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Competing plastic deformation mechanisms in nanophase metals

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The mechanisms of plastic deformation in nanocrystalline Ni are studied using three-dimensional molecular-dynamics computer simulations for samples with mean grain sizes ranging from 3 to 12 nm under uniaxial load at finite temperatures. At the lower limit of this size range, we observe a plastic regime controlled by intergrain sliding; at the upper limit, however, we observe a regime with two competing mechanisms: intergrain sliding and dislocation emission from the grain boundaries (GB's). The latter mechanism constitutes a transition behavior, precursor to the dislocation-dominated regime typical of large grain polycrystals. In samples with mainly low-angle GB's, the transition occurs at a smaller grain size. [S0163-1829(99)00525-1]

Grain size is one of the most important variables characterizing the microstructure of polycrystalline metals. It has significant influence in the plastic behavior of materials. In going from single crystal to polycrystals, plasticity is affected in various ways by the presence of grain boundaries (GB's). Dislocations are the carriers of plastic deformation in crystalline materials and depending on the nature of interface between grains they can travel across them or not. In general terms, the energetics of GB's is such that for low-angle missorientations between neighboring crystals the GB's energy is small, while the converse is true for high-angle missorientations, with the notable exception of some special coincident site lattice boundaries. High-energy GB's act as efficient obstacles for dislocation motion because they usually do not find a plane-matching Burgers vector in the neighboring grain. Dislocations generated by a given source inside a grain repel each other. As a consequence of this mutual interaction and the external applied stress, their distribution peaks close to the boundaries in the so-called pileup effect. When the stress field resulting from the addition of individual dislocation contributions reaches some critical value, it activates sources in neighboring grains. This stress field can be calculated in the continuum approximation giving a $d^{-1/2}$ dependence for the yield stress of polycrystals as a function of grain size d. This is the well-known Hall-Petch relation[1,2] verified in numerous experiments.

Nanocrystalline phases have become a focus of attention to material scientists because the Hall-Petch relation, when extrapolated to grain sizes in the nanometer range, predicts extremely hard materials. However, experimental evidence suggests that in this range the Hall-Petch relation apparently fails to describe the observations; a new regime appears, whose quantitative description is still controversial.[3–6]

In nanophase solids a large fraction of atoms (up to 50%) are boundary atoms; thus intercrystalline deformation mechanisms are expected to become relevant, as opposed to intracrystalline mechanisms based on dislocation activity. At the smallest grain sizes, dislocation sources inside grains can hardly exist because size and image force limitations; only dislocation emitted from a boundary can eventually travel across the grain. From these arguments it is then likely to expect a change in regime when decreasing grain size, from dislocation-dominated Hall-Petch to a boundary-dominated new one.

In previous works, we studied the properties of nanophase samples in the 3.5–8 nm grain size range.[7–9] Here, by extending the grain size to 12 nm and by deforming textured nanostructures, we present evidence of two competing mechanisms leading to such change of regime, obtained from molecular-dynamics (MD) computer simulations in nanophase Ni.

For some simple materials (late transition metals and their compounds), MD computer simulations provide an atomistic view of the deformation process through the mean-field approximation for the atomic interactions.[10,11] It is simple enough to deal with about a million atoms in present day computers, allowing computer-generated samples to be in a one-to-one scale with real nanograins. Many physical properties such as the lattice parameter, cohesive energy, elastic constants, phonon-dispersion relations, point defect behavior, phase diagrams, stacking fault energies, surface structure, reconstruction and energy, etc., are well reproduced within this model. We performed MD simulations of deformation in three-dimensional (3D) nanophase Ni samples, in the temperature range 300–500 K, at constant applied uniaxial tensile stress between 0 and 3 GPa, in the grain size range 3.2–12 nm. The nature of the interface structure in real nanophase samples may go from random to quite relaxed or even textured orientations.[12,13] Consequently, we used two procedures to create them: a stochastic method, and a constrained stochastic method. In the first one, the simulation cell volume was filled with nanograins grown from seeds with random location and crystallographic orientation, filling the space according to the Voronoi construction. In the

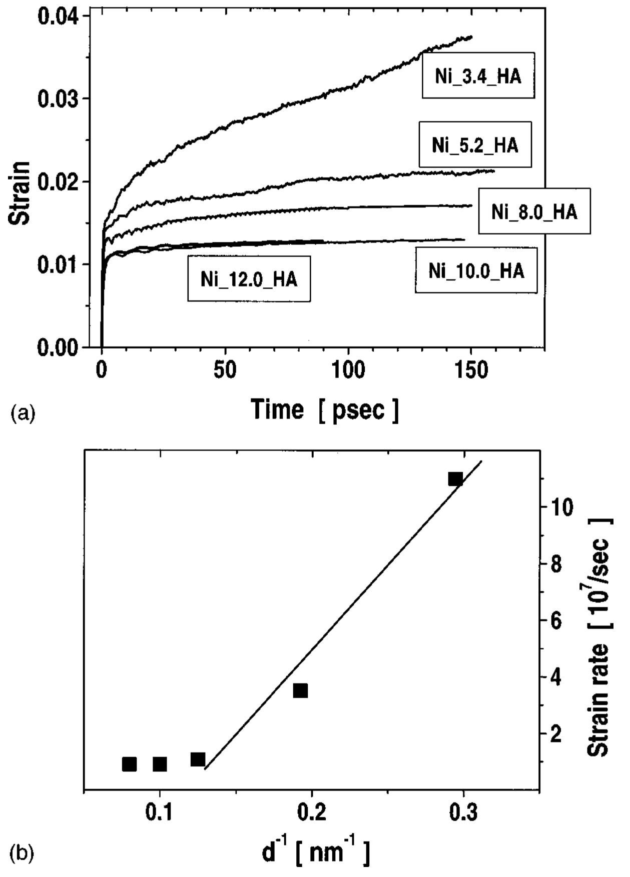

FIG. 1. (a) Strain-time curves for nanophase Ni between 3.4 and 12 nm grain size, with high-angle GB's, at a stress of 1.5 GPa. (b) Strain rate versus inverse of the grain size, from (a).

second procedure, the grain missorientations are restricted to be less than a given angle (between 3° and 17°). We call these high-angle (HA) and low-angle (LA) samples, respectively. They were then annealed at 300 K giving a final density at 0 K above 97% of the perfect crystal value.

We used a second moment (tight-binding) Ni potential[14] in the Parinello-Rahman[15] approach and periodic boundary conditions. Sample sizes were between 10^5 and 10^6 atoms. We analyzed the deformation results in terms of the grain size, and the evolution of the microstructure in terms of energy, density, and atomic bond analysis. At the early stages of deformation at a stress of 1.5 GPa, strain increases linearly with time in all cases, as shown in Fig. 1(a) for samples with several grain sizes. This suggested to us the use of a general nonlinear viscous plasticity model whose microscopic process is sliding at the interface. For details we refer the reader to our previous work.[7–9]

At the smallest grain sizes explored previously, the plastic activity is concentrated at the GB's; strain rate increases for decreasing grain size, at equal applied stress. An energy balance indicated that deformation takes place keeping constant the total amount of GB's. This is shown in Fig. 2, where histograms of the potential energy and coordination number for a Ni sample of 5.2-nm grain size are shown for the undeformed and 2% deformed states (the latter with 1.5 GPa) at 300 K, and subsequently unloaded. The number of atoms with perfect crystal energy only decreases by 1% after deformation, and most of them are shifted into the nearest-neighbor energy bin in the histogram. At 300 K, only a small decrease of 2% in the 12-coordinated atoms is observed. These observations suggested an important characteristic of plasticity in nanophase metals at these sizes and under the present conditions: there is no damage accumulation during deformation, similar to the conditions for superplasticity.[7–9] This assumption is valid at temperatures equal to or higher than room temperature; at 0 K we observed a small increase in non-fcc (or defect) atoms,[9] also confirmed by a recent report on zero-temperature simulations.[16]

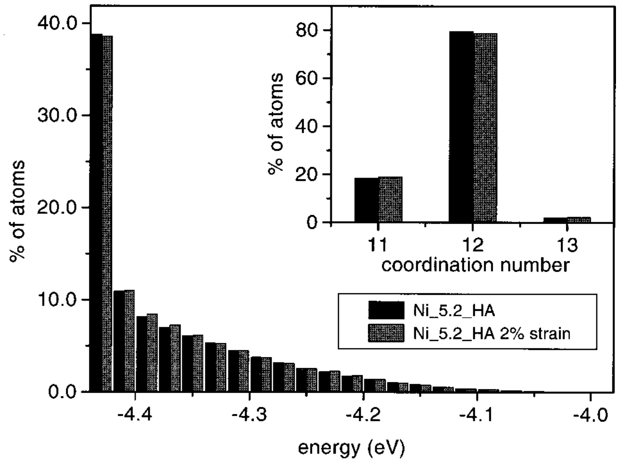

FIG. 2. Histograms of potential-energy distribution for all atoms in a Ni nanophase sample with 5.2 nm mean grain size and high-angle boundaries, undeformed and with 2% strain. Inset: Histograms of coordination number for the same cases.

To interpret the observations of our previous work at small grain size, we assumed that macroscopic displacement is the result of grains sliding against each other, with a general nonlinear viscous behavior. No contribution to plasticity from the grain interior was assumed. From these hypotheses we assumed a standard stress-assisted activation process. We further considered geometric arguments to incorporate the grain size, which resulted in a d^{-1} dependence. We obtained the following relationship for the strain rate as a function of grain size, temperature, and stress:

$$\dot{\varepsilon} = \frac{d_0}{d} e^{-(U/kT)} \sinh\left(\frac{\sigma v}{kT}\right),$$

where d_0 is a constant, U and v are the activation energy and volume, and σ is the applied stress. For details about this equation and values of the parameters, see Ref. 9.

In contrast to the complex time dependence of deformation in creep tests in microcrystalline metals, which is the consequence of work hardening, the linear time dependence of ε is the result of a simple approximation that reflects the absence of damage accumulation. It is confirmed in those cases where we performed deformation longer than those reported here, where we do not see any significant change in slope. The results analyzed with this expression, for random high-angle samples, show a well-characterized behavior of intergrain plasticity in the lower limit of grain size, whose salient feature is a softening as grain size decreases. The

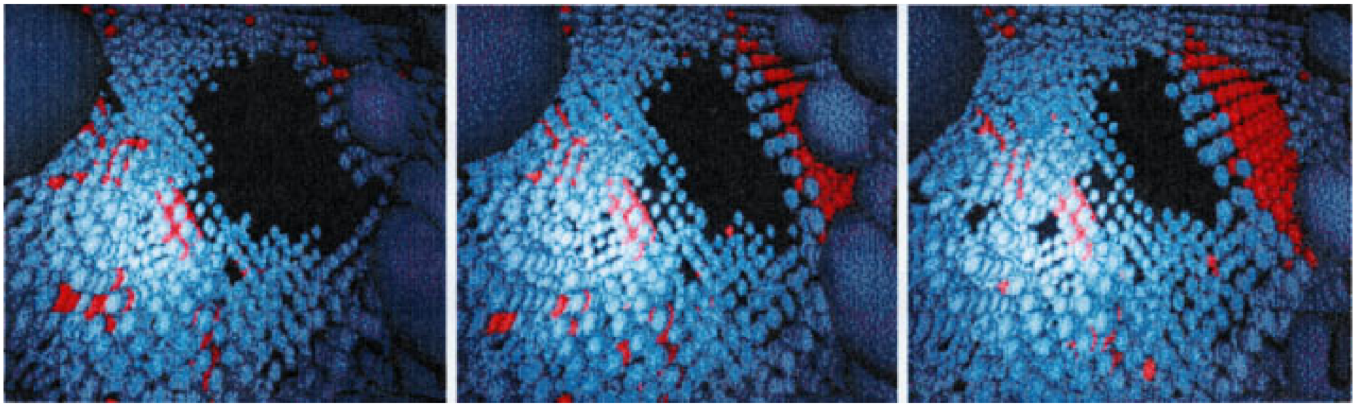

FIG. 3. (Color) 2D projections of three spots during deformation of a 5.2 nm low-angle (textured) Ni nanosample under traction. Red atoms represent a stacking fault created by a moving partial edge dislocation. For details see text.

predicted $1/d$ dependence, and the dependence on the other variables (stress and temperature), has been reported elsewhere.[7–9]

By further increasing the grain size, however, a clearly different behavior is observed [see Fig. 1(b)], which represents a transition into a new regime that should lead, for sufficiently large grain size, to the intragrain plastic behavior described by the Hall-Petch relation. For Ni, our simulations reveal the end of the slide-dominated regime above around 10 nm. It is to be expected that the geometric argument leading to the $1/d$ dependence certainly has its limit of applicability when going to larger grain sizes, because the boundaries do not form channels in the limit $\Delta/d \rightarrow 0$, where Δ is the GB width. Figure 1(b) shows a transition between an intergrain channeled slip behavior for $d \leqslant 10\,\mathrm{nm}$, and an intermediate mechanism controlled by a decreasing contribution from GB sliding and eventually an increasing contribution of intragrain dislocation slip. There are several experimental indications for such a transition.[3–6]

To characterize this transition regime and find the mechanisms responsible for the plastic deformation, we performed observations of computer images in the 3D CAVE™ virtual reality environment at Virginia Tech. (www.cave.vt.edu). We particularly focus our attention into atoms with hexagonal-close-packed (hcp) environment because they reflect the possible presence of $a_0/6[112]$ Shockley partial dislocations. In fact, a grain traveled across by such a dislocation shows an intrinsic stacking fault formed by a pair of neighboring (111) planes with local hcp stacking. In these HA samples (Figs. 1 and 2), we observe small clusters of atoms with hcp environment, but we do not observe significant dislocation activity. We find an increasing number of small hcp planes in the GB's of the deformed samples. We conclude that for these sizes in randomly oriented (HA) samples the sliding mechanism is clearly decreasing in importance, but the dislocation-dominated regime is not yet reached.

We explored then the textured, LA samples, where the larger degree of coherence in the interfaces helps transferring the shear component of the applied stress into the grain interior, facilitating the dislocation activity and favoring the dislocation mechanism. Analysis of the textured samples shows significant differences when compared to high-angle nanophase structures. Whereas the mean energy per atom is approximately the same, the HA sample has most of its excess energy in the GB's, while in the LA sample the energy is distributed among the boundary and the interior of the grains, as elastic strain. This reflects the close relation between dislocation emission from GB's and relaxation of strain in the grain interior.

Simulation results obtained in LA samples reveal the presence of atoms with hcp environment inside the grains and in the GB in a number larger than in the HA case, as well as clear motion of Shockley partial dislocations already at an average grain size of 5.2 nm. hcp atoms inside the grains are grouped in double planar arrays, and are intrinsic stacking faults. They are left behind by those Shockley partial dislocations that can either be produced in a GB or come from another grain.

Figure 3 shows three pictures taken in the CAVE™ at three different moments of deformation. For clarity we removed the fcc atoms, colored the GB atoms blue and the hcp atoms red. On the first picture we look inside the grain and observe in the upper right corner a small hcp cluster. On the second picture a partial dislocation traveling inside the grain produces two hcp planes behind it, which are larger in the third picture. For a movie of this process visit www.cmsms.vt.edu/~diana/nanoni.gif. We interpret this process with dislocations generated at the GB's as being dominant in the intermediate grain size regime, between Hall-Petch and slide regimes. It is important to mention that on increasing deformation, we do not observe a second partial in the same or neighboring plane that would remove the stacking fault or produce twinning, but other partials appear in different grains.

In conclusion, we have shown that for small grain size ($d < 10\,\mathrm{nm}$) plastic deformation in nanophase Ni has a regime controlled by GB sliding in which the strain rate increases with decreasing mean grain size. Above a critical value in the range of 10 nm, the strain rate becomes almost independent of the grain size, indicating a transition into a new regime. This regime is intermediate between the sliding regime and the intragrain dislocation-dominated regime, typical of coarse-grained polycrystals. We have also shown that there is a considerable influence of the GB structure on the deformation process of similar size nanosamples. In samples with mainly low-angle GB's, the deformation also received contributions from intragrain slip due to Shockley partial dislocations generated at the GB's that create intrinsic stacking faults inside the grains, already at a grain size as small as 5 nm.

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