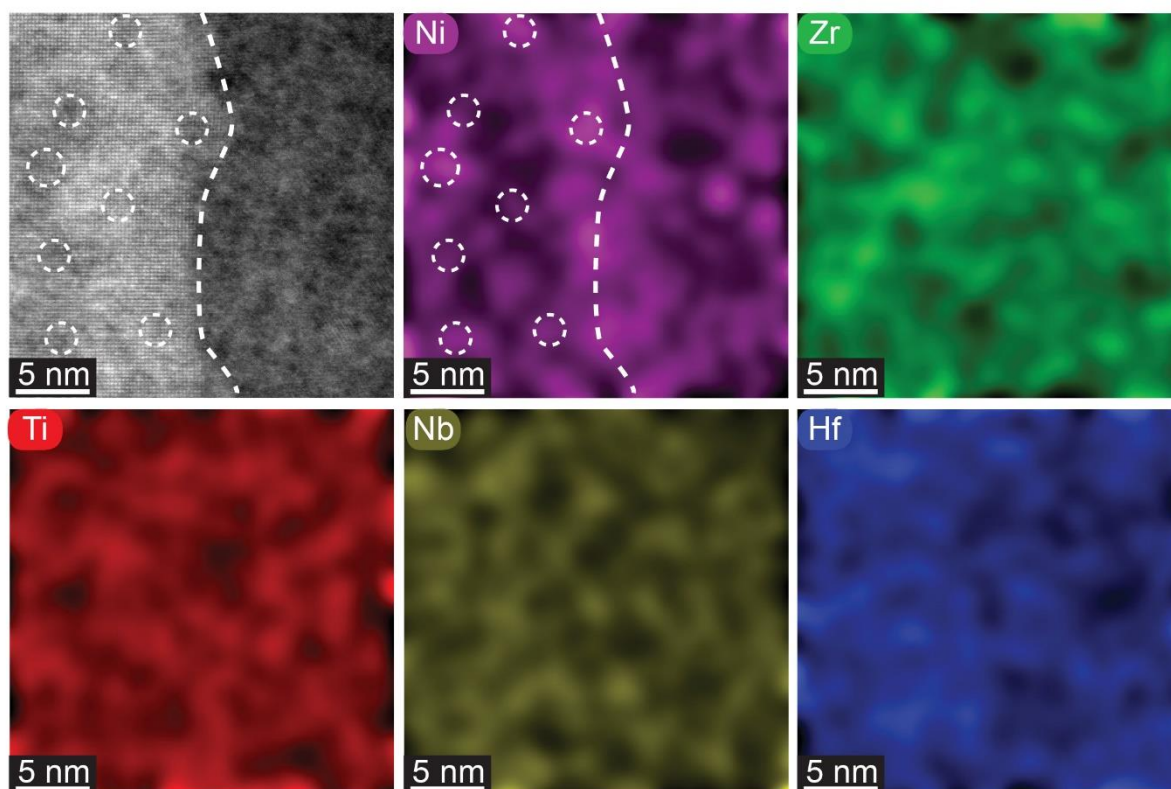
Supplementary Figure 2. DFT calculation of GBs of Ni-TiZrNbHf alloy. Schematic description of simulated structure of a typical grain boundary of Ni-segregated TiZrNbHf alloys before and after decohesion.



Supplementary Figure 3. Structure of the TiZrNbHf base alloy. Typical side-view transmission electron microscope (TEM) image, showing ~100 nm diameter columnar grains. The inset is the corresponding selected-area electron diffraction (SAED) pattern.

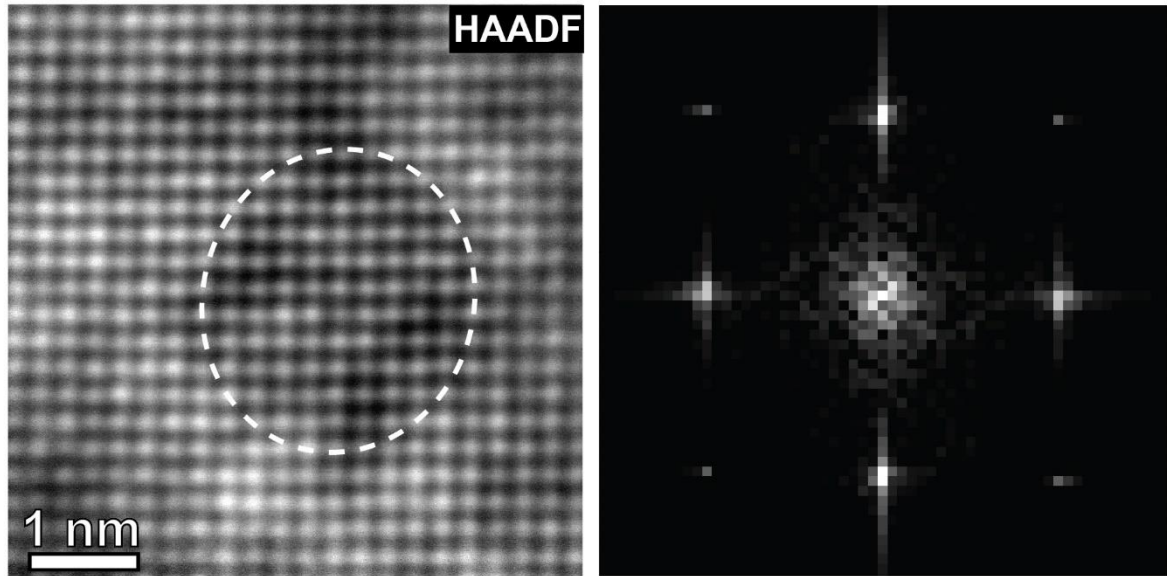


Supplementary Figure 4. Typical bright-field plane-view and side-view TEM images of the $(\text{TiZrNbHf})_{98}\text{Ni}_2$ alloy. The x-y plane denotes plane-view probing, and the z axis indicates the growth direction of the material. The top-right inset presents the frequency distribution of the columnar grain diameter. The bottom-right inset is the SAED pattern, revealing a single-phase bcc structure.

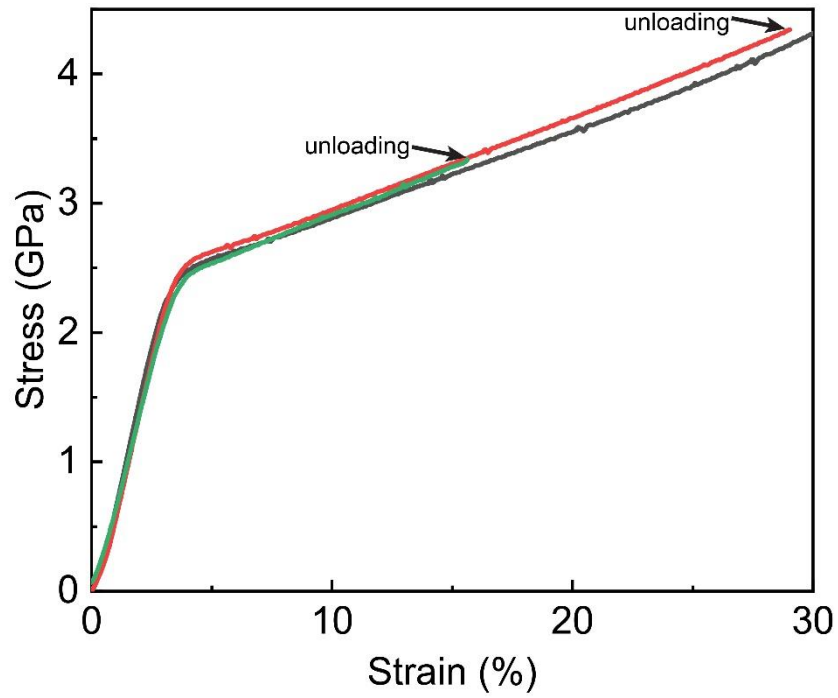


Supplementary Figure 5. STEM imaging and EDS mapping of the $(\text{TiZrNbHf})_{98}\text{Ni}_2$ alloy.

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.

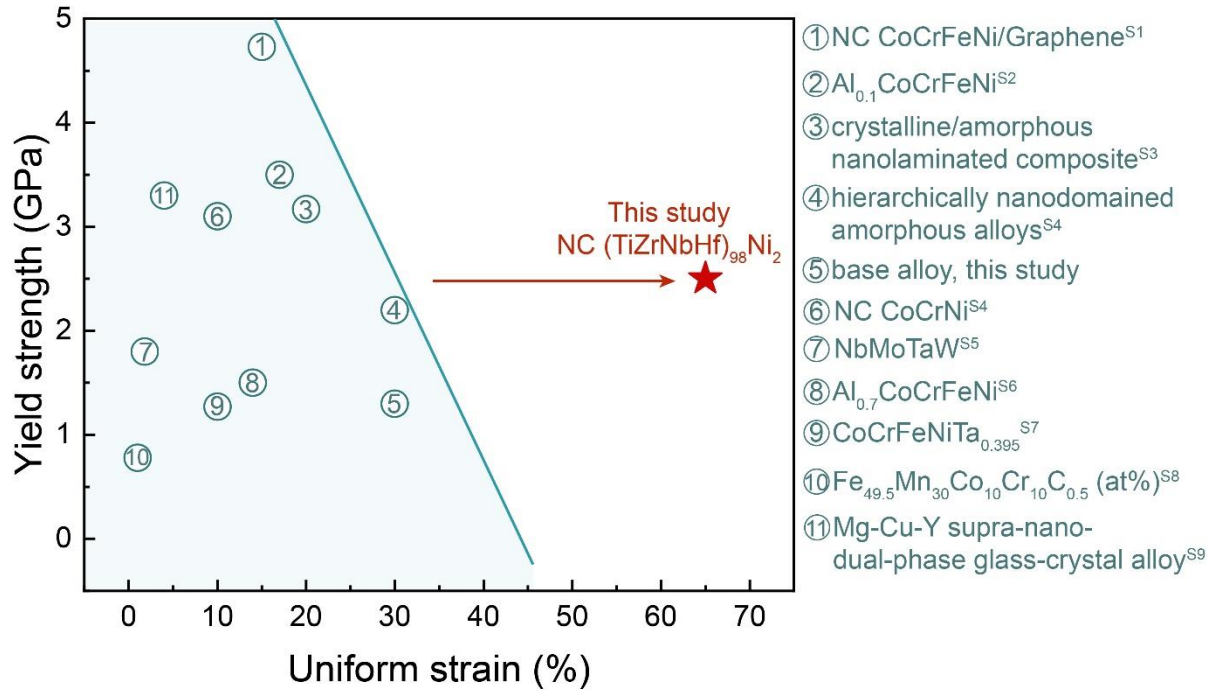


Supplementary Figure 6. HAADF-STEM image (a) and the corresponding fast Fourier transformation (FFT) pattern (b) of the $(\text{TiZrNbHf})_{98}\text{Ni}_2$ alloy. a, The STEM image shows that the ~ 3 -nm-sized cluster in the nanograin is coherent with the matrix. The white dashed curve highlights the cluster. **b,** FFT pattern suggests that the alloy adopts a single-phase bcc structure.

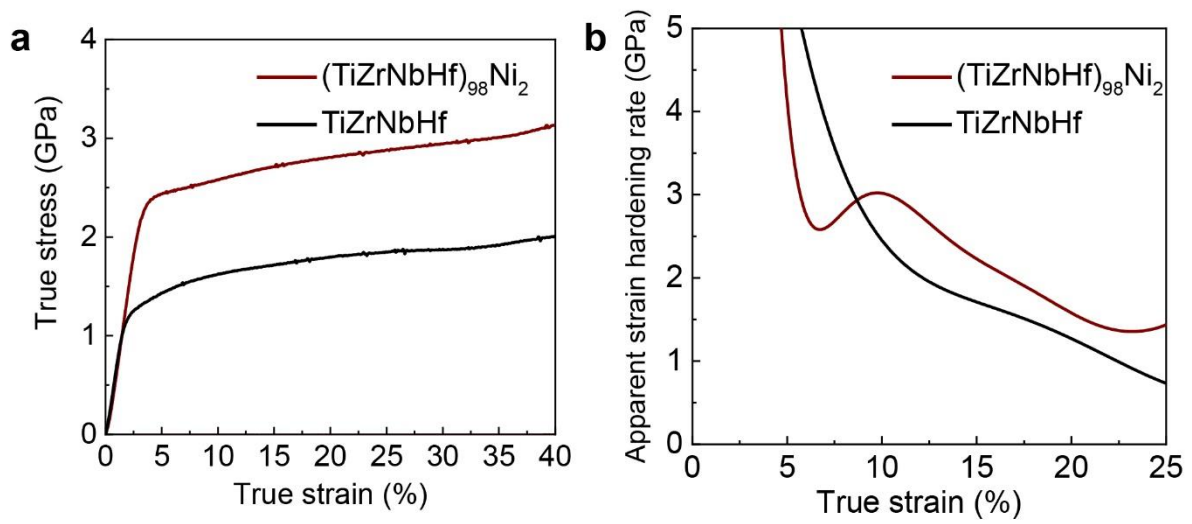


Supplementary Figure 7. Stress-strain curves of the $(\text{TiZrNbHf})_{98}\text{Ni}_2$ alloy measured in micro-pillar compression, demonstrating the repeatability of the measured properties.

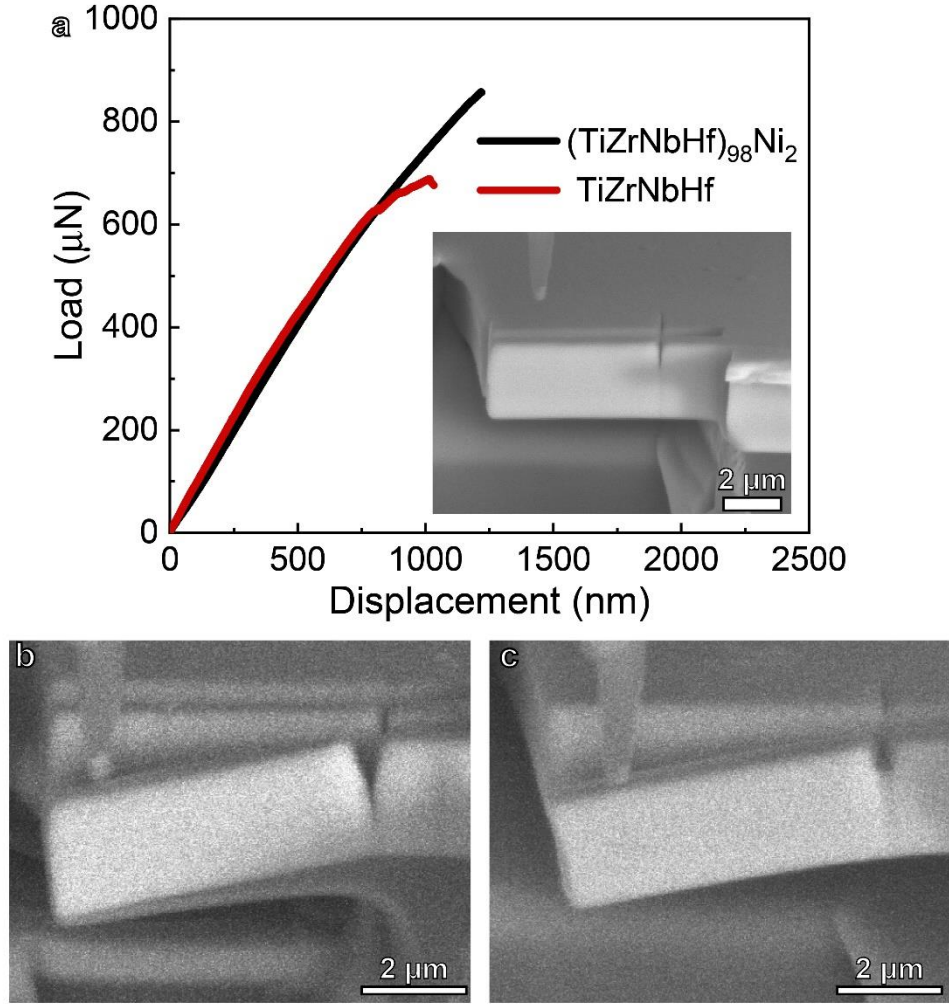
Source data are provided.



Supplementary Figure 8. Yield strength vs. uniform strain of the (TiZrNbHf)₉₈Ni₂ alloy, in comparison with other HEAs¹⁻⁸ and a supra-nano-dual-phase glass-crystal alloy⁹ tested in micropillar compression at ambient temperature. Source data are provided.

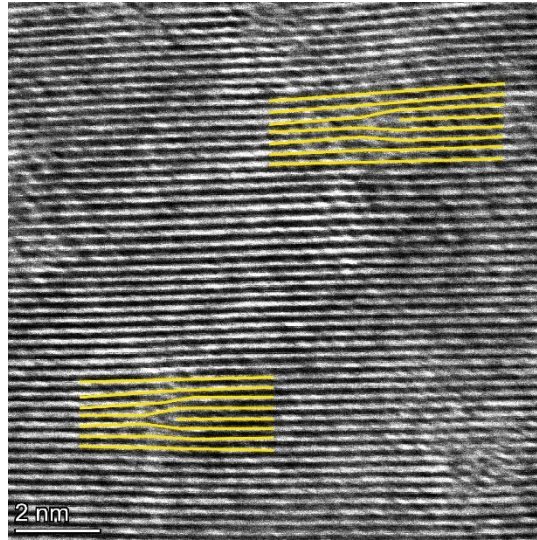


Supplementary Figure 9. True stress versus true strain curves (a) and apparent strain hardening rate (b) of the $(\text{TiZrNbHf})_{98}\text{Ni}_2$ and TiZrNbHf alloys. Source data are provided.

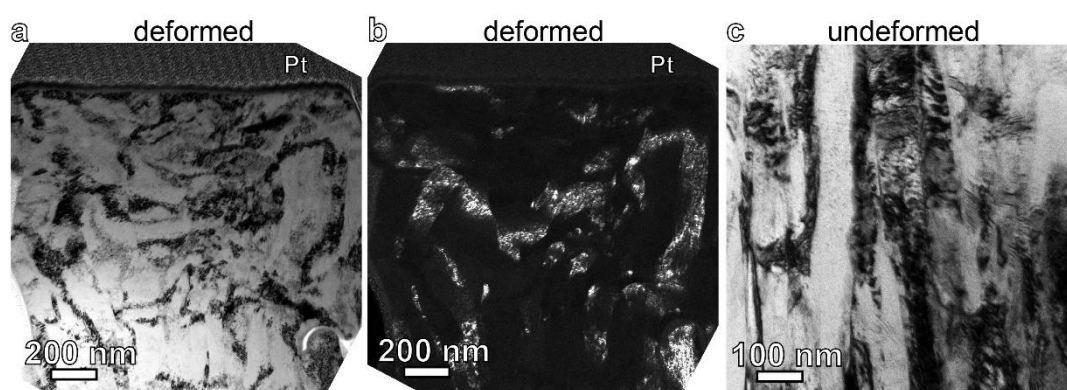


Supplementary Figure 10. Fracture toughness of the NC $(\text{TiZrNbHf})_{98}\text{Ni}_2$ and TiZrNbHf alloys. (a) Load-displacement curves of the pre-notched microcantilevers prepared in the $(\text{TiZrNbHf})_{98}\text{Ni}_2$ and TiZrNbHf alloys. The inset shows a notched $(\text{TiZrNbHf})_{98}\text{Ni}_2$ microcantilever. (b, c) Snapshot SEM images of TiZrNbHf (b) and $(\text{TiZrNbHf})_{98}\text{Ni}_2$ (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 $(\text{TiZrNbHf})_{98}\text{Ni}_2$ 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 applicable¹⁰. The NC $(\text{TiZrNbHf})_{98}\text{Ni}_2$ alloy requires a higher load for crack initiation, showing a maximum

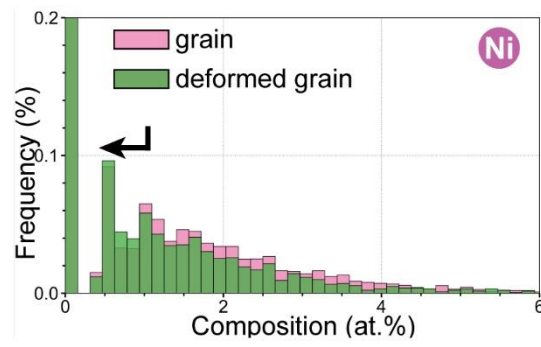
load of 857 μN . The fracture toughness is calculated using the equation described in Methods. The NC TiZrNbHf and (TiZrNbHf)₉₈Ni₂ alloy has a fracture toughness of 4.3 $\text{MPa}\cdot\text{m}^{1/2}$ and 6.0 $\text{MPa}\cdot\text{m}^{1/2}$, respectively. Source data are provided.



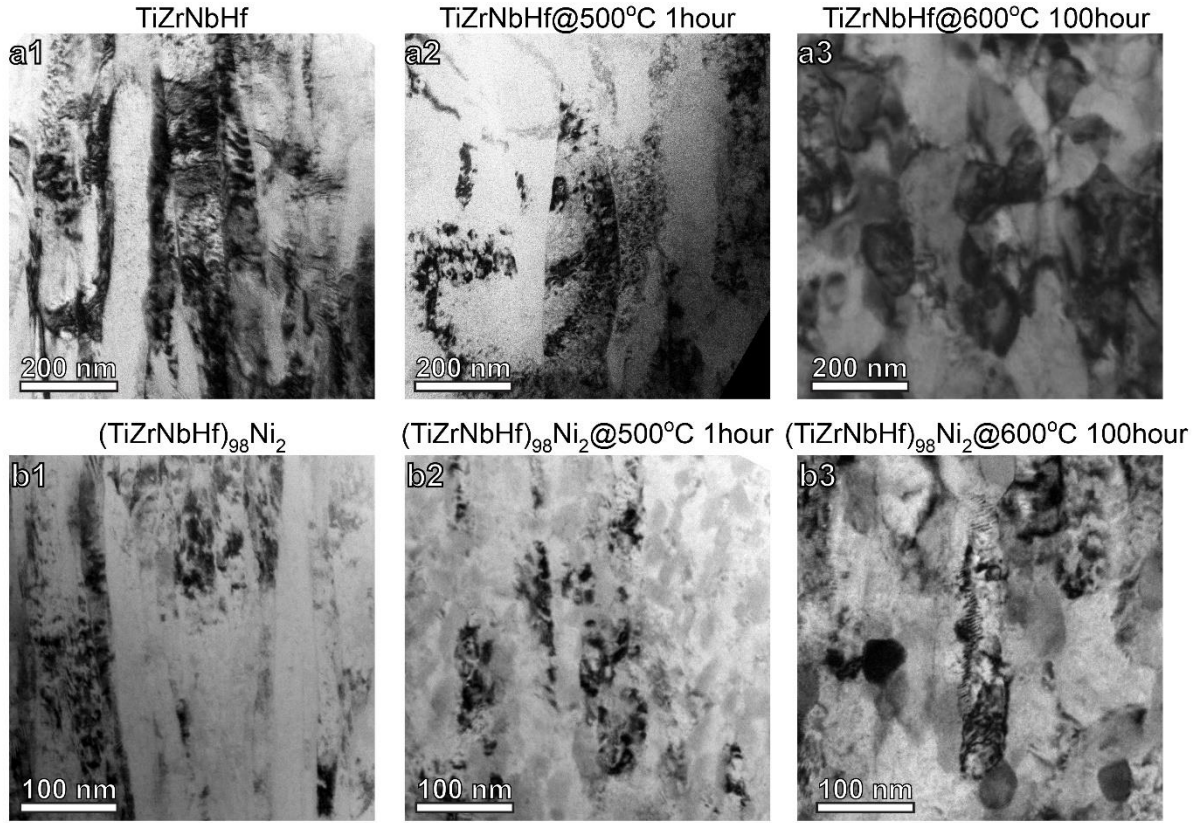
Supplementary Figure 11. BF-STEM image of the deformed (TiZrNbHf)₉₈Ni₂. This is the same region as that for HAADF-STEM imaging in Fig. 4b2. Edge dislocations are highlighted using yellow lines.



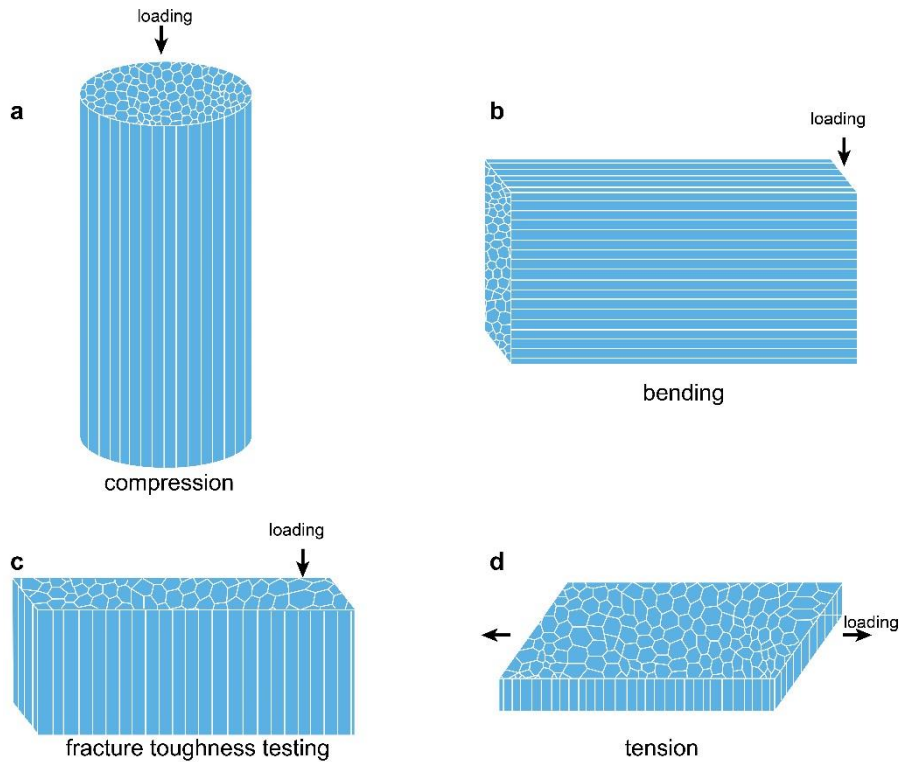
Supplementary Figure 12. Structure of the TiZrNbHf nanocrystalline alloy after compression. Bright-field (a) and dark-field (b) TEM image of the deformed pillar. c, TEM image of the undeformed alloy (for comparison).



Supplementary Figure 13. Statistical concentration histograms of Ni obtained from the APT dataset. The distributions of Ni in the ‘deformed grain’ shift to left compared with that in the original grain.



Supplementary Figure 14. 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.



Supplementary Figure 15. 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.

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