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

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Abstract:

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 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 (HP) 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); i.e., in a new class of nc and nt materials (we term them as nnt-materials from here on). The existing theories suggest drastically different HP breakdown mechanisms in these two types of materials; i.e., the former is caused by GB sliding[3] and the latter by dislocation-nucleation governed plasticity[6]. 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[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 HP strengthening and softening in nnt-materials. Ag is a low stacking fault energy metal (~16 $mJ \cdot m^{-2}$)[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[18]; i.e., 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 solutes[19], or a change of stacking fault energies in Ag caused by alloying that alters fundamental deformation mechanisms. For above 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 (SI), Fig. S1). Neither will Cu affect the stacking fault energy of Ag at a concentration <1.0 wt.%. Moreover, Cu atoms are ~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 defects[15]. We have successfully fabricated a series of Cu- and Al-microalloyed (<1.0 wt.%) nnt-Ag samples (SI, Table S1). The strongest material has an average d of 49 ± 15 nm and twin spacing λ = 3.6 ± 1.5 nm. We find that these materials

retain a continuous HP strengthening behavior down to the smallest twin size, which markedly differs from the projected HP breakdown from ref.[6]. We performed atomic simulations with comparable *d* value to experiments and varying λ. In contrast to popular belief, three HP strengthening and softening regions are uncovered. Importantly, 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 molecular dynamics (MD) simulations involving a total of 2.2 billion atoms were used to study ten λ values from 1.4 to 21.9 nm, with either kinked (i.e., defective) or perfect coherent TBs (Methods). The *d* in our nt-Ag models is fixed at 45 nm (i.e., 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. Fig. 1a displays a simulated nt-Ag microstructure containing equally spaced nanotwins of size λ = 3.5 nm, and the equilibrium impurity distribution of 0.47 wt.% Cu atoms after 500 K annealed conditions. It indicates that under the equilibrium conditions most Cu atoms are preferentially segregated into GBs and TB kink-step defects, inset of Fig. 1b. This is consistent with our ab-initio density-functional theory (DFT) calculations finding largely positive segregation enthalpies for Cu at several atomic sites of a (112) TB kink step and a high-energy Σ9(221) symmetric tilt GB in Ag, compared to the negative energies of an element presenting no GB segregation such as Al, Fig. 1b. Interestingly, 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 materials[20]. 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 (SI, Fig. S2), while yield stresses at the initiation of GB sliding and GB-nucleated dislocations rise dramatically (SI, Fig. S3). Dislocation nucleation mechanisms occur at higher stresses, because solute segregation to GBs significantly reduces the excess GB free volume[21,22] (SI, Fig. S4). 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 nt-Ag materials, respectively (SI, Fig. S3c). This impurity-segregated

strengthening is well beyond the hardening normally expected from solid solution strengthening based upon Fleischer model or solute pinning model proposed for heavily alloyed nc metals[23,24] (SI, Discussion S1). 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.% (SI, Fig. S1a).

Hall-Petch Strengthening and Softening Mechanisms

Above simulation results demonstrate that selective impurity segregation provides a means for probing the HP limit and associated softening mechanisms currently unknown in nnt metals. Fig. 1c-d exhibit the HP plots of flow strength (i.e., 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 HP strengthening region is observed for $\lambda \geq 6.3$ nm, which is determined from the relationship

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

where σ_0, K_{GB} and K_{TB} are material-dependent constants (SI, Discussion S2). As the HP 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 (Movie S1). 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 (SI, Fig. S5 and Movie S2). The existing understanding in pure nt-Cu[6] is that the softening is associated with twinning partial dislocations nucleating from GB – TB junctions and propagating freely inside TBs, leading to a negative HP slope as the junction density increases.

To our surprise, however, the strengths of both pure and Cu-segregated nt-Ag with perfect TBs (i.e., ideal materials) reach a plateau without any sign of softening, as λ decreases below 7 nm, 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 HP region with a negative slope becomes evident for materials with high density of kinked TBs when $\lambda < 2.8$ nm, Fig. 1d. At the same time, a region where the HP slope is near zero, between

λ = 2.8 nm and 6.3 nm, is observed. Similar transition regions are also predicted with a smaller *d* value of 20 nm (27 grains) when λ < 3.5 nm (SI, Fig. S6a-b). Therefore, these results indicate the existence of three distinct HP zones in "real world" materials, but only two for ideal ones.

Our MD results in nt-Ag show very different softening mechanisms than the literature[6]. First, we identify a slip transition from hard to soft modes, accompanied by a breakdown of non-Shockley dislocations, at λ = 6.3 - 7.7 nm (SI, Fig. S5d) that does not match the simulated transition spacing for softening at λ = 2.8 nm. Second, we observe that most dislocation emissions occur outside GB-TB junctions along slip planes parallel to TBs when λ ≤ 4.9 nm (SI, Fig. S7). 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 λ = 1.4 nm, Fig. 2b and Movie S3. We have developed a continuum theory predicting the softening behaviour from kink motion (SI, Discussion S3). Because each kink has an effective length of *d* (they extend through the entire grain), the density of kink steps in motion ρ_κ can be estimated as:

$$\rho_k = \frac{\alpha}{\lambda}, \tag{2}$$

where α is the average number of kink steps per unit of TB length. Here, we fixed α = 1/10 kink/nm in our MD simulations based on the previous experimental observations[15]. Fig. 2c demonstrates that the theoretical kink density dominates the density of Shockley dislocations that can actively participate in plastic deformation, when λ ≤ 3.5 nm. Our continuum model shows that the softening stress associated with kink motion can be expressed as

$$\sigma = \sigma^* + \left(\frac{\dot{\gamma}_{GB} B}{\alpha h^2}\right)\lambda, \tag{3}$$

where σ^* is a threshold stress, *B* is a friction coefficient, *h* is the height of a kink step, and $\dot{\gamma}_{GB}$ is the maximum GB shear-strain rate. MD predictions and the proposed theory from Eq. (3) show agreement when λ ≤ 2.8 nm, Fig. 2d. This defect-induced softening is consistent with the original experimental report in nt-Cu[5].

To better understand the origin of a zero-slope HP region, we conducted a detailed study of

atomic-scale mechanisms of GB plasticity as function of λ, Fig. 3. We find from Fig. 3a-e and Movies S4-S5 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 λ = 3.5 nm is doubled that of nc-Ag without TBs (when d = 45 nm). In fact, Fig. 3f reveals that the local GB shear-strain rates attain a maximum plateau of 0.0015 ps^{-1} in Cu-segregated nnt-Ag when λ ≤ 4.2 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, 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 (SI, Fig. S8). 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 (SI, Fig. S9), but the GB shear rate and HP limit are lower, because GB stresses drop dramatically without impurity segregation, Fig. 3g. These findings point at a direct relationship between HP limit and impurity-segregated local GB stresses – an observation that appears also consistent with recent experimental results in heavily alloyed nc metals[12].

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-Cu[6]. We thus performed further simulations in nt-Cu (SI, Fig. 6d), which suggests that non-standard multi-time-step algorithm used in previous work, probably the anisochronous updating of slow and fast force, could be responsible for the stress overshoot during plastic flow that dramatically reduced GB-mediated mechanisms (SI, Discussion S4). Overall, significant GB sliding observed in our work (SI, 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 modeling 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 Table S1). The microstructure length-scale can be controlled by the content of Cu element (<1.0 wt.%). Fig. 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 HP zone in MD simulations. The as-synthesized nnt-Ag has mostly equiaxed grains from plane-view transmission electron micrograph (TEM), Fig. 4a and SI, Fig. S10a-b. High-density growth twins are evident from cross-sectional TEM images, Fig. 4b and SI, Fig. S10c. TB defects are stable at this λ, as small kink steps and incoherent TBs are also visible under high-resolution TEM, inset of Fig. 4b. Through in-situ x-ray diffraction heating experiments, we find that the microstructure of pure nt-Ag (*d*=147±15 nm, λ=8.0±2.0 nm) becomes unstable at 438 K (SI, Fig. S11). In contrast, that of a 0.19±0.02 wt.% Cu-microalloyed sample remains unchanged up to 653 K; i.e., 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 crystals[27], are shown in Fig. 4e and SI, Fig. S12. The HP relationship (Eq. 1) shows good quantitative agreement with the experimental results down to λ~7.0 nm. For Al-microalloyed nnt-Ag, interestingly, we observe a hardness plateau (1.96±0.17 GPa) with a twin spacing between 3.5-6.5 nm (SI, Table S1, and Fig. S10d-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 HP line, down to the smallest *d* and λ synthesized. This continuous HP strengthening to λ~3.6 nm is significant from several aspects. First, hardening down to λ ~ 3.8 nm has been reported in a covalent-bonded material[28], 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 λ = 12-37 nm was previously observed experimentally in nt-Cu with large equiaxed grains[5,10]. Yet we observe a continuous HP strengthening in Cu-mixed nnt-Ag films containing either small equiaxed grains (for 1 μm thickness film) or a mixture of small equiaxed- and columnar-grains (for 2 μm

thickness film, see Methods and SI, Fig. S12). Third, we performed low-temperature annealing experiments to enhance impurity segregation in Cu-mixed nnt-Ag. Strikingly, 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 – a 11% increase over already-impressive hardness values. The 3.05±0.18 GPa value is ~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, in order to limit GB segregation, exhibit similar strength to that of pure and Al-microalloyed nnt-Ag materials (Fig. 4e and SI, Table S1).

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]. Fig. 5a compares the temperature-dependent ρ behaviour for the pure nt-Ag, Cu-mixed nnt-Ag, Ag nanowire (227 nm in diameter)[32], bulk Ag[32], and nc-Cu[33] 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 ~ 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 materials, 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 ~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. Interestingly, Fig. 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-Cu[35], nano-Cu-alloys[35], Cu-ceramics

composites[36], ufg-Al[37], nano-Al[35], and nano-Al-alloys[35]. Notably, the performance of nnt-Ag extends even beyond the current benchmark pure nt-metals (i.e., nt-Cu and nt-Ag), signaling 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 alloying[38] and hierarchical interface-design strategies[39] 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, should be expected to exist in the future. Combined computational and experimental efforts are powerful tools to identify these new materials systems.

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Acknowledgements: The authors thank Drs. Alison Engwall for synthesis help, and Enrique Martinez for the helpful discussion. XK, ZP and FS gratefully thank support from the U.S. Department of Energy (DOE) grant DE-SC0016270. The work at the Lawrence Livermore National Laboratory (LLNL) was performed under the auspices of DOE Contract DE-AC52-07NA27344. JG, MFB, and RTO at Ames Laboratory were supported by the DOE Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Contract DE-AC02-07CH11358. AC at Los Alamos National Laboratory are supported under DOE Contract DE-AC52-06NA253. YMW and DQ acknowledge the support of LDRD program (17-ERD-048) at LLNL. JM acknowledges support from the National Science Foundation (NSF) grant DMR-1611342. The simulations in this research used resources of the National Energy Research Scientific Computing Centre, supported by DOE Contract DE-AC02-05CH11231, and those of the Extreme Science and Engineering Discovery Environment, supported by NSF grant ACI-1548562.

Author Contributions: YMW and FS conceived and guided the research. JY, MFB, JG, RTO, and YMW performed the synthesis, mechanical testing, and characterizations. DQ performed the electrical measurements. AC developed the initial MC/MD code. XK and FS performed the MC/MD simulations and atomistic analysis. ZP performed the DFT calculations and MD analysis on Cu metals. JM and FS developed the continuum softening model. All authors contributed to the data discussion and manuscript preparation.

Competing interests: The authors have no competing interests.

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Supplementary Information is available online for this paper.

Figure Legends

Fig. 1 | Hall-Petch strength transition zones in pure and impurity-segregated nanotwinned Ag metals containing either perfect or kinked twin boundaries (TBs) obtained by large-scale atomistic simulations. a. Snapshot of hybrid Monte-Carlo and molecular dynamics simulation of microstructure relaxation and equilibrium impurity segregation after 500 K annealing in nt-Ag with a target concentration of 0.47 wt.% Cu, λ = 3.5 nm and d = 45 nm. First, common neighbor analysis is performed to differentiate atoms from coherent TBs (magenta color), incoherent interface defects (dark purple), and face-centered cubic (FCC) 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 colored in green, dark purple and blue when found at incoherent interfaces, coherent TBs and FCC lattice, respectively. 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 twin-boundary kink step and a high-energy Σ9 (211) tilt grain boundary, respectively. Sites 1-6 of the kink defect are indicated in inset. Scale bar is 0.5 nm. Hall-Petch flow strength plots for pure and Cu-segregated nt-Ag with **c.** perfect coherent TBs and **d.** kinked TBs, as a function of λ. All error bars include flow stress predictions between 5% and 7% strain.

Fig. 2 | Twin-boundary defect-motion softening mechanism (negative HP slope). a. Simulated stress-strain curves for different twin spacings λ for both kinked and perfect twin boundaries in Cu-segregated nt-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 5% strain inside a grain containing kinked twin boundaries when λ = 1.4 nm. All face-centered cubic atoms have been removed for clarity. The arrows indicate partial dislocations from splitting or motion of twin-boundary 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 Eq. 2, showing that the dislocation density is dominated by kink motion when λ < 3.5 nm. **d.** Comparison of plastic flow stresses predicted by MD and theoretical model for kink-motion softening, Eq. 3. All error bars include flow stress predictions between 5% and 7% strain.

Fig. 3 | Transition from positive Hall-Petch strengthening to GB-stress-controlled (near-zero HP slope) mechanisms. MD snapshots of **a.** and **b.** initial microstructure before deformation and **c.** and **d.** of local von-Mises shear strain accumulated from 5% to 7% applied strains in Cu-segregated nt-Ag with λ = 14.8 and 3.5 nm, respectively. The GB-mediated plasticity by sliding increases as λ decreases. **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.

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 ~1.5 μm film thickness. The inset is a high-resolution TEM image of incoherent twin boundaries (ITBs) and twin steps. **c**. and **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 contents[27]. A black line indicates the ideal Hall-Petch prediction (Eq. 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 (λ=3.6nm). Error bars include a minimum of nine hardness measurements.

Fig. 5 | Electrical conductivity and yield strength of Cu-impurity-mixed nnt-Ag. a. The electrical resistivity of nnt-Ag-0.81wt.%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 Ag[32]. **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 the nanoindentation hardness), pure nt-metals, nanostructured Cu (nano-Cu), nano-Cu-alloys, 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 a guide for the eye only.

Methods

Materials synthesis. Thin film samples of pure nt-Ag and Cu- or Al-microalloyed nnt-Ag were synthesized by magnetron sputtering onto <100> oriented 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 revolutions per minute 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 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, MA, USA) wavelength/energy dispersive combined microanalyzer. To map out the composition of a large area, a dot-by-dot scan method (2mm×2mm) 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 K, 423 K, and 473 K, respectively. Ramping rate is 10 K/min. They were held at target temperatures for 30 minutes and furnace cooled back to room temperature.

Nanoindentation. Two types of films were used in the nanoindentation experiments. The first type has the thickness of 1 μm, which contains equiaxed grains from the cross-section. The second type has a thickness of 2 μm, which contains a mixture of equiaxed and columnar grains. The indentation depths for the first and second types of films are 100 nm and 200 nm, respectively. Nanoindentation experiments were performed using Hysitron TI900 TriboIndenter (Eden Prairie, MN, USA) equipped with a Diamond Berkovich tip. Displacement control mode was adopted to make sure the hardness values for different samples were measured at similar contact depth. We find that the hardness values of nt-Ag and nnt-Ag are stabilized at an indentation depth of 200 nm for 2μm-thickness samples (Fig. S12), consistent with the literature reports[14,40]. It was also found that the hardness variations obtained from 1μm- and 2μm-thick samples are relatively small. Therefore, the hardness values reported in this work are from 2μm-thick samples. Three segments were set for the load profile with 20s loading, 5s holding and 20s unloading followed by 40s drift correction period. 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 μN was applied on the Berkovich indenter tip. The scanning frequency is 1 Hz.

Electrical resistivity measurements and calculations. Both pure nt-Ag and nnt-Ag-0.81wt.%Cu thin films (2 μm thick) were cut into the standard Hall-bar configuration with the dimensions of 2.14×0.56 mm^2 (length × width). The four leads were attached with silver paint. The resistance measurements were performed with a Janis ST-500 probe station (Woburn, MA, USA) 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 $\rho_o = m/(ne^2\tau_o)$, where m=0.99m_e is the effective mass of electron, m_e=9.11×10^{-31} kg the electron mass, n=5.85×10^{28} m^{-3} the electron density of Ag[32], e=1.60×10^{-19} C the electron charge, and τ_o the relaxation time. The Fermi velocity V_F of Ag is 1.39×10^6 m/s[32]. The mean electron free path induced by the structural scattering can be calculated as $\lambda_o=V_F\tau_o$.

In-situ X-ray diffraction (XRD) heating analysis. For in situ XRD heating experiments, free-standing films ~50 μm in thickness were prepared using a 180-minute deposition time. The experiments were performed with a Panalytical X'Pert Pro Diffractometer with 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. The thermal expansion of the stage was accounted for by offsetting the sample *z*-height during heating. The XRD scans were collected every 2 minutes over a selected 2θ range to include {111} and {200} reflections. For 50 μm thick films, the grain sizes measured from the top surface are ~450 nm for pure nt-Ag, and ~300 nm for Cu-microalloyed nnt-Ag.

TEM specimen preparation and characterizations. Plan-view transmission electron microscopy (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 200KV. 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, Oregon, USA). The average grain size and average twin spacing shown in Figs. 4c and 4d were counted from 149 grains and 154 twin boundaries (TBs), respectively.

Molecular-dynamics (MD) simulations. Large-scale MD simulations were performed using the massively parallel software LAMMPS[41] with the embedded-atom-method potential for Ag-Cu by Wu and Trinkle[42]. 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 (Fig. S1d). The atomistic samples consisted of a cubic simulation box with periodic boundary conditions on each of the *xyz* spatial directions. This box was 90nm × 90nm × 90nm in dimensions 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 A were automatically removed at this stage. Each grain contained constantly spaced twin boundaries perpendicular to the [111] direction. The twin spacing was varied from 1.4 nm to 21.9 nm between different models. A TB kink defect of 0.7 nm (3 atomic layers) in height in the [111] direction was introduced on each twin boundary. Each kink formed two steps perpendicular to the $[11\bar{2}]$ direction and separated by 10 nm, following past experimental observations[15]. The total energy of each sample was minimized at 0 K by 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 1·10^8 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 Ovito[43]. The MD simulations were performed on SuperMIC supercomputer of the Extreme Science and Engineering Discovery Environment (XSEDE) and Cori supercomputer of 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 behavior (segregation of Cu atoms) and the MD approach simulating the structural change due to the segregation. The MC simulation was performed in a variance-constrained semi-grand-canonical (VC-SGC) ensemble, where the total number of atoms is kept constant and the global composition of Cu atoms is 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 10 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

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

where β is $1/k_BT$, 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, $\hat{c}$ 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 eV, variance of κ = 100, and target concentration up to 1.3 at.% (or 0.77 wt.%). The simulation output showed that standard deviation of impurity at. % was about 10^{-5} and the acceptance ratio was close to $2.5\cdot10^{-6}$. 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 NPT ensemble under zero pressure from 500 K 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) twin-boundary kink steps and Σ9 (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 without and with 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 generalized gradient approximation scheme[47]. Interaction between ions and electrons was modelled using the projector augmented wavefunction method pseudopotentials. The convergence criterion is 10^{-6} eV for wave function optimization and 10^{-4} eV/Å for geometry optimization. The atomistic models used for kink steps and high energy GB are shown in Fig. S14, along with the number of each atomic site used to compute the different segregation enthalpies. The ab-initio calculations were all performed on the NERSC's Cori supercomputer.

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Data availability: All data needed to evaluate the conclusions in the paper are present in the paper or the supplementary materials.