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Grain boundary sliding in nanomaterials at elevated temperatures

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Abstract The unique deformation behavior of nanocrystalline materials is considered to be caused by suppression of conventional lattice dislocation slip (which dominates in coarse-grained materials) and effective action of alternative deformation mechanisms occurring through motion of grain boundary defects. A significant role of grain boundary sliding in deformation processes in nanocrystalline materials was shown in models and was revealed experimentally.

Introduction

In conventional polycrystalline materials, grain boundary sliding (GBS) only manifests itself at temperatures above $0.5T_\mathrm{m}$ (T_m is a melting point). With a decreasing grain size, softening effects have been observed experimentally in a number of nc materials in contrary with classical Hall–Petch relationship [1–3]. The negative Hall–Petch slope with decreasing grain size in nanometer range led Chokshi et al. [4] to propose that GBS plays a major role in deformation process in nanocrystalline (nc) materials with grain sizes smaller than 10 nm even at ambient temperatures. Recently, Champion et al. [5] demonstrated exceptional mechanical properties in nc copper. This nanomaterial was produced by differential cold extrusion of ultrafine metal powder synthesized by a cryogenic evaporation–condensation technique. Nc copper was three times more resistant to deformation than coarse-grained copper and deformed homogeneously with no apparent necking by a steady deformation flow until sample failure occurred, i.e., the material displayed near-perfect elasto-plastic behavior. Similar perfect elasto-plasticity in nanomaterials was observed by other researchers [5–10] both in tension and compression. This behavior could be explained by high atomic diffusion and the small size of the grains, which would make it possible to activate superplastic-type mechanisms at room temperature. The possibility of having higher effective diffusion coefficients in nanostructures [11] raised the hope that such diffusion-based mechanisms could become active at room temperature. Unfortunately, there is still a lack in technological approaches that can allow the production of high-quality nanomaterials with grains smaller than 20–30 nm in a volume large enough for appropriate mechanical testing. The most important and significant results on the physical and mechanical processes occurring during plastic deformation of nc metals have been obtained by molecular dynamic simulations (MDS). This technique is well suited for the study of nc metals where a volume of only approximately 1 $\mu\mathrm{m}^3$ can be tested. For conventional polycrystals, such a volume would not be representative of the material. Collective sliding of a few tiny grains on a shear plane has been recently predicted in computer simulations by Hasnaoui et al. [12]. A formation of local shear planes during plastic deformation of nc Ni with mean grain size of 5 nm was clearly observed after plastic strain of 3.6% at room temperature. Despite very little direct experimental evidence for

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GB sliding at low temperatures [13–15], some observations might be considered as indirect evidence for this deformation mechanism. Several experimental results on large-strain deformation of nanocrystalline metals demonstrate a lack of texture formation and the retention of equiaxed grains [16]. These observations are compatible with the operation of a GBS related superplasticity-type mechanism. Remarkably, some of the micrographs of the nc materials after cold deformation show neighboring segments of grain boundaries to be aligned (Fig. 3b in [16] and Fig. 4 in [17]) as the signature of macroscopic GBS.

Experimental data on elevated temperature plasticity of nanostructures is even more limited because of high thermal instability of such nanostructures. Results on deformation behavior of nc materials revealed a clear *correlation between microstructural instability and enhanced plasticity* [18]. The driving force for grain growth is quite high in nc materials because of the high interfacial area per unit volume. In some ways this is to be expected because both grain boundary migration and grain boundary sliding involve diffusion. Extensive grain growth clearly results in transformation of deformation mechanisms. In this paper, an analysis of experimental observations on deformation behavior of nc materials at elevated temperatures in correlation with existing models is presented.

Experimental observations

High density of grain boundaries and high probability of GBS in nc materials even at room temperature (see above) leads to a suggestion that deformation of these materials at elevated temperatures should be mostly controlled by processes in grain boundaries.

An important prediction for materials with decreasing grain size is their great potential to enhanced plasticity at elevated temperatures. In the most intensively investigated materials with grains smaller than 100 nm, high temperature deformation in the temperature range where the *microstructure is stable* results in a slight increase in ductility but is far from predicted superplastic behavior [19]. Moreover, a number of features observed in nc materials that did undergo superplastic flow, are different from the typical superplastic behavior of microcrystalline materials [18, 20, 21]. That includes high flow stresses and extensive strain hardening (Fig. 1). Superplasticity in microcrystalline materials is well established as a grain size dependent phenomenon that can be described by the constitutive equation for conventional superplasticity [22]:

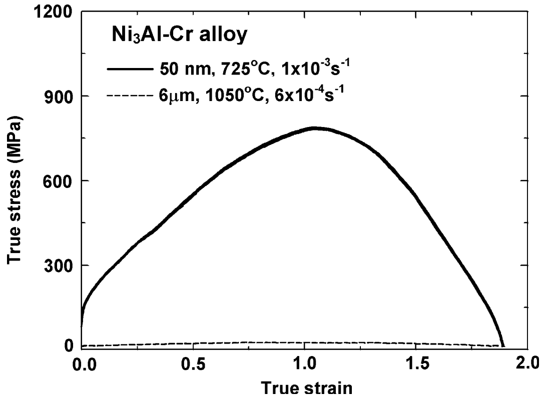

Fig. 1 A comparison of flow curves for Ni_3Al alloy in microcrystalline and nanocrystalline state. Note the higher flow stress in nanocrystalline state, although both specimens showed similar ductility (From Ref. [17])

$$\dot{\varepsilon} = A\frac{DGb}{kT}\left(\frac{b}{d}\right)^{p}\left(\frac{\sigma}{E}\right)^{2} \qquad (1)$$

where $\dot{\varepsilon}$ is the strain rate, D is the appropriate diffusivity (lattice or grain boundary), G is the shear modulus, b is the Burger's vector, k is the Boltzmann's constant, T is the test temperature, d is the grain size, p is the grain size exponent (usually 2 for lattice diffusion controlled flow and 3 for grain boundary diffusion controlled flow) and σ is the applied stress. Behavior described by this equation has been observed for metals, intermetallics and ceramics materials. Because of the grain size dependence in the constitutive relationship for superplastic flow, strain hardening during superplasticity has been conventionally explained in terms of grain growth. However, grain growth alone cannot account for the entire strain hardening in all these materials. At constant temperature, the stress dependence n, and grain size dependence p, have been experimentally determined for nanocrystalline Ni_3Al during the present investigation. Both of these values are equal to 2. An examination of Eq. 1 will reveal that at constant T and constant $\dot{\varepsilon}$: $\sigma \infty (d)^{p/n}$; with $n = 2$ and $p = 2$, $\sigma \propto d$, i.e., the increase in stress should be directly proportional to increase in grain size. However, the results on Ni_3Al alloy at 650 °C and 1×10^{-3} s^{-1} strain rate shows a flow stress increase by a factor of ~5 where the grain size increased only by a factor of ~2 [23]. A theoretical model developed by Gutkin et al. [24] attributes a strengthening effect that dominates at the first long stage of superplastic deformation to the formation of sessile grain boundary dislocations at triple junctions. Their theoretical analysis of the energy characteristics of the transformations indicates that the transformations of grain boundary dislocations at triple junctions are energetically favorable in certain ranges of parameters of the defect configuration. The corresponding flow stress is caused mostly by the critical shear stress, which is highly sensitive to both the level of plastic strain and the triple junction geometry. At the same time, the movement of grain boundary dislocations across triple junctions can be accompanied with grain boundary migration driven by a decrease of the total length and thereby energy of grain boundaries (Fig. 2). As a result of numerous possibilities of movement of grain boundary dislocations across triple junctions and the accompanying grain boundary migration, the grain boundary planes temporarily become parallel to each other at the shear surface (Fig. 2). In these circumstances, triple junctions stop being geometric obstacles for the movement of new grain boundary dislocations, leading to enhanced GBS. Recently, we have obtained experimental evidence for this process in nc materials during in-situ tensile testing of nc Ni_3Al alloy [19]. The bright field micrograph in Fig. 3 is showing a formation of sliding surfaces marked by arrows that supports the idea that cooperative grain boundary sliding took place during deformation of nanocrystalline Ni_3Al alloy. The mechanism associated with sliding and rotation of entire grain groups along common sliding surfaces was experimentally observed and analyzed in detail for microcrystalline materials [25, 26].

Discussion

To create a plane interface, the peaks and troughs of the mesoscopic grain boundary plane must be removed, i.e., the grain boundary area along the mesoscopic glide plane must be minimized to an acceptable degree. In those cases when part of the grain boundaries are oriented non-favorably for the realization of sliding with respect to operating stresses, the transfer of deformation from one grain boundary to another boundary might occur via intergranular

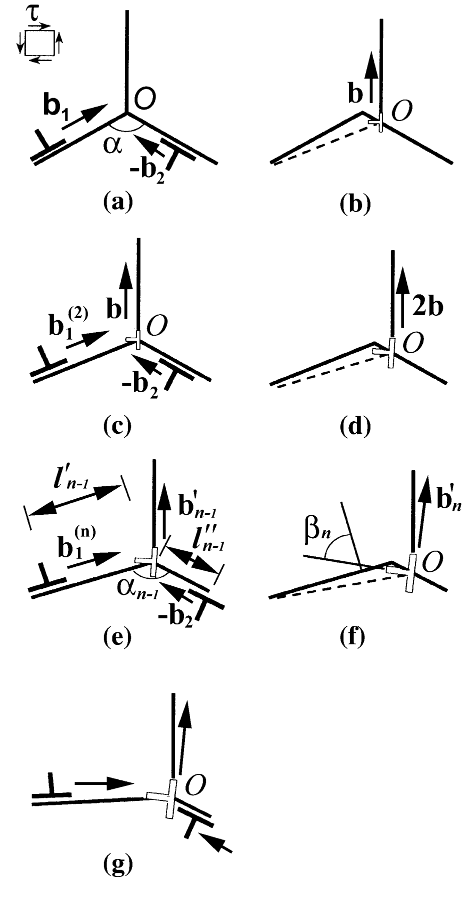

Fig. 2 Numerous acts of transfer of GB dislocations across a triple junction and accompanying local migration of GBs make GB planes (adjacent to the triple junction) to be temporarily parallel to each other (From Ref. [21])

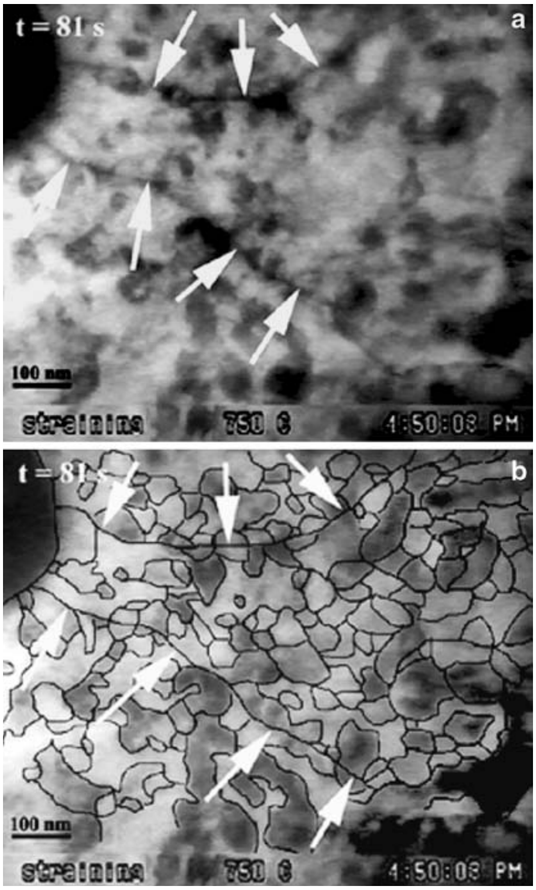

Fig. 3 (**a**) TEM image of nanocrystalline Ni_3Al extracted from a real-time video of in-situ tensile test at 750 °C. Highlighting of recognizable GB in (**b**) helps to see sliding surfaces that are pointed by arrows (From Ref. [16])

dislocation glide (grain I, Fig. 4). In nc materials, as it was shown recently [27], the partial dislocation slip occurs at lower shear stresses compared with the perfect dislocation slip in grains having a size smaller than some critical value. In this case, the shear stress needed to activate the partial dislocation sources at grain boundaries controls the flow stress in nc materials deformed through emission and movement of partial dislocations and twins. Direct evidence of intragranular deformation by partial emission and twining has been obtained by TEM and HREM for a number of nc materials [16, 27–34]. The root cause of emission of partial dislocations from the grain boundaries has been commented upon extensively [35–37] and has also been observed in MDS [36–44]. The MDS indicated the appearance of twin networks where two twin planes operate on an equal basis. However, in contrast to the MDS, the twins in nc Pd [34] and Al [27] were found to form on only one slip plane per grain; thus the twins were always coplanar within each grain. As one slip plane is not enough to accommodate general deformation on a larger scale, an additional deformation mechanism is required. Roesner et al. [34] suggested that grain rotation will allow the grains to orient their active twin plane along the principal shear direction. In addition, simulations predict that intragranular deformation by partial dislocation emissions accounts for only a small portion of the macroscopic deformation, especially at very small grain sizes, where the existence of any intragranular dislocations is rare or is entirely in doubt [39, 45]. Moreover, it has been shown that emission of partial dislocations aids in relaxation of grain boundaries during the sliding process [46, 47]. Gutkin et al. [48] have shown theoretically that the emission of partial dislocations from triple junctions of grain boundaries is energetically favorable in nc materials where GBS contributes to plastic flow. In such nc materials, GBS leads to storage of grain boundary dislocations at triple junctions and gradual increase of the system strain energy. The energy can effectively relax through the emission of Shockley partial dislocations into the adjacent grain interior. This theoretical statement accounts for experimental observations [27, 33, 49–51] of partial dislocations carrying deformation twinning in nc materials. Moreover, when the partial dislocation emission is enhanced, the emission events cause a decrease in the rate of the dislocation accumulation at triple junctions and hamper the nanocrack generation in the vicinities of triple junctions. This effect is worth being taken into account in the explanation of the experimentally observed [33, 49–51] good ductility of nc materials (fabricated by the cryomilling method) showing the enhanced emission of partial dislocations from grain boundaries.

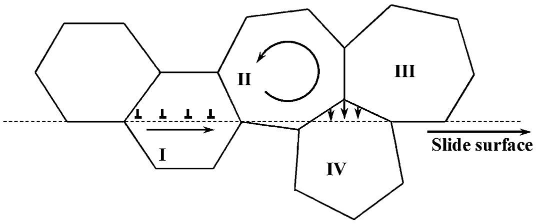

Fig. 4 Possible mechanisms of the formation of the sliding surface for CGBS in microcrystalline materials: I—dislocation glide; II—grain rotation; II–III—grain boundary sliding; IV—-grain boundary migration (From Ref. [16])

A localization of migration of grain boundaries and their fine adjustment along the common surface (grain IV, Fig. 4) might also play an important role in a plane interface formation. One of such local grain boundary migration was described in Gutkin et al.'s model (see above) when numerous acts of transfer of grain boundary dislocations across a triple junction cause a local migration of grain boundaries and lead to an increase in a triple junction angle (Fig. 2). Same authors have also theoretically described stress-driven grain boundary migration as a special mode of rotational plastic deformation in nc materials. It has been shown that there are three main ranges in the value of the external shear stress τ acting on a grain boundary in a nc material. When $\tau < \tau_{c1}$, the grain boundary migration is not possible. If $\tau_{c1} < \tau < \tau_{c2}$ the grain boundary can migrate in a stable regime when its propagation is determined by the level of τ. If $\tau > \tau_{c2}$ the grain boundary migration becomes unstable when the grain boundary propagation does not depend on the level of τ. The numerical values of these two critical stresses, τ_{c1} and τ_{c2}, strongly depend on the elastic modulus of the material, as well as on the strength of disclination-like defects appearing at the grain boundary junctions in the process of migration. Estimates have shown that stress-induced grain boundary migration can substantially contribute to plastic deformation of nc materials.

In the context discussed, of particular interest are experimental data [52–54] and models [55] on observations of both grain rotation and GBS occurring simultaneously in deformed nc materials (grains II and III, Fig. 4). The primary carriers of the rotational plastic deformation in solids are believed to be dipoles of grain boundary disclinations [56]. A disclination is a line defect characterized by a rotation of the crystalline lattice around its line [57]. A disclination dipole consists of two disclinations causing crystal lattice rotation between them; such dipoles are energetically permitted only for disclinations that are close to each other. Motion of a disclination dipole along grain boundaries causes plastic flow accompanied by crystal lattice rotation behind the disclinations. The disclination dipole motion has been suggested to be intensive in nc materials, where the volume fraction of grain boundaries is high and disclinations are close to each other [58]. Murayama et al.'s atomic-level observation of disclination dipoles in deformed nc materials [59] provides experimental support for this suggestion. It should be pointed out that grain rotation occurs in nc materials when it is effectively accommodated by enhanced diffusion along grain boundaries [60]. However, grain boundary migration involves diffusion as well. Extensive grain growth clearly results in transformation of deformation mechanisms [61]. Thus, in order to retain a nc structure in the material, deformation temperature might be too low for long-range grain boundary diffusion. It was suggested that GBS in nanomaterials is accommodated by atom shuffling similar to that considered in free volume model for stress-driven atomic re-arrangement in amorphous materials by Spaepen [62]. Such mechanism might be considered as ''stress-induced'' (i.e., athermal) grain boundary diffusion [63, 64].

In the absence of grain boundary relaxation during GBS, stresses might reach locally such extreme values that displacement of individual atoms is not expected, and the most natural expectation is the shifting of atomic planes, along or close to the direction of the Burgers vector in the glide planes of normal dislocations [65]. Such displacement of atomic planes occurs simultaneously leading to mesoscopic shear and the softening of the materials that eventually leads to fracture. Extensive shear banding was experimentally observed in a number of nc materials [66–68]. Bobylev et al. [69] have theoretically shown that shear band development occurs in the presence of mostly low-angle grain boundaries in a nc structure. Lattice dislocations released from the decayed low-angle boundary enhance decay of neighboring low-angle tilt boundaries. Also, decay of a low-angle tilt boundary leads to the formation of a dipole of disclinations at the grain boundary junctions adjacent to the decayed boundary. The disclination dipole elastically interacts with the lattice dislocations there by forming neighboring low-angle tilt boundaries and enhances decay of these boundaries. Thus, the shear-stress-induced decay of a low-angle tilt boundary can trigger the formation of a shear band (thin, sheet-like region where high plastic strain is localized) in the nc solid. It is worth noting that a similar process of decay of a low-angle boundary has recently been observed in MDS [12] of plastic deformation in nc Ni. Van Swygenhoven et al. [70] have also shown that due to presence of grain boundaries that are resistant to sliding (i.e., special low angle grain boundaries or misorientation close to twin boundary), local shear planes can concentrate around these grain boundaries creating a cluster of grain embedded in a sliding environment. Impurities have also strong effect on deformation mode in nc materials [67].

It is most likely that, such processes responsible for nc plasticity as, local grain rotation and local GBS take place simultaneously in order to form planar interfaces for subsequent cooperative GBS. Emission of partials and grain boundary migration by grain boundary diffusion (thermal and/or athermal) play an important role for accommodation both local events and cooperative sliding controlling the ductility of a nc material.

Conclusion

In the absence of classical intragranular slip, GBS in nc materials is controlled by such mechanisms as specialized intragranular slip (mostly partial dislocation emission and twining) and grain boundary diffusion (thermal and/or athermal by atomic shuffling). In order for GBS to be activated and, as a result, for nc materials to show an enhanced plasticity, there is a number of specific requirements for microstructural characteristics and for testing conditions. First of all, a nc material must have high-angle grain boundaries and mobile triple junctions. Any impurities that lock grain boundary and triple junctions need to be avoided. The ideal temperature range for deformation process should be in the narrow temperature range in which there is enough thermal activation for GBS but where the grain growth kinetics is low or minimum.

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