



Up-hill diffusion of solute atoms towards slipped grain boundaries: A possible reason of decomposition due to severe plastic deformation [☆]

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ABSTRACT

Supersaturated solid solutions subjected to severe plastic deformation often exhibit decomposition of the solid solution, leading to a peculiar grain boundary phenomenon, the formation of few nanometer thin layer enriched in solute atoms along grain boundaries. Based on localized grain boundary sliding, this phenomenon can be explained by the formation of hydrostatic stress field, which induces up-hill diffusion in the solute atmosphere, resulting in solute atom accumulation along the stressed grain boundaries.

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It is well-established that both the strength and ductility of bulk materials can be improved by grain refinement. This was a strong motivation of the first efforts to get finer grain sizes in conventional materials using severe plastic deformation (SPD) techniques such as high-pressure torsion (HPT) [1–10] and equal-channel angular pressing (ECAP) [11–19]. In general, during plastic deformation different crystal defects, such as vacancies, dislocations, stacking faults and grain boundaries may form, increasing the strength and/or enhancing the creep ability of the material [3]. In the case of alloys, severe plastic deformation can change dramatically the initial microstructure, resulting in the formation of new phases and/or phase transformations inside both grains and grain boundaries (GB) [20–22]. For instance, the phenomenon of GB wetting due to HPT process is well-known in several recent works [23–26]. A typical example on the decomposed microstructure and wetted grain boundaries of Al-30wt%Zn alloy ultrafine-grained by HPT at room temperature, reported by Straumal et al. [23]. In details, the initially supersaturated solid solution is decomposed into fine Al grains, Zn particles and an Al/Al grain boundaries wetted by Zn-rich layer. Although the features of the wetting behavior were deeply discussed [23,24], the physical reason of the solid solution decomposition and the explanation of the migration of solute atoms into grain boundaries during SPD is still an open question. In the followings, a possible explanation will be given for

this phenomenon, which provides further insight into the significance of the SPD techniques.

First of all, we have to start from the fact that atoms are typically less strongly bonded in grain boundaries than in the bulk material. Furthermore, SPD processes induce intense dislocation motion through grain boundaries and produce additional defects, i.e. disconnections [27], with extra energy contribution. The increased shear stress of SPD processed materials can lead to the formation of grain boundary disconnection pairs during the SPD process. These pairs result in coupled localized sliding and bending out of the grain boundary between triple junctions [28]. Thermal activation ($T > 0.6T_m$) of the high energy state of grain boundaries biases the coupling between the normal and sliding motions toward sliding of the grain boundary [28]. Although high temperature is not reached in a typical, room temperature SPD process even for Al alloys ($T \approx 0.4–0.5T_m$), strong vacancy formation and accompanied increase in atomic mobility may facilitate grain boundary sliding at lower temperatures during the SPD process. For the sake of simplicity, only one sliding grain boundary between two grains is discussed here (see the schematic image in Figure 1a). Grain boundary sliding at the triple junctions requires substantial diffusion of the atoms through the grains, therefore, in the following, the slip offset between the neighboring grains is considered zero at the triple junctions (see Fig. 1b). Between the triple junctions, the slip along grain boundary may vary and form an $f(x)$ offset distribution, which leads to the relaxation of the stress at the grain boundary. In the idealized case, when slip occurs in a straight grain boundary without any resistance, the grain boundary behaves similarly as a mode II crack [29]. In this specific situation, the shear stress field –

[☆] This work is dedicated to Prof. Ruslan Z. Valiev on the occasion of his 70th birthday.

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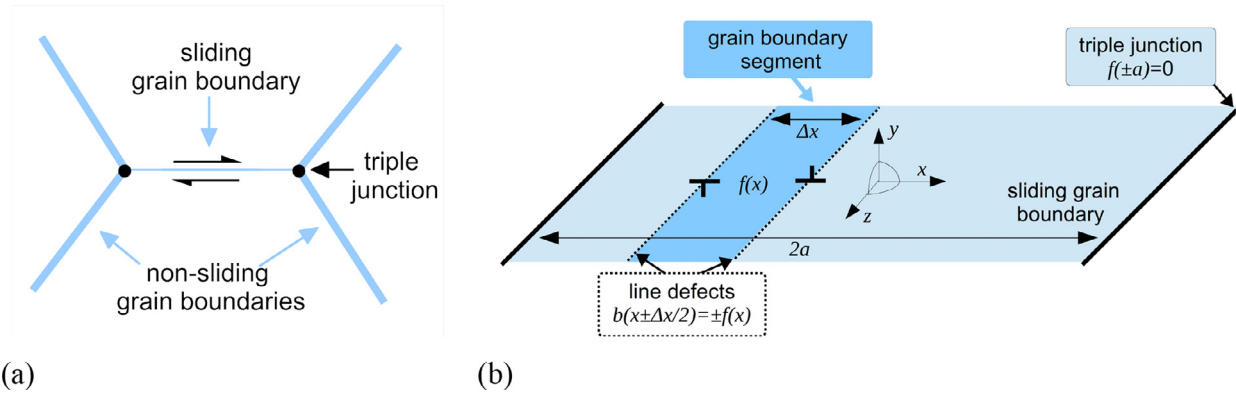


Fig. 1. (a) Schematic 2D image of one sliding grain boundary between triple junctions. (b) 3D model of the same grain boundary in which the offset distribution of the local $f(x)$ slip is realized in discrete grain boundary segments by edge dislocation dipoles with $\pm f$ Burgers vectors.

including the external stress – relaxes fully along the grain boundary and the relaxation (so that the offset distribution) becomes a reversible linear function of the external stress field [29]. In minor extent, this linear elastic behavior contributes to the resilience of nanocrystalline samples, reducing the apparent shear modulus of the materials [30]. Therefore, we anticipate that grain boundary sliding is present in SPD processed alloys, irrespectively of solute atom content or the purity of material.

In order to determine the effect of grain boundary sliding on the surrounding material, a simple elastic continuum model is constructed, which approximates the contribution of a single grain boundary to the external stress. For this purpose, the grain boundary was divided into discrete, Δx wide segments with $f(x)$ offset and the stress field of each segment was approximated by that of a pair of line defects enclosing the segment (see Fig. 1b). In the pair, each line defect was straight and had infinite length and equal Burgers vector, but with opposite sign ($b = \pm f(x)$). The Burgers vector of the line defects was in the plane of the grain boundary to reproduce the slip of the boundary, thus each grain boundary segment can be characterized by an edge dislocation dipole (denoted by $\perp$ and $\top$ in Fig. 1b). Normal displacement, i.e. bending out, of the grain boundary due to the dipole formation was neglected in the model. Due to the linear behavior of the model, stress contributions of the different segments can be summed up in a selected point and the stress field of the grain boundary can be calculated as the convolution of the sum of local Burgers vector with the stress field of an edge dislocation [31]. In this grain boundary model, simulations were performed for load-unload cycles with different grain boundary parameters. In the present simulations, instead of the quantization of the Burgers vectors of the edge dislocations, the $f(x)$ offset distribution was varied freely to decrease the sum of the external stress (τ_{ext}) and the stress contribution of the grain boundary to the shear strength of the grain boundary (τ_{GB}). Based on the simulations of load-unload cycles with non zero τ_{GB} values, the $f(x)$ offset distribution changed irreversibly during unloading. Mathematically, $\tau_{GB} \neq 0$ introduced a non-linearity into the model. Thus, for τ_{GB} being comparable to the external stress, the $f(x)$ and the stress distribution around the grain boundary of the maximum loaded state were preserved after complete unloading. This indicates, that grain boundaries with finite strength, remember to their stress history and can exhibit a residual stress field at zero external stress due to their preceding deformed state. Since, this continuum model is very general, it can be applied in other problems where localized slip occurs along a surface. For example, recently we used a similar model to determine residual stress field in the analogous system of shear bands in metallic glasses [32].

The demonstration of the stress field around the slipped boundary can be seen in Figs. 2 and 3. Fig. 2a shows that the σ_{xy} shear

component of the residual stress field develops back stress along the grain boundary and strong stress concentrations occur only at the triple junctions (see the enlarged area near the triple junction in Fig. 2b). The offset distribution related to the residual stress field can be described as (see the inset of Fig. 2a),

$$f(x) = f_{\max} \sqrt{1 - \frac{x^2}{a^2}}, \quad (1)$$

where $f_{\max} = 2a(1 - \nu)(\tau_{ext} - \tau_{GB})/G$, ν is the Poisson number, G is the shear modulus and $2a$ is the length of grain boundary. Due to the simple form of non-linearity (using a constant τ_{GB} parameter), solutions of the model can be analytically obtained in the typical form of Eq. (1) and the corresponding residual shear stress together with other stress components can be described by harmonic functions for the case when slip occurs only in a single grain boundary. It should be noted that this result can be applied as a first order approximation for slips in multiple grain boundaries, because strong shear stresses are localized outside of the neighboring grain boundaries (see Fig. 2b).

Let us see now how the stress field affects the decomposition and migration of solute atoms in a solid solution. Diffusion is typically driven by concentration differences in materials. However, in general, the chemical potential determines the equilibrium distribution of the atomic concentration. In solid solutions with cubic symmetry, the chemical potential, Φ depends on the $p\Delta V$ term [33–36], where p is the hydrostatic pressure and ΔV is the volume difference between the solute and matrix atoms. Therefore, gradients in the hydrostatic stress field also induce diffusion currents of solute atoms (j), which can be given by the following formula:

$$j = -\frac{Dc}{kT} \text{grad}(\Phi(p\Delta V)) - D \text{grad}(c), \quad (2)$$

where c is the local concentration of the solute atoms, D is the diffusivity, k is the Boltzmann constant and T is the absolute temperature. This process is analogous to the formation of Cottrell atmosphere in the hydrostatic stress field of an edge dislocation [33]. Calculations are focused on the mechanical driving force originating from the hydrostatic component of the stress field on the alloying atoms, as a typical case for the diffusion of solute atoms in stressed bodies [34].

Fig. 3 exhibits the calculated hydrostatic component of the residual stress field around the slipped grain boundary. It can be seen that large pressure gradient exists across the slipped grain boundary, where the sign of the hydrostatic stress changes within the width of the grain boundary, i.e. in one atom sized interval (Fig. 3b). Proportionally to the variation of $b(x)$, the local Burgers vector distribution (see the inset of Fig. 3a), hydrostatic pressure along the grain boundary also changes moderately and reaches high values only at the triple junctions due to the stress local-

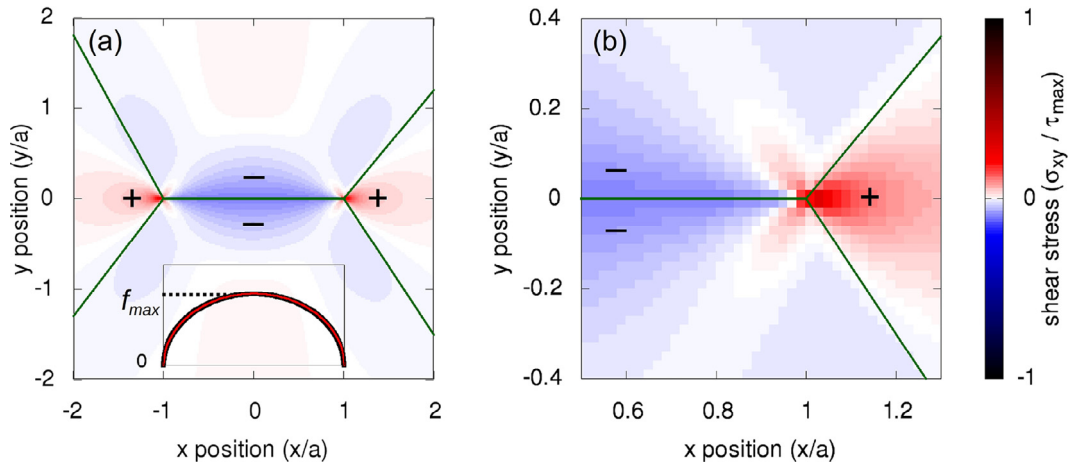


Fig. 2. (a) The σ_{xy} shear component of the residual stress field around a slipped grain boundary calculated by the model. Green lines indicate the trajectories of grain boundaries. The inset shows the corresponding $f(x)$ offset distribution (black curve) with a fitted analytical (red) curve. (b) The enlarged view of the same shear stress field near a triple junction. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

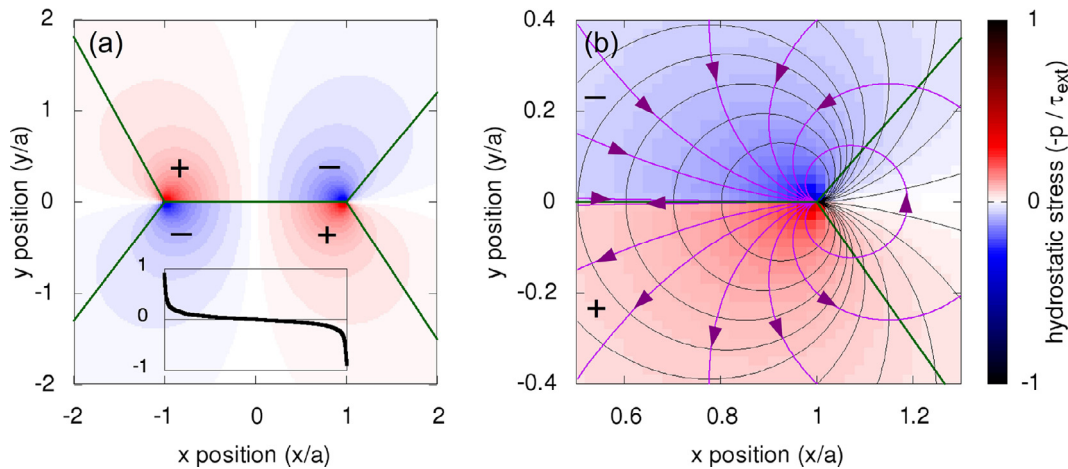


Fig. 3. (a) Calculated hydrostatic component of the residual stress field around a slipped grain boundary. The inset shows the local $b(x)$ Burgers vector density in arbitrary unit. (b) Enlarged views of the same hydrostatic stress field near a triple junction. Analytical iso-pressure lines (black curves) and the perpendicular diffusion current trajectories (purple lines with arrows) are also indicated. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

ization. This indicates that local concentration changes can be expected at the triple junctions and along the grain boundary. More precisely, based on the continuity equation, three terms arise from the derivation of Eq. (2), which determine the accumulation rate of the solute atoms,

$$\frac{\partial c}{\partial t} = \frac{Dc}{kT} \text{div}(\text{grad}(\Phi)) + \frac{D}{kT} \text{grad}(c) \text{grad}(\Phi) + D \text{div}(\text{grad}(c)). \quad (3)$$

The first two terms of the right hand side of Eq. (3) account for the role of pressure gradient in the sample and the third one describes the concentration gradient driven diffusion, which is equivalent to the well-known first Fick law. For homogeneous concentration distribution, only the first term is non-zero. Therefore this first term is responsible for the formation of initial concentration inhomogeneities in a solid solution. In the present model, the term $\text{div}(\text{grad} \Phi) - \text{div}(\text{grad} p)$ is equal to zero within the grains as the stress field can be described by harmonic functions, but it diverges along the sides of the grain boundaries as seen in Fig. 4a. This indicates that due to the first term of Eq. (3) solute atoms, vacancies and other point defects can accumulate very selectively at the two sides of the slipped grain boundary. Primarily, this up-hill diffusion process, which works against the normal diffusion, explains

qualitatively the formation of solute atom layer along grain boundaries. Moreover, the binding energy between solute atoms and an edge dislocation ($\sim 37 \text{ meV}$ for Zn in Al matrix [31]) in the grain boundary leads to a reduced surface energy which results in easy wetting and a preferred inhomogeneous nucleation for the equilibrium phases along the slipped grain boundary. However, full wetting of the Zn phase along the grain boundary is expected only if a sharp change in the hydrostatic stress takes place due to the grain boundary slip, and partial wetting is anticipated along other grain boundaries as demonstrated experimentally in Fig. 4b from Ref. [23].

Secondary effects, such as the easy slip between the Al grains, may also contribute to the full picture and explain characteristics of the forming sharp Zn walls. On one hand, local concentration change depends also on the availability of solute atoms along solute current trajectories. Therefore iso-pressure lines and the perpendicular diffusion current trajectories [35] were also indicated near a triple junction in an enlarged view in Fig. 3b. It can be seen that the diffusion current trajectories around the horizontal slipped grain boundary drive solute atoms toward the triple junctions and, typically, the currents are parallel to the grain boundary between the triple junctions in a similar way as it was pinpointed for an analogous system (diffusion near a mode II crack) [35,36]. The con-

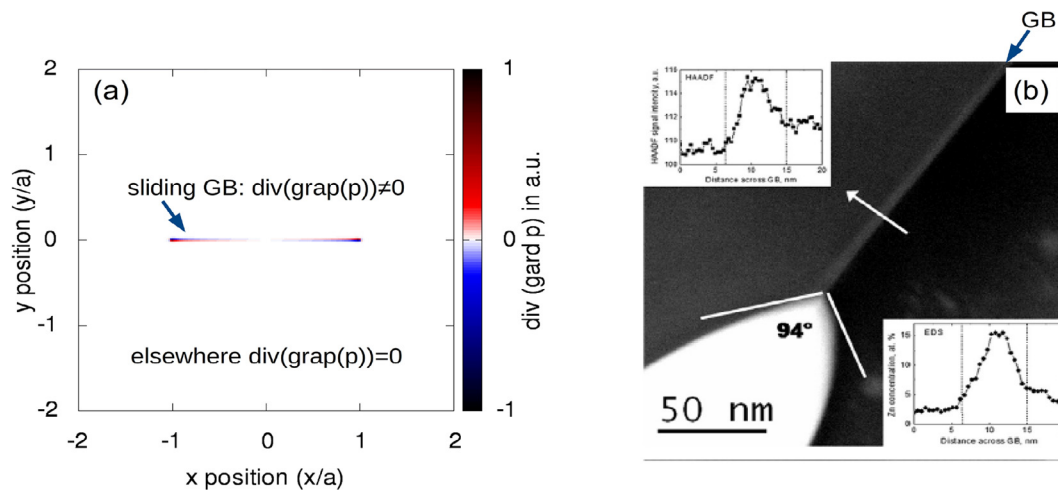


Fig. 4. (a) Distribution of $\text{div}(\text{grad}(p))$, which is proportional to the local accumulation rate of solute atoms, as calculated from the modeled hydrostatic stress field. Accumulation points are in coincidence with the trajectory of the slipped grain boundary. (b) Z-contrast image obtained by high angle annular dark field in scanning mode of transmission electron microscope (HAADF STEM) showing a Zn particle (bright) in the bottom left corner and an Al/Al grain boundary (aligned from left bottom to right top) wetted by a Zn-rich layer in the Al-30wt%Zn alloy processed by HPT. Reproduced with permission [23]. Copyright 2014, Elsevier.

tribution of the normal diffusion and the stress field of neighboring grain boundaries may modify the diffusion currents slightly, driving and thus trapping the solute atoms into the grain boundaries. As an additional effect, the parallel diffusion of the solute atoms and vacancies can take place simultaneously due to the formed hydrostatic stress field. As a result, vacancy concentration may also increase substantially along the grain boundaries compared to the high value reached during SPD process in the bulk material. Due to the increase of vacancy concentration, localized sliding can produce non-equilibrium state in grain boundaries with enhanced diffusion (sometimes referred as extra free volume) in any SPD materials [37], which suggests a generalization of the model for pure materials as well. Independently from this effect, in Al-Zn alloys, diffusivity grows rapidly with Zn content [38]. Therefore, the additional high vacancy concentration can effectively produce fast diffusion and easy shearability in Zn rich boundary phases, leading to a positive feedback (reduction in τ_{GB}) during the process. On the other hand, a negative feedback to the diffusion process also exists along the slipped boundaries due to the finite ΔV value of the solute atoms. Hydrostatic stress field of the accumulating atoms in the grain boundary phase compensates the hydrostatic stress field of the sheared boundary, reducing and smoothing the term $\text{div}(\text{grad } p)$ near the slipped grain boundary. This feedback ceases the further diffusion towards grain boundaries in time and conserves the decomposed microstructure. For Al-Zn solid solution, however, ΔV is substantially smaller than for other (e.g. for Al-Cu or Al-Mg) solid solutions, which allows the formation of a thicker grain boundary layer in Al-Zn alloys. Finally, besides kinetic factors, the stability of the formed Zn rich layer is preserved also by thermodynamic effects, as Al-Zn form an eutectic of the Al and Zn phases practically in the full composition range at room temperature [38], therefore the supersaturated Al-Zn solid solution becomes more stable if it decomposes into the mixture of Al rich and Zn rich phases.

In summary, formation of disconnection pairs in the grain boundaries of SPD materials can lead to localized grain boundary sliding. This minor effect relaxes the external shear stress partially along the grain boundary and forms a stress field around the sliding grain boundary. Hydrostatic component of this stress field induces diffusion currents and forms accumulation sites for both vacancies and solute atoms specifically at the atomically thin grain boundary, because the divergence of the diffusion currents is non zero exclusively along the grain boundaries. In Al-Zn solid solution,

this process leads to the wetting of the slipped boundaries by Zn phase and the accumulation of Zn atoms in grain boundaries. Analogously, vacancy concentration may also increase in grain boundaries, which gives a positive feedback to the process and explains enhanced grain boundary sliding in Al-Zn solid solutions subjected to severe plastic deformation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.scriptamat.2020.07.055](https://doi.org/10.1016/j.scriptamat.2020.07.055).

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