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Is diffusion creep the cause for the inverse Hall–Petch effect in nanocrystalline materials?

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Abstract

It has previously been demonstrated by means of molecular-dynamics (MD) simulation that for the very smallest grain sizes (typically below 20–30 nm), nanocrystalline f.c.c. metals deform via grain-boundary diffusion creep, provided the applied stress is low enough to avoid microcracking and dislocation nucleation from the grain boundaries. Experimentally, however, the nature of the deformation process in this "inverse Hall–Petch" regime (in which the yield stress decreases with decreasing grain size) remains controversial. Here we illustrate by MD simulation that in the absence of grain growth a nanocrystalline model b.c.c. metal, Mo, and a model metal oxide, UO_2, also deform via diffusion creep. However, in the case of Mo both grain-boundary and lattice diffusion are observed to contribute to the creep rate; i.e., the deformation mechanism involves a combination of Coble and Nabarro-Herring creep. While our results on Mo and UO_2 are still preliminary, they lend further support to the observation of diffusion creep previously documented in f.c.c. metals and in covalently bonded Si.

Keywords: Inverse Hall–Petch; Diffusion creep; Coble creep; Nanocrystalline; Molecular dynamics

1. Introduction

We feel privileged to have this opportunity to contribute to this special volume celebrating the vision, accomplishments and leadership of Professor Carl Koch. His critical approach to what experimentation can teach us about the structure and physical properties of nanocrystalline materials [1] and his equally critical view of what can be learned from atomic-level simulations on what are necessarily highly idealized nanocrystalline model systems have provided – and will continue to provide – invaluable leadership in this complex field. It is in this spirit that we contribute our paper to this special volume, hoping to further stimulate the discussion on the relationship, if any, between experiments and simulations on the thermo-mechanical behavior of nanocrystalline materials.

It is well established from experiments that, in accordance with the well-known Hall–Petch relation, resistance to plastic deformation by dislocation motion increases steadily as grain size is reduced. Gleiter and co-workers [2] were the first to predict that, beyond this expected behavior, at the very smallest grain sizes there may be a limit to plastic strengthening, giving rise to an inversion and a diminishing strength with ever smaller grain size. In subsequent investigations [3–5], it was suggested that diffusion creep might be the dominant deformation mechanism resulting in this decrease in the strength in nanocrystalline materials with decreasing grain size, even at room temperature.

Inspired by Gleiter's intuitive prediction and the early experimental results, we have previously demonstrated by molecular-dynamics (MD) simulation that fully dense nanocrystalline–Si [6] and Pd model microstructures [7], indeed, deform via the Coble-creep mechanism [8], lending support to the suggestions based on the early experiments. Due to their well-known time-scale limitations, such simulations are necessarily restricted to elevated temperatures. However, based on the insights gained from them it has been suggested that even at room-temperature the deformation of nanocrystalline materials should, indeed, proceed by the Coble-creep mechanism [9]. In fact, this mechanism has been shown to be entirely consistent with extensive room-temperature simulations [10–16] that suggested that grain-boundary (GB) sliding is responsible for the decrease in the yield stress with decreasing grain size. These simulations, performed on f.c.c. model systems with more or less randomly

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chosen grain orientations, showed that the observed GB sliding involved uncorrelated atom shuffling and, to some extent, stress-assisted diffusion [16]. These apparently contradictory observations are readily reconciled [9] by realizing that the Coble-creep mechanism for homogeneous grain elongation via GB diffusion requires Lifshitz sliding as an accommodation mechanism [17,18].

If GB sliding alone (rather than the Coble-creep mechanism) were, indeed, responsible for the inverse Hall–Petch behavior reported in the room-temperature simulations [10–16], an accommodation mechanism would be required so as to ensure continuous deformability while avoiding microcracking. From extensive studies of superplastic deformation, dislocation processes and GB-diffusion have been identified as the only viable accommodation processes, provided no cracking occurs. Concerning dislocation accommodation, it is well-known that dislocation sources inside the grains can operate only down to a grain size of typically about 1 μm, since the size of a Frank–Read source cannot exceed the grain size and the stress needed for its operation is inversely proportional to the size of the source. For smaller grain sizes, mobile dislocations must be nucleated from other sources, such as the GBs or grain junctions. Recent simulations have demonstrated that a threshold stress, σ_c, exists below which, at least on an MD time scale, dislocations cannot be nucleated from the GBs or grain junctions. For the case of Al these simulations yielded a value of $\sigma_c \sim 2.3$ GPa [19], similar to MD values of yield and flow stresses ranging between 1.5 and 3 GPa reported for other f.c.c. metals [10–16]. Since these stresses are at least an order of magnitude higher than typical experimental stresses, it is likely that in real nanocrystalline materials dislocations are unavailable to accommodate GB sliding, at least for the smaller grain sizes.

In the absence of dislocation processes and microcrack formation, GB diffusion therefore seems to offer the only viable accommodation process for GB sliding. From the deformation of coarse-grained materials under conditions where dislocation processes are unimportant, it is well-known that, just as GB sliding must be accommodated by GB diffusion [20], GB-diffusion creep in turn requires GB sliding (known as Lifshitz sliding [17]) as an accommodation process [18]. The intricate interplay between the two mechanisms therefore represents two different aspects of the same deformation process, and a spectrum of different MD simulations performed to date, albeit on highly idealized model systems, seem to confirm this scenario. It therefore appears that the inverse Hall–Petch effect is merely a manifestation of GB-diffusion creep, with the characteristic $\sigma \sim d^3$ decrease of the flow stress, σ, with decreasing grain size, d, predicted from the well-known Coble-creep formula for coarse-grained materials. [6–9].

In this work, by presenting preliminary MD simulations on a nanocrystalline model b.c.c. metal, Mo, and a model metal oxide, UO_2, we further elaborate on the importance of diffusion creep in the deformation of nanocrystalline materials. The model materials, Mo and UO_2, were selected due to their significance to nuclear fission reactor systems. B.C.C. metals, including Mo, are the primary component of alloys used for the structural components of fission reactors at elevated temperatures [21,22]. UO_2 is the primary reactor fuel in these reactors. By contrast with our previous f.c.c.-metal simulations, in the case of Mo we find that both GB and lattice diffusion contribute to the creep rate; i.e., the deformation mechanism involves a combination of Coble and Nabarro-Herring creep. Moreover, in the case of UO_2 we are able to identify chemical diffusion of both ionic species through the GBs as the rate-controlling process during Coble creep.

2. Simulation methodology

The Voronoi tessellation method [23] was used to construct [1 0 0] columnar samples containing 12 grains of identical hexagonal shape and size ($d = 12$ nm) within the three-dimensionally (3d) periodic simulation cell. The grains were populated by placing atoms on a rotated b.c.c. lattice site (for Mo) and on a fluorite lattice (for UO_2) in the simulation cell. For Mo, the individual grains were rotated progressively by 30° with respect to one-another, thus producing only high-energy [1 0 0] 30° asymmetric tilt GBs. By contrast, for UO_2 the grain orientations were chosen randomly by using a Monte-Carlo procedure; however, to ensure that only high-angle GBs were generated, only misorientation angles greater than 15° were allowed. The Mo simulation cell contains 20 (1 0 0) atomic planes in the periodically repeated column direction whereas the UO_2 simulation cell contains 10 (1 0 0) atomic planes.

Throughout this study, Mo was modeled using the Finnis-Sinclair (FS) potential [24] with shifted-force modification for both the pair-wise repulsion and electron-density contributions. This potential was fitted to several experimental quantities including the lattice parameter ($a_o = 0.3147$ nm), cohesive energy (6.82 eV) and the three elastic constants. For UO_2 we use the point-ion potential recently developed by Basak et al. [25]. The short-range contribution of this potential was fitted to the lattice parameter, the bulk modulus and the low-temperature thermal expansion. The potential successfully predicts the melting of the oxygen sub-lattice around 2300 K, which was confirmed by our simulations. We use the exact method for the evaluation of the Coulomb energy, forces and stresses by direct $1/r$ summation with spherical truncation at the cutoff radius $R_c = 1.08$ nm and with a damping parameter of 1.5 [26]. This method is computationally more efficient than the widely used Ewald [27] or fast-multipole [28] methods, yet produces identical and physically more transparent results. The trajectories of all the atomic species are obtained by a 5th-order predictor–corrector algorithm with an MD time step of $\Delta t = 2 \times 10^{-15}$ s (for Mo) and 0.5×10^{-15} s (for UO_2) for which the energy was conserved to four significant digits over several thousand time steps.

The unrelaxed zero-temperature MD input structures are gradually heated up to the desired temperature in a stepwise fashion and allowed to anneal isothermally for 100,000 time steps. We estimated the GB-induced melting to occur at $T_m = 3150 \pm 50$ K for Mo and at 3450 ± 50 K for UO_2. To compare the two materials under similar deformation conditions, equal homologous temperatures of $0.84T_m$ and $0.87T_m$ are chosen. The Mo simulations were thus carried out at 2700 and 2800 K and those for UO_2 at 2900 and 3000 K. The snapshot