Strain-Induced Ultrahard and Ultrastable Nanolaminated Structure in Nickel
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they reproduce the observed larger scatter and possibly higher normalization in SMBH-galaxy scaling relations for the most massive SMBHs (1, 2). Other physical effects will also be built into the next generation of GWB models. For example, recent numerical simulations of massive galaxy mergers predict binary SMBHs with eccentricities ranging between 0.1 (31) and 0.9 (32). If binaries radiating gravitational waves at frequencies relevant to pulsar timing arrays are considerably eccentric or predominantly evolving under environmental interactions (33), the spectral shape of $\Omega_{\text{GW}}(f)$ may differ from current predictions (34).

References and Notes
18. The data sets are described in supplementary text section S1.
19. Additional description of the algorithm is found in supplementary text section S2.
22. Details of the data check and other tests can be found in supplementary text section S2 and table S2.
23. The algorithm used for calculating $f_{\text{pulsar}}$ is described in supplementary text section S3.
24. Corrections to previous models for the GWB are outlined in supplementary text section S4. The models for the GWB are described in additional detail in supplementary text sections S5 and S6. The probability used to compare these models to the PPTA limit are calculated in supplementary text section S7.

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Data used in this analysis can be accessed via the Australia National Data Service (www.ands.org.au).

Supplementary Materials
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Supplementary Text
Fig. S1
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Strain-Induced Ultrahard and Ultrastable Nanolaminated Structure in Nickel

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Heavy plastic deformation may refine grains of metals and make them very strong. But the strain-induced refinement saturates at large strains, forming three-dimensional ultrafine-grained (UFG, sub-micrometer–sized) structures with random orientations. Further refinement of this microstructure is limited because of the enhanced mobility of grain boundaries. Very high-rate shear deformation with high strain gradients was applied in the top surface layer of bulk nickel, where a 2D nanometer-scale laminated structure was induced. The strongly textured nanolaminated structure (average lamellar thickness of 20 nanometers) with low-angle boundaries among the lamellae is ultrahard and ultrastable: It exhibits a hardness of 6.4 gigapascal—which is higher than any reported hardness of the UFG nickel—and a coarsening temperature of 40 kelvin above that in UFG nickel.

Metals can be strengthened by introducing more grain boundaries (GBs) via grain refinement (1, 2) or alternatively by generating more dislocations (3). Remarkable hardening in metals and alloys induced through heavy plastic deformation originates from both mechanisms: Grains are refined to the sub-micrometer or nanometer scales, and stored

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of $10^2$ and $10^3\, s^{-1}$ to a strain of 2.9, a smaller boundary spacing with a higher dislocation density is formed relative to that under low-rate ($10^{-2}\, s^{-1}$) deformation, such as cold rolling and torsion, at comparable strains ($10$, $11$). Lowering deformation temperature may elevate stored dislocation density and reduce grain sizes in deformed copper (Cu) ($12$, $13$). Strain gradient in plastic deformation is proportional to the density of stored geometrically necessary dislocations ($14$). A very high density of dislocations ($1.8 \times 10^{16}$ to $3.6 \times 10^{16}\, m^{-2}$, which is one order of magnitude higher than the dislocation density limit in deformed Cu) is observed in thin shear bands in the nanotwinned structure in Cu, owing to the very high strain gradients ($10^2$ and $10^3\, s^{-1}$) deformation, such as cold rolling and torsion at ambient temperature ($15$, $16$), in which the rod surface layer is plastically sheared with gradient distributions of applied strain rates and strains. In the top surface layer of a pure bulk Ni sample, where nanometer-thick laminated (NL) structures were induced. A pure Ni rod [purity of 99.88 weight percent (wt %)] of 10 mm in diameter was subjected to surface mechanical grinding treatment (SMGT) (Fig. 1A) at ambient temperature ($15$, $16$), in which the rod surface layer is plastically sheared with gradient distributions of applied strain rates and strains. In the top surface layer of $\sim 80\, \mu m$ thick, the estimated strain rate varies from $10^2$ to $10^3\, s^{-1}$ (topmost surface) to $10^2$ to $10^3\, s^{-1}$ (80 $\mu m$ deep from the treated surface), with corresponding accumulative equivalent strains of 30 to $\sim 15$. Strain gradients in the top 80 $\mu m$ vary from 0.4 to 0.1 $\mu m^{-1}$, which is 10 times greater than that in the high-pressure torsion process ($17$). After the treatment, a depth-dependent gradient microstructure was formed (Fig. 1B): a nanostructured layer in the top surface of $\sim 80\, \mu m$ thick with characteristic sizes below 100 nm, an UFG layer in a depth span of 80 to $\sim 140\, \mu m$, and a deformation layer at $140\, \mu m$~1 mm deep with various strain-induced defects, including dislocations and subboundaries. Deeper than 1 mm is deformation-free substrate.

The UFG layer is characterized by roughly equiaxed 3D grains (with an aspect ratio of $\sim 2$), with an average size of $\sim 230\, nm$ and random orientations (Fig. 1, C and D). A large fraction of high-angle GBs (>80%) was noticed from misorientation distribution measured by means of electron back-scattering diffraction (EBSD) and convergent beam electron diffraction (CBED) [in a transmission electron microscope (TEM)] ($15$). These are the typical characteristics of the steady-state UFG structures of Ni processed via heavy plastic deformation ($4$, $5$, $18$). The observed grain sizes and misorientation distribution agree quantitatively with those in the high-pressure torsion Ni samples with a strain of $\sim 10$, which is comparable with the estimated accumulative strains in this section ($6$ to $14$).

The topmost few micrometers of thickness are characterized by randomly oriented equiaxed nanograins with an average size of $\sim 11\, nm$. Deeper than 10 $\mu m$ are elongated nanosized grains (parallel to the sample surface), with an average transversal size of $18 \pm 5\, nm$ in cross-sectional TEM observations. With increasing depth from 10 to 50 $\mu m$, no obvious change is seen for transversal sizes of the nanograins, but their aspect ratios increase markedly from a few to greater than 100. Most grains are several micrometers in length, whereas some are broken into sub-micrometer–long segments (Fig. 1, E and F). Similar morphologies were seen in the longitudinal-section TEM images, with but smaller aspect ratios (ranging from a few to $\sim 15$) (Fig. 1E) than the cross-sectional. Clearly, the subsurface layer in a depth span of 10 to $50\, \mu m$ consists of 2D laminated grains, a kind of layer-shaped nanostructures ($19$). Rather uniform thickness is seen across the depth span of 10 to $50\, \mu m$, ranging from 5 to 50 $\mu m$, averaging $20 \pm 7\, nm$ (Fig. 1E). Such NL structures are distinct from the steady-state UFG structures (Fig. 1C) from heavy plastic deformation.

In a depth span of 50 to ~80 $\mu m$ is a transition layer from the NL structures to the 3D UFG or nanograined (NG) structures, characterized by alternative layers consisting of slightly elongated nanograins (with an average transversal size of 70 nm) and NL structures. Thicknesses of both layers are roughly comparable.

The elongated diffraction spots in the selected area electron diffraction pattern (SAED) indicate a strong texture in the NL structures (Fig. 1E), High-resolution TEM (HRTEM) observations were performed in order to identify the structure characteristics of boundaries between adjacent lamellae. Shown in 2A is a typical HRTEM observation of four lamellae (I to IV) along the <110> zone axis. From the fast Fourier transformation (FFT) (Fig. 2A, inset), one can see a small misorientation of $\sim 7^\circ$ along the <110> zone axis existing among these lamellae. HRTEM images showed that one of the closely packed {111} planes of II (Fig. 2C) is inclined by $7^\circ$ to that of III (Fig. 2D), which is in accordance with the splitting of {111} spots by an angle of $7^\circ$ in the FFT. A zoom-in observation of the boundary (Fig. 2B) showed an inclination by $3^\circ$ between the {111} planes in II and III, implying an orientation gradient existing within the nanolamellae. Plenty of HRTEM images showed most boundaries in the NL structures exhibit similar misorientations along a certain axis, ranging from $1^\circ$ to $8^\circ$.

Texture of the NL structures was determined with EBSD in a sample partially recovered at $540^\circ$C for 1 hour in order to improve the index rate while retaining the deformation texture. The {111} pole figure (Fig. 2E) and orientation distribution function maps (Fig. 2F) showed that the texture components are major {100} and minor {111}<112> and {111}<110> typical torsion textures (pure shear) in FCC metals ($20$). The presence of the strong shear textures (with a

**Fig. 1. Processing and microstructure overview of the Ni sample.** (A) A schematic illustration of the SMGT setup. (B) A cross-sectional scanning electron microscope image of the SMGT Ni sample. The treated surface is outlined by a yellow dashed line. (C) An EBSD image of the region outlined by dashed blue line in B. (D and E) Typical bright-field cross-sectional (SD-ND) and longitude-sectional (TD-ND) TEM images of the UFG structures (110 $\mu m$ deep from the surface) and NL structures (40 to 50 $\mu m$ deep from the surface) indicated in (B), respectively. Insets in (D) and (E) are the corresponding distribution of boundary spacing (left) and the SAED pattern (right). The sample coordinates in (D) and (E) are identical to that in (A). (F) A dark-field longitude-sectional TEM image corresponding to that in (E).
maximum intensity of ~6), which is consistent with the elongated SAED spots (Fig. 1E), indicates heavy shear deformation in the top surface layer during SMGT processing and operative dislocation activities in the 2D NL structures (21).

Vickers hardness measurements in the cross-sectional samples indicated that in the UFG layer in a depth span of 80 to ~600 μm, hardness varies from $2.76 \pm 0.26$ to $1.40 \pm 0.05$ GPa corresponding to different structural sizes. These results are consistent with the reported data for pure Ni (10, 18, 22) and the Hall-Petch relation (Fig. 2E). Measured hardness of the NL structures at 10 to ~50 μm deep averaged $6.4 \pm 0.32$ GPa. This value is much higher than that in Ni samples processed via plastic deformation reported in the literature (5, 10, 11, 18) and is comparable with that of the electrodeposited Ni with grain sizes of ~20 nm (23). Taking lamellar thickness as the equivalent grain size, we found that its hardness lies on the extrapolated Hall-Petch line (Fig. 2E). Such an agreement suggests that the NL boundaries are as effective in resisting dislocation motion as the conventional high-angle GBs. In fact, previous studies showed that contribution of low-angle boundaries to strength is comparable with that of high-angle GBs in strain-induced NG metals (11, 24).

In addition, presence of substructures inside lamellae [such as dislocations and twin boundaries as revealed in HRTEM observations (fig. S3)] may provide additional hardening.

Dislocations are mainly presented at the low-angle boundaries in deformed metals, whereas the dislocation density within the volumes between the boundaries is one or two orders of magnitude lower and hence can be neglected (10, 11, 24). The dislocation density in low-angle boundaries ($\rho_{LAB}$) is calculated by $\rho_{LAB} = f_{LAB} \cdot S \cdot p_A$, where $f_{LAB}$ is the fraction of low-angle boundaries, $S$ is the boundary area per unit volume, and $p_A$ is the dislocation density per unit area of boundary [for a mixed tilt and twist boundary $p_A = 1.56/b$ (10, 24), $\theta$ is the average misorientation angle of low-angle boundaries and $b$ is the Burgers vector]. With the measured parameters (table S1), a dislocation density of $\sim 1 \times 10^{15}$ m$^{-2}$ was obtained for the UFG structures (120 μm deep from the surface), which is in accordance with the measured result ($\sim 2 \times 10^{15}$ m$^{-2}$) in a torsion-deformed Ni at a comparable strain (25). For the NL structures (40 μm deep from the surface), dislocation density is $\sim 2.4 \times 10^{16}$ m$^{-2}$, which is 20 times greater than that in the UFG. With this dislocation density, hardness of the NL structures can be calculated in terms of the Taylor hardening mechanism by taking it as 3 times the yield stress (10, 24)

$$H_v = 3(\sigma_0 + M \alpha G b \sqrt{\rho_{LAB}})$$  \hspace{1cm} (1)$$

where $\sigma_0$ is the frictional stress, $M$ is the Taylor factor, $\alpha$ is a constant, and $G$ is the shear modulus. The calculated hardness is 6.7 GPa, which is very close to the measured result (6.4 GPa), verifying the estimated dislocation density.

Thermal stabilities of these microstructures were examined by measuring boundary spacing under TEM after isothermal annealing at 300° to
900°C for 1 hour: 3D UFG structures at ~100 μm deep, 3D NG structures (average size of ~70 nm) at 60 to ~70 μm deep, and 2D NL structures. As in Fig. 3A, no obvious increment in the boundary spacing was detected for these structures after annealing below 300°C. The onset temperature for obvious grain coarsening (T_on) is ~443°C for the NG structures and is slightly higher for the UFG (467°C). This is in accordance with the general trend that coarsening temperature decreases for smaller grains (26). For the NL structures, it is surprising to see a much higher onset temperature for lamella thickening of ~506°C. This instability temperature is in agreement with that for the dislocation boundaries in deep layers of the sample (varying from 500° to 540°C, de- }

Fig. 4. Correlation of thermal stability and hardness. The onset temperature (T_on) versus hardness for various microstructures [UFG, NG, and dislocation boundaries (DBs)] in the SMGT Ni at different depths. Solid triangles denote DBs at depths of ~150, 200, and 300 μm from the treated surface. 

lamellae (28), as well as the suppressed recrystallization nucleation kinetics by the laminated structure in extremely small dimensions (29), may also contribute to the elevated stability. Formation of the NL structures is reasonably attributed to the large shear deformation with very high rates and large strain gradients in the top surface layer of the SMGT sample, which is distinct from the conventional heavy plastic deformation processes such as high-pressure torsion (HPT) and cold rolling. High strain rates promote dislocation multiplication relative to their annihilation (11, 30). The much larger strain gradients in the top surface layer of the SMGT sample than that in the HPT process (typically ~0.04 μm⁻¹) means a much higher geometrically necessary dislocation density is generated because it is proportional to the strain gradient (14). Formation of more low-angle boundaries in form of nanoscale laminated structures is energetically favorable, with an increased density of stored dislocations for minimizing the overall excess energy. Nano-scale laminated structures have also been observed in shear bands that are locally sheared at high rates with large strain gradients in UFG iron samples after compressive deformation (31) and in the nanotwinned Cu during dynamic compression (12). Most boundaries in the sheared regions (or shear bands) in the Cu are of low angle, with an average misorientation of ~7° (12). These observations, in accordance with our present study, suggest that formation of 2D NL structures with a very high dislocation density is a general scenario for strain-induced grain refinement in extremely small dimensions deformed at high strain rates with large strain gradients.

By generating such ultrahard and ultrastable NL structures in surface layers of engineering materials, enhancement in their wear resistance and fatigue properties is anticipated that are sensitive to the surface hardness and structure stability. The very high stored energy of the NL structure may elevate diffusion kinetics and chemical reactivity, facilitating surface modification of engineering alloys. With the simple and cost-effective processing technique, this nanostructure will find potential technological applications in a wide range of industrial manufacturing processes. 

References and Notes
15. Materials and methods are available as supplementary materials on Science Online.
17. J. Sevillano Gil, in Evolution of Deformation Microstructures in 3D, C. Gundlach et al., Eds. (Denmark Rice National Laboratory, Denmark, 2004), pp. 1–11.

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Supplementary Materials
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Materials and Methods
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