

Ideal maximum strengths and defect-induced softening in nanocrystalline-nanotwinned metals

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Strengthening of metals through nanoscale grain boundaries and coherent twin boundaries is manifested by a maximum strength—a phenomenon known as Hall–Petch breakdown. Different softening mechanisms are considered to occur for nanocrystalline and nanotwinned materials. Here, we report nanocrystalline-nanotwinned Ag materials that exhibit two strength transitions dissimilar from the above mechanisms. Atomistic simulations show three distinct strength regions as twin spacing decreases, delineated by positive Hall–Petch strengthening to grain-boundary-dictated (near-zero Hall–Petch slope) mechanisms and to softening (negative Hall–Petch slope) induced by twin-boundary defects. An ideal maximum strength is reached for a range of twin spacings below 7 nm. We synthesized nanocrystalline-nanotwinned Ag with hardness 3.05 GPa—42% higher than the current record, by segregating trace concentrations of Cu impurity (<1.0 weight (wt)%). The microalloy retains excellent electrical conductivity and remains stable up to 653 K; 215 K better than for pure nanotwinned Ag. This breaks the existing trade-off between strength and electrical conductivity, and demonstrates the potential for creating interface-dominated materials with unprecedented mechanical and physical properties.

Although the mechanisms underpinning Hall–Petch hardening and softening in nanocrystalline (NC) and nanotwinned (NT) materials have been investigated separately for several decades^{1–13}, an interesting scenario may arise when a metal is strengthened by both grain boundaries (GBs) and twin boundaries (TBs); that is, in a new class of NC and NT materials (we term them nanocrystalline-nanotwinned materials (NNTs) from here on). The existing theories suggest drastically different Hall–Petch breakdown mechanisms in these two types of material; that is, the former is caused by GB sliding³ and the latter by dislocation-nucleation governed plasticity⁶. To date, the atomic softening mechanisms have been garnered by molecular dynamics (MD) simulations of materials containing nanosized grains (≤ 70 nm)^{2,3,6–9}. It has been a longstanding challenge to experimentally verify or disapprove these mechanisms due to the technological difficulty of synthesizing nanostructured materials with microstructures that are as ideal and infinitesimal as those used in these models. For pure NT metals, the grain sizes (d) of as-synthesized materials are typically larger than 100 nm (refs. ^{5,14,15}), precluding experimental investigations of the truly NC region. It thus remains scientifically significant to experimentally interrogate the strength behaviour in NT materials with d well below 100 nm, where GBs and TBs could become competing mechanisms. In essence, the strengthening and softening behaviour in NNT metals is largely unknown at present.

We choose silver (Ag) as a model material system to investigate the Hall–Petch strengthening and softening in NNT-materials. Ag is a low stacking-fault energy metal (~ 16 mJ m^{−2})¹⁶ and known to form copious growth nanotwins during magnetron sputtering processes^{17,18}. However, the smallest d achieved using this method is ~ 150 nm (ref. ¹⁸); that is, outside the NC region. Heavily alloying

is a common strategy to reducing d but inevitably complicates the fundamental mechanism studies due to the hardening effects of solutes¹⁹, or a change of stacking-fault energies in Ag caused by alloying that alters deformation mechanisms. For these reasons, we developed a microalloying (or doping) strategy by carefully selecting Cu as the primary impurity—a solute that is predicted by our own simulations to have no solid-solution strengthening effect in Ag when its content is below 3.0 wt% (Supplementary Information and Supplementary Fig. 1). Neither will Cu affect the stacking-fault energy of Ag at a concentration <1.0 wt%. Moreover, Cu atoms are $\sim 12\%$ smaller than Ag ones, and Ag–Cu is an immiscible system, which facilitates the segregation of Cu into high-energy interface sites such as GB and TB defects¹⁵. We have successfully fabricated a series of Cu- and Al-microalloyed (<1.0 wt%) NNT-Ag samples (Supplementary Table 1). The strongest material has an average d of 49 ± 15 nm and twin spacing $\lambda = 3.6 \pm 1.5$ nm. We find that these materials retain a continuous Hall–Petch strengthening behaviour down to the smallest twin size, which markedly differs from the projected Hall–Petch breakdown from ref. ⁶. We performed atomic simulations with comparable d value to experiments and varying λ . In contrast to popular belief, three Hall–Petch strengthening and softening regions are uncovered. We observe that the softening behaviour is fundamentally different between ‘ideal’ materials with perfect TBs and ‘real world’ materials that contain TB defects. A strength plateau region is observed for pure NT-Ag and Al-microalloyed NNT-Ag, which qualitatively agrees with our simulation predictions.

Atomistic simulation of selective impurity segregation

Large-scale hybrid Monte Carlo (MC) and MD simulations involving a total of 2.3 billion atoms were used to study ten λ

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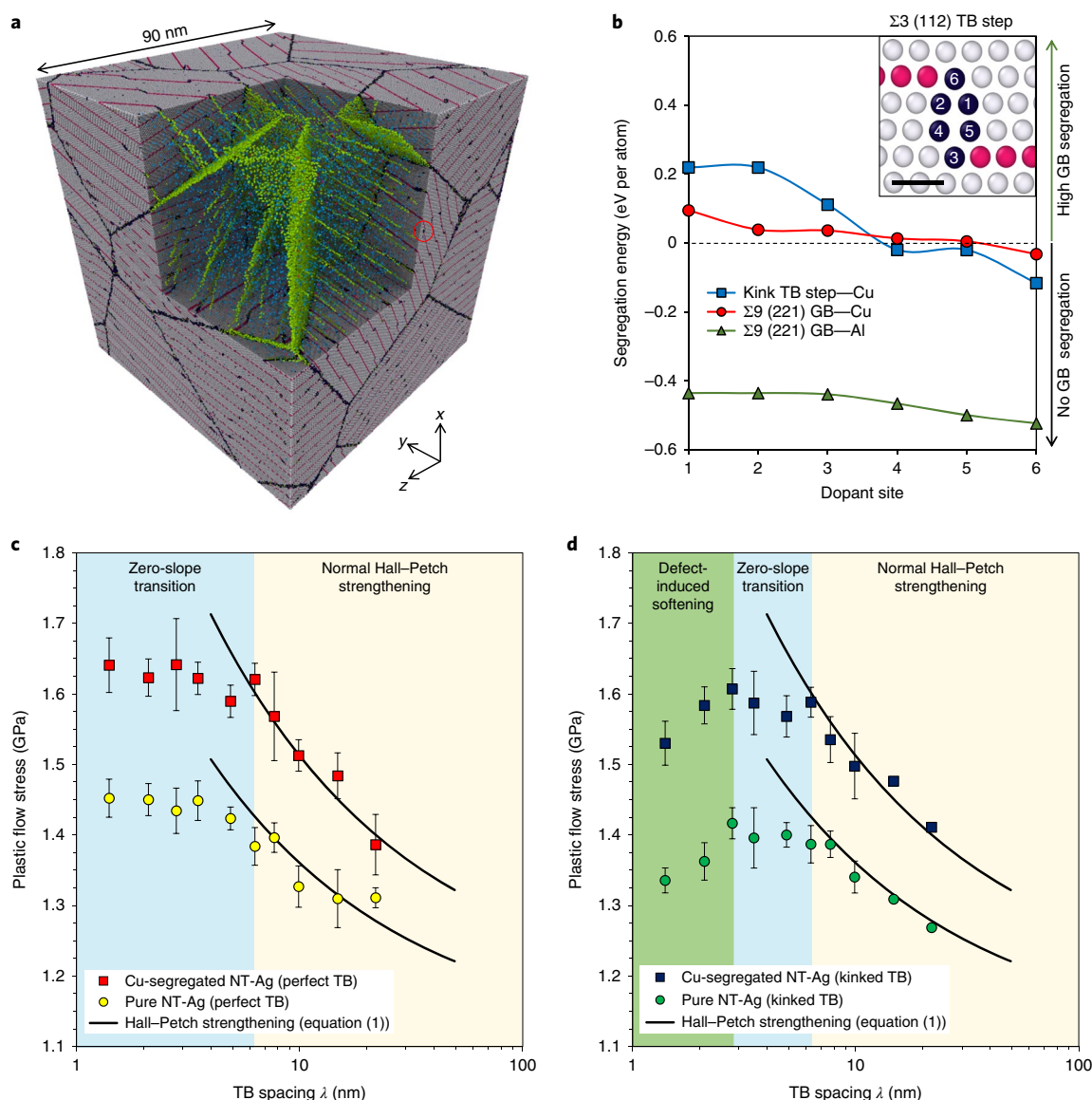


Fig. 1 | Hall-Petch strength transition zones in pure and impurity-segregated nanotwinned Ag metals containing either perfect or kinked TBs obtained by large-scale atomistic simulations. **a**, Snapshot of hybrid MC and MD simulation of microstructure relaxation and equilibrium impurity segregation after 500 K annealing in NT-Ag with a target concentration of 0.47 wt% Cu, $\lambda = 3.5$ nm and $d = 45$ nm. First, common neighbour analysis is performed to differentiate atoms from coherent TBs (magenta colour), incoherent interface defects (dark purple) and face-centred cubic atoms (light grey). Second, Ag atoms are removed from one of the corner regions to highlight its Cu-impurity distribution. In this region, Cu atoms are coloured in green, dark purple and blue when found at incoherent interfaces, coherent TBs and face-centred cubic lattice, respectively. The red circle highlights an internal TB kink-step defect added to the atomistic model. **b**, First-principles density-functional theory calculations of the six highest substitutional segregation energies at different local sites of a TB kink step and a high-energy $\Sigma 9$ (221) tilt grain boundary, respectively. Sites 1–6 of the kink defect are indicated in the inset. Scale bar is 0.5 nm. **c,d**, Hall-Petch flow strength plots for pure and Cu-segregated NT-Ag with perfect coherent TBs (**c**) and kinked TBs (**d**), as a function of λ . All error bars include flow stress predictions between 5 and 7% strain.

values from 1.4 to 21.9 nm, with either kinked (that is, defective) or perfect coherent TBs (Methods). The d in our NT-Ag models is fixed at 45 nm (that is, like the experiments), corresponding to a GB atom fraction of 3%. Twin-free NC-Ag is also simulated as a comparison, since this material has never been studied before. Figure 1a displays a simulated NT-Ag microstructure containing equally spaced nanotwins of size $\lambda = 3.5$ nm, and the equilibrium impurity distribution of 0.47 wt% Cu atoms after 500 K annealed conditions. It indicates that under equilibrium conditions most Cu atoms are preferentially segregated into GBs and TB kink-step defects, see the inset of Fig. 1b. This is consistent with our ab initio

density-functional theory calculations finding largely positive segregation enthalpies for Cu at several atomic sites of a (112) TB kink step and a high-energy $\Sigma 9$ (221) symmetric tilt GB in Ag, compared to the negative energies of an element presenting no GB segregation such as Al (Fig. 1b). These calculations predict a maximum Cu segregation enthalpy in TB defects twice as large that in GBs. Selective Cu segregation gives rise to marked strengthening effects in NT-Ag materials²⁰. From our MC/MD simulations, it is evident that, by segregating a small amount of Cu atoms, GBs and TB defects are firmly pinned down during plastic deformation (Supplementary Fig. 2), while yield stresses at the initiation of GB sliding and

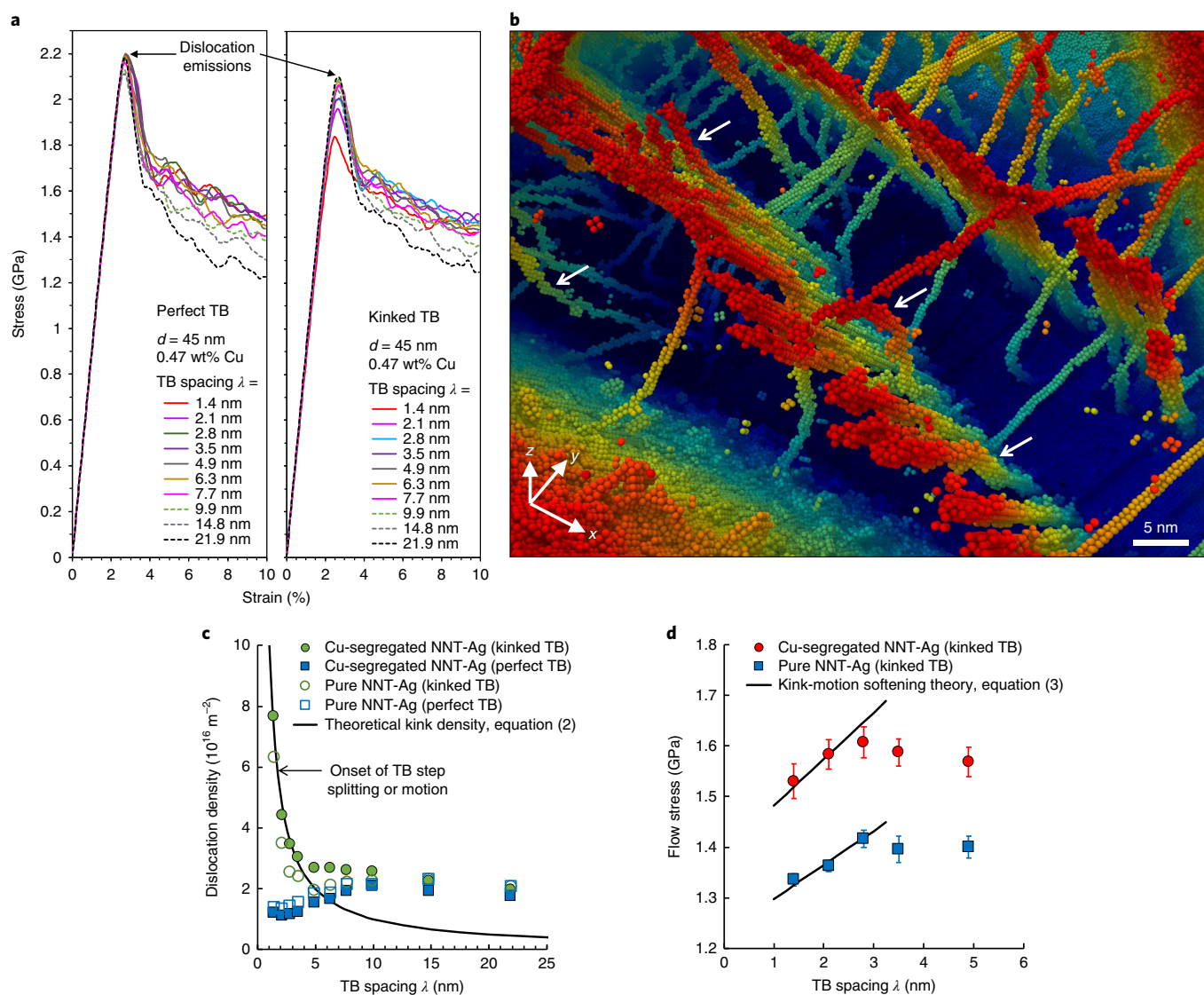


Fig. 2 | Twin-boundary defect-motion softening mechanism (negative Hall-Petch slope). **a**, Simulated stress-strain curves for different twin spacings λ for both kinked and perfect TBs in Cu-segregated NNT-Ag, 0.47 wt% Cu and $d = 45$ nm. The onset of dislocation-nucleation mechanisms is shown by an arrow at the peak of stress. **b**, Atomistic deformation snapshot at 7% strain inside a grain containing kinked TBs when $\lambda = 1.4$ nm. All face-centred cubic atoms have been removed for clarity. The arrows indicate partial dislocations from splitting or motion of TB kink steps that are responsible for the softening behaviour. **c**, Density of Shockley partial dislocations at 5% applied strain, as a function of λ . The solid line represents a theoretical estimate of the initial kink density from equation (2), showing that the dislocation density is dominated by kink motion when $\lambda < 3.5$ nm. **d**, Comparison of plastic flow stresses predicted by MD and theoretical model for kink-motion softening, equation (3). All error bars include flow stress predictions between 5 and 7% strain.

GB-nucleated dislocations rise dramatically (Supplementary Fig. 3). Dislocation-nucleation mechanisms occur at higher stresses, because solute segregation to GBs significantly reduces the excess GB free volume^{21,22} (Supplementary Fig. 4). Furthermore, steady plastic flow is established by applying more than 4% strain. In this state, the average flow strength increases with impurity addition, with a maximum reached at only 0.12 and 0.47 wt% Cu in twin-free NC-Ag and NNT-Ag materials, respectively (Supplementary Fig. 3c). This impurity-segregated strengthening is well beyond the hardening normally expected from solid-solution strengthening based on the Fleischer model or the solute pinning model proposed for heavily alloyed NC metals^{23,24} (Supplementary Discussion 1). In fact, our atomistic simulations suggest that solid-solution strengthening is totally absent in this material with random Cu distributions up to 3.0 wt% (Supplementary Fig. 1a).

Hall-Petch strengthening and softening mechanisms

The above simulation results demonstrate that selective impurity segregation provides a means for probing the Hall-Petch limit and associated softening mechanisms currently unknown in NNT metals. Figure 1c,d exhibits the Hall-Petch plots of flow strength (that is, the average stress from 5 to 7% applied strain) as a function of λ , simulated for pure and Cu-segregated NNT-Ag metals with either perfect or kinked TBs, respectively. For the Cu-segregated models, the impurity concentration is fixed at 0.47 wt% Cu. A normal Hall-Petch strengthening region is observed for $\lambda \geq 6.3$ nm, which is determined from the relationship

$$\sigma_{\text{flow}} = \sigma_0 + \frac{K_{\text{GB}}}{\sqrt{d}} + \frac{K_{\text{TB}}}{\sqrt{\lambda}} \quad (1)$$

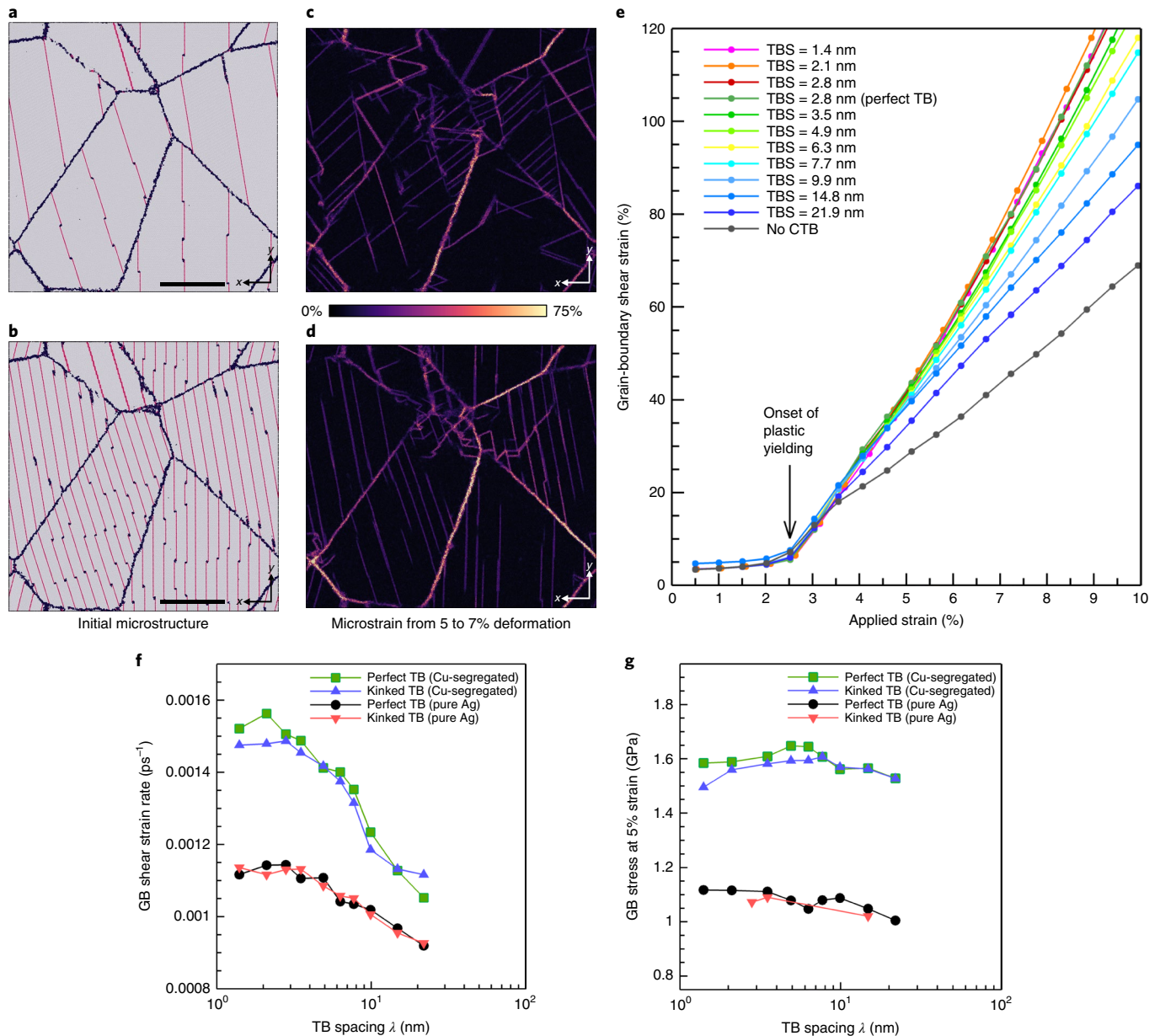


Fig. 3 | Transition from positive Hall-Petch strengthening to GB stress-controlled (near-zero Hall-Petch slope) mechanisms. a–d, MD snapshots of the initial microstructure before deformation (**a,b**) and of local von-Mises shear strain accumulated from 5 to 7% applied strains (**c,d**) in Cu-segregated NT-Ag with $\lambda = 14.8$ and 3.5 nm, respectively. The GB-mediated plasticity by sliding increases as λ decreases. Scale bars: **a**, 50 nm; **b**, 10 nm and inset, 5 nm. **e**, Average shear strain per GB atom as a function of applied strain. Strong dependence on λ is only seen with the plastic flow regime, but not at yielding. **f**, The average shear-strain rate per GB atom increases substantially as both λ and impurity segregation increase, but also reach a plateau below a critical twin spacing transition. **g**, Average atomic tensile stress σ_{xx} per GB atom at 5% applied strain in pure and Cu-segregated NT-Ag, showing significantly higher GB stresses with Cu-impurity segregation.

where σ_0 , K_{GB} and K_{TB} are material-dependent constants (Supplementary Discussion 2). As the Hall–Petch plots are similar for materials with kinked and perfect TBs, the TB defects appear to have no impact for the most part. At $d = 45$ nm, emission of extended Shockley partial dislocations, rather than GB sliding, is predicted to dominate the plastic deformation of NC-Ag (Supplementary Video 1). TBs actively strengthen this material by promoting hard slip mechanisms at dislocation–TB intersections, which is accompanied by non-Shockley sessile dislocations forming progressively as the λ decreases (Supplementary Fig. 5 and Supplementary Video 2). The existing understanding in pure NT-Cu⁶ is that the softening is associated with twinning partial dislocations nucleating from

GB–TB junctions and propagating freely inside TBs, leading to a negative Hall–Petch slope as the junction density increases.

However, the strengths of both pure and Cu-segregated NT-Ag with perfect TBs (that is, ideal materials) reach a plateau without any sign of softening, as λ decreases below 7 nm, see Fig. 1c. The strength in this previously unobserved transition zone is mostly independent of λ , suggesting that GB behaviour governs this transition. Remarkably, softening accompanied by a third Hall–Petch region with a negative slope becomes evident for materials with a high density of kinked TBs when $\lambda < 2.8$ nm, Fig. 1d. At the same time, a region where the Hall–Petch slope is near zero, between $\lambda = 2.8$ and 6.3 nm, is observed. Similar transition regions are

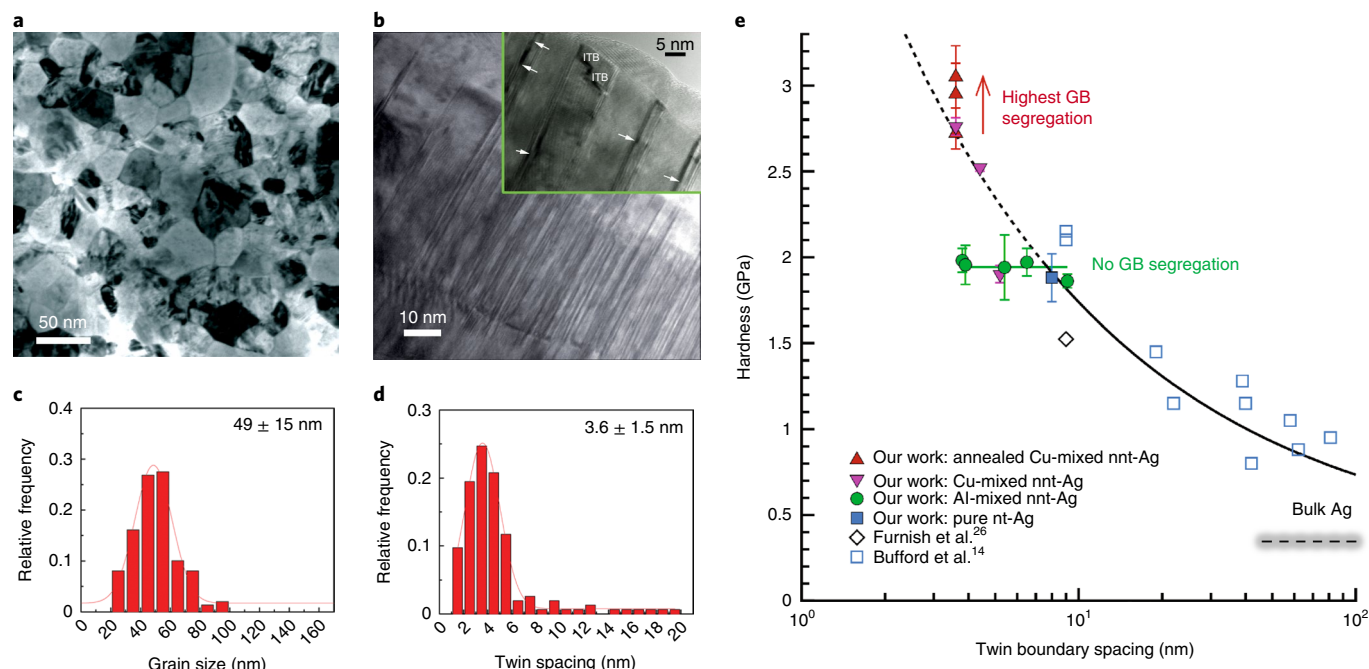


Fig. 4 | Cu-impurity-mixed nanocrystalline-nanotwinned Ag (NNT-Ag) synthesized by magnetron sputtering. **a**, Plan-view TEM image of NNT-Ag-0.81wt% Cu sample. **b**, Cross-sectional view of high-density growth twins of the same sample in **a**. The image is taken at $\sim 1.5\ \mu\text{m}$ film thickness. The inset is a high-resolution TEM image of incoherent TBs (ITBs) and twin steps. **c,d**, The grain size (d) and twin spacing (λ) distribution, respectively. **e**, A Hall-Petch plot for hardness of pure NT-Ag, Cu-mixed NNT-Ag and Al-mixed NNT-Ag metals synthesized, along with references for high-purity NT-Ag^{14,26} and a range of values for well-annealed bulk Ag crystals with different dislocation contents²⁷. A black line indicates the ideal Hall-Petch prediction (equation (1)). A hardness plateau in Al-mixed samples is observed when λ falls between 3.8–6.5 nm, in qualitative agreement with our simulation results. A green line shows a fitted average for all Al-mixed specimens in this range. However, Cu-mixed samples with high segregation exhibit continuous strengthening behaviour up to the smallest length scale investigated ($\lambda = 3.6\ \text{nm}$). Error bars include a minimum of nine hardness measurements.

also predicted with a smaller d value of 20 nm (27 grains) when $\lambda < 3.5\ \text{nm}$ (Supplementary Fig. 6a,b). Therefore, these results indicate the existence of three distinct Hall–Petch zones in ‘real world’ materials, but only two for ideal ones.

Our MD results in NT-Ag show very different softening mechanisms than the literature⁶. First, we identify a slip transition from hard to soft modes, accompanied by a breakdown of non-Shockley dislocations, at $\lambda = 6.3\text{--}7.7\ \text{nm}$ (Supplementary Fig. 5d) that does not match the simulated transition spacing for softening at $\lambda = 2.8\ \text{nm}$. Second, we observe that most dislocation emissions occur outside GB–TB junctions along slip planes parallel to TBs when $\lambda \leq 4.9\ \text{nm}$ (Supplementary Fig. 7). Third, Fig. 2a indicates that, with perfect TBs, the initial yield stress for dislocation emission mechanisms does not depend on λ . On the contrary, reducing λ down to 1.4 nm markedly decreases the initial yield stress in the presence of kinked TBs.

The softening behaviour of defective NT materials is identified to be caused by the motion or splitting of TB kink steps, which is particularly pervasive at $\lambda = 1.4\ \text{nm}$, see Fig. 2b and Supplementary Video 3. We have developed a continuum theory predicting the softening behaviour from kink motion (Supplementary Discussion 3). Because each kink has an effective length of d (they extend through the entire grain), the density of kink steps in motion ρ_k can be estimated as:

$$\rho_k = \frac{\alpha}{\lambda} \quad (2)$$

where α is the average number of kink steps per unit of TB length. Here, we fixed $\alpha = 1/10$ kinks per nm in our MD simulations on the basis of the previous experimental observations¹⁵. Figure 2c demonstrates that the theoretical kink density dominates the

density of Shockley dislocations that can actively participate in plastic deformation, when $\lambda \leq 3.5\ \text{nm}$. Our continuum model shows that the softening stress associated with kink motion can be expressed as

$$\sigma = \sigma^* + \left(\frac{\dot{\gamma}_{\text{GB}} B}{a h^2} \right) \lambda \quad (3)$$

where σ^* is a threshold stress, B is a friction coefficient, h is the height of a kink step and $\dot{\gamma}_{\text{GB}}$ is the maximum GB shear-strain rate. MD predictions and the proposed theory from equation (3) show agreement when $\lambda \leq 2.8\ \text{nm}$, Fig. 2d. This defect-induced softening is consistent with the original experimental report in NT-Cu³.

To better understand the origin of a zero-slope Hall–Petch region, we conducted a detailed study of atomic-scale mechanisms of GB plasticity as function of λ , see Fig. 3. We find from Fig. 3a–e and Supplementary Videos 4 and 5 that GB sliding in Cu-segregated NNT-Ag is considerably intensified as λ decreases. Remarkably, Fig. 3e demonstrates that GB sliding at 7% strain in NNT-Ag with $\lambda = 3.5\ \text{nm}$ is double that of NC-Ag without TBs (when $d = 45\ \text{nm}$). In fact, Fig. 3f reveals that the local GB shear-strain rates attain a maximum plateau of $0.0015\ \text{ps}^{-1}$ in Cu-segregated NNT-Ag when $\lambda \leq 4.2\ \text{nm}$, which is more than one order of magnitude higher than the strain rate imposed in the model overall. This phenomenon is governed by local GB stress effects, rather than by dislocation-nucleation mechanisms, because it is not observed at the onset of plastic yielding, see Fig. 3f. During plastic flow from 5 to 7% strain, the maximum atomic stresses shift entirely from the grain interior to the GB region, as λ decreases from 14.8 to 3.5 nm (Supplementary Fig. 8). The transition to soft crystal slip modes strictly parallel to TBs is expected to accelerate this effect, by introducing some incompatibility to the deformed grains, which, however, can be

accommodated by GB motion. The same GB-controlled mechanism is found with pure NNT-Ag metals (Supplementary Fig. 9), but the GB shear rate and Hall–Petch limit are lower, because GB stresses drop dramatically without impurity segregation, Fig. 3g. These findings point at a direct relationship between Hall–Petch limit and impurity-segregated local GB stresses—an observation that also appears consistent with recent experimental results in heavily alloyed NC metals¹².

The zero-slope GB-dictated intermediate regime predicted in NT-Ag for two grain sizes ($d=20$ and 45 nm) is at odds with the sharp softening transition and stress overshoot reported previously in NT-Cu⁶. We thus performed further simulations in NT-Cu (Supplementary Fig. 6d), which suggests that non-standard multi-time-step algorithm used in previous work, probably the anisynchronous updating of slow and fast force, could be responsible for the stress overshoot during plastic flow that dramatically reduced GB-mediated mechanisms (Supplementary Discussion 4). Overall, significant GB sliding observed in our work (Supplementary Fig. 6c) is consistent with a body of MD simulation studies in the literature^{7,25}.

Hardness and stability of nanocrystalline-nanotwinned metals

Nonetheless, the modelling results above suggest that a maximum strength is achievable in Cu-segregated NNT-Ag materials with a λ down to ~ 2.8 nm (Fig. 1d). The preferential segregation of Cu into TB defects over GBs provides an interesting mechanism to suppress TB defect migration and thus increase the stability of nanoscale twins. This affords opportunities for us to make a new class of high strength, high thermal stability and high electrical conductivity materials (Methods and Supplementary Table 1). The microstructure length scale can be controlled by the content of Cu element (<1.0 wt%). Figure 4a,b shows an example of such materials with an observed d of 49 ± 15 nm (Fig. 4c) and a λ of 3.6 ± 1.5 nm (Fig. 4d). The small length scales achieved are scientifically and technologically attractive, as they match well with those used above to determine the zero-slope Hall–Petch zone in MD simulations. The as-synthesized NNT-Ag has mostly equiaxed grains from a plane-view transmission electron micrograph (TEM, Fig. 4a and Supplementary Fig. 10a,b). High-density growth twins are evident from cross-sectional TEM images (Fig. 4b and Supplementary Fig. 10c). TB defects are stable at this λ , as small kink steps and incoherent TBs are also visible under high-resolution TEM, see the inset of Fig. 4b. Through in situ X-ray diffraction heating experiments, we find that the microstructure of pure NT-Ag ($d=147 \pm 15$ nm, $\lambda=8.0 \pm 2.0$ nm) becomes unstable at 438 K (Supplementary Fig. 11). In contrast, that of a 0.19 ± 0.02 wt% Cu-microalloyed sample remains unchanged up to 653 K; that is, 215 K higher than for pure NT-Ag. The much higher thermal stability of the impurity-mixed NNT-Ag is impressive, considering that this material has much smaller d (55 ± 4 nm) and λ (5.2 ± 2.3 nm).

The hardness measurements of as-deposited pure NT-Ag, Cu-mixed NNT-Ag and Al-mixed NNT-Ag samples, along with past references for high-purity NT-Ag^{14,26} and well-annealed bulk Ag crystals²⁷, are shown in Fig. 4e and Supplementary Fig. 12. The Hall–Petch relationship (equation (1)) shows good quantitative agreement with the experimental results down to $\lambda \approx 7.0$ nm. For Al-microalloyed NNT-Ag, we observe a hardness plateau (1.96 ± 0.17 GPa) with a twin spacing between 3.5–6.5 nm (Supplementary Table 1 and Supplementary Fig. 10d,e). These results qualitatively agree with our simulated predictions in Fig. 1d, where a strength plateau occurred when λ falls below 6.3 nm.

For Cu-microalloyed NNT-Ag, however, we observe a continuous increase in hardness along the Hall–Petch line, down to the smallest d and λ synthesized. This continuous Hall–Petch strengthening to $\lambda \approx 3.6$ nm is significant from several aspects. First, hardening down to $\lambda \approx 3.8$ nm has been reported in a covalent-bonded

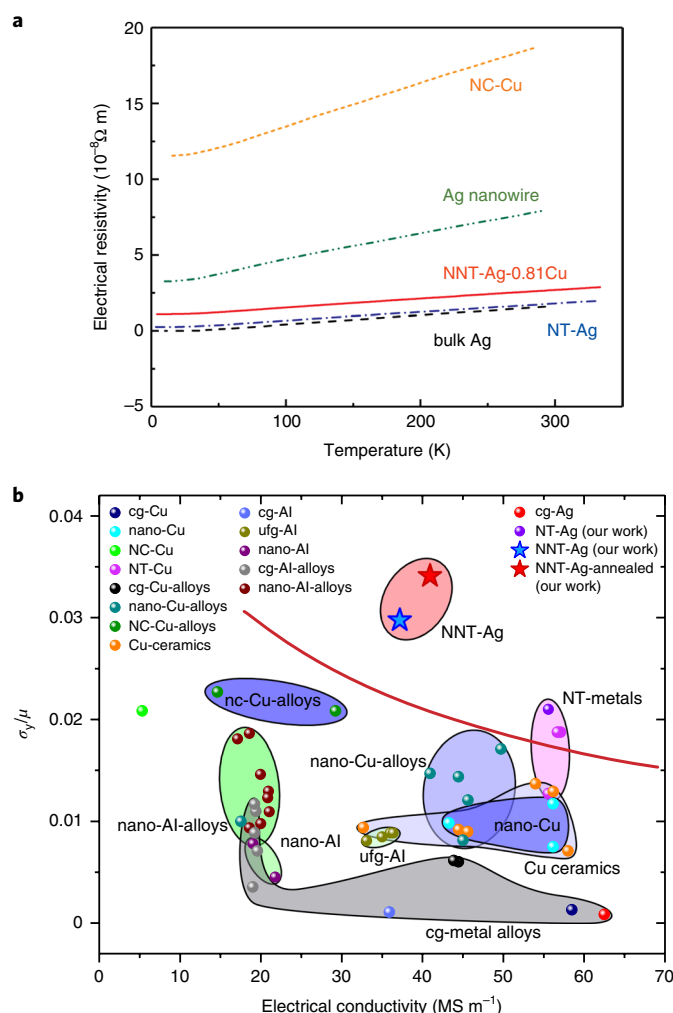


Fig. 5 | Electrical conductivity and yield strength of Cu-impurity-mixed NNT-Ag.

a, The electrical resistivity of NNT-Ag-0.81 wt%Cu between 4 and 300 K, in comparison with that of pure NT-Ag, nanocrystalline Cu (NC-Cu)³³, Ag nanowire (227 nm in diameter)³² and bulk Ag³². **b**, A summary of yield strength/shear modulus (σ_y/μ) versus electrical conductivity of various metals and alloys, including NNT-Ag (our work where $\sigma_y = H/3$ with H being the nanoindentation hardness), pure NT metals, coarse-grained Cu (cg-Cu), nanostructured Cu (nano-Cu), nano-Cu-alloys, ultrafine-grained Al (ufg-Al), nano-Al, nano-Al-alloys, Cu-ceramics composites and conventional commercial Cu alloys. The exceptional combination of strength and electrical conductivity in NNT-Ag exceeds that of existing materials, including the current benchmark NT metals. The solid red line is only a guide for the eye.

material²⁸, the mechanism of which was attributed to the quantum confinement effect that is considered impossible in bulk metals^{28,29}. Second, a softening transition at $\lambda=12$ –37 nm was previously observed experimentally in NT-Cu with large equiaxed grains^{5,10}. Yet we observe a continuous Hall–Petch strengthening in Cu-mixed NNT-Ag films containing either small equiaxed grains (for a 1 μm thickness film) or a mixture of small equiaxed and columnar grains (for a 2 μm thickness film, see Methods and Supplementary Fig. 12). Third, we performed low-temperature annealing experiments to enhance impurity segregation in Cu-mixed NNT-Ag. The hardness value of NNT-Ag can be further increased from 2.76 ± 0.16 GPa to 3.05 ± 0.18 GPa at 423 K annealing conditions—an 11% increase over already-impressive hardness values. The 3.05 ± 0.18 GPa value is $\sim 42\%$ above those reported in the literature

for NT-Ag (the previous record value is ~ 2.15 GPa)¹⁴ and surpasses the maximum hardness observed in NT-Cu (~ 2.7 GPa)⁵. In contrast, NNT-Ag metals containing few Cu impurities (0.19 wt%) and no annealing, to limit GB segregation, exhibit similar strength to that of pure and Al-microalloyed NNT-Ag materials (Fig. 4e and Supplementary Table 1).

Electrical resistivity of nanocrystalline-nanotwinned metals

We further investigate the electrical resistivity (ρ) of Ag nanostructures, as they are of potential interest for applications as transparent electrodes, catalysts and plasmonic materials^{30,31}. Figure 5a compares the temperature-dependent ρ behaviour for the pure NT-Ag, Cu-mixed NNT-Ag, Ag nanowire (227 nm in diameter)³², bulk Ag³² and NC-Cu³³ as a reference. At room temperature, the ρ values for NT-Ag, 0.81 wt% Cu-mixed NNT-Ag, Ag nanowire and NC-Cu are 1.80×10^{-8} (Ω m), 2.69×10^{-8} (Ω m), 7.78×10^{-8} (Ω m) and 1.90×10^{-7} (Ω m), respectively. The ρ value of Cu-mixed NNT-Ag is three and seven times lower than that of Ag nanowire and NC-Cu ($d \approx 15$ nm), respectively, and is only marginally higher than that of pure NT-Ag. The electron mean free paths due to the structural defect scattering at 0 K for NT-Ag and 0.81 wt% Cu-mixed NNT-Ag are estimated to be 33 and 8 nm, respectively (Methods). These values are larger than the λ measured in both types of material, indicative that TBs are not the dominant scattering sources for electrons. Thermal annealing of Cu-mixed NNT-Ag at 423 K is found to further reduce the electrical resistivity by $\sim 10\%$, and increases the electron mean free path by 12.5%. As the intrinsic strength of metals and alloys is linked to their shear modulus (μ)³⁴, we normalize the yield strength (σ_y , hardness divided by 3) of Cu-mixed NNT-Ag by μ for fair comparison with the literature data. Figure 5b indicates that the σ_y/μ values of our NNT-Ag well surpasses those reported in various nanostructured (nano) metals and alloys with similar electrical conductivities. This leads to an exceptional combination of strength and electrical conductivity that is far outside the inversely correlated strength-electrical conductivity zone typically seen in conventional commercial alloys and high-strength nano metals and alloys such as nano-Cu³⁵, nano-Cu-alloys³⁵, Cu-ceramics composites³⁶, ultrafine-grained Al (ufg-Al)³⁷, nano-Al³⁵ and nano-Al-alloys³⁵. Notably, the performance of NNT-Ag extends even beyond the current benchmark pure NT metals (that is, NT-Cu and NT-Ag), signalling that our materials are of technological importance.

Outlook

Our work collectively demonstrates that NNT metals strengthened by impurity segregation mechanisms have clear advantages over existing heavy alloying³⁸ and hierarchical interface-design strategies³⁹ that may inevitably lead to the trade-off of strength and electrical conductivity. While the present focus was primarily on Ag-Cu alloys, a broader range of alloy materials with similar impurity-segregated strengthening behaviour could exist in the future. Combined computational and experimental efforts are powerful tools for identifying these new material systems.

Online content

Any methods, additional references, Nature Research reporting summaries, source data, statements of code and data availability and associated accession codes are available at <https://doi.org/10.1038/s41563-019-0484-3>.

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Author contributions

Y.M.W. and F.S. conceived and guided the research. J.Y., M.F.B., J.G., R.T.O. and Y.M.W. performed the synthesis, mechanical testing and characterizations. D.Q. performed the electrical measurements. A.C. developed the initial MC/MD code. X.K. and F.S. performed the MC/MD simulations and atomistic analysis. Z.P. performed the density-functional theory calculations and MD analysis on Cu metals. J.M. and F.S. developed the continuum softening model. All authors contributed to the data discussion and manuscript preparation.

Competing interests

The authors declare no competing interests.

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Methods

Materials synthesis. Thin film samples of pure NT-Ag and Cu- or Al-microalloyed NNT-Ag were synthesized by magnetron sputtering onto (100) orientated Si wafers. Three 50 mm diameter Ag targets were arranged in a confocal geometry to sputter onto the 152-mm diameter substrate, which was rotated at 15 r.p.m. and cooled with liquid nitrogen. For the microalloyed samples, a fourth target of Cu or Al metal, 76 mm in diameter, was arranged in a confocal geometry outside the circle of Ag targets. The distance from the Ag and impurity sputtering targets to the centre of the substrate were 120 and 156 mm, respectively. For all sputtering runs, the base pressure was $<5 \times 10^{-8}$ torr and the working pressure was 5 mtorr of Ar. Three sputtering guns with Ag targets were operated at 300 W for each deposition run, while the sputtering gun with the impurity target was operated at 20 to 100 W for different runs. Our extensive transmission electron microscopy (TEM) characterizations of as-synthesized pure NT-Ag and Cu- or Al-microalloyed NNT-Ag materials indicate that the grain size of these films depends on the film thickness, whereas the average twin spacing (λ) remains relatively constant throughout the thickness. For consistency, the grain size reported in the main text is measured from the bottom side of the films except where noted.

Impurity level analysis. The compositions of as-deposited films were measured by electron microprobe analysis using a JEOL JXA-8200 (Peabody) wavelength/energy dispersive combined microanalyser. To map out the composition of a large area, a dot-by-dot scan method ($2 \times 2 \text{ mm}^2$) was used.

Thermal annealing. Pure NT-Ag and Cu-microalloyed NNT-Ag samples were annealed using a tube furnace (with 1-inch diameter quartz tube) under 100-sccm Argon (ultrahigh purity 99.999 + %) flow at temperatures of 373, 423 and 473 K, respectively. Ramping rate is 10 K min^{-1} . They were held at target temperatures for 30 min and furnace cooled back to room temperature.

Nanoindentation. Two types of film were used in the nanoindentation experiments. The first type had a thickness of $1 \mu\text{m}$, which contained equiaxed grains from the cross-section. The second type had a thickness of $2 \mu\text{m}$, which contained a mixture of equiaxed and columnar grains. The indentation depths for the first and second types of film were 100 and 200 nm, respectively. Nanoindentation experiments were performed using a Hysitron TI900 TriboIndenter equipped with a Diamond Berkovich tip. The displacement control mode was adopted to make sure the hardness values for different samples were measured at similar contact depths. We found that the hardness values of NT-Ag and NNT-Ag were stabilized at an indentation depth of 200 nm for $2 \mu\text{m}$ -thickness samples (Supplementary Fig. 12), consistent with the literature reports^{14,40}. It was also found that the hardness variations obtained from $1 \mu\text{m}$ - and $2 \mu\text{m}$ -thick samples were relatively small. Therefore, the hardness values reported in this work are from $2 \mu\text{m}$ -thick samples. Three segments were set for the load profile with 20 s loading, 5 s holding and 20 s unloading after 40 s drift correction period. The Oliver–Pharr method was used to extract the effective modulus and hardness. The changes of surface morphology and roughness after thermal annealing were measured using the scanning mode of the nanoindentation system. A constant load of $2 \mu\text{N}$ was applied on the Berkovich indenter tip. The scanning frequency was 1 Hz.

Electrical resistivity measurements and calculations. Both pure NT-Ag and NNT-Ag-0.81 wt% Cu thin films ($2 \mu\text{m}$ thick) were cut into the standard Hall-bar configuration with the dimensions of $2.14 \times 0.56 \text{ mm}^2$ (length $\times$ width). The four leads were attached with silver paint. The resistance measurements were performed with a Janis ST-500 probe station and a home-made liquid helium cryostat. The DC current of 1 mA was applied over a temperature range of 4 to 339 K in our experiments. The resistivity of a metal can be written as $\rho_0 = m/(ne^2\tau_0)$, where $m = 0.99m_e$ is the effective mass of electron, $m_e = 9.11 \times 10^{-31} \text{ kg}$ the electron mass, $n = 5.85 \times 10^{28} \text{ m}^{-3}$ the electron density of Ag^{32} , $e = 1.60 \times 10^{-19} \text{ C}$ the electron charge and τ_0 the relaxation time. The Fermi velocity V_F of Ag is $1.39 \times 10^6 \text{ m s}^{-1}$ (ref. ³²). The electron mean free path induced by the structural scattering can be calculated as $\lambda_0 = V_F\tau_0$.

In situ X-ray diffraction (XRD) heating analysis. For in situ XRD heating experiments, free-standing films $\sim 50 \mu\text{m}$ in thickness were prepared using a 180-min deposition time. The experiments were performed with a Panalytical X'Pert Pro Diffractometer with a Co K_α radiation and X'Celerator detector. The samples were heated in an Anton–Paar HTK 1200N hot-stage in flowing helium gas at a constant rate of 5 K min^{-1} . The thermal expansion of the stage was accounted for by offsetting the sample z -height during heating. The XRD scans were collected every 2 min over a selected 2θ range to include {111} and {200} reflections. For $50 \mu\text{m}$ thick films, the grain sizes measured from the top surface are $\sim 450 \text{ nm}$ for pure NT-Ag and $\sim 300 \text{ nm}$ for Cu-microalloyed NNT-Ag.

TEM specimen preparation and characterizations. Plan-view TEM specimens were prepared using ion milling at liquid nitrogen temperature. The ion milling was done on the free-side (top) of the films to examine the structure closer to the substrate side (film bottom). The average grain size of pure NT-Ag and

Cu-microalloyed NNT-Ag samples were measured from plan-view using an FEI Tecnai G2 F20-XT TEM operated at 200 kV. Some cross-sectional samples were also examined by a Philips CM-30 TEM operated at 300 kV. The cross-sectional TEM samples were prepared by a focused-ion-beam (FIB) machine (FEI Nova 600 Dual-Beam FIB). The average grain size and average twin spacing shown in Fig. 4c,d were counted from 149 grains and 154 TBs, respectively.

MD simulations. Large-scale MD simulations were performed using the massively parallel software LAMMPS⁴¹ with the embedded-atom-method potential for Ag-Cu by Wu and Trinkle⁴². This potential was fitted from ab initio data to match surface atom diffusivities and generalized stacking-fault energy curves in this system. Our own simulations with this potential showed that the unstable and stable stacking-fault energies in pure Ag were equal to 115.3 mJ m^{-2} and 16.6 mJ m^{-2} , respectively (Supplementary Fig. 1d). The atomistic samples consisted of a cubic simulation box with periodic boundary conditions on each of the xyz spatial directions. This box had dimensions of $90 \times 90 \times 90 \text{ nm}^3$ and contained 42.6 million atoms. Seven grains with random crystal orientations and random centres were created by placing atoms in the simulation box using a Voronoi tessellation scheme. GB atoms closer than 0.5 Å were automatically removed at this stage. Each grain contained constantly spaced TBs perpendicular to the (111) direction. The twin spacing was varied from 1.4 to 21.9 nm between different models. A TB kink defect of 0.7 nm (three atomic layers) in height in the (111) direction was introduced on each TB. Each kink was formed two steps perpendicular to the (112) direction and separated by 10 nm, following past experimental observations¹⁵. The total energy of each sample was minimized at 0 K by a conjugate gradient method. The structure was further relaxed under zero pressure using an isothermal–isobaric (NPT) ensemble at 450 K for 100 ps, then cooled to 300 K in 50 ps and held at the same temperature for another 50 ps. Temperature was rescaled after every 500 steps. The time step was 5 fs, which was found to conserve the total energy of the system. The samples were deformed in pure tension by stretching the simulation box at an engineering strain rate of $1 \times 10^8 \text{ s}^{-1}$ along the x direction until 10% strain was reached after 1 ns. We used the NPT ensemble at 300 K and applied zero pressure laterally along the z and y directions. Atomic stresses from the Virial theorem and the deformed volume of the simulation box were used to compute the true stress–true strain diagrams. Atomistic snapshots were created by common-neighbour analysis, atomic-strain analysis and dislocation-extraction analysis in the visualization software Ovito⁴³. The MD simulations were performed on the SuperMIC supercomputer at the Extreme Science and Engineering Discovery Environment (XSEDE) and the Cori supercomputer at the National Energy Research Scientific Computing Centre (NERSC).

Hybrid MC/MD simulations. A hybrid MC/MD approach^{44,45} was developed in LAMMPS, together with the *vcsgc-lammps* package, to simulate the segregation of Cu atoms in NNT-Ag, with MC approach simulating the chemical behaviour (segregation of Cu atoms) and the MD approach simulating structural change due to segregation. The MC simulation was performed in a variance-constrained semi-grand-canonical (VC-SGC) ensemble, where the total number of atoms was kept constant and the global composition of Cu atoms was controlled to a predetermined target value. The hybrid MC/MD simulation was run at 500 K for 1 million MD steps with a time step of 2 fs and calls to MC every 10 MD steps. Temperature in MD was controlled by rescaling every ten steps and pressure was maintained to 0 bar using a Berendsen barostat. The MC algorithm involved the following steps: (1) select an atom randomly, (2) swap its atomic type, (3) calculate the change in energy and global composition of Cu and (4) accept the trial swap with a probability function given by

$$A_r = \min(1, \exp\{-\beta[\Delta U + N\Delta c(\phi + 2\kappa\bar{c})]\})$$

where β is $1/k_B T$, ΔU is the energy difference between two configurations, N is the total number of atoms, Δc is the concentration difference, ϕ and κ are Lagrange multiplier constraints for the first and second moments of the concentration, respectively, and $\bar{c}$ is the averaged concentration before and after the trial move. In practice, the MC simulation required an initial guess of a chemical potential difference $\Delta\mu = 2.5 \text{ eV}$, variance of $\kappa = 100$, and target concentration up to 1.3 atomic% (or 0.77 wt%). The simulation output showed that standard deviation of impurity concentration was about 10^{-5} and the acceptance ratio was close to 2.5×10^{-6} . Such a low acceptance ratio is due to the low impurity concentration and is sufficient to reach convergence since additional MC steps led to no considerable chemical and structural changes. Before deformation, each segregated model was further relaxed in the NPT ensemble under zero pressure from 500 to 300 K for 100 ps and kept at 300 K for another 100 ps. The MC/MD simulations were performed on the XSEDE's SuperMIC and NERSC's Cori supercomputers.

Ab initio calculations. Calculations of segregation enthalpies for solute Cu or Al atoms in (112) TB kink steps and $\Sigma 9$ (221) grain-boundary in Ag were performed using the Vienna Ab initio Simulation Package (VASP)⁴⁶. Gamma point geometry optimization was used to obtain the minimum potential energy of each single-crystal, kink and GB configurations with and without impurity at specific sites. We used plane wave basis sets to expand Kohn–Sham orbitals with a cutoff energy of 350 eV, and the exchange–correlation functional based on a generalized gradient

approximation scheme⁴⁷. Interaction between ions and electrons was modelled using the projector augmented wavefunction method pseudopotentials. The convergence criterion was 10^{-6} eV for wave function optimization and 10^{-4} eV/+ for geometry optimization. The atomistic models used for kink steps and high energy GB are shown in Supplementary Fig. 14, along with the number of each atomic site used to compute the different segregation enthalpies. The ab initio calculations were all performed on NERSC's Cori supercomputer.

Data availability

All data needed to evaluate the conclusions in the paper are present in the paper or the Supplementary Materials.

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