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Abstract

Nanophase metallic materials show a maximum in strength as grain size decreases to the nano scale, indicating a break down of the Hall-Petch relation. Grain boundary sliding, as a possible accommodation mechanisms, is often the picture that explain computer simulations results and real experiments. In a recent paper, Bringa et al. Science **309**, 1838 (2005), we report on the observation of an ultra-hard behavior in nanophase Cu under shock loading, explained in terms of a reduction of grain boundary sliding under the influence of the shock pressure. In this work we perform a detailed study of the effects of hydrostatic pressure on nanophase Cu plasticity and find that it can be understood in terms of pressure dependent grain boundary sliding controlled by a Mohr-Coulomb law.

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The Hall-Petch relation predicts that as grain size decreases the hardness of polycrystalline materials increases as the inverse square root of the grain size. But the possibility of taking full advantage of this feature by designing hard materials by grain size refinement seems to be limited to grain sizes above a critical value (10-30 nm for Cu or Ni); below it, the strength ceases to increase, or eventually decreases, with decreasing grain size. Grain boundary (GB) sliding or other types of grain boundary accommodation mechanisms are thought to become dominant in this regime, that has been widely investigated both via simulation techniques and modeling [1–10].

Inhibiting softening by GB plasticity is then a key issue to obtain harder materials. Also for practical applications of these materials the stabilization of GB on aging is of importance. Both goals, namely GB plasticity and GB stability, can probably be achieved by the addition of carefully chosen alloying elements. However there seems to exist another mean to avoid sliding, although in a very peculiar set up, as we recently proved in molecular dynamics simulations and experiments of shock loading nanophase Cu [11]. The high pressure developed on the wake of a shock wave appears to efficiently prevent GB sliding. A preliminary explanation based on the assumption that GB sliding is similar to mechanical friction between two rough surfaces in contact, justified us to use a simple Mohr-Coulomb law [12], for the pressure dependence of the friction coefficient to satisfactorily interpret the results of our simulations. The ability to lock the boundaries in this way would extend the region of normal Hall-Petch behavior to smaller grain sizes and for some particular applications where pressure is relevant, like damage of spacecrafts by dust particles or targets for inertial confinement fusion, may provide a way to design materials with even greater hardness.

Computer simulations of plasticity at the nanoscale provides a plausible picture of the processes in terms of a crossover between dislocation - dominated regime for large grain size, and grain boundary sliding for small grain size. Qualitative and simple quantitative interpretation of grain boundary sliding as linear viscous flow was given in Ref. [13].

Systematic simulation studies covering a large grain size domain have recently been published [3], confirming the end of the validity of the Hall-Petch relation at about 15 nm in nc-Cu. It is then quite accepted now that the increase in hardening by reducing the grain size has a limit when the competing softening mechanisms of GB sliding comes into play.

Even if that kind of computer simulations are done at extremely high deformation rates, the results belong to the category of homogeneous strain, in the sense that there no stress gradients developed in the sample. Moreover, samples are uniaxially strained while the transverse cross section is allowed to relax. In shocks, where we found the ultra-high strength [11], the situation is quite different. Shock waves develop a huge pressure behind the front since they travel faster than the speed of sound and lateral relaxation cannot therefore occur. Volume is reduced by a significant amount and plastic deformation is the way the material follows to relax stress from uniaxial towards hydrostatic.

In our work on shock loading of nc-Cu we interpreted the pressure-induced hardening via two mechanisms, one is what we are discussing here, i. e. GB sliding inhibition, and the other is the dislocation mobility sensitivity to pressure. The latter is a well know mechanisms developed to interpret the results of shock loading in single or coarse grain polycrystals [11, 14]. Using a very simple picture for the competition and overlap between both mechanism at the crossover scale, we got the hardness behavior represented in Fig 1 in Ref. [11].

In this work we address a simple question in a clear simulation set up: is Gb sliding affected by pressure as it is implicit in the elementary idea of friction? To answer this question we use computer simulations to study the effect of hydrostatic pressure on the grain boundary motion under homogeneous stress at two (both high) strain rates, namely 3.0 10^8 and 1.0 10^9 $1/sec$. We note that these strain rates are similar to those in shocks.

A similar question was recently addressed in [15] by simulations at ultra fine grain sizes in different states of uniaxial and biaxial loading. An asymmetry in tension-compression, as well as a failure of standard yield criteria lead also the authors to propose a Mohr-Coulomb law to interpret the results, in a similar way as we report here, although they did not consider hydrostatic load and their stresses where one order of magnitude smaller that ours.

$$\sigma_{zz} = \sigma^0_{zz} + \alpha P \tag{1}$$

In these simulations, with uniaxial stress along z in addition to hydrostatic load, we monitor the zz component of the stress tensor minus the hydrostatic pressure, i. e. $\sigma_{zz} - P$, that gives us a quantitative measurement of how easy is for the material to plastically flow under pressure. To extract conclusions regardless of the strain rate dependence of the response of the material, which induces an additional variable that affects the response, we measure in particular the stress necessary to induce some *fixedvalue* (0.5, 1 or 2%) of

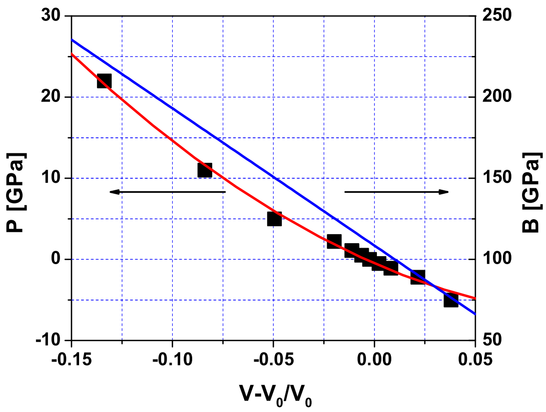

FIG. 1: Hydrostatic pressure vs volume for nanophase Cu (squares); also shown is a quadratic fit and its derivative, the bulk modulus B.

plasticstrain versus pressure. Because we use these fixed values of plastic strain, we need the elastic response of the material under pressure to subtract the elastic contribution to deformation. This elastic response is sample-dependent as the small number of grains in a simulation sample precludes the use of the statistical treatment of elastic response of an anisotropic medium.

The conditions used in these simulations, in particular the small grain size (5 nm), are such that no dislocation activity is present, i. e. all plasticity is related to GB's activity, as we carefully checked.

We first then study the elastic response of a cubic nanophase sample constructed using Voronoy cells and containing half a millon atoms distributed in 72 randomly oriented grains with average grain size of 5 nm. The EAM potential used in these simulations is taken from [16]. Figure 1 shows the P-V relation and its derivative, the bulk modulus. It is evident that due to the large deformation range explored and the highly defected structure of the sample, the response in not linear; we fit a quadratic polynomial to this curve and extract a bulk modulus that depends linearly on pressure. For comparison purposes, the bulk modulus of a perfect crystal for this potential is 181 GPa [16]. For the type of loading used in the deformation runs, the Young modulus Y is used for the elastic part, which shows a similar behavior.

Stress-strain results for $\dot{\epsilon} = 3.0\ 10^8/sec$ and several hydrostatic pressures are shown in

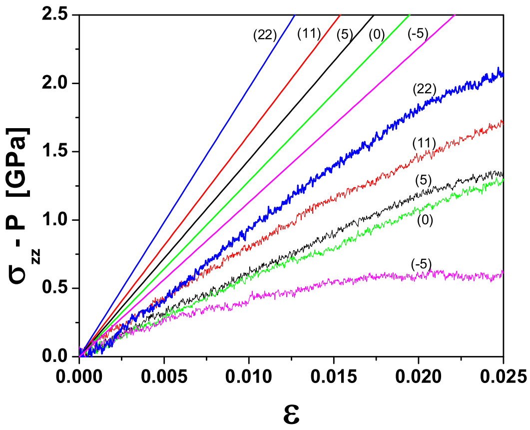

FIG. 2: Stress-strain curves for different hydrostatic pressures at $\dot{\epsilon} = 3.010^8/sec$. Straight lines are the elastic responses at each pressure. Values in parenthesis indicate pressure in GPa.

Figure 2, together with the measured elastic response to uniaxial load (straight lines with slope = Y(P). For negative pressures (tension) grater than 5 GPa the sample breaks. By subtracting the elastic to the total strain, we get the plastic contribution to it, and by looking at the stress corresponding to different pre-set values of plastic deformation, namely 0.5, 1, and 2%, we obtain the shear stress versus pressure reported in Figure 3 and represented by Eq.(1).

It is important to realize that our definition of shear stress is peculiar. The $\sigma - \epsilon$ plots at these strain rates do not show well defined yield and flow stresses. They are very strain rate sensitive and may, at these strain rates, show a maximum. Our definition of strength as the stress needed to reach a given percentage of plastic deformation is a sensible way to avoid this complexity in the analysis of the response curve.

It is remarkable in this figure the strong linear correlation between the points and the similarity of the slopes, α's, at different plastic deformation. In fact $\alpha(0.5\%) = 0.03$, $\alpha(1.0\%) = 0.036$, $\alpha(1.5\%) = 0.04$. Similar results were obtained for the other set of runs at $\dot{\epsilon} = 1.0\ 10^9/sec$.

The hypothesis is then clearly confirmed: if one considers GB sliding to occur against some "friction" force, this force would increase directly proportional to the pressure, making the barrier for GB sliding higher with pressure. This mechanism suppresses the sliding for the stress levels studied under shock conditions [11].

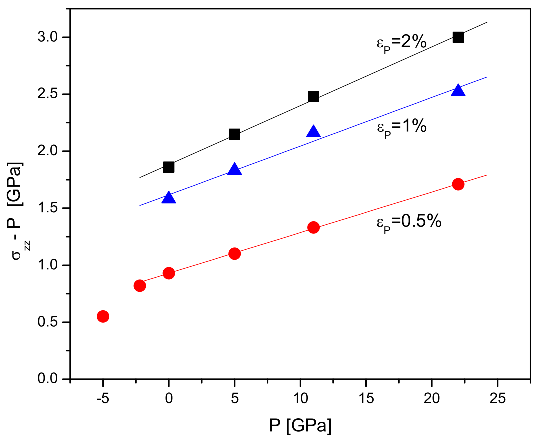

FIG. 3: Stress necessary to produce a given amount of plastic deformation versus hydrostatic pressure, as obtained form Fig (2). A remarkable linear correlation, at all 3 levels of plastic strain used for the definition of strength, supports the interpretation of GB plasticity in terms of a Mohr-Coulomb law.

The high values of hydrostatic pressure used in this work, within the range of pressures induced by shock waves, introduces a significant tension - compression asymmetry, as shown in the lower curve of Fig 3, that leads to failure for negative pressures grater than 5 GPa. It is therefore not possible to explore the validity of the Mohr-Coulomb law in tension, in contrast to the situation studied in [15] using biaxial stresses ten times smaller than ours.

In summary, in this work we prove that the relation between the stress needed to deform plastically a nanophase sample and hydrostatic pressure is remarkable linear, like in a simple friction mechanisms, and can therefore be captured with a Mohr-Coulomb law developed for granular materials. We provide the slope in the linear relation and find it to be quite insensitive to the total plastic deformation or the strain rate used to calculate it.

The implications of this findings support our previous results on ultra-high hardness under shock conditions. In computer simulations of shocks in nc Cu, where the Poisson volume relaxation effect is restrained from occurring, we found that the flow stress reaches ultra-high values not seen before for this model material, in striking contrast with the results reported so far for simulations and experiments under quasi-static, uniform stress, where volume relaxation is naturally allowed [11]. The softening of the flow stress of nc metals below $\sim$ 15 nm grain size does not happen, or is significantly reduced, under shock loading because the transition from dislocation mediated plasticity at large grain sizes, to GB sliding at small grain sizes is suppressed. Suppression arises because the barriers for GB sliding increase with pressure, as proved in this work. The quantitative evaluation of the pressure sensitivity reported here is of direct use in continuum models of plasticity [17].

Comment on the barriers for dislocations

Acknowledgments

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