that are normally FCC, such as gold, to maintain local, close-packed arrangements that are compatible with the constraints imposed by the surrounding environment. This result establishes a physically useful connection between dislocations and grain boundaries, the two most fundamental microstructural elements underpinning the behavior of polycrystalline materials.

References and Notes

Deformation Twinning in Nanocrystalline Aluminum

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We report transmission electron microscope observations that provide evidence of deformation twinning in plastically deformed nanocrystalline aluminum. The presence of these twins is directly related to the nanocrystalline structure, because they are not observed in coarse-grained pure aluminum. We propose a dislocation-based model to explain the preference for deformation twins and stacking faults in nanocrystalline materials. These results underscore a transition from deformation mechanisms controlled by normal slip to those controlled by partial dislocation activity when grain size decreases to tens of nanometers, and they have implications for interpreting the unusual mechanical behavior of nanocrystalline materials.

The extremely high strength and hardness of nanocrystalline materials relative to their coarse-grained counterparts suggest that normal dislocation activity—the dominant plastic deformation mode of ductile coarse-grained materials—is suppressed in nanocrystalline grains. The resulting high strength of nanocrystalline materials may give rise to unique plastic deformation mechanisms that are not seen in coarse-grained materials (1–7). Twinning in aluminum, which has been suggested by recent molecular dynamics (MD) simulations (7, 8), is an interesting case. Deformation twins have been observed in face-centered cubic (fcc) metals, such as copper and nickel (9–11), when deformed at subambient temperatures and/or high strain rates, but deformation twins have not been experimentally confirmed in single or polycrystalline pure aluminum (7, 8, 11, 12), even when shock-loaded at low temperatures (13, 14). The appearance of Shockley partial dislocations at a crack tip of aluminum has been regarded as an indication of deformation twinning (13), but supporting evidence for this claim has not been forthcoming.

Nanocrystalline aluminum films with thickness of ~200 and ~400 nm were prepared by physical vapor deposition of pure aluminum (99.9%) onto oxidized (001) silicon substrates that were cooled with liquid nitrogen. The deposition was performed at a pressure of ~5 × 10⁻⁸ Torr and a deposition rate of 5 to 10 nm/min. To suppress columnar grain structures, we interrupted the deposition for 1 min at ~20-nm thickness intervals during film growth. Texture was negligible in these films, as indicated by x-ray diffraction analysis. The as-deposited films had grain sizes in the range of 10 to 35 nm (Fig. 1A). High-resolution transmission electron microscope (HRTEM) observations with a point-to-point resolution of 0.2 nm revealed that most of the nanograins were separated by high-angle boundaries and that no grain boundary phases were present in these samples. Occasionally, growth twins were observed with the twin boundary appearing as a perfectly flat interface (Fig. 1B). Such sharp interfaces have been previously

![Fig. 1. Microstructure of as-prepared nanocrystalline aluminum. (A) Bright-field TEM micrograph showing nanocrystalline grains with sizes ranging from 10 to 35 nm. No dislocations or deformation twins can be seen. (B) HRTEM image of a growth (111) twin boundary (marked by a white arrow).](image-url)
observed in deposited or annealed aluminum and have been referred to as the \( \{111\} \) twin boundary \((16, 17)\).

The nanocrystalline aluminum films were deformed by microindentation and by manual grinding to allow the introduction of large plastic strains and to facilitate TEM observations of the deformation defects. We chose these methods because the thin films cannot be tested in compression, and they fail with little plastic deformation in tension \((18)\). The indented samples were thinned from the back using tripod polishing, dimpling, and finally low-temperature ion milling. The insert in Fig. 2A shows a bright-field TEM micrograph of a micro-indent with the fourfold geometry. No cracks can be seen, even at the corners of the indent, indicating that the formation of the indent is fully plastic. Around the edges of the indent, planar defects with two parallel flat boundaries were seen in a number of grains and were identified as deformation twins. The width and orientation of the twin bands vary from grain to grain. The twinning seems to occur preferentially in smaller grains and propagates across the entire grain. An example is shown in the HRTEM micrograph of Fig. 2B, together with a fast Fourier transform (FFT) pattern. The deformation twin can be recognized by the mirror symmetry between the band and the matrix in the atomic resolution image, in which the bright spots correspond to individual atomic columns. The twin boundaries are determined to be parallel to one set of the \( \{111\} \) planes. In addition, the HRTEM image reveals that the deformation twin boundaries are several atomic planes thick, caused by twinning dislocations that are tilted relative to the electron beam and not clearly imaged. A large number of dislocations rather than deformation twinning were found in coarse-grained aluminum deformed under the same indenter as shown in Fig. 2C, confirming the grain-size dependence of the twinning mechanism.

To rule out the possibility that deformation twinning can only be induced under the very high pressures generated by a diamond indenter \((19)\), we used a different deformation scheme. Freestanding nanocrystalline aluminum films were released from sodium chloride substrates and manually ground into small fragments with an agate mortar and pestle in pure methanol for \( \sim 1 \) min. This procedure is generally used to crush materials for TEM observations by applying complex stresses. These stresses are much lower than those generated by a sharp diamond indenter. The original film thickness was \( \sim 200 \) nm, whereas the thickness of the fragments used for subsequent TEM observations was measured to be less than 100 nm by electron energy loss spectroscopy. The reduction in thickness appears to result from large plastic deformation, and the bright-field TEM micrograph in Fig. 3A illustrates the features of the heavily deformed nanocrystalline aluminum. The high density of planar defects that is shown in this figure is not seen in the as-deposited samples and is found to appear preferentially in smaller grains. Some of the defects were confirmed to be deformation twins by HRTEM. In these cases, multiple narrow twins often resided in a single grain, and the twinning planes were determined to be of the \( \{111\} \) type \((19)\). The FFT pattern of Fig. 3B demonstrates the twin relationship among the bands and the matrix \((19)\). The multiple twins are highlighted in the Fourier-filtered image \((19)\) for a
selected region in Fig. 3B. Stacking faults, dislocations, and microbands were also observed in the samples.

The TEM observations provide direct experimental evidence confirming the MD predictions of twinning during plastic deformation of nanocrystalline aluminum (7, 8). Regarding the twinning mechanism of fcc materials, several models have been proposed in which deformation twins are created by stacking faults led by 1/6⟨112⟩ Shockley partial dislocations (20–23). The preference for twinning and stacking fault formation in nanocrystalline grains can be understood by comparing the critical shear stress needed to nucleate a perfect dislocation (1/2⟨110⟩) with an approximation of the source size equal to the grain size (D), \( \tau_N \), with that required to initiate the Shockley partial (1/6⟨112⟩) twinning dislocation to generate stacking faults and deformation twins, \( \tau_p \).

Such a comparison can be made using formulations given by classical dislocation theory (22, 23), where

\[
\tau_N = \frac{2\alpha \mu b_N}{D}
\]

and

\[
\tau_p = \frac{2\alpha \mu b_p}{D} + \frac{\gamma}{b_p}
\]

Here \( \mu \) is the shear modulus (~35 GPa for aluminum), \( \gamma \) is the stacking fault energy [104 to 142 mJ/m² for aluminum (7)], and \( b_N \) and \( b_p \) are the magnitudes of the Burgers vectors of the perfect dislocation and the Shockley partial dislocation, respectively. The parameter \( \alpha \) reflects the character of the dislocation [\( \alpha = 0.5 \) and 1.5 for edge and screw dislocations, respectively (23)] and contains the scaling factor between the length of the dislocation source and the grain size. The grain boundaries are taken as dislocation sources, as predicted by computer simulations for nanocrystalline grains (~6–12, 24). When the grain size becomes smaller than a critical value, \( D_c \), determined by equating Eqs. 1 and 2

\[
D_c = \frac{2\alpha \mu (b_N - b_p)}{g}
\]

\( \tau_p \) becomes smaller than \( \tau_N \). Taking \( \alpha = 1 \), the estimated \( D_c \) is approximately 10 to 15 nm for aluminum. For simplicity, this model for nanocrystalline materials does not include the influence of elastic anisotropy, the small Peierls-Nabarro stress, localized stress concentrations, and the interactions of dislocations with grain boundaries. Nevertheless, the predictions given by this simple model shed light on the experimentally observed trends in several ways. First, twinning becomes a preferred deformation mode in aluminum with a grain size on the order of 10 nm, which is consistent with our HRTEM observations of deformation twins in the grains with sizes of ~10 to 20 nm. The model also provides a physical explanation of the preferential generation of partial dislocations, which results in the formation of stacking faults and deformation twins in nanocrystalline grains as suggested by computer simulations (6–8, 12, 24). Second, the \( \tau_p \), estimated from Eq. 2 is much higher than \( \tau_N \) in large aluminum grains, which is in agreement with the dominance of the normal dislocation plasticity in conventional aluminum. Third, for other fcc materials with lower \( \gamma \) and higher \( \mu \), the \( D_c \) values are much larger and can be used to interpret the observation that deformation and growth twins are found in nanocrystalline copper and nickel (9, 25–27) at \( D_c \) values that are more than twice that of aluminum. Fourth, the generation of twin interfaces and stacking faults offers an alternative interpretation to dislocation pile-up at grain boundaries to explain the continuous grain-size strengthening, as suggested by Eq. 2, and the strain hardening of nanocrystalline materials (25–27).

References and Notes

\[ \text{n-Type Conducting CdSe Nanocrystal Solids} \]

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A bottleneck limiting the widespread application of semiconductor nanocrystal solids is their poor conductivity. We report that the conductivity of thin films of n-type CdSe nanocrystals increases by many orders of magnitude as the occupation of the first two electronic shells, \( 1s_n \) and \( 1p_n \), increases, either by potassium or electrochemical doping. Around half-filling of the \( 1s_n \) shell, a peak in the conductivity is observed, indicating shell-to-shell transport. Introducing conjugated ligands between nanocrystals increases the conductivity of these states to \(~10^{-2}\) siemens per centimeter.

During the past decade, it has become apparent that solids of monodispersed nanocrystals provide the opportunity for developing materials with novel properties (1, 2). In particular, semiconductor nanocrystals (3) offer great promise for fabricating optoelectrical devices (4–6). In these “artificial atoms,” the inorganic cores allow precise tuning of the discrete electronic states by size confinement. To stabilize against sintering, retain solubility, and maintain good optical properties, the surfaces are capped by organic ligands, as in the prototypical CdSe system (7). However, these ligands and traps on the nanocrystal surfaces are thought to inhibit electronic

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\[ \text{REPORTS} \]

www.sciencemag.org SCIENCE VOL 300 23 MAY 2003 1277