Fracture toughness and bond trapping of grain boundary cracks

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Abstract
The fracture toughness of materials in which brittle cracks initiate and propagate along grain boundaries depends not only on the energy of the grain boundary, but also on its microscopic structure. How exactly and to which degree brittle grain boundary fracture is affected by the local atomic structure at the crack tip has not yet been studied in detail. Here, we use molecular static simulations to study the atomic-scale fracture behavior of six large angle tilt grain boundaries in tungsten bicrystals. The fracture toughness depends critically on the propagation direction and on the position of the crack tip within the structural units of the grain boundary. Furthermore, the grain boundary fracture toughness can be significantly larger than for single crystals in the same orientation. These results cannot be explained by the usual thermodynamic approach in continuum-scale fracture mechanics but can be understood by considering the effect of bond trapping of grain boundary cracks.

Keywords:
Grain boundary, Fracture, Atomistic Simulation, Bond trapping, Tungsten

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1. Introduction

The resistance against crack propagation is undoubtedly one of the most important properties of structural materials. Whether a stressed component fractures by brittle cleavage or by ductile rupture is determined by the competition between bond-breaking at the crack tip and plastic deformation in the vicinity of the crack [1, 2]. Which of these processes dominates at a given temperature and strain rate depends on the nature of the chemical bond between the atoms [3] as well as on the microstructure of the material [2, 4–6]. In linear elastic fracture mechanics (LEFM), the fracture toughness (or brittle crack initiation toughness) is defined as the critical stress intensity factor $K_{lc}$ at which an atomically sharp crack would start to propagate under mode I loading [7]. In the case of negligible plastic deformation, the theoretical value $K_G$ is related to the critical energy release rate $G_c$, i.e., the change in elastic strain energy per unit area of crack advance, by

$$K_{lc} = \sqrt{E'G_c}, \quad (1)$$

where $E'$ denotes an appropriate elastic modulus [8]. For completely brittle fracture of a single crystal (SC) the critical energy release rate $G_c$ is according to Griffith [9] equal to the surface energy $2\gamma_{surf}$ of the two newly created surfaces of unit area:

$$G^{SC}_c = 2\gamma_{surf}. \quad (2)$$

In case the crack propagates along a grain boundary (GB) between two grains 1 and 2, the energy required to create the two surfaces, which can be
crystallographically different, has to be considered relative to the GB energy $\gamma_{GB}$ [7, 10]:

$$G_{c}^{GB} = \gamma_{surf}^1 + \gamma_{surf}^2 - \gamma_{GB}.$$  \hspace{1cm} (3)

In brittle materials, fracture along symmetrical GBs should therefore always be more favorable than cleavage on a plane parallel to the GB ($\gamma_{surf}^1 = \gamma_{surf}^2 = \gamma_{surf}$). Whether fracture in a brittle polycrystal takes place by transgranular cleavage or intergranular fracture however depends, besides geometrical factors, on the ratio of $G_{c}^{GB}$ to the lowest possible $G_{c}^{SC}$ [10].

Above thermodynamic treatment of fracture in terms of continuum properties neglects however the underlying atomic nature of the material. At the atomic scale, the propagation of cleavage cracks is determined by the forces required to break the bonds directly at the crack tip. The breaking of discrete atomic bonds manifests itself in the so-called lattice trapping effect [11–13]: an atomically sharp crack tip can remain stable until a load $K^+$ larger than $K_G$ is reached. This load is called the upper trapping limit. Similarly, a lower trapping limit $K^- < K_G$ exist, above which the crack will not heal [14]. The trapping range is defined as $\Delta K = K^+/K^- - 1$. Lattice trapping was identified as the reason for the preference of $\{100\}$ cleavage over cleavage on the lower energy $\{110\}$-planes in tungsten [15], and has been shown to lead to anisotropy with respect to the propagation direction along different crystallographic directions within the same fracture plane [16] as well as crack velocities [17] in silicon.

The concept of lattice trapping can be readily expanded to include GBs, where the atoms are not arranged on a regular lattice, and consequently the more general term bond trapping is used [12, 18]. Although experiments
on oxide ceramics have hinted at the importance of bond trapping in the selection of the transgranular mode of fracture over intergranular fracture [12, 19], a systematic study of the influence of bond trapping on GB fracture is currently lacking.

Knowledge about the fracture toughness of GBs is of particular importance for continuum models of intergranular fracture [20–32], which allow to investigate failure of polycrystalline materials at the macroscale as well as for grain boundary engineering of structural materials [33, 34]. The experimental determination of the fracture toughness of individual GBs is however challenging, as it requires the preparation of notched flat and defect-free GBs with defined misorientation. Therefore, only few measurements of GB fracture toughness exist [35, 36]. Most experiments instead determine the fracture strength of GBs by measuring the tensile stress at which a GB fails in an uniaxial tensile test. The fracture strength of GBs was however investigated that way only for relatively few materials, e.g., high-purity Mo [37–40], Ni$_3$Al [41, 42], Ni-20Cr [43] and Si [44]. In the context of the present work, it is interesting to note that these experiments often show that samples with GBs normal to the tensile direction can have fracture stresses of the order of single crystals [33, 39, 40, 43] or higher [38, 41, 42, 44] and even show intergranular instead of transgranular fracture [40–43]. In most cases the strong GBs are $\Sigma 3, \Sigma 9, \Sigma 17$ coincidence site lattice (CSL) GBs [38, 41–43], but there are exceptions [40, 44]. In addition, low $\Sigma$ GBs like $\Sigma 5$ and $\Sigma 7$ showed lower fracture stresses than the strong GBs and intergranular fracture [41], and the GB fracture stress is not always correlated to the GB energy [42, 43]. The determination of the fracture stress in tensile tests involves plastic de-
formation, which in turn depends on the crystallographic orientation of both grains. Such experiments therefore cannot provide direct information on the GB strength. However, these experiments show that GBs are not per-se weak and that their strength is not directly predictable [41].

Atomistic simulations have played an important role in providing fundamental insights on crack tip processes [45] and on the way GBs influence the mechanical properties of materials [46]. The study of intergranular fracture using a GB crack in a bicrystal set-up dates back to the 1990s [26, 47–54]. However, many of these studies focus on ductile metals [26, 50, 53, 54], and very few quantitative calculations of the fracture toughness of brittle GBs exist [48, 51, 52].

Here we report on atomistic calculations of grain boundary fracture of a series of tilt GBs in tungsten, focusing on the quantitative determination of the fracture toughness and its direction and position dependence.

2. Methods

In order to study bond trapping in GB fracture, we performed molecular statics (MS) simulations of mode I cracks in five symmetrical and one asymmetrical tilt GBs under variation of their reciprocal density of coincidence sites, Σ, [10], and on single crystals of corresponding orientations.

2.1. Interatomic potential

Tungsten is chosen as model material because its brittle fracture behavior at low temperatures has been studied extensively, both by simulations [5, 48, 55] and experiments [15, 56–61]. In pure polycrystalline tungsten, brittle intergranular fracture has been observed experimentally for both textured,
elongated [57, 59, 60] as well as untextured, equiaxial grain structures [56, 58]. Moreover, tungsten’s near-perfect elastic isotropy simplifies the simulation set-up and analysis.

The atomic interaction is modeled by a Finnis-Sinclair potential [62, 63] which has been shown to represent well the experimentally observed fracture behavior of tungsten [15]. The potential properties relevant for this study are summarized in in Tab. 1.

2.2. Construction of grain boundaries

The GBs are constructed following the approach detailed in [64]. Two crystal grains are rotated with respect to each other according to the rotation axes and angles provided in Tab. 2 and joined along the GB plane. Periodic boundary conditions (PBC) are used for the $x-$ and $z$-directions within the GB plane whereas free boundary conditions are used along the GB normal ($=y$-direction). The GB structure is optimized with respect to the microscopic degrees of freedom by rigidly translating the two crystals with respect to each other and subsequently minimizing the energy while only allowing for motion of the atoms in direction of the GB normal. Using the microscopic translations of the two crystals which lead to the structure with the minimal potential energy as initial condition, the GB is fully relaxed without restriction of atomic motion and allowing for changes of the box size in the $x$- and $z$-direction to obtain a stress-free structure.

The exact size of the simulation box in the $x$- and $y$-directions is determined by the periodicity of the coincidence site lattice. The width in the $z$-direction is chosen such that it is at least three times the cut-off radius $r_{\text{cut}}$ of the potential, the extension of the GB in $y$-direction is chosen such that
it is larger than 30 nm, as is the sample size in the \( x \)-direction.

Throughout this study the FIRE algorithm [65] is used to minimize the potential energy of a system. Samples are considered to be in a minimum energy configuration when the force norm per degree of freedom is smaller than \( 10^{-8} \text{eV/Å} \). The so obtained GB structures and energies agree well with the literature, see e.g. [48, 66].

2.3. Simulation set-up

The simulation set-up is schematically shown in Fig. 1. From the relaxed configurations, cylindrical samples with radius \( R = 15 \) nm which contain the GB in the middle are cut out. Atoms within a distance \( R - 2r_{\text{cut}} \leq r \leq R \) from the center of the cylinder are held fixed. An atomically sharp crack is introduced at the center by displacing the atoms according to the displacement field \( u_{xy}(r, \theta, K) \) around a crack tip in an anisotropic body obtained from LEFM under plane strain conditions [8]. For more details on the introduction of cracks see [67]. PBC are used along the cylinder axis which corresponds to the crack front direction as well as the GB tilt axis.

In addition, cracks with the same crack plane and crack front direction were studied using the set-up in SCs with crystallographic orientations corresponding to the rotated grains.

2.4. Determination of critical stress intensity factors

The determination of the critical stress intensity factor at which the crack either propagates or crack tip plasticity is initiated requires a well-defined initial structure. I.e., upon energy minimization, the crack tip has to remain stable and at the exact center of the cylindrical set-up. The stress intensity
factor at which this is the case, \( K_{in} \), is determined by displacing the atoms according to the displacement field \( u_{xy}(r, \theta, K_{test}) \) for various test values \( K_{test} \) and subsequently minimizing the energy of the system. The values for \( K_{test} \) are chosen to be slightly below the stress intensity factor \( K_G \) according to the Griffith criterion for the given GB or SC (Eqs. (1-3)). The initial stress intensity factor \( K_{in} \) then corresponds to the value of \( K_{test} \) at which the crack tip remains stable at the initial position at the center of the cylinder.

From the initial stress intensity \( K_{in} \) the crack is loaded by incrementally displacing the atoms according to \( u_{xy}(r, \theta, \Delta K_I) \), which corresponds to an increase in load of \( \Delta K_I = 0.007 \text{ MPa}\sqrt{\text{m}} \). The crack structure is subsequently relaxed with the FIRE algorithm, and if no significant change of the bond lengths at the crack tip or of their configuration is detected, the relaxed structure is loaded by applying a further displacement field increment. The stress intensity factor at which the bond configuration at the crack tip changes either by brittle fracture or by crack tip plasticity is in the following referred to as \( K_{Ic} \). For more details on the iterative loading procedure and determination of \( K_{Ic} \) see [68].

For brittle propagating cracks, \( K^+ \) is identical to \( K_{Ic} \). \( K^- \) is determined by incremental unloading of the crack tip, i.e., by the application of a displacement field \( u_{xy}(r, \theta, \Delta K_I) \) with \( \Delta K_I = -0.007 \text{ MPa}\sqrt{\text{m}} \) to the atomistic configuration derived from the previous unloading step. Finally, the stress intensity factor where the crack closes is denoted as \( K^- \).

The influence of the boundary conditions were tested by performing simulations on selected GB cracks using four times larger cylinder radii. The observed fracture mechanisms were identical to the ones in the larger set-up,
and the values of $K_{ic}$ varied only within $2 - 3\Delta K_I$, the resolution of the stepwise iterative loading procedure.

3. Results

3.1. Cracks in single crystals

Nine different combinations of crack plane and crack front directions were studied in the SC set-up. The theoretical fracture toughness according to Eq. (1) and the determined fracture toughness and fracture behavior are summarized in Tab. 3. The lowest fracture toughness of tungsten SCs was determined for crack propagation on the (110) plane with [1 10] crack front direction to $K_{ic}^{SC} = 1.547 \text{ MPa}\sqrt{\text{m}}$, which is in excellent agreement with the values determined by Kohlhoff et al. [55] and agrees well with experiments [15]. This value exceeds $K_{G}^{SC}$, which has been attributed to lattice trapping [55]. The lattice trapping in this case was determined to $\Delta K_{SC} = 0.17$, see Tab. 4. Similarly, all other cleavage cracks require higher loads than $K_{G}^{SC}$ to propagate.

With the exception of the (710)[001] crack, which kinked out onto the (110) low-energy plane, all brittle cracks propagated on the initial cleavage plane. An example for brittle crack propagation is shown in Fig. 3 and Video 1, see Supplemental Material at [URL will be inserted by publisher], for the (112) [111] crack. Crack tip plasticity occurred typically by emission of twins, see Tab. 3. Crack tip dislocations were only observed for the (111) [112] crack system, where a full $a_0/2[111]$ (110) edge dislocation was emitted.
3.2. Grain boundary cracks

The grain boundary energies $\gamma_{GB}$ of the six studied GBs are summarized in Tab. 2, together with the corresponding surface energies $\gamma_{surf}$, and the theoretical critical energy release rates $G^e_{GB}$ according to Eq. (3). Tab. 3 compares the critical stress intensity factors $K^G_{IC}$ determined from the simulations to the theoretical fracture toughness $K^G_{IC}$ calculated from $G^e_{GB}$ according to the Griffith theory, Eqs. (1-3). This table also includes the information of the type of event at $K^G_{IC}$, i.e., whether the crack propagated by cleavage or plastic deformation was observed. Note that GB fracture was always studied using at least two opposite crack propagation directions within the GB plane.

Fig. 2a) is a graphical representation of the information in Tab. 3.

The simulation results show in all cases a significantly larger $K^G_{IC}$ than the theoretically predicted $K^G_{IC}$, independent of the event type, i.e. cleavage (open symbols in Fig. 2) or formation of twins (full symbols). Furthermore, even though $K^G_{IC}$ is smaller than $K^SC_{IC}$ for all studied GBs, the determined $K^G_{IC}$ can actually be larger than $K^SC_{IC}$. In particular, the GBs $\Sigma 3 (112) 60^\circ/ [11\bar{1}]$ and $\Sigma 25 (710) 16.3^\circ/ [001]$, which both show brittle fracture, have significantly higher fracture toughness than the equally brittle SC cracks on the same crack planes.

The results in Fig. 2a) show furthermore, that for GB fracture the toughness as well as fracture behavior depends on the direction in which the crack propagates. I.e., whether the crack propagates parallel or antiparallel to the cross product between crack plane normal and crack front direction. This is even the case when the fracture takes place in both directions in a purely brittle manner without emission of dislocations (open symbols in Fig. 2a).
The direction dependence of GB fracture is further exemplified in Fig. 2b) where the fracture toughness for ten different crack front directions in the Σ3 (111) 70.5°/[110] GB are shown.

The fracture behavior of the Σ3 (112) 60°/[111] GB is shown in Fig. 3b, where it is compared to a SC crack with the identical [111] crack front direction and (112) crack plane. The crack propagation under incremental loading is also shown in Video 1, see Supplemental Material at [URL will be inserted by publisher]. At $K_I = 1.661 \text{ MPa}\sqrt{\text{m}}$ the crack tip is stable in both the SC and the GB. In the SC, the first crack tip bond is broken at $K_{IC}^{SC} = 1.860 \text{ MPa}\sqrt{\text{m}}$, whereas the bonding topology at the crack tip in the GB remains unchanged. At higher loads, the crack in the SC propagates further on the initial (112) crack plane. The grain boundary crack in contrast starts to propagate at $K_{IC}^{GB} = 1.896 \text{ MPa}\sqrt{\text{m}}$, producing $\{110\}$ facets on the (112) crack plane. This difference in fracture surfaces is related to the bond breaking process. Fig. 3 shows that the SC crack advances by successive breaking of single bonds whereas quasistatic crack propagation within the GB takes place by simultaneous breaking of two different bonds.

The atomic crack tip configuration for this crack system is shown in more detail in Fig. 4a,b). As expected, the bonding situation is clearly different in the GB compared to the SC. In particular, the two atoms forming the critical bond at the crack tip see a different environment: in the grain boundary, the atoms directly at the crack tip interact with more atoms and have a lower potential energy as compared to the single crystal (see Fig. 4).

Fig. 4c) shows the lengths of the marked crack tip bonds as function of the applied stress intensity factor during iterative loading and unloading.
Following [16], the breaking of atomic bonds at the crack tip is determined by monitoring the bond distances across the crack plane for the two bonds indicated in Figs. 4a,b) as function of the applied load, Fig. 4c). Upon loading, the bond distances remain about constant up to a critical load $K^+ > K_G$ where the bond distance suddenly increases. When the crack is unloaded from this configuration, the distance between the now separated atoms decreases nearly linearly, until the bond forms again at $K^−$ which is lower than $K_G$. Further unloading leads to the formation of a new bond with an atom behind the original location of the crack tip (dashed lines in Fig. 4).

In the SC case, the breaking of the first bond (marked by arrows in Fig. 4a and b, solid line in subfigure c) at $K^+_{SC} = 1.860 \text{ MPa}\sqrt{m}$ is followed by the breaking of a second bond when the load is increased by additional $0.028 \text{ MPa}\sqrt{m}$. In the GB, two bonds break simultaneously at $K^+_{GB} = 1.896 \text{ MPa}\sqrt{m}$, which leads to the different fracture surfaces. The bond trapping range can be determined from Fig. 4e) to $\Delta K_{GB} = 0.30$ which is significantly larger than for the SC, $\Delta K_{SC} = 0.24$. Tab. 4 presents the lower and upper bond trapping limits, $K^−$ and $K^+$, as well as the corresponding bond trapping ranges, $\Delta K$, for selected GB and SC cracks.

The structure of the $\Sigma25\{710\}16.3^\circ/\langle001\rangle$ GB is shown in Fig. 5a). The GB can be described by three structural units, which repeat themselves along the $\langle\overline{1}70\rangle$ direction with a period of $\lambda_{\overline{1}70} = 11.2 \text{ Å}$ (the GB supercell contains two of these periods). As indicated by the colors in Fig. 5a), the GB consists of alternating regions of compressive and tensile hydrostatic stress, in which the bond lengths are correspondingly increased or decreased relative to the SC nearest neighbor distance, see Fig. 5b). Crack tips for the
two propagation directions $\pm[1\bar{7}0]_1$ were initially positioned at $x_{GB} = 0.8, 2.4, 4.0, 5.7$ and $10.3$ Å (for symmetry reasons, only positions above the symmetry plane were tested). Upon relaxation, stable crack tips could only be observed at the locations indicated in Fig. 5a). In particular, for cracks propagating in the $[1\bar{7}0]_1$ direction, a stable crack tip could only be obtained at one position ($x_{GB}=5.7$ Å) within the structural units. In this case the crack propagates through all structural units once $K_{ic} = 2.627$ MPa$\sqrt{m}$ is reached. The bond trapping range in this case is $\Delta K = 1.37$, compared to $\Delta K = 0.95$ in the opposite direction. The crack propagation under incremental loading for cracks positioned at $x_{GB} = 5.7$ Å with $\pm[1\bar{7}0]_1$ propagation directions is also shown in Video 2, see Supplemental Material at [URL will be inserted by publisher]. The fracture toughness and behavior of this GB depends sensitively on the exact position of the crack tip. As can be seen in Fig. 5b), the fracture toughness is inversely proportional to the bond length. The fracture toughness can differ up to 30% depending whether the crack tip is positioned in front of the shortest bond in the compressive region or in front of the longest bond in the tensile region. Similarly, the bond trapping range depends on the crack tip position: $\Delta K(x_{GB} = 0.8$ Å) = 0.41 compared to $\Delta K(x_{GB} = 5.7$ Å) = 0.95 for propagation in the $[\bar{1}70]_1$ direction. The influence of the initial crack tip position on the fracture behavior is demonstrated in Fig. 5c)-f). The atomic configurations at a load level just below $K_{ic}$ are shown in Figs. 5c) and d) for a crack tip at $x_{GB} = 0.8$ Å and at $x_{GB} = 4.0$ Å. An increase in load by $\Delta K_1$ leads to the breaking of the bond directly in front of the crack at $x_{GB} = 0.8$ Å, whereas the crack at $x_{GB} = 4.0$ Å breaks through the remaining period of the structural units and kinks out.
onto a low-energy \{110\} plane in the upper grain. The configurations at $K_{IC}$ of the respective crack tip positions are shown in Figs. 5e) and f). For higher loads, this kinking out is seen at all crack tip positions for the $[\bar{1}70]_1$ crack propagation direction.

Similarly to the GB cracks which were presented here in more detail, all other studied brittle cracks require higher loads than the theoretical value $K_G^{SC}$ according to Eq. 3 to start propagating (see open symbols and dashed lines in Fig. 2a). In general, brittle crack propagation is observed to take place in a zig-zag fashion (GB cracks on the (111) and (111)/(\bar{1}15) planes), by kinking out of the plane (GB cracks on the (112) and (710) planes) or by propagating within the plane (the GB crack on the (114) plane). In the SC case, in contrast, kinking out of the crack plane from the original plane onto a low-energy plane is only observed for the (710)[001] crack.

4. Discussion

The usual thermodynamic description of brittle GB fracture in a continuum mechanics framework implies that the fracture toughness of GBs is lower than the fracture toughness of a perfect single crystal in the same orientation, and that the fracture toughness does not depend on the crack tip position within the GB or on the crack propagation direction. Our simulation results show clearly, that at the atomic scale these assumptions can no longer be used.

Direction dependent fracture behavior of GBs has been already reported for experiments [69] and simulations [50] on Cu bicrystals. In these cases, the direction dependence can be explained as a direct consequence of the
Rice-Thomson model [69–71]: for GB fracture, the angles between the crack propagation direction and the slip systems in the two grains are different for a crack propagating along the +[hkl]-direction from a crack propagating in the −[hkl]-direction. I.e. in one direction emission of dislocations or twins is easier than in the other. Our simulations however show that also for purely brittle fracture $K_{fc}$ can depend on the crack propagation direction.

Comparing in Fig. 2a) the fracture toughness for SC and GB cracks shows clearly that two GBs, namely $\Sigma3$ (112) 60°/[111] and $\Sigma25$ (710) 16.3°/[001], have significantly higher fracture toughness than the SC cracks on the same crack plane (see also Video 1 and 3 in Supplemental Material at [URL will be inserted by publisher]). It is important to note that also in these cases, fracture takes place in a perfectly brittle manner, and the differences in fracture toughness are not caused by plasticity. These GBs can also be tougher than perfect single crystals oriented for fracture on the primary cleavage plane. A large number of such tough GBs could therefore favor transgranular over intergranular fracture. In this context it is important to note that the increased toughness, i.e., a significantly higher $K_{fc}$ than $K_{GB}^{G}$, is not correlated with the GB energy. E.g., the $\Sigma25$ GB has a significantly higher fracture toughness than the lower energy $\Sigma3$ and $\Sigma9$ GBs.

The deviation of the fracture toughness from the thermodynamic prediction $K_{G}$ has to be rooted in the nature of the atomic bonds at these GBs. The increased fracture toughness is correlated with an increased bond trapping range compared to the lattice trapping range in the SC. Several factors can contribute to the increased toughness, e.g., shorter bond lengths in the GB (which are correlated with local compressive regions), increased number
of neighbors in the GB (i.e. more bonds need to be broken) or different load sharing of the atoms at the crack tip in the GB compared to the SC crack. Although the used potential might not exactly model the energies and forces of atoms in tungsten GBs, the observed behavior should be generally valid: the bonding situation in GBs can vary largely from the bonding in SCs, including the possibility of local GB bonds which are stronger than regular bonds in the SC. The observations that for brittle fracture on the same plane GBs can be tougher than SCs and that the GB fracture toughness depends on the crack tip position and crack front direction should therefore be independent of the details of the atomic interaction model. This has been verified by additional simulations of cracks in molybdenum bicrystals which show similarly increased fracture toughness of GB cracks compared to SC cracks on the same cleavage plane [72]. The deviations from the thermodynamic description of GB fracture in a continuum framework are caused by the atomic nature of GBs, and should therefore be generalizable and relevant for GB fracture in brittle and semi-brittle materials. In this context it is also interesting to note that atomistic simulations of graphene showed an increased yield strength of sheets containing GBs compared to defect free graphene [73].

All these atomistic aspects observed in the simulations can be expressed as effects due to bond trapping in GBs. They are summarized and compared to lattice trapping in SCs in the classical schematic representation of surface energy vs. crack length, see Fig. 6. Contrary to lattice trapping, bond trapping in GBs depends on the position within the GB as the atomic bonding varies with the local environment. For CSL-GBs, the fracture toughness has
to be furthermore a periodic function of the position with at least the same periodicity as the GB. For these GBs, the structural units are also usually not mirror symmetric with respect to the plane normal to the crack propagation direction. A backward-forward direction dependence of the fracture toughness as shown in Fig. 2 can therefore be expected even for completely brittle fracture.

The thermodynamic relation between critical energy release rate and the energy of the surfaces and GBs, see Eqs. (2-3), of course still holds, however only when averaged over a certain number of broken bonds. I.e., the average slope of the surface energy vs. crack length graph for the GB, Fig. 6, has to correspond to Eq. (3), and consequently has to be lower than for the SC. Locally, the required energy release rate for crack advance can however be larger in the GB than in the SC case.

Although GBs show regions with low fracture toughness, it is the region with the highest $K_{ic}$ which determines ultimately the crack initiation toughness of a GB. This is clearly shown in Fig. 5c-f): under quasi-static loading, the crack tip located initially at the weakest spot of the GB just propagates by breaking one bond and is arrested at the next, stronger unit. Yet, if the crack tip is positioned at the strongest bond, the crack propagates through all GB units. This situation might be different for dynamically propagating cracks. The determination of the crack arrest toughness is, however, beyond the scope of this study.

Similar to studies on lattice trapping [16, 55], the present study of the effect of bond trapping on grain boundary cracks is limited to static calculations in a quasi two dimensional set-up. Temperature effects and the presence
of kinks on the crack front are neglected. However, the 2D quasi-static simulations on lattice trapping were able to explain macroscopically observed fracture behavior, e.g., the occurrence of primary \(\{100\}\) cleavage planes in tungsten [15], or the anisotropy with respect to the propagation direction along different crystallographic directions within the same fracture plane in silicon [16]. Similarly, bond trapping of GB cracks could have macroscopic implications e.g. on the selection of the transgranular mode of fracture over intergranular fracture as speculated in [12, 19].

In general, controlled experiments on GB cracks are very difficult to perform [41]. The presence of GB defects like steps or absorbed dislocations, segregated atoms, and the often non-planar nature of GBs and curved crack fronts, as well as the presence of dislocations in the grains, make a direct comparison of our simulation results with experiments nearly impossible. Recent developments in nanomechanical testing however now allow the determination of the fracture toughness of interfaces from in-situ bending tests of notched cantilever beams [74]. Such tests could be performed with well-characterized GBs in polycrystalline materials, avoiding the difficulties in preparing bicrystal specimens. In our simulations, the difference of the GB fracture toughness for different crack propagation directions is rather small (see Fig. 2) and will therefore most probably not be detectable in experiments. However, according to our simulations, the determined fracture toughness can deviate from the thermodynamic prediction according to Eq. (3) by up to 90%, see Fig. 2 and Tab. 3. Comparing the experimentally determined GB fracture toughness in an inherently brittle material with the corresponding theoretical prediction or with a numerical calculation using a
cohesive zone model (CZM) [20, 75, 76] could thus allow to reveal the influence of bond trapping on GB fracture toughness. In fact, bond trapping might be one of the underlying reasons for the reported extraordinary high tensile strengths of some GBs [38, 41, 42, 44, 61], in particular when they are not directly correlated with the GB energy [42, 43] or otherwise not directly predictable [41].

Currently, GB fracture is typically modeled on the meso- and continuum scale using a cohesive zone approach [20–32]. Commonly used CZMs [20, 75, 76] require as parameters the ultimate/maximum tensile strength of the GB and the work of fracture needed to separate the cohesive zone. This information can be determined from atomistic [25, 26, 30, 32] or ab-initio simulations [77]. However, the crack is often not directly modeled in these approaches, and instead these values are derived from tensile straining of GBs [25, 77]. Such simulations are averaging over the atomic structure of GBs, and continuum simulations with CZM parameters derived that way failed to reproduce the atomistic simulation results [29]. By their very nature, simple CZMs are furthermore not able to properly describe the direction dependence of the fracture toughness of GBs. Here, theories like quantized fracture mechanics [78], which take into account lattice trapping, could be extended to include bond trapping of GB cracks. Ultimately, however, parameterized GB CZMs would need to be validated using fracture experiments on defined GBs. To our knowledge, such direct comparisons are currently still lacking.

A deeper understanding of GB fracture on the atomic level and improved mesoscale models would be particularly useful for the study of microstructurally short cracks or fracture of nanosized structures, where the influence
of individual GBs on the fracture behavior is accentuated. Taking bond trapping effects into account could also open up new possibilities for grain boundary engineering of fracture resistant materials.

5. Summary

The present study highlights the role of bond trapping effects on the fracture toughness of GBs. The fracture toughness and failure mode of six tilt grain boundaries in tungsten was determined and compared to the fracture in single crystals of the same orientation. Even in the case where no crack tip plasticity is involved, the fracture toughness of GBs was shown to depend on the crack propagation direction and the exact crack tip position within the GB. Furthermore, the local fracture toughness of GB cracks can surpass the fracture toughness of single crystals oriented for cleavage on the same crystallographic plane and direction, and the maximum GB fracture toughness is not necessarily correlated with the GB energy. These observations can not be explained by the classical thermodynamic description of fracture in terms of continuum properties, but are direct atomistic effects of the locally varying bonding situation in the GB and can be summarized in a bond trapping framework.

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Table 1: Summary of the properties of the Finnis-Sinclair potential [62, 63] relevant to the simulation of fracture in tungsten in comparison to experimental and DFT data. The elastic constants are denoted by $C_{ij}$, and $\gamma_{\text{surf}}(hkl)$ are the surface energies of the corresponding (hkl) planes.

| Property     | Experimental data | DFT data | F-S Potential |
|--------------|-------------------|----------|---------------|
| $C_{11}$ (GPa) | 522.4\textsuperscript{a} | 552\textsuperscript{c} | 522.44        |
| $C_{12}$ (GPa) | 204.4\textsuperscript{a} | 204\textsuperscript{c} | 204.43        |
| $C_{44}$ (GPa) | 160.6\textsuperscript{a} | 149\textsuperscript{c} | 160.62        |
| $\gamma_{\text{surf}}$(100) (mJ/m$^2$) | 2800\textsuperscript{b} | 4635\textsuperscript{d} | 2922.6        |
| $\gamma_{\text{surf}}$(110) (mJ/m$^2$) | — | 4005\textsuperscript{d} | 2575.4        |
| $\gamma_{\text{surf}}$(111) (mJ/m$^2$) | — | 4452\textsuperscript{d} | 3301.2        |
| $\gamma_{\text{surf}}$(112) (mJ/m$^2$) | — | 4177\textsuperscript{d} | 3045.8        |
| $\gamma_{\text{surf}}$(114) (mJ/m$^2$) | — | — | 3159.3        |
| $\gamma_{\text{surf}}$(115) (mJ/m$^2$) | — | — | 3139.8        |
| $\gamma_{\text{surf}}$(710) (mJ/m$^2$) | — | — | 3001.7        |
| $r_{\text{cut}}$ (Å) | — | — | 3.25          |

\textsuperscript{a} Elastic constants at 300 K according to Bujard [79]

\textsuperscript{b} Surface energies for average orientation taken from Miedema [80]

\textsuperscript{c} Elastic constants calculated by Einarsdotter 	extit{et al.} [81] (using DFT with the local density approximation, a plane-wave basis set, and norm-conserving pseudopotentials)

\textsuperscript{d} Surface energies calculated by Vitos 	extit{et al.} [82] (using DFT with the generalized gradient approximation, full charge density linear muffin-tin orbitals method)
Table 2: List of studied grain boundaries and their grain boundary energy $\gamma_{GB}$. The grain boundaries are characterized by their grain boundary plane and the axis and angle of rotation as well as their CSL value. In addition, the surface energy $\gamma_{surf}$ of a free surface corresponding to the crystallographic orientation of the grain boundary plane is provided.

| Grain boundary | $\gamma_{GB}$ (mJ/m$^2$) | $\gamma_{surf}$ (mJ/m$^2$) | $G_{GB}^{c}$ (mJ/m$^2$) |
|----------------|--------------------------|--------------------------|----------------------|
| $\Sigma 3 (111) 70.5^\circ / [\bar{1}10]$ | 2353.6 | 3301.2 | 4248.8 |
| $\Sigma 3 (111) 180^\circ / [11\bar{2}]$ | 2353.6 | 3301.2 | 4248.8 |
| $\Sigma 3 (112) 60^\circ / [11\bar{1}]$ | 390.5 | 3045.8 | 5701.1 |
| $\Sigma 9 (114) 38.9^\circ / [110]$ | 956.0 | 3159.3 | 5362.6 |
| $\Sigma 25 (710) 16.3^\circ / [001]$ | 1680.9 | 3001.7 | 4322.5 |
| $\Sigma 3 (111)_{1} (\bar{1}15)_{2} 70.5^\circ / [1\bar{1}0]$ | 2010.5 | 3301.2/3139.8$_{2}$ | 4430.5 |
Table 3: Summary of theoretical and determined critical stress intensity factors $K_G$ and $K_{lc}$ in single crystals (SC) and corresponding tilt grain boundaries (GB). $K_{lc}$ is the stress intensity when the crack tip either propagates by cleavage (brittle) or deforms plastically (ductile). The ductile deformation mode is mechanical twinning except for the (111)[112] crack system.

| Crack system (plane)[front] | $K_{SC}^G$ in MPa$\sqrt{m}$ | $K_{SC}^{lc}$ in MPa$\sqrt{m}$ (behavior) | $K_{GB}^G$ in MPa$\sqrt{m}$ | $K_{GB}^{lc}$ in MPa$\sqrt{m}$ (behavior) |
|-----------------------------|----------------------------|--------------------------------|--------------------------|--------------------------------|
| (001)[110]                  | 1.612                      | 1.711 (brittle)                |                          |                                |
| (110)[110]                  | 1.514                      | 1.547 (brittle)                |                          |                                |
| (111)[110]                  | 1.713                      | 1.697 (ductile)                | 1.375                    | 1.583 (ductile) 1.470 (brittle) |
| (111)[112]                  | 1.713                      | 1.768 (ductile)                | 1.375                    | 1.519 (brittle) 1.519 (brittle) |
| (111)[111]                  | 1.646                      | 1.860 (brittle)                | 1.592                    | 1.896 (brittle) 1.896 (brittle) |
| (114)[110]                  | 1.676                      | 1.569 (ductile)                | 1.383                    | 1.583 (ductile) 1.633 (brittle) |
| (710)[001]                  | 1.633                      | 2.080 (brittle)                | 1.385                    | 2.627 (brittle) 2.329 (brittle) |
| (111)[110]                  | 1.713                      | 1.697 (ductile)                |                          | 1.670 1.754 (ductile) 1.725 (brittle) |
| (115)[110]                  | 1.670                      | 1.583 (ductile)                |                          |                                |

- **a** Emission of a perfect $a_0/2[111]$ (110) edge dislocation.
- **b** This value is given at the same position in the GB as for the opposite direction since $K_{GB}^{lc}$ varies strongly within the GB (between 1.867 and 2.435 MPa$\sqrt{m}$ for this direction.)
- **c** The crack deviates from its initial (710) crack plane onto low-energy planes.
Table 4: Summary of bond trapping ranges $\Delta K = K^+ / K^- - 1$ of selected single crystals and grain boundaries.

| Crack system | Propagation direction | $K_G$ in MPa $\sqrt{m}$ | $K^-$ in MPa $\sqrt{m}$ | $K^+$ in MPa $\sqrt{m}$ | $\Delta K$ |
|--------------|-----------------------|-------------------------|-------------------------|-------------------------|----------|
| (001)[110]   | [110]                 | 1.611                   | 1.462                   | 1.711                   | 0.17     |
| (112)[111]   | [110]                 | 1.646                   | 1.498                   | 1.860                   | 0.24     |
| $\Sigma 3$ (112) | [110] | 1.592                   | 1.448                   | 1.896                   | 0.30     |
| (710)[001]   | [110]                 | 1.697                   | 1.434                   | 2.080                   | 0.45     |
| $\Sigma 25$ (710) | [101] | 1.385                   | 1.320                   | 1.867                   | 0.41     |
| $\Sigma 25$ (710) | [101] | 1.385                   | 1.107                   | 2.627                   | 1.37     |
Figure 1: Schematic illustration of the set-up for simulations of mode I grain boundary cracks. Atoms are displaced according to the linear-elastic displacement field around a crack tip in a semi-infinite anisotropic body [8, 83]. The outer region of minimum thickness $2r_{\text{cut}}$ is fixed during the molecular statics simulation while atoms in the inner region are free to move. Periodic boundary conditions (PBC) are applied along the tilt axis ($z$).
Figure 2: Overview of critical stress intensity factors $K_{IC}$ in dependence on (a) the crack system and (b) the crack front direction along the $\Sigma 3 (111)/[\bar{1}10]$ GB; $\diamond$, single crystals; $\triangleright/<$, tilt GBs with crack propagation direction parallel/antiparallel to the cross product between crack plane normal and crack front direction; open symbols indicate brittle crack propagation; solid symbols indicate plastic crack tip deformation; the error, i.e. the stepwidth of load increase $\delta K_I$, is smaller than 1/8 of the symbol size.
Figure 3: Illustration of the crack propagation in the (112) [110] single crystal (a) and the symmetrical Σ3 (112) 60°/ [111] tilt grain boundary; the sequences show the initial crack tip positions followed by configurations after quasi-static incremental loading; the fracture surfaces are indicated at 1.952 MPa√m for the SC and at 2.080 MPa√m for the GB; the atoms are colored according to their potential energy; the atomic radii represent their distance to the plane of projection (perpendicular to the crack front direction).
Figure 4: Crack tip configuration in the single crystal (a) and the Σ3 (112) 60°/[111] GB (b) and bond trapping (c) for fracture on the (112) plane with [111] crack front direction. The critical crack tip bonds are indicated by an arrow. The color in (a,b) corresponds to the number of neighboring atoms within the cut-off radius of the potential, $r_{\text{cut}} = 3.25 \, \text{Å}$ (grey: 8, pink: 9, green: 10, red: 11, yellow: 12, blue 13, white: 14). (c) shows the length of the critical bond (—) as function of the applied stress intensity factor for loading (→) and unloading (←); dashed lines (—) represent the distance of the first created bonds due to crack closure upon unloading, which are represented by the dashed lines in (a) and (b).
Figure 5: Position-dependence of fracture toughness in the $\Sigma 25 (710) 16.3^\circ / [001]$ GB: (a) GB structure and distribution of hydrostatic pressure $p$ ($p < 0$: tension). The structural units of the GB are indicated by grey lines. Different crack tip positions are indicated by triangles ($\triangleright/\triangleleft$) positioned at $x_{\text{GB}} = 0 \ldots 1/2 \lambda_{170}$, where $\lambda_{170}$ is the length of the structural unit in $[\bar{1}70]$ direction. The triangles point in the crack propagation direction, only positions which resulted in a stable crack tip upon relaxation are shown. (b) Corresponding values of the fracture toughness $K_{\text{leGB}}^c$ (black triangles) and equilibrium distance of crack tip bonds normalized by the nearest neighbor distance (nnd) (filled blue triangles). For the crack tip positions indicated by yellow and pink filled triangles in subfigures (a) and (b), the corresponding crack paths are compared in a sequence of loaded crack tip configurations showing the breaking of the crack tip bond for $x_{\text{GB}} = 0.8 \, \AA$ (c,e) and the simultaneous breaking of structural units and kinking out onto a low-energy $\{110\}$ plane for $x_{\text{GB}} = 4.0 \, \AA$ (d,f).
Figure 6: Schematic comparison of the energy of the surface created by the advance of a crack with respect to the energy of a perfect crystal, showing the trapping behavior in crystal lattices (red, according to [7]), GBs (blue) and the corresponding linear continuum limits. The periodicity of bond trapping corresponds to the repeat distance of the structural units, and the magnitude of the bond trapping can be significantly larger than the lattice trapping. The toughness of a GB can therefore locally surpass that of a crystal fracturing along the same plane. The magnitude of the bond trapping effect can furthermore show a backward-forward or direction dependence since the GB structure is generally asymmetric.