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Grain boundary stability dictates the rate-limiting deformation process in nanocrystalline metals

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ABSTRACT

Nanocrystalline metals can exhibit both dislocation-mediated and grain boundary (GB)-mediated plasticity, making it difficult to identify the rate-controlling unit process. Here, we vary GB structural stability in Ni- and Pt-based films through deposition route and alloying, and determine the governing deformation mechanisms by coupling transient activation-parameter measurements with simultaneous *in situ* transmission electron microscopy observations. Despite having comparable mean grain sizes, the films with different nonequilibrium GB states separate into two reproducible mechanical regimes. In the grain-coarsening regime, rapid stress-assisted grain growth influences the plastic flow rate, and the measured activation volume is small ($\sim 4\text{--}5b^3$ in Ni and $3\text{--}4b^3$ in Pt). In the stable-grain regime, the plastic flow rate is controlled primarily by dislocation activity, and the measured activation volume is larger ($\sim 7\text{--}12b^3$ in Ni and $5\text{--}10b^3$ in Pt₉₀Au₁₀). The measured activation volumes for the stable-grain condition agree quantitatively with atomistic predictions for GB dislocation nucleation, whereas the smaller values measured during grain coarsening are attributed to diffusion-assisted GB motion. These results show that, in addition to grain size, GB structural stability is a key variable influencing which localized process controls plastic flow in nanocrystalline face-centered cubic metals.

1. Introduction

The high strength of nanocrystalline materials arises primarily from the suppression of dislocation activity by small grain sizes and the resulting large volume fraction of grain boundaries (GBs). This suppression is associated with the enhanced activation of GB-mediated deformation mechanisms that are typically less important in coarse-grained materials [1–9]. These processes play a central role in both accommodating and controlling thermally activated plastic flow. The kinetics of plasticity can be characterized by the activation volume, V^* , which provides a quantitative fingerprint of the underlying rate-limiting process [10]. As grain size decreases, the density of interfaces increases and plasticity becomes confined to increasingly localized events at or near GBs [11–16]. Accordingly, the characteristic V^* can decrease by one to two orders of magnitude relative to coarse-grained metals, often accompanied by enhanced strain-rate sensitivity [17–22]. For example, Wang et al. reported a markedly smaller V^* in electrodeposited nanocrystalline Ni (with an average grain size of ~ 30 nm) than in

coarse-grained Ni, interpreting this reduction as evidence for a shift from conventional forest-controlled dislocation glide [21,22] to GB-mediated dislocation processes [20].

Such measurements have established that V^* in nanocrystalline and ultrafine-grained metals is far smaller than in their coarse-grained counterparts. However, order-of-magnitude arguments alone cannot reliably distinguish among the several candidate mechanisms that produce similarly low V^* values, including dislocation nucleation from GBs, dislocation-mediated GB sliding, and diffusion-assisted GB disconnection processes [3,23–32]. The present work addresses this limitation by extending our micro-electro-mechanical system (MEMS)-based *in situ* transmission electron microscopy (TEM) transient testing method, which measures physical activation volumes with high precision while directly imaging the evolving microstructure [33–35]. This approach makes it possible to connect V^* to flow stress and to the deformation mode observed in the same material state, providing a more discriminating link between kinetics and the underlying mechanisms. In addition, the grain sizes examined here lie on the same ~ 10 -nm length scale

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as atomistic calculations of GB dislocation nucleation, allowing direct comparison between experiment and simulation without relying on the grain-size scaling relationships for V^* used in Conrad-type models [21, 36,37].

In this work, we examine Ni- and Pt-based systems with comparable grain sizes but different nonequilibrium GB states. Thermal exposure during deposition provides one route for stabilizing GBs by promoting boundary relaxation and defect annihilation, whereas alloying kinetically pins boundary motion through solute segregation [38–42]. Across these systems, two reproducible regimes emerge: a stable-grain regime, in which GB migration is suppressed and the measured activation volumes remain relatively large, and a grain-coarsening regime, in which pronounced stress-assisted grain growth accompanies deformation and the measured activation volumes shift to substantially smaller values. These results indicate that GB structural stability is a critical variable governing the kinetics of plastic flow.

2. Methods

2.1. Specimen fabrication

Dog-bone-shaped, freestanding nanocrystalline Ni specimens were produced using three deposition conditions. The nominal thickness of all samples was 100 nm. The first set was deposited by electron-beam evaporation at a deposition rate of $1 \text{ \AA/s}$ under a base pressure of 7×10^{-7} Torr. The second set was deposited by DC magnetron sputtering without substrate preheating, at a deposition rate of $1 \text{ \AA/s}$ under a base pressure of 1×10^{-7} Torr and working pressure of 7.5 mTorr with Ar gas. The third set was deposited by DC magnetron sputtering with the substrate preheated to of 100°C , using the same deposition rate and pressure. Although the actual film temperature may increase during deposition even without intentional substrate heating, for simplicity these films are referred to throughout the manuscript as “evaporated”, “sputtered (no preheat)”, and “sputtered (preheat)”, respectively. Film thickness was measured by Dektak profilometry. The evaporated Ni films with no preheat substrates were 95 nm thick, whereas the sputtered films were 75–95 nm thick. This variation arises from differences in deposition angle after resist masking at different locations on the wafer. These samples have previously been investigated in ref [43]. Pt and $\text{Pt}_{90}\text{Au}_{10}$ films (97 nm thick) were deposited onto patterned Si wafers by pulsed DC magnetron sputtering without substrate heating. Before deposition, a 5 min descum step was performed at 50 W using an $\text{Ar}:\text{O}_2$ mixture to clean the patterned surface. The chamber base pressure was below 10^{-7} Torr, and deposition was carried out in 22 mTorr Ar gas.

All the specimens had the same dog-bone geometry (shown in Fig. 1b) defined on Si wafers by electron-beam lithography using S1813

photoresist. After pattern development, the metal layer was deposited onto the patterned wafer and released by a lift-off process. The resulting patterned films were converted into freestanding structures using XeF_2 dry etching. The detailed lift-off procedures follow our established protocol [44–47]. The measured thicknesses were used to calculate engineering stress for each test. The lithographically defined pattern contains many discrete islands of specimens distributed across the substrate. Because the deposition flux arrived at slightly different angles at different island locations, the film thickness varied from island to island. However, within a given island, the thickness was uniform as confirmed by profilometry. Accordingly, mechanical tests and TEM observations were performed on specimens taken from one island with uniform thickness, while *in situ* high-resolution TEM (HRTEM) observations were conducted on a different island with a slightly lower thickness. Cross-sectional TEM lamellae were prepared by FIB lift-out on a Thermo Fisher Helios 5CX dual-beam (FIB/SEM) using standard lift-out and polishing steps.

2.2. In situ TEM nanomechanical testing

In situ tensile experiments were performed in a 300 kV FEI Tecnai F30 using a custom MEMS-based platform to obtain quantitative mechanical data, as developed and validated in our prior work [33–35]. The MEMS tensile device is shown in Fig. 1a. For the *in-situ* TEM observations, specimens were strained and then held at a fixed actuator position to conduct transient experiments, with the dashed box in Fig. 1c indicating the stress range where microstructural evolution was monitored. The peak stress was defined as the maximum stress reached before the hold segment, while the relaxation magnitude was calculated as the stress drop during the hold. For the high-resolution TEM observations, the stress was obtained from matching the applied power to a calibrated test performed on another specimen with identical geometry. The strain values reported for the monotonic and *in situ* observations correspond to local strains measured from a DIC code [34]. Importantly, although *in situ* observations at high magnification may locally enhance diffusion-assisted processes [47], all activation parameters reported here were measured at low magnification. To minimize beam-induced artifacts, imaging was performed under a relatively low dose (spot size 4 with a spread beam). Using the measured screen current ($\sim 3 \text{ nA}$), the corresponding dose rate was estimated to be $\sim 2 \text{ e}^- \text{ \AA}^{-2} \text{ s}^{-1}$. 4D-STEM maps were acquired in a 300 kV FEI Tecnai F30 (STEM mode) using a 0.7 mrad convergence semi-angle and a Gatan Metro 300 pixelated detector. Orientation maps were constructed from the collected 4D-STEM datasets using the Gatan STEMx template matching software. Diffraction patterns were averaged with their nearest neighbors to increase the signal-to-noise ratio and improve indexing consistency [48,

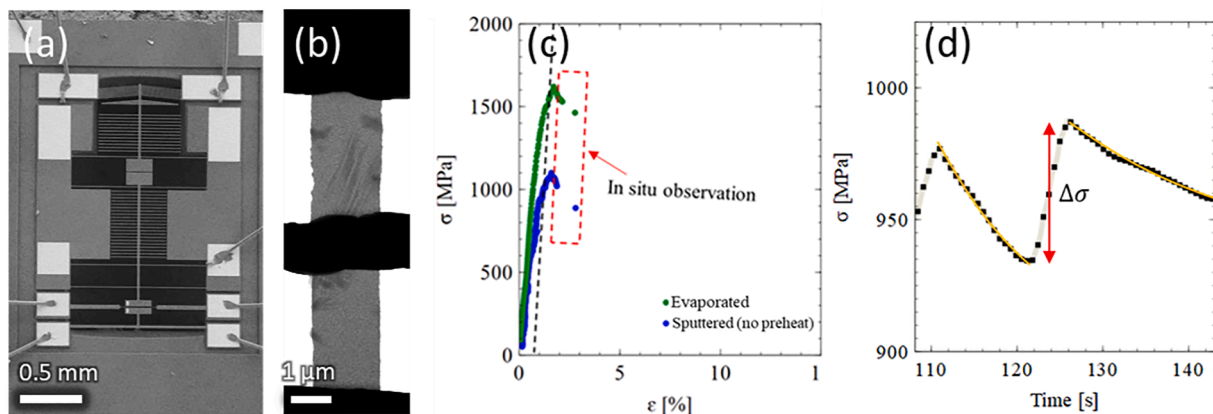


Fig. 1. (a) SEM image of the MEMS tensile device used for quantitative *in situ* mechanical testing. (b) TEM image of a specimen on the specimen pad. (c) Stress-strain curves showing the loading regime used for *in situ* TEM observations. (d) Representative stress-time response during a stress relaxation transient experiment used to measure activation volume.

49]. The orientation data were analyzed using OIM Analysis.

To quantify stress-dependent mechanically driven grain growth during monotonic loading, *in situ* TEM experiments were performed at a nominal strain rate of $\sim 10^{-4} \text{ s}^{-1}$ for the three Ni deposition conditions. Bright-field TEM images were acquired during loading. Individual grains that could be confidently identified in successive frames were manually tracked, following the protocol used in our prior study [44]. For each tracked grain, the grain area was manually outlined and converted to an equivalent circular diameter. The normalized grain-size increment was then calculated as $\Delta d/d_0 = (d - d_0)/d_0$, where d_0 is the grain diameter in the first frame in which that grain was tracked. In each experiment, the field of view covered approximately one-fourth of the gauge length. For each stress range, grain size measurements included at least 25 confidently tracked grains acquired under good two-beam imaging conditions. For each specimen type, the applied power was correlated with separately measured monotonic stress-strain curves, allowing individual frames to be assigned to an approximate stress value. Complementary interrupted 4D-STEM measurements were performed before loading and after deformation to prescribed strain levels, following a hold until the stress stabilized. For Pt and Pt₉₀Au₁₀, the same region was mapped before and after loading. Because the much smaller Ni grains prevented reliable registration of the same region, the initial and deformed maps were acquired from different regions of the same specimen.

2.3. Strain-rate sensitivity and activation-volume measurements

The strain-rate sensitivity was measured from monotonic tensile tests performed over a range of applied strain rates, with the flow stress extracted at a fixed plastic strain of 0.2%. Because yielding in nanocrystalline films can extend over a finite strain interval, some grains may remain elastically loaded at this strain. Although evaluation at a larger plastic strain would more fully represent developed plastic flow, this could not be applied consistently because the usable plastic-strain range of the Ni specimens tested at the highest rates was $< 1\%$. We therefore adopted 0.2% plastic strain as a uniform reference across all testing conditions, consistent with our prior work and that of Jonnalagadda et al. on nanocrystalline and ultrafine grained Au [35,50]. Accordingly, the strain-rate sensitivity, defined as $m = \partial \ln \sigma / \partial \ln \dot{\epsilon}$, is interpreted here as an effective macroscopic strain-rate sensitivity at a consistently defined stage of deformation, rather than as the response of a uniformly plastic specimen. Activation volumes were obtained from repeated stress relaxation transients using the same MEMS platform, as recently demonstrated [35]. During the transient segment, the plastic strain rate after and before a reloading segment ($\dot{\epsilon}_{pl,i2}$ and $\dot{\epsilon}_{pl,f1}$, respectively), as well as the stress difference, $\Delta \sigma_{12}$, defined in Fig. 1d, were measured as detailed in [35]. The activation volume was then calculated as $V^* = \sqrt{3} k T \frac{\ln(\dot{\epsilon}_{pl,i2}/\dot{\epsilon}_{pl,f1})}{\Delta \sigma_{12}}$, where k is Boltzmann's constant and T is temperature during testing. Reported values are normalized by b^3 , where b is the

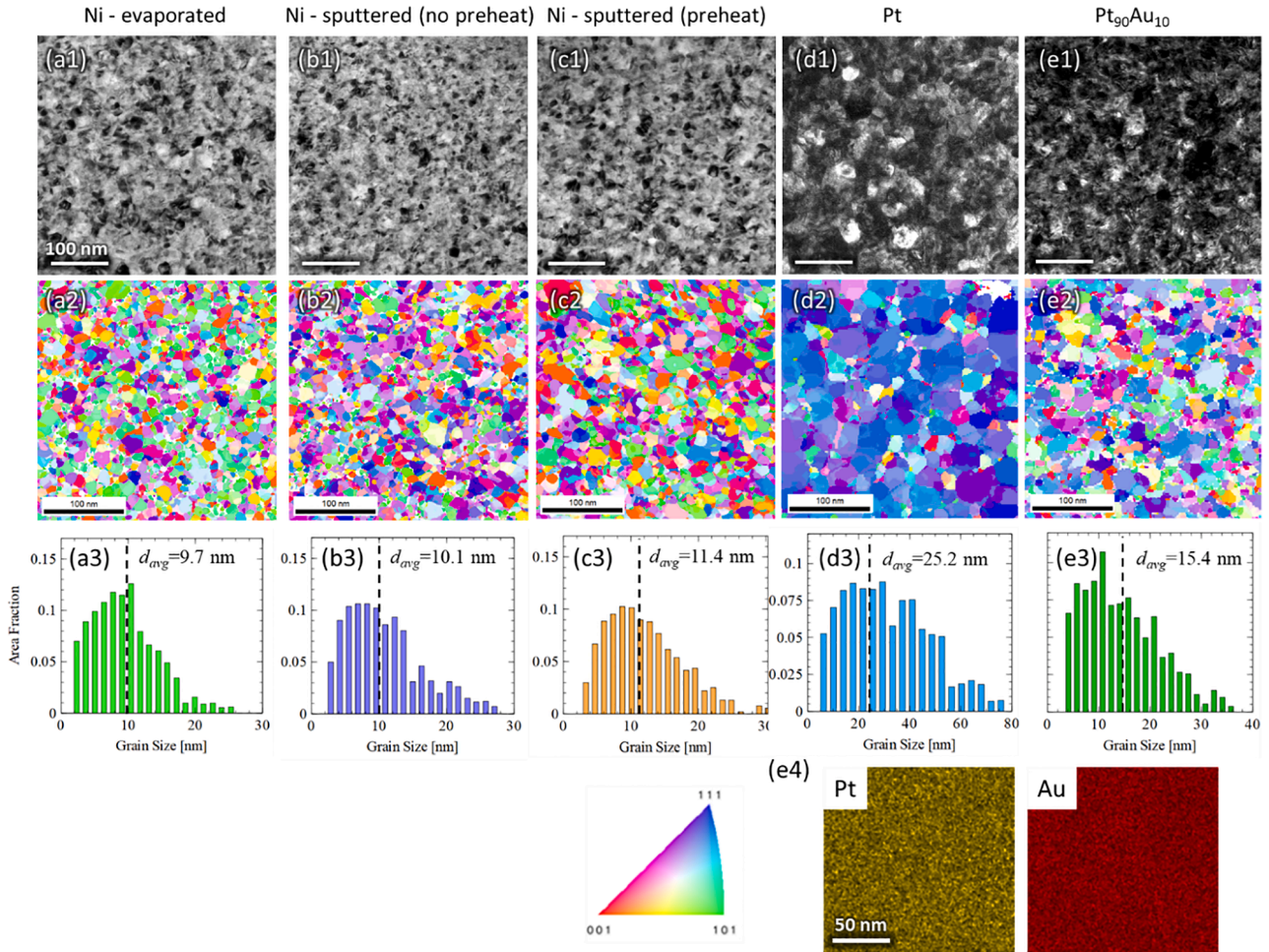


Fig. 2. (a–e) Representative as-deposited microstructures of (a) evaporated Ni, (b) sputtered (no preheat) Ni, (c) sputtered (preheat) Ni, (d) Pt, and (e) Pt₉₀Au₁₀ films. For each condition, the first row shows bright-field TEM images, the second row shows representative out-of-plane IPF orientation maps obtained by 4D-STEM, and the third row shows grain-size distributions. Dashed lines indicate the mean grain size, d_{avg} , for each film. The IPF color key is shown below the maps. The TEM-EDX elemental maps show the spatial distributions of Pt and Au in the Pt₉₀Au₁₀ film.

magnitude of the Burgers vector. The activation volumes were measured from multiple transient experiments conducted on different specimens. Activation volumes obtained at different flow stresses were then combined and plotted together as a function of stress.

3. Results

3.1. Initial microstructure

Bright-field TEM images of the initial microstructures for the Ni, Pt, and Pt₉₀Au₁₀ films are shown in Fig. 2a1–e1, with the corresponding representative 4D-STEM orientation maps shown in Fig. 2(a2–e2). Grain sizes quantified from the orientation maps (Fig. 2a3–e3) show that all three Ni films have average grain sizes of ~ 10 nm: the evaporated Ni films (Fig. 2a3) have an average grain size (d_{avg}) of 9.7 nm; the sputtered (no preheat) films have $d_{\text{avg}} = 10.1$ nm; and the sputtered (preheat) films (Fig. 2c3) have $d_{\text{avg}} = 11.4$ nm. In all cases the grain size distributions are narrow, with most grains lying between roughly 5 and 25 nm. The out-of-plane textures of the Ni films are compared in Supplementary Fig. S4. The Pt and Pt₉₀Au₁₀ films exhibit d_{avg} of 25.2 nm and 15.4 nm, respectively. The d_{avg} values for all specimens are indicated by the dashed lines in Fig. 2a3–e3. The Au elemental map in Fig. 2e4 shows a spatially uniform Au distribution in the Pt₉₀Au₁₀ film, indicating a chemically homogeneous Pt–Au solid solution at the mapped length scale. This result is consistent with previous studies on as-deposited Pt–Au films [51].

Despite their nearly identical mean grain sizes for Ni, these films

differ substantially in defect content and GB structural state, providing a controlled basis for examining how GB stability influences the subsequent deformation response. Representative cross-sectional TEM images of FIB-prepared specimens from the three films are shown in Fig. 3. Dislocations were identified from lattice-fringe terminations and extra half-planes, while periodically spaced fringe terminations along an interface were identified as a grain-boundary dislocation array accommodating the lattice misorientation. Dislocation content was first evaluated from representative HRTEM images acquired for each deposition condition (Fig. 3a–c). Among the three Ni films, the sputtered Ni (no preheat) film exhibits the highest dislocation content, followed by the sputtered Ni (preheat) film, while the evaporated film shows microstructure free of dislocations. Dislocation density is difficult to quantify from HRTEM fields of view, as it varies with grain size and crystallographic orientation—hence, we examined multiple regions for each condition to establish a qualitative trend, shown in Supplementary Fig. S1–3. Although a statistically complete assessment of lattice coherency across GB interfaces is experimentally challenging, direct HRTEM observations show that the sputtered (no preheat) film contains frequent GB-associated lattice-fringe offsets and dislocation-like interfacial defects, as highlighted in Fig. 3b2–b3. Such features are not observed in the evaporated and sputtered (preheat) films.

3.2. Mechanical properties: monotonic properties and plastic flow kinetics

Fig. 4 summarizes the monotonic tensile response of the Ni, Pt, and Pt₉₀Au₁₀ films. For Ni (Fig. 4a), the evaporated and sputtered (preheat)

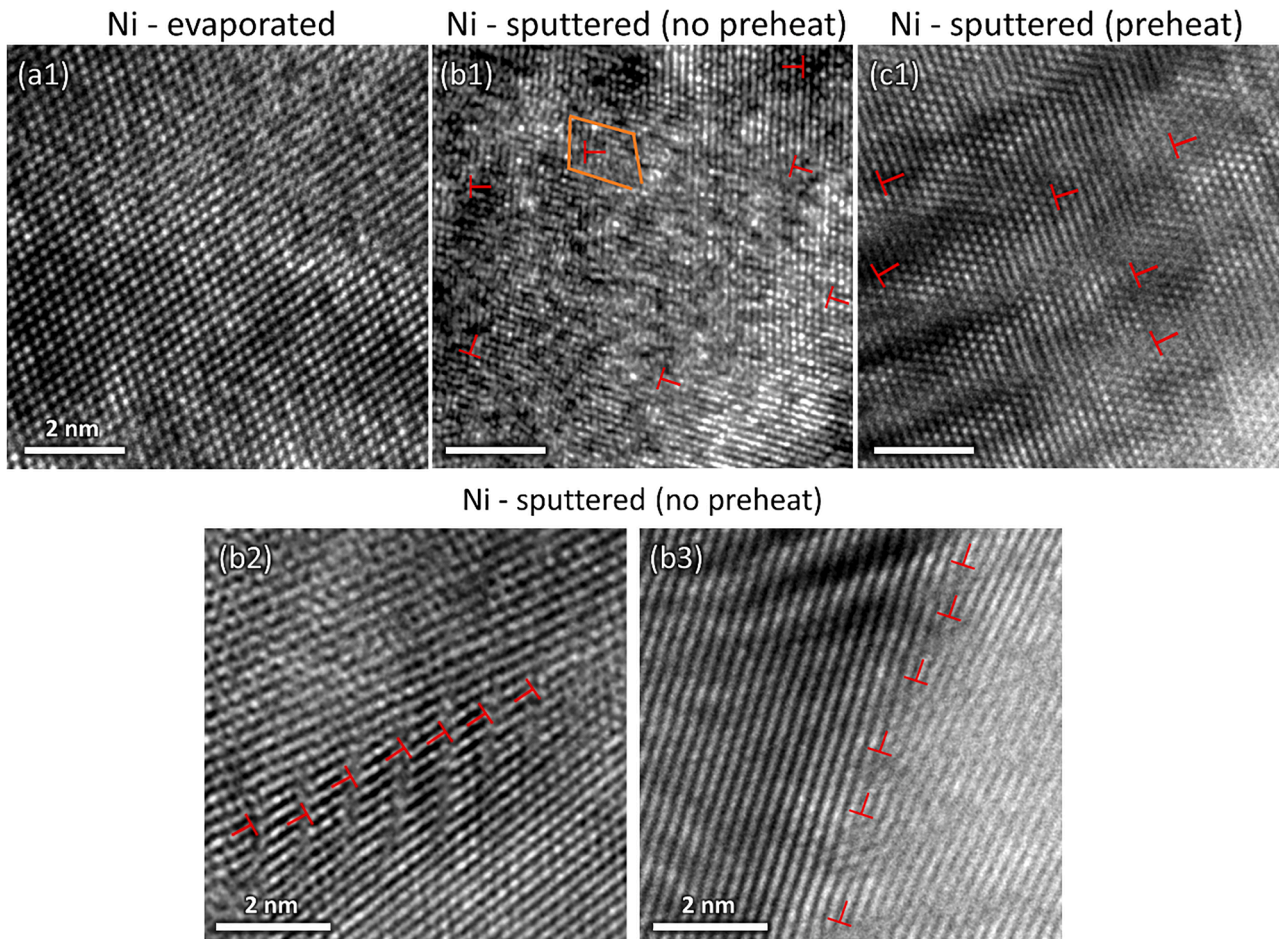


Fig. 3. Atomic-scale lattice defects in the three Ni films. Representative HRTEM images of grain interiors in the as-deposited evaporated Ni film (a1), sputtered (no preheat) Ni film (b1), and sputtered (preheat) Ni film (c1). HRTEM images in (b2, b3) show representative GB regions in the sputtered (no preheat) Ni film, where interfacial defect structures are marked by red symbols.

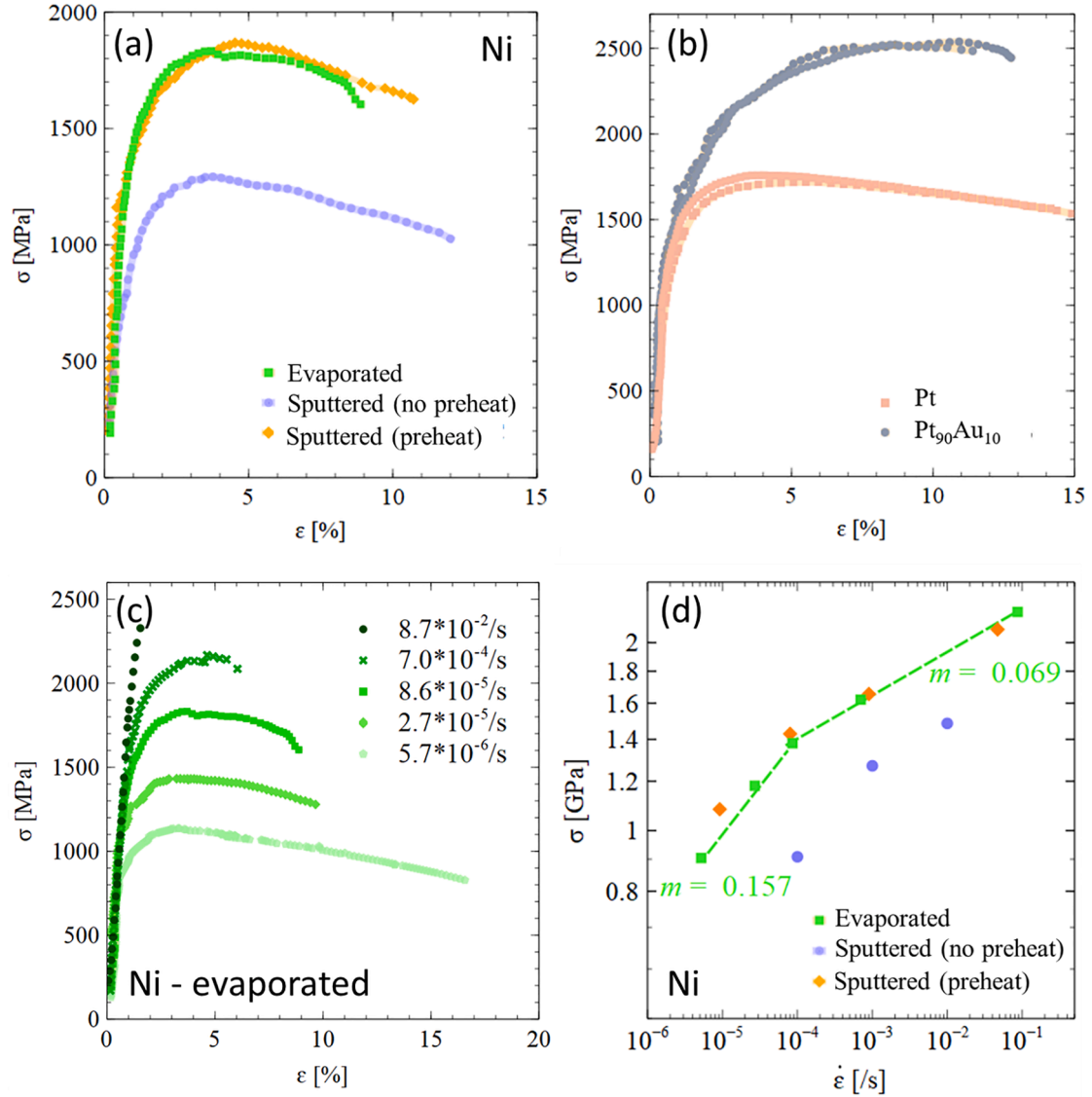


Fig. 4. (a) Representative engineering stress–strain curves for Ni films fabricated by evaporation, sputtering (no preheat), and sputtering (preheat). (b) Representative engineering stress–strain curves for Pt and Pt₉₀Au₁₀ films. (c) Strain-rate-dependent tensile response of the evaporated Ni film measured over applied strain rates from 5.7×10^{-6} to 8.7×10^{-2} s⁻¹. (d) Flow stress as a function of strain rate for the three Ni film types. The strain-rate sensitivity, m , was obtained from power-law fits to the flow stress–strain rate data, with the fitted curves indicated by green dashed lines for evaporated Ni.

films exhibit yield strengths, defined as the 0.2% plastic strain offset, of 1.4 GPa, whereas the sputtered (no preheat) film yields at 0.9 GPa. This contrast indicates that the three deposition conditions produce distinct mechanical responses despite their comparable initial grain sizes. The Pt and Pt₉₀Au₁₀ films provide an additional comparison with different GB stability (Fig. 4b). Pt₉₀Au₁₀ exhibits substantially higher strength (1.8 GPa) than Pt (1.4 GPa). These values are consistent with previous studies of Pt and Pt₉₀Au₁₀ films [52]. Pt₉₀Au₁₀ also maintains strain hardening over the measured plastic-strain window of approximately 10%, whereas Pt reaches necking at approximately 3% strain. The monotonic responses for Pt and Pt₉₀Au₁₀ were measured using two specimens each to demonstrate reproducibility. The measured elastic modulus are similar among the three Ni films, ranging from ~177 to 183 GPa, while the Pt and Pt₉₀Au₁₀ films exhibit moduli of ~170 GPa and 183 GPa, respectively.

Representative strain-rate-dependent tensile curves for the evaporated Ni film are shown in Fig. 4c. Fig. 4d summarizes the strain-rate dependence of the flow stress measured at a fixed plastic strain of 0.2% for all specimens. For the evaporated Ni films, the strain-rate

sensitivity, m , was extracted by fitting the flow stress versus strain rate data at a fixed plastic strain of 0.2% to the power-law relation, $\sigma \propto \dot{\epsilon}^m$. These data were fit using two power law relations. The results reveal a clear transition between two rate-sensitivity regimes: m evolves from a high- m regime at low rates (10^{-6} – 10^{-4} s⁻¹, $m = 0.157$) to a low- m regime at elevated rates (10^{-3} – 10^{-1} s⁻¹, $m = 0.069$). The decrease in m with increasing strain rate has previously been observed in nanocrystalline [50] and ultrafine-grained Au [35], and suggests a switch in governing mechanisms. Insufficient data points (see Fig. 4d) were obtained for the other two Ni films to perform the same strain rate analysis. Instead, activation volume measurements were performed across all films.

Fig. 5 shows the activation volume measurements from repeated transient experiments [35], plotted as a function of flow stress. The measured values fall into two distinct bands that correlate directly with microstructural stability, for both Ni and Pt systems. Ni films prepared by evaporation and sputtering (preheat) show a decrease in activation volumes from ~12b³ at ~1 GPa to ~7-8b³ at ~1.6-1.8 GPa (see Fig. 5 (a)). In contrast, for sputtered (no preheat) Ni films, substantially smaller activation volumes of ~4-5b³ were measured. Similarly, for

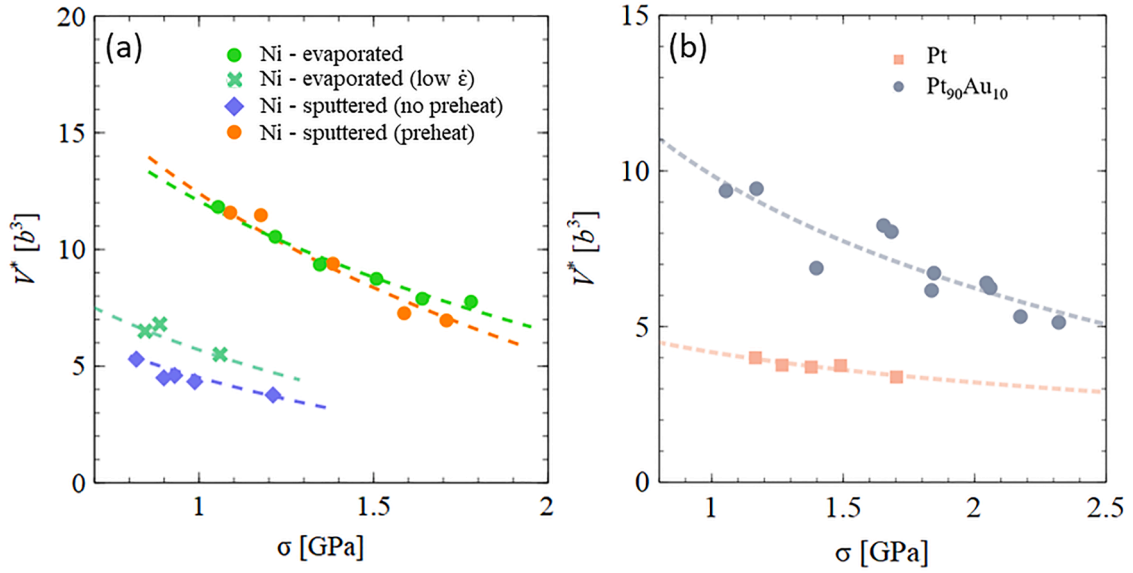


Fig. 5. (a) Activation volume, V^* , as a function of applied stress for evaporated Ni, sputtered (no preheat) Ni, and sputtered (preheat) Ni. (b) V^* as a function of stress for Pt and Pt₉₀Au₁₀ films.

evaporated Ni films, the activation volume measurements performed at 10^{-5} s^{-1} , provide much lower values ($\sim 5\text{--}7 b^3$) compared to the same films measured at 10^{-4} s^{-1} . This comparison between lower (10^{-5} s^{-1}) and normal (10^{-4} s^{-1}) strain rate follows our prior protocol [35]. Similarly, despite smaller initial d_{avg} , Pt₉₀Au₁₀ shows systematically larger activation volumes than pure Pt over the measured stress range (Fig. 5b). For Pt₉₀Au₁₀, V^* decreases from $\sim 10b^3$ to $\sim 5b^3$ with increasing flow stress from 1 to 2.3 GPa, whereas for pure Pt, V^* is around $3\text{--}4b^3$ for flow stresses of $\sim 1.1\text{--}1.7$ GPa.

3.3. In situ TEM observation of microstructural evolution

To facilitate observation of active deformation mechanisms in the plastic regime, samples were loaded to 1% plastic strain. The subsequent transient segments show pronounced differences in time-dependent deformation, consistent with the difference in activation volumes highlighted in the previous section. As shown by the stress–strain curves in Fig. 1c, despite the lowest peak stress of ~ 1.10 GPa, the sputtered (no preheat) film exhibits the largest stress relaxation (215 MPa). In contrast, the evaporated film relaxes substantially less (160 MPa), even at a higher peak stress of ~ 1.63 GPa. *In situ* TEM observations directly associate these transient mechanical responses with concurrent microstructural evolution (Figs. 6 and 7). Grain coarsening is observed in both the evaporated and sputtered (no preheat) Ni films during the transient segment, but its extent differs markedly. The evaporated film exhibits only limited microstructural evolution, with grain growth remaining minor over the observation window (Fig. 6a,b, Supplementary Video S1). In contrast, the sputtered (no preheat) film undergoes much more pronounced coarsening, with selected grains between the yellow arrows growing at the expense of adjacent grains (Fig. 6c,d, Supplementary Video S2). Substantial grain growth is already evident in the sputtered (no preheat) film before the onset of the relaxation/observation segment (Fig. 6c). Figure 6e,f shows a complementary high-resolution *in situ* experiment on the sputtered (preheat) Ni film (Supplementary Video S3). The applied stress was slightly above the macroscopic yield strength, 1.6 GPa, corresponding to approximately 1% plastic strain. At this stress level, the lattice remains largely coherent, with several pre-existing dislocations already visible. During the subsequent load-hold segment, a new dislocation segment nucleates, producing a localized lattice-fringe offset highlighted in red in Fig. 6f. This behavior was observed in several grains. The insets show masked IFFT images from

the dashed-box regions, highlighting the emergence of the new dislocation contrast, while the pre-existing dislocations show no observable motion.

In situ TEM observations further highlight the difference in microstructural stability between Pt and Pt₉₀Au₁₀. By the onset of high-magnification observation after loading to 4% strain, the Pt film had already undergone pronounced coarsening. During the subsequent transient segment, dislocation nucleation from GBs and propagation across grain interiors was observed, as indicated by the red arrows in Fig. 7b, c (Supplementary Video S4). In contrast, Pt₉₀Au₁₀ shows no obvious grain growth at the onset of observation and no resolvable GB motion during the transient segment. Instead, deformation is carried primarily by successive dislocation motion within a comparatively stable grain structure, as indicated in Fig. 7e, f and Supplementary Video S5..

3.4. Stress-assisted grain growth behavior

Fig. 8 quantifies the evolution of mechanically driven coarsening across the different films from the two complementary experiments described in 2.2. Fig. 8a shows the normalized grain-size increment, $\Delta d/d_0$ as a function of stress for the *in situ* tests on Ni. Fig. 8b shows the final grain-size distributions measured by 4D-STEM after loading to approximately 4% strain, followed by a 30 min transient segment. Both analyses show that coarsening is strongly film-type dependent, but they emphasize different aspects of the response. The post-deformation distributions indicate that the sputtered (no preheat) film undergoes the largest overall coarsening, with the average grain size increasing from 10.1 ± 5.5 nm to 27.7 ± 17.5 nm. In comparison, the evaporated film increases from 9.7 ± 4.6 nm to 18.1 ± 15.3 nm, while the sputtered (preheat) film increases from 11.4 ± 4.6 nm to 20.1 ± 11.6 nm. However, the kinetic contrast is even more pronounced in the *in situ* measurements during loading. The sputtered (no preheat) film exhibits the largest $\Delta d/d_0$ throughout the measured stress range, indicating substantially faster stress-assisted GB migration than the other films. At comparable stresses near 1.1 GPa, the measured $\Delta d/d_0$ in the sputtered (no preheat) film is more than an order of magnitude larger. This difference is partly associated with its lower yield stress (~ 0.9 GPa): at 1.1 GPa, this film is already undergoing substantial plastic deformation, whereas the evaporated and preheated films remain below their yield stresses of ~ 1.4 GPa. Its larger $\Delta d/d_0$ therefore reflects both the earlier

Ni - evaporated

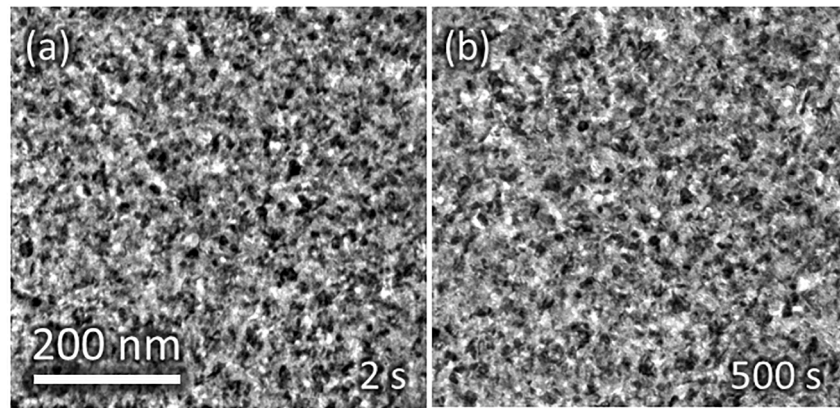
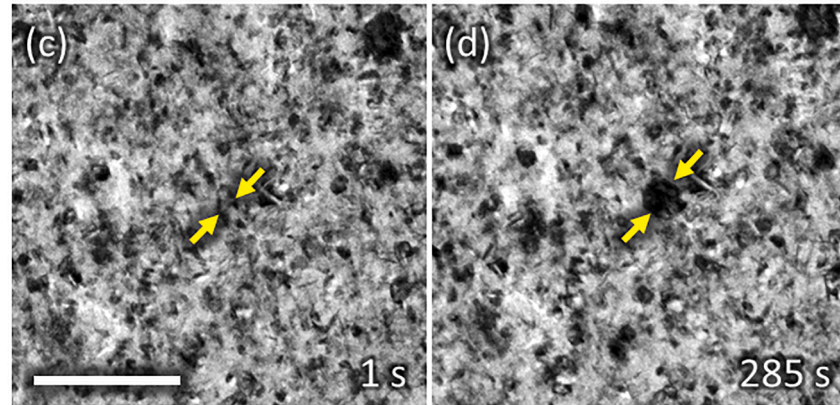
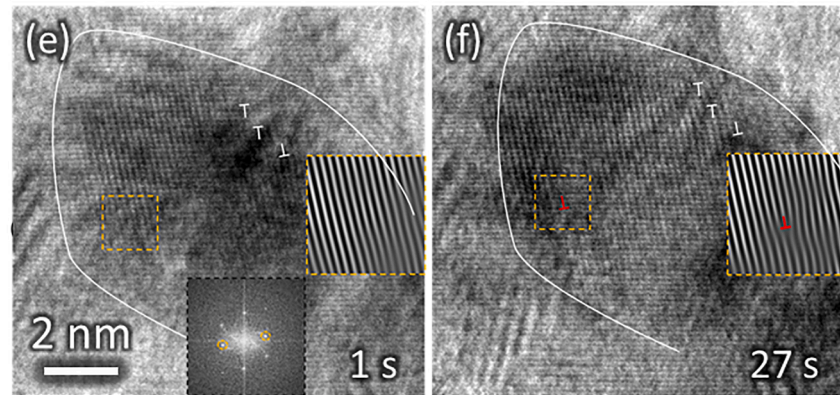
Ni - sputtered
(no preheat)Ni - sputtered
(preheat)

Fig. 6. *In situ* bright-field TEM snapshots for Ni prepared by evaporation (a, b), sputtering (no preheat) (c, d), and sputtering (preheat) (e, f). Yellow arrows in c–d track a coarsening grain. HRTEM snapshots acquired during a transient segment in a sputtered (preheat) Ni film (thickness ≈ 70 nm). Pre-existing dislocations are highlighted in white. The orange dashed boxes mark the corresponding masked IFFT reconstructions of the selected g vectors, smoothed using a 5-pixel kernel (indicated in the inset of (e)). The newly nucleated dislocation is highlighted in red.

onset of plastic flow and a greater propensity for stress-assisted GB motion. In contrast, the sputtered (preheated) film remains close to the evaporated film over the full measured stress range.

The same load–hold protocol was then applied to the Pt-based films using interrupted 4D-STEM, with orientation maps acquired from the same region before deformation and after loading to 4% strain followed by a 30 min hold at constant actuator displacement. The corresponding grain-size distributions and orientation maps are summarized in Fig. 8c. Sputtered Pt undergoes pronounced stress-assisted coarsening, with the mean grain size increasing from 25.2 ± 15.1 to 48.2 ± 29.6 nm within the tracked area. In contrast, Pt₉₀Au₁₀ remains comparatively stable in the same-area comparison, with the mean grain size changing only slightly from 15.6 ± 7.5 to 16.4 ± 8.1 nm.

The *in situ* grain-size measurements in Fig. 8a show that grain growth begins near yielding in the Ni films and becomes more pronounced at higher applied stress, which covers the stress range used during

activation volume measurement. This effect is strongest in sputtered (no preheat) Ni, which exhibits a rapidly evolving grain structure during loading and after the subsequent hold. A similar microstructural evolution is observed in sputtered Pt, where the mean grain size nearly doubles after deformation. These are the same two conditions that define the lower branch of activation volume observed in Fig. 5. Notably, despite the large changes in grain size, their activation volumes show little stress dependence and remain confined to a narrow range, of $\sim 4\text{--}5 b^3$ for sputtered (no preheat) Ni and $\sim 3\text{--}4 b^3$ for sputtered Pt. During the fixed-actuator transients used for microstructural observation, the plastic strain rate progressively decreases as the stress relaxes. The transient therefore samples lower effective strain rates and longer time scales than the preceding monotonic loading, potentially increasing the contribution of slow, diffusion-assisted GB processes and amplifying the observed grain growth. The magnitude of coarsening during the hold is consequently protocol dependent and should not be interpreted as a

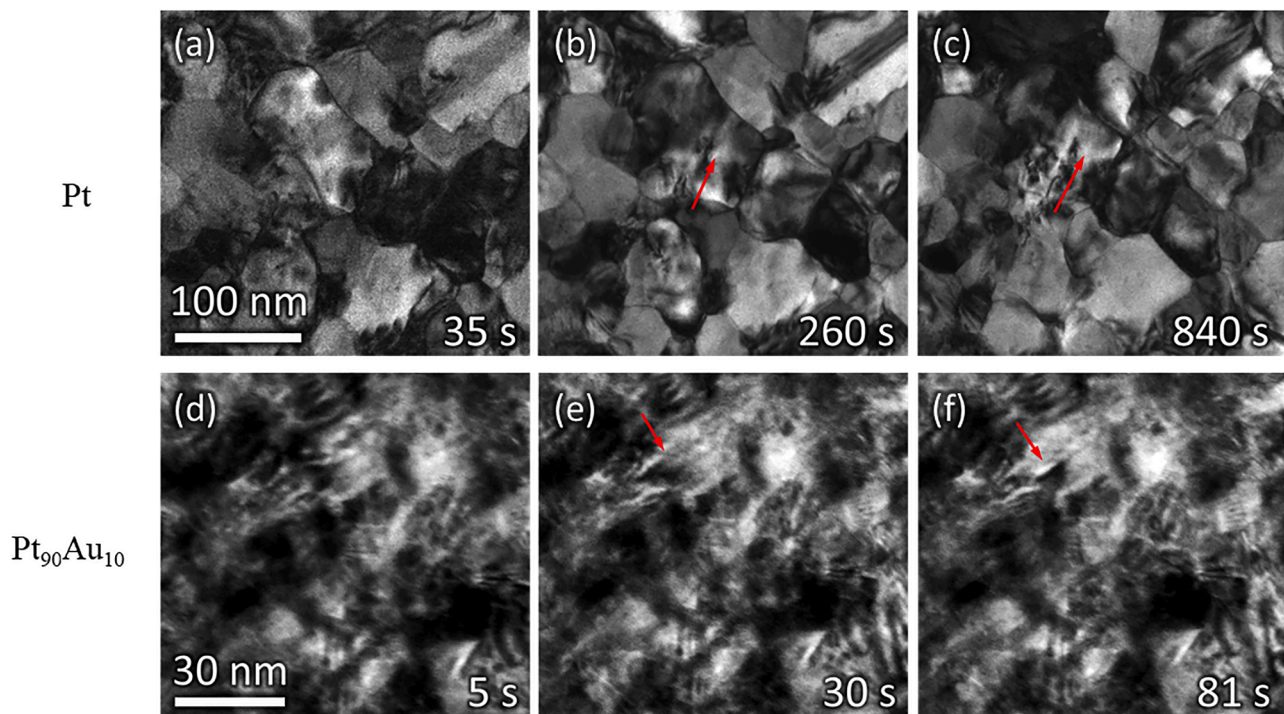


Fig. 7. (a–c) *In situ* TEM snapshots of sputtered Pt acquired during the transient segment after prior loading to 4% strain. (d–f) Snapshots of $\text{Pt}_{90}\text{Au}_{10}$ acquired under the same protocol. Red arrows mark dislocations nucleated from GBs and gliding across coarsened grains during the transient segment.

direct measure of grain-growth kinetics during continuous loading. Nevertheless, substantial coarsening is already present before the hold in sputtered (no preheat) Ni and Pt, while the independent measurements in Fig. 8a show the same relative difference in GB mobility among the Ni films during monotonic loading. The transient observations are therefore interpreted together with the pre-hold microstructure and the monotonic-loading measurements, rather than as standalone evidence.

4. Discussion

This study reveals a clear and systematic connection between mechanical response, microstructural evolution, and activation parameters in both nanocrystalline Ni and Pt. Two complementary routes were used to vary GB stability: low-energetic bombardment or mild thermal exposure during deposition, which promotes GB relaxation and defect annihilation [42], and Au alloying in Pt, which provides chemical stabilization and solute-mediated kinetic pinning [53].

For the Ni films, the three deposition methods were selected because they are expected to generate different nonequilibrium GB states while limiting the structural and texture variability reported in the literature [54,55]. This design allows the subsequent mechanical responses to be interpreted primarily as a function of GB stability. The evaporated films involve lower incident particle energies (~ 0.1 – 0.5 eV [56]), and are therefore expected to accumulate less bombardment-induced defect storage during growth [55]. Similar deposition-dependent differences in defect storage have been reported in other material systems, and metal evaporation carried out under moderate vacuum (e.g. $\sim 5 \times 10^{-6}$ Torr) can preserve nearly no defect at grain boundaries [57,58]. As a result, the evaporated Ni films are expected to possess a comparatively relaxed and structurally stable GB network. In contrast, the room-temperature sputtered Ni films are exposed to more energetic species extending to tens of eV [59]; such conditions are more likely to produce densification, knock-on damage, excess defect storage, and thus a more nonequilibrium GB structure [60,61]. This understanding is consistent with prior studies linking high-energetic bombardment during sputter deposition to enhanced defect incorporation and microstructural disorder [55,60].

The sputter-deposited (preheat) films exhibit greater stability due to the higher substrate temperature, which promotes thermally assisted defect rearrangement and partial annihilation [42]. Prior studies show that even low-temperature annealing can relax nonequilibrium GB structures and drive the boundary network toward a more equilibrated state [39, 42]. Sputtering (preheat) is therefore expected to retain some disadvantages of sputter deposition while developing more stabilized boundary structures than films deposited by a similar procedure at room temperature. These expected differences in structural state are examined directly in Fig. 3. $\text{Pt}_{90}\text{Au}_{10}$ was deposited by the same sputtering route as Pt, but the addition of Au provides a chemically modified boundary network while maintaining a spatially homogeneous alloy.

Across both routes, the measured V^* values identify two reproducible regimes associated with comparatively stable and strongly evolving GB networks, respectively. Stable GB networks, including evaporated Ni, sputtered (preheat) Ni, and $\text{Pt}_{90}\text{Au}_{10}$, exhibit suppressed stress-assisted coarsening and larger activation volumes, whereas unstable GB networks, including sputtered (no preheat) Ni and sputtered pure Pt, show pronounced grain growth and smaller activation volumes. The strongly evolving GB regime is consistently associated with sputtered films, including sputtered (no preheat) Ni and Pt, even though the larger grain size of Pt would ordinarily be expected to favor more dislocation-dominated plasticity [62,63]. Importantly, the small activation volumes measured in the unstable films persist even at higher stresses, corresponding to later stages of loading where substantial grain coarsening has already occurred, as shown by the grain-size measurements for sputtered (no preheat) Ni in Fig. 8a and sputtered Pt in Fig. 8c. Although these films have evolved toward a coarsened microstructure, their activation volumes remain in the lower range of ~ 4 – $5 b^3$ for sputtered (no preheat) Ni and ~ 3 – $4 b^3$ for sputtered Pt, rather than shifting toward the larger activation volumes associated with the dislocation-associated processes. The out-of-plane textures of Ni films are compared in Supplementary Fig. S4. All films exhibit relatively low maximum MRD values, indicating that their textures are close to random and thus could not explain the present result.

In the following sections, we interpret these experimental signatures

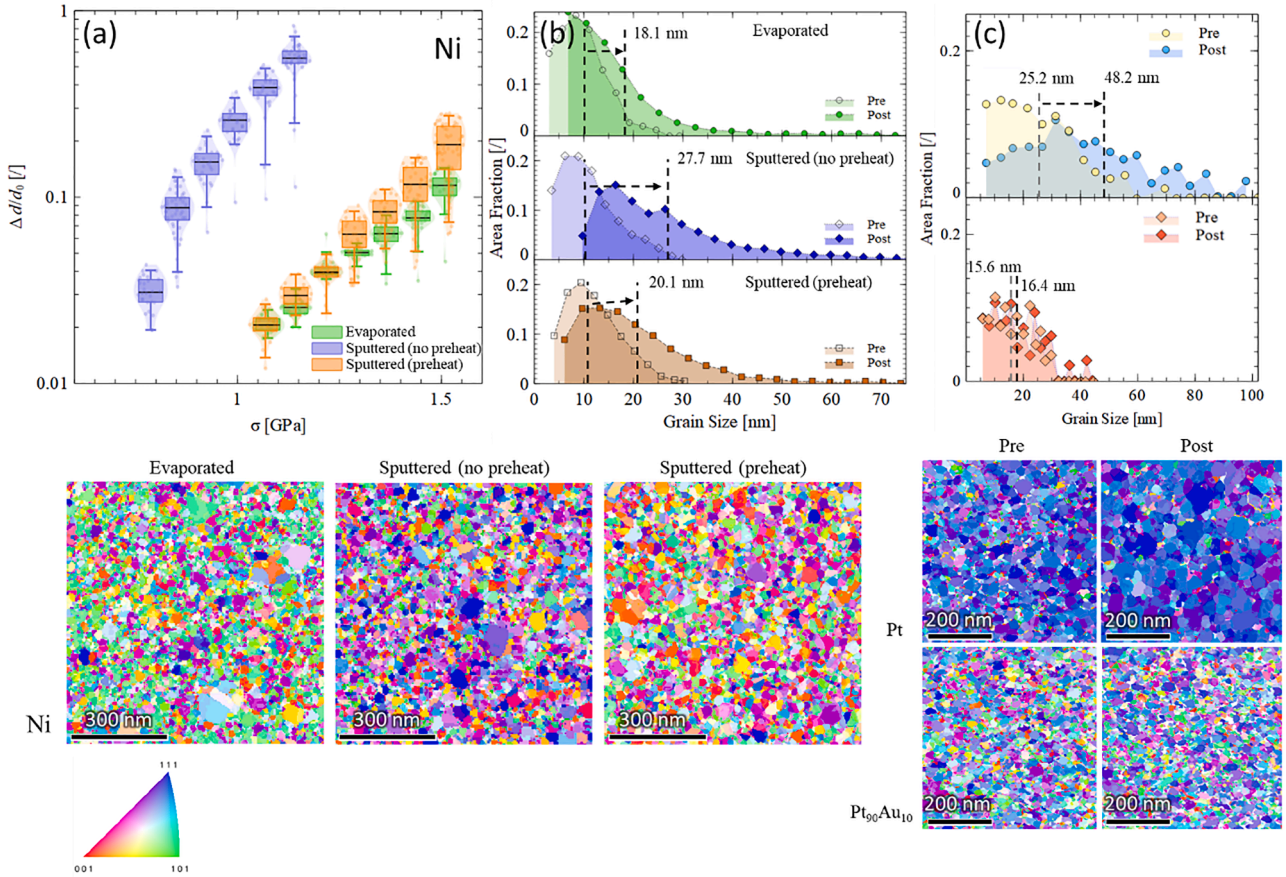


Fig. 8. Quantification of mechanically driven grain coarsening in the Ni and Pt-based films. (a) Normalized grain-size increment, $\Delta d/d_0$, during monotonic loading as a function of applied stress for evaporated Ni, sputtered (no preheat) Ni, and sputtered (preheat) Ni. (b) Area-weighted grain-size distributions of the three Ni films after loading to 4% strain followed by a 30 minute hold. Representative post-deformation 4D-STEM orientation maps are shown below. Dashed lines indicate the average grain size after the load-hold sequence. (c) Same-area interrupted 4D-STEM comparison for Pt and Pt₉₀Au₁₀ before and after loading to 4% strain followed by a 30 min hold. Sputtered Pt shows pronounced coarsening, whereas Pt₉₀Au₁₀ remains comparatively stable. Representative pre- and post-deformation orientation maps are shown below the grain-size distributions.

in terms of the underlying rate-limiting unit processes, compare the Ni results with atomistic predictions, and clarify the role of GB stability in selecting the rate-controlling deformation mechanism.

4.1. Dislocation nucleation at GBs

For Ni specimens with low GB defect concentrations, such as evaporated Ni and sputtered (preheat) Ni, the measured activation volumes at typical laboratory strain rates of $\sim 10^{-4} \text{ s}^{-1}$ cluster within a range of $\sim 7\text{--}12b^3$. Direct *in situ* TEM observations (Fig. 6e, f, and Supplementary Video S3) provide compelling evidence that plastic flow in this regime is dominated by dislocation nucleation at GBs. HRTEM imaging of sputtered (preheat) Ni reveals the emergence of short dislocation segments from a nearby GB.

Quantitative support for this rate-controlling step is provided by direct comparison with atomistic free-end nudged elastic band (FENEb) simulations of GB dislocation nucleation. Our prior FENEb simulations [21] focused primarily on symmetric tilt GBs, which represent energetically favorable but structurally idealized configurations. The atomistically calculated activation volume for these boundaries is $\sim 20b^3$. The enhanced stability of these boundaries raises the barrier for dislocation nucleation, requiring cooperative activation of a larger number of atoms and thereby increasing the activation volume. However, such special boundaries constitute only a small fraction of the GB population in nanocrystalline materials. In contrast, most GBs in these films are not symmetric or low coincidence site lattice (CSL) value, with relatively

high boundary energies.

To investigate the activation volume associated with dislocation nucleation from a more relevant GB, we performed FENEb simulations for one experimentally reported asymmetric tilt GB [30] with a $\langle 110 \rangle$ tilt axis and a misorientation of 21.8° as shown in Fig. 9a. The structure was relaxed using an embedded atom method potential for Ni [64]. To highlight the GB configuration, atoms with a face-centered cubic structure are colored green, those with a hexagonal close-packed structure are red, and all other atoms are colored white. The simulated bicrystal has in-plane dimensions of approximately $10 \text{ nm} \times 10 \text{ nm}$ with free surface boundary conditions, and a thickness of $\sim 15 \text{ nm}$ along the tilt axis with periodic boundary conditions.

Fig. 9b presents the minimum energy path for dislocation nucleation at this asymmetric GB obtained from FENEb calculations, while Fig. 9c shows the corresponding atomic configurations at the initial state, saddle point, and final state along the minimum energy path. The simulation reveals that dislocation nucleation initiates as an embryonic dislocation loop emanating from the junction between the GB and the free surface. By varying the applied axial load along $\langle 110 \rangle$, the stress-dependent activation energy $E(\tau)$ was determined as a function of the resolved shear stress τ , as shown in Fig. 9d. The circles represent direct FENEb results, and the solid line is a fitted curve. The activation volume, defined as $V^* = -\frac{\partial E(\tau)}{\partial \tau}$, is plotted in Fig. 9e. The dislocation process with a characteristic E value of 0.7 eV corresponds to a typical laboratory strain rate of 10^{-3} s^{-1} at room temperature [65]. Consequently, the corresponding simulated V^* is $\sim 7b^3$, which is approximately 1/3 of that

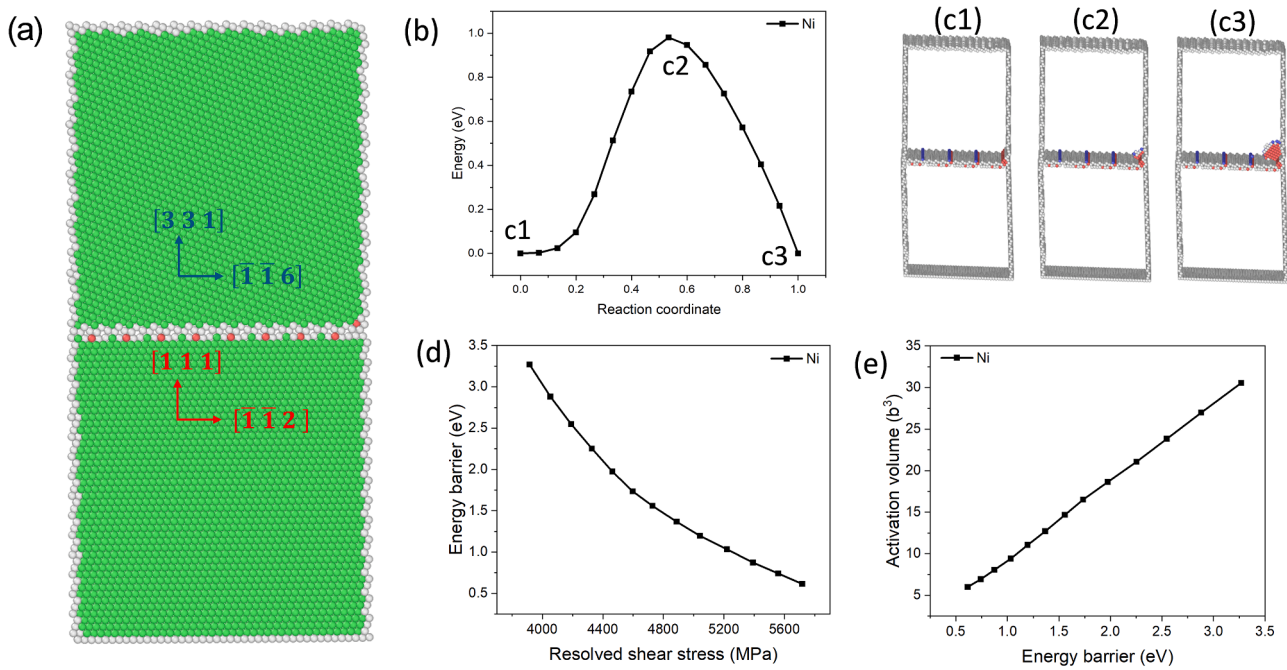


Fig. 9. FENEb results for GB dislocation nucleation at an asymmetric tilt GB with a $\langle 110 \rangle$ tilt axis and a misorientation of 21.8° . (a) Atomistic FENEb simulation setup for GB dislocation nucleation. (b) Minimum energy path calculated by FENEb. Each symbol represents the energy of a replica along the minimum energy path under an applied resolved shear stress. (c1–c3) Atomic configurations (marked in (b)) along the minimum energy path. (d) Activation energy as a function of resolved shear stress. Circles represent the FENEb results and the solid line is the fitted curve. (e) Activation volume as a function of energy barrier.

calculated for symmetric tilt GBs.

Taken together, these results suggest that symmetric tilt GBs provide a high-end estimate of the activation volume associated with GB dislocation nucleation ($20b^3$), while the asymmetric boundary examined here demonstrates that more general GB structures can produce substantially lower values, down to $7b^3$. The experimentally measured activation volumes for both evaporated and sputtered (preheat) Ni ($7\text{--}12b^3$) fall within this predicted range, indicating quantitative consistency between atomistic simulations and macroscopic measurements. This close correspondence, together with direct *in situ* TEM observations, establishes GB dislocation nucleation as the rate-limiting deformation mechanism when the GB network remains stable against stress-assisted coarsening. If the GB network is unstable, as in sputtered (no preheat) Ni, the experimentally measured activation volumes are much lower ($3\text{--}5b^3$), indicating the involvement of competing rate-limiting steps.

The expected range of activation volume for GB dislocation nucleation in the Pt-based films can be estimated from the dependence of activation volume on shear modulus using the Ni FENEb values. For consistency, the shear moduli were calculated from the measured elastic moduli using $G = E/[2(1 + \nu)]$, where ν is the Poisson's ratio, giving $G \approx 68\text{--}70$ GPa for the Ni films, $G \approx 62$ GPa for Pt, and $G \approx 67$ GPa for Pt₉₀Au₁₀. This scaling gives an expected GB dislocation-nucleation range of $\sim 8\text{--}23b^3$ for Pt and $\sim 7\text{--}21b^3$ for Pt₉₀Au₁₀. Because the lower bound of the measured V^* values for Pt₉₀Au₁₀ is $\sim 5b^3$, it is closer to the controlling step of dislocation nucleation. Interestingly, near the peak stress, where dislocation nucleation, glide, and junction formation are directly observed in the drastically coarsened Pt grains in Fig. 7, the measured activation volume is still $\sim 3\text{--}4b^3$, which falls well below the nucleation range, indicating that these dislocation-mediated processes are not the rate-limiting step. Similarly, sputtered (no preheat) Ni retains a small activation volume after substantial grain growth. These results show that substantial grain growth alone does not necessarily shift the transient response toward the dislocation-nucleation regime; instead, the rate-controlling process remains governed by the competing steps discussed next.

4.2. Diffusion-assisted mechanisms

The grain-coarsening deformation mode identified in this study is characterized by the smallest activation volumes, with V^* reaching values as low as $\sim 3b^3$. Such values are substantially lower than those expected for dislocation nucleation or glide by cutting forest dislocations, indicating that the rate-limiting unit process shifts to a more localized mechanism when the GB network is mechanically unstable.

A natural class of mechanisms consistent with these observations involves diffusion-assisted GB processes. Nonequilibrium GBs are known to contain intrinsic and extrinsic interfacial dislocations, excess free volume, and long-range elastic strain fields, all of which enhance short-circuit diffusion along GBs and promote stress-assisted boundary migration [66]. Under applied stress, GB migration can be accommodated by the nucleation and motion of GB disconnections—line defects that carry both a Burgers vector component (associated with sliding) and a step height (associated with migration) [13,30,31,67–72]. When the Burgers vector component is non-zero, the motion of disconnections generally requires climb-assisted processes mediated by point-defect diffusion [73], leading to intrinsically small activation volumes.

It has been proposed that GB sliding can become the dominant deformation mechanism even at room temperature [74,75]. *In situ* tensile studies and simulations on nanocrystalline Ni films indicate that, as the grain size gradually approaches ~ 10 nm, GB sliding increasingly occurs in tandem with the nucleation of partial dislocations [76–80]. These conditions place diffusion-assisted boundary motion on a comparable kinetic footing with displacive processes.

The experimental trends observed here provide direct support for the bifurcation in the activation volume measurement. All conditions exhibiting measurable grain coarsening—either due to intrinsically unstable boundary structures (sputtered (no preheat) Ni) or due to extended time scales at low strain rate (evaporated Ni tested at $\sim 10^{-5}$ s⁻¹)—also exhibit the smallest activation volumes and the highest strain-rate sensitivities. Conversely, when GB motion is more restricted—either by increasing the strain rate or by stabilizing the boundary structure through increased structural order or solute

segregation—the activation volume increases, and the deformation kinetics shift away from this diffusion-assisted regime. Similar behavior was reported in nc Al films, where Gianola et al. found that stress-coupled grain growth accompanied strain-rate sensitivities up to $m \approx 0.14$ [81]. Subsequent experiments showed that increasing oxygen-related impurity content stabilized the Al grain structure against stress-driven coarsening and produced a strong but brittle response, whereas lower-impurity films underwent discontinuous grain growth and sustained more than 15% plastic strain [82].

4.3. Role of GB stability

The results presented above demonstrate that, among the films examined here with comparable grain sizes, differences in GB stability strongly influence the rate-limiting deformation mechanism. Although prior studies have primarily interpreted activation parameters in terms of grain size [35], the present work shows that materials with comparable grain sizes can exhibit fundamentally different kinetic responses depending on the structural state and kinetic stability of their GB networks. Even after stress-assisted grain growth produces grains large enough to accommodate dislocation activity [43,62,63,80], diffusion-related GB processes can remain rate controlling despite the increased contribution of intragranular dislocation motion.

Specifically, GB stability governs the competition between displacive and diffusion-assisted processes by controlling both the availability of fast diffusion pathways and the propensity for stress-assisted boundary migration. Nonequilibrium GBs, such as those introduced by energetic sputter deposition (e.g., sputtered (no preheat) Ni and pure Pt), contain excess free volume, structural disorder, and interfacial defects, which enhance short-circuit diffusion and facilitate shear-coupled GB motion. Under these conditions, plastic deformation becomes strongly coupled to GB migration and grain coarsening, leading to small activation volumes and elevated strain-rate sensitivities, as discussed in Section 4.2.

In contrast, structurally stabilized GB networks—either through lower-energy deposition routes (as in evaporated Ni), thermally assisted relaxation (sputtered (preheat) Ni), or solute segregation ($\text{Pt}_{90}\text{Au}_{10}$)—suppress stress-assisted GB motion and limit the contribution of diffusion-mediated processes. As a result, plastic flow is primarily accommodated by dislocation nucleation at GBs, as evidenced by direct *in situ* TEM observations and the quantitative agreement with atomistic FENEBC predictions described in Section 4.1. The corresponding activation volumes in this regime are consistently larger, reflecting the more collective nature of the nucleation process. Trace oxygen may also be present in these films and could weakly segregate to GBs [83,84]; however, its concentration is below the detection limit of TEM-EDX in the present measurements, so its contribution cannot be quantified directly.

Importantly, GB stability not only determines the dominant deformation mechanism under a given condition but also controls the transition between mechanisms through its interaction with external parameters such as strain rate. For example, even structurally stable GB networks can exhibit grain-coarsening behavior when sufficient time is available for diffusion-assisted processes (e.g., at low strain rates), whereas increasing the strain rate effectively suppresses these processes and shifts the response toward dislocation-controlled plasticity. This interplay highlights the need to consider GB stability in terms of both structural state and kinetic response.

Taken together, these results establish GB structural stability as a unifying parameter governing the plastic flow in nanocrystalline metals. By modulating the balance between diffusion-assisted boundary processes and displacive dislocation activity, GB stability could influence the operative rate-limiting unit mechanism and, consequently, the measured activation parameters. This framework provides a consistent interpretation for the wide range of activation volumes reported in the literature and resolves apparent discrepancies between experimental observations and atomistic predictions.

These findings reveal a performance trade-off between microstructural stability and rate-sensitive strain accommodation in nanocrystalline metallic films. GB stabilization promotes retention of the grain structure and strength, whereas positive strain-rate sensitivity can delay strain localization; this latter effect has been associated with enhanced tensile ductility in nanocrystalline Al and ultrafine grained Au undergoing GB-mediated deformation [35,85]. However, when the rate-dependent response is coupled to diffusion-assisted processes, the same boundary kinetics that accommodate strain also drive irreversible coarsening, potentially reducing strength and strain-hardening capacity while increasing deformation heterogeneity. The early necking of pure Pt, despite its pronounced GB activity and small activation volume, demonstrates that an unstable GB network alone does not ensure stable plastic flow. The relevant design objective is therefore to control the extent of microstructural change during deformation. Limited and spatially distributed grain growth may be beneficial if it facilitates strain accommodation and enables dislocation storage, whereas extensive or localized coarsening can erode strength and accelerate localization. Establishing the quantitative relationships among GB migration, strain hardening, and localization will be necessary to identify this processing and loading window.

5. Conclusions

Nanocrystalline metals reside in a crossover regime where both dislocation activity and GB-mediated accommodation can contribute to plastic flow. The present results show that the rate-limiting process for nanocrystalline Ni and Pt is not governed by grain size alone, but is highly sensitive to the structural stability of the GB network. By varying boundary stability through deposition route, mild thermal exposure during sputtering, and alloying, two reproducible kinetic regimes are identified.

When the GB network is comparatively stable, as in evaporated Ni, sputtered (preheat) Ni, and $\text{Pt}_{90}\text{Au}_{10}$, stress-assisted grain coarsening is suppressed. These films exhibit higher yield strengths and larger activation volumes, consistent with a displacive process controlled by GB dislocation nucleation. In Ni, this stable-grain regime corresponds to yield strengths of 1.4 GPa and activation volumes of $\sim 7\text{--}12b^3$, in quantitative agreement with atomistic predictions for GB dislocation nucleation.

In contrast, unstable GB networks, as in sputtered (no preheat) Ni and sputtered pure Pt, exhibit lower yield strengths, pronounced stress-assisted grain growth, and smaller activation volumes despite evolving microstructure. For the sputtered (no preheat) Ni film, the yield strength decreases to 0.9 GPa and V^* decreases to $\sim 4\text{--}5b^3$. This shift indicates that the rate-limiting process moves away from dislocation nucleation toward a more localized, diffusion-assisted boundary process.

CRediT authorship contribution statement

Yichen Yang: Writing – original draft, Investigation, Formal analysis, Data curation. **Kunqing Ding:** Writing – original draft, Investigation, Formal analysis. **Kyle R. Dorman:** Writing – review & editing, Methodology. **Brad L. Boyce:** Writing – review & editing, Resources, Methodology. **Ting Zhu:** Writing – review & editing, Supervision, Methodology, Investigation, Funding acquisition, Conceptualization. **Josh Kacher:** Writing – review & editing, Supervision, Investigation, Funding acquisition, Conceptualization. **Olivier Pierron:** Writing – original draft, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.actamat.2026.122746](https://doi.org/10.1016/j.actamat.2026.122746).

Appendix: Details of the FENEB calculations

The atomistic model used for the FENEB calculations contained 225,918 Ni atoms. The bicrystal consisted of an asymmetric $[1\bar{1}0]$ tilt GB formed between the (331) plane of the upper grain and the (111) plane of the lower grain, with a misorientation angle of 21.8° . The simulation cell had in-plane dimensions of approximately $10\text{ nm} \times 10\text{ nm}$ and a thickness of approximately 15 nm along the $\langle 110 \rangle$ tilt axis. Periodic boundary conditions were applied along the tilt axis, while free surfaces were employed in the other two directions.

Prior to constructing the FENEB pathway, the bicrystal was mechanically preloaded to identify the preferred dislocation-nucleation event. The nucleation site and Burgers-vector direction observed during preloading were then used to construct a nucleated partial-dislocation configuration. The nucleated defect was a $1/6\langle 112 \rangle\{111\}$ Shockley partial dislocation. This configuration was used to initialize the reaction pathway between the defect-free grain-boundary state and the state containing one nucleated partial dislocation. In this way, the preloading calculation was used only to identify a physically relevant nucleation site and slip system, whereas the subsequent FENEB calculation determined the corresponding minimum-energy pathway and saddle-point configuration.

The FENEB calculations were performed using 16 replicas. A displacement-controlled loading condition was employed. Mechanical loading was imposed by prescribing displacement in the x direction to boundary layers consisting of five atomic layers at the top and bottom free surfaces. For each prescribed displacement, the corresponding applied stress was obtained from the atomistic calculation and converted to the resolved shear stress, τ , acting on the identified $1/6\langle 112 \rangle\{111\}$ slip system. A separate FENEB calculation was then performed at each loading level to determine the stress-dependent activation barrier. The minimum-energy pathway was relaxed using the Quickmin algorithm. A spring constant of $1\text{ eV}/\text{\AA}^2$ was used between neighboring replicas, with a force convergence criterion of $1 \times 10^{-3}\text{ eV}/\text{\AA}$ and a maximum of 5×10^5 minimization steps. The free-end NEB treatment was applied to the final replica. The activation energy at each applied stress, $E(\tau)$, was determined from the energy difference between the saddle point and the initial state along the converged minimum-energy pathway. The stress dependence of the activation barrier was fitted using $E(\tau) = A(1 - \tau/\tau_0)^n$, where A , τ_0 , and n are fitting parameters. The activation volume was subsequently obtained from $V^* = -\frac{\partial E(\tau)}{\partial \tau} = \frac{An}{\tau_0}(1 - \tau/\tau_0)^{n-1}$. The resulting activation volume was normalized by b^3 , where b is the magnitude of the full Burgers vector. The comparison with experiment was made at an activation barrier of approximately 0.7 eV , corresponding to a typical laboratory deformation rate at room temperature, as discussed in Section 4.1.

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