Chapter 3
Incipient plasticity at grain boundaries in bcc metals

3.1 Introduction
Subgranular microhardness testing has been used for a long time to probe grain boundary hardening effects due to solute segregation in polycrystalline materials [1,2]. Hardening in these experiments is typically found up to tens of micrometers from the grain boundary and can be explained by the varying concentrations of solute atoms close to the grain boundary, which may affect the mobility of dislocations. In the absence of solute gradients near the boundary, no hardening is observed at this scale [3]. The possibility to measure an intrinsic hardening contribution of the grain boundary, as a result of the difficulty in slip transfer across the boundary, has recently come under investigation with the widespread availability of the nanoindentation technique. Low-load indentation experiments [4,5] have shown significant hardening effects within a distance of the order of 1 µm from the boundary. Such experiments could potentially offer detailed information about the intrinsic mechanical properties of individual grain boundaries. So far however, a thorough understanding of the mechanical response is lacking.

The results presented in this chapter [5,6] show that nanoindentation in close proximity of a grain boundary may lead to detectable slip transfer across the boundary. This behavior can be evaluated quantitatively by recourse to a Hall-Petch type analysis. While the Hall-Petch relation is traditionally described in terms of dislocation pile-ups at grain boundaries, other obstacles may also bound dislocation activity and thus control the pile-up distance. The yield stress of these systems has been observed to obey a similar $d^{-1/2}$ dependence, where $d$ is the characteristic distance between the obstacles. For example, it has been found that both cementite particles and (sub)grain boundaries affect the strengthening of spheroidized steel in a Hall-Petch type manner [7]. In the present experiments, the volume between the indenter and the boundary confines the dislocation pile-up. This leads to the unique ability of locally probing the slip transmission characteristics of an individual grain boundary, as a measure of which a value for
the Hall-Petch slope \( k_y \) as given by Eq. (2.10) can be calculated. Alternatively, since the strain gradients in the indentations at hand are appreciable, the results may be analyzed in the framework of a strain gradient plasticity theory in which the boundary is accounted for by an interfacial energy-like term [8]. A physical interpretation of this theory and a comparison with the Hall-Petch approach are presented in Section 3.7.

Body-centered cubic metals generally show a higher resistance to slip transfer than face-centered cubic metals as shown by typical values of the Hall-Petch slope \( k_y \), which are of the order of 0.3-1.8 MNm\(^{-3/2}\) for bcc metals and 0.05-0.1 MNm\(^{-3/2}\) for fcc metals at room temperature. Consequently, to facilitate the detection of dislocation pile-up and transmission, bcc metals have been selected for this study. However, also in the absence of slip transmission, the indentation experiments provide valuable information on the incipient plastic behavior of the boundary and on the nature of the interaction between the boundary and the indentation-induced dislocations.

### 3.2 Experimental procedure

The measured indentation response near a grain boundary in general may be affected by many microstructural and geometrical parameters such as the presence of second phases, gradients in solute or defect concentrations, the inclination of the boundary plane, the curvature of the boundary, the presence of triple junctions and the surface topology at the boundary. Therefore, in order to isolate the intrinsic indentation response of an individual grain boundary, bicrystalline or at least coarse-grained single-phase specimens are required. In this study, one Fe-14%Si alloy bicrystal with a general grain boundary and two pure Mo bicrystals with symmetric coincident site lattice (CSL) <110> tilt boundaries were used. All three specimens were prepared by floating-zone melting from a bicrystal seed consisting of two semicylindrical single-crystalline pieces joined together [9]. The geometrical parameters are summarized in Table 3.1. The Fe-Si specimen (having all Si in solid solution) contained traces of phosphorus and carbon [9]. Auger spectroscopy showed no detectable impurities on the grain boundaries in the Mo bicrystals [10,11].

The specimen surfaces were polished using a final polishing colloidal silica suspension. For the Mo bicrystals, 96 ml of the suspension was mixed with 2 ml ammonia solution (25%) and 2 ml hydrogen peroxide solution (30%). By atomic force microscopy it was confirmed that no severe preferential grain
boundary attack resulted from these additives. Over a lateral distance of 30 µm across the boundary, a smooth height profile was found as shown in Figure 3.1. With a maximum slope of less than 0.2°, this topology is not expected to influence the local indentation response. Electron backscatter diffraction (EBSD) was employed to locate the grain boundaries with respect to a grid of marker indents.

Nanoindentation measurements were carried out employing an MTS Nano Indenter XP (MTS Nano Instruments, Oak Ridge, TN) with a pyramidal Berkovich tip using the continuous stiffness measurement (CSM) technique. Load-controlled indentations were made to a maximum depth of 200 nm with a targeted strain rate of 0.05 s$^{-1}$, which corresponds to a maximum loading rate of the order of 0.1 mN/s. The azimuthal orientation of the indenter was chosen to

Table 3.1
Grain boundary parameters and indentation direction in crystal coordinates. The Rodrigues notation used for the Fe-Si specimen defines the misorientation by a vector that is parallel to the rotation axis and has a magnitude of $\tan \omega / 2$, where $\omega$ is the rotation angle.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Material</th>
<th>Misorientation</th>
<th>Boundary plane</th>
<th>Indentation direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mo</td>
<td>$\Sigma 3$</td>
<td>(121)$_g$ // (121)$_a$</td>
<td>[101]$_a$ // [101]$_a$</td>
</tr>
<tr>
<td>2</td>
<td>Mo</td>
<td>$\Sigma 11$</td>
<td>(323)$_g$ // (323)$_a$</td>
<td>[101]$_a$ // [101]$_a$</td>
</tr>
<tr>
<td>3</td>
<td>Fe-14%Si</td>
<td>[-0.29 0.12 0.03] Rodrigues vector</td>
<td>(-0.75 0.56 0.35)$_g$ // [0.34 -0.13 0.93]$_a$ // [0.05 0.40 0.91]$_a$</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3.1: Height profile across $\Sigma 11$ grain boundary in polished Mo bicrystal as measured by atomic force microscopy. The maximum slope with respect to the surface is less than 0.2° and hence no effect on the indentation response is expected.
have one side of the triangular impression parallel to the grain boundary under investigation. In order to vary the distance to the boundary with the smallest possible increments, lines of indentations were drawn across the grain boundary at angles smaller than 3° with a spacing of 3 µm between the indents. An example of a line of indents crossing the boundary in the Fe-Si bicrystal is shown in Figure 3.2. Although the plastically deformed zones of consecutive indents are likely to overlap at such a close spacing, no significant effect of any cross-talk interaction on the measured response was found in a test comparing lines of indents of 200 nm depth with spacings ranging from 3 to 10 µm in the Fe-Si matrix. This is likely due to a slight work hardening introduced by mechanical polishing of the surfaces, compared to which the additional hardening effect from adjacent indentations is very small.

3.3 Dislocation nucleation at grain boundaries

3.3.1 Detection of preferential nucleation

On both Mo bicrystals, results were obtained from three lines of 60 indents across the boundary. The initial yield behavior of the Mo grain interior showed multiple yield excursions up to a load of around 1.5 mN, in which the indentation depth suddenly increased by typically tens of nanometers at constant load. The loads at which these excursions occurred varied considerably throughout the grain interior. This is thought to be mainly due to variations in dislocation density and surface stresses introduced by mechanical polishing of the surface. Oxide films are not expected to play a significant role as the oxidation rate of molybdenum at room temperature is relatively low.

A significant effect of the boundaries on this staircase yielding was found, as shown in Figure 3.3. Indentations made within 0.2 µm of the Σ3 boundary showed only very small excursions of less than 10 nm, and in some cases, the deformation appeared to be plastic at the onset of contact and no excursions were found altogether. For indentations further from the boundary, the
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Figure 3.3: Load vs. displacement curves recorded in the Mo grain interior and close to the coherent $\Sigma 3$ boundary. The initial yield excursions ("staircase yielding") in the grain interior are marked with arrows. In the indentation near the boundary, the yield excursions are attenuated.

Figure 3.4: Initial loading response of four consecutive indentations close to the Mo $\Sigma 3$ boundary. At 0.03 $\mu$m from the boundary, loading appears to be plastic from the onset of contact and no yield excursions are found. With increasing distance, the initial loading approaches elastic behavior and the subsequent yield excursions rapidly become more pronounced.
excursions rapidly become more pronounced, as illustrated by the initial loading response of four subsequent indentations plotted in Figure 3.4. Beyond 0.3 µm from the boundary, the load at which the excursions occur seems to be arbitrary and shows no correlation with the distance to the boundary. A similar but less pronounced effect was observed at the Σ11 boundary. In this case, excursions were present in all indentations at the interface, including the ones that showed immediate plastic contact.

The loading response prior to the initial yield point is well described by purely elastic loading [12]. The maximum elastic shear stress $\tau_{\text{max}}$ under a rounded Berkovich indenter can be approximated by the relation for a spherical indenter with the same tip radius $R$ following Eq. (2.35):

$$
\tau_{\text{max}} = 0.31 \left( \frac{6P E_r}{\pi R^2} \right)^{1/3}
$$

where $P$ is the indentation load and $E_r$ is the reduced modulus of the indenter and the specimen. In the indentations in the Mo grain interior, the first yield point occurred at loads ranging from 0.1 up to 0.6 mN. With a tip radius of 200 nm, as estimated from the calibration of the tip area function, the maximum shear stress under the indenter at a load of 0.6 mN is found to be of the same order as the theoretical shear strength of molybdenum $\tau_{\text{th}} \approx \mu / 2\pi = 20$ GPa. Evidently, the absence of an existing dislocation field is not a prerequisite to attain values close to this shear stress, as was observed earlier for indentation of tungsten single crystals [13]; the investigated surfaces were mechanically polished and hence contained many dislocations. The perception that dislocations may exist or be nucleated prior to the first yield excursion is supported by atomistic simulations of indentation of Mo (100) and (111) surfaces [14].

The observed attenuation of grain interior yield excursions for indentations near the grain boundaries is presumably caused by preferential nucleation of dislocations at the boundary. This phenomenon has been considered by Lilleodden et al. [15], who performed atomistic simulations of grain boundary proximity effects on the indentation behavior of gold thin films. It was found that indentation by a 40 Å radius indenter within 25 Å of a Σ79 tilt boundary leads to a significant reduction of the critical load for initial yielding. In the present experiments, the indenter radius is two orders of magnitude larger, and a boundary proximity effect is therefore measured at accordingly larger distances. Up to 0.3 µm from the Mo Σ3 boundary, initial yielding occurs at significantly
lower loads than away from the boundary as shown in Figure 3.5. Beyond this distance, dislocations nucleate in the grain interior at varying loads depending on the local density of statistically stored dislocations.

Dislocation nucleation from grain boundaries was also believed to be predominant in indentation experiments of nanocrystalline Cu as reported by Chen et al. [16]. Although other deformation mechanisms govern plasticity at these grain sizes, the initial yield point during indentation was observed at the same load as in coarse-grained copper. This was interpreted to be indicating that initial plasticity is still controlled by dislocation-based mechanisms. The fact that the easy nucleation from the grain boundary was not observed to decrease the load for the initial yield point, as in the present case, may be explained by the fact that the newly nucleated dislocations were confined to the nanosized grains. In our experiments, the nucleated dislocations could freely propagate into the crystal and thus significantly contribute to plasticity.

3.3.2 Determination of the nucleation shear stress

From the interaction range of 0.3 µm, an estimate for the nucleation shear stress of dislocations at the boundary can be obtained. In order for dislocations to nucleate from the boundary, the nucleation shear stress must be attained at the

![Figure 3.5: Correlation between initial yielding and distance to the boundary in the Mo $\Sigma 3$ bicrystal. The indentations represented by data points on the horizontal axis showed plastic loading from the onset of contact. For the other data points, the initial yield point is defined as the first excursion from elastic loading of at least 5 nm indentation depth. Close to the boundary, the yield load is reduced due to preferential nucleation at the grain boundary.](image-url)
boundary before grain interior yielding occurs, as shown in Figure 3.6. We can approximate the elastic stress fields at the boundary by using the two-dimensional analytical solution for cylindrical contact as outlined in Section 2.3.4. The principal shear stress at any point \((x,z)\) may then be calculated as

$$\tau = -\frac{\sigma_x}{2\pi} x \tau + \tau_{xz} \frac{z}{2},$$

(3.2)

with \(\sigma_x\), \(\sigma_z\) and \(\tau_{xz}\) as defined by Eqs. (2.36)-(2.38). Figure 3.7 shows a plot of the principal shear stress as a function of depth at a distance \(x = 300\) nm from the center of symmetry. The values of the maximum indentation pressure \(p_0 = \tau_{th}/0.31\) and contact half-width \(a = \pi p_0 R/2E_r\) have been chosen so as to

![Figure 3.6: Two-dimensional representation of homogeneous nucleation vs. preferential nucleation at the grain boundary under cylindrical elastic contact.](image)

![Figure 3.7: Absolute value of the principal elastic shear stress as a function of depth, evaluated at a distance \(x = 300\) nm from a cylindrical contact with contact half-width \(a = 65\) nm and maximum pressure \(p_0 = 64.5\) GPa. Local maxima of the shear stress are attained at 120 and 720 nm depth.](image)
represent indentation up to the first homogeneous nucleation of dislocations in the grain interior according to Eq. (3.1). Under these conditions, local maxima of the shear stress at the boundary are obtained at 120 and 720 nm below the surface with a shear stress value of approximately 1.8 GPa. This value is therefore an estimate for the nucleation shear stress for dislocations at the boundary; as expected, it is considerably lower than the theoretical shear stress of 20 GPa. The transition from nucleation at the boundary to nucleation in the grain interior was less clear for the $\Sigma 11$ boundary; therefore, the nucleation stress has not been calculated for this case. It should be noted that the ease of dislocation nucleation can be greatly affected by the presence of grain boundary steps. The present results can thus only provide a rough estimate of the extent of dislocation nucleation at grain boundaries.

A physical explanation of preferential nucleation at the boundary may be given by the grain boundary dislocation having a shear stress component on the slip plane, which assists the applied shear stress in generating a lattice dislocation loop. The maximum shear stress is attained at a distance of the width of the grain boundary dislocation, $\xi$. Assuming that nucleation of a dislocation loop occurs in the vicinity of the grain boundary when the total shear stress reaches a value of $\mu / 2\pi$ as suggested by the experiments far away from the boundary, the applied shear stress necessary for nucleation becomes

$$\tau_n = \frac{\mu}{2\pi} - \frac{\mu b}{\pi(1-\nu)\xi}$$

For the experimental value of $\tau_n = 1.8$ GPa, the width of the grain boundary dislocation is found to be $\xi = 0.9$ nm, which compares well to other estimates [17,18]. From Eq. (3.3) it follows that when the grain boundary dislocation core becomes more delocalized, the necessary nucleation shear stress at the grain boundary increases. As a consequence, localized cores at lower temperatures will act as concentrators, while at higher temperatures, the grain boundary dislocation cores spread out and homogeneous nucleation near grain boundaries becomes less likely [18,19].

### 3.4 Dislocation pile-up and transmission across grain boundaries

#### 3.4.1 Detection of slip transmission

Results for the Fe-Si bicrystal were obtained from four lines of 60 indentations crossing the grain boundary. The initial yield point was evidenced in all
indentations by a single displacement excursion at a constant load of around 50 µN, rather than by the staircase yielding observed in Mo. In each of the lines however, a few consecutive indentations that crossed the boundary, exhibited one or two additional characteristic yield excursions well beyond the initial yield plateau. Figure 3.8 shows EBSD scans of the boundary crossings in which these indents are circled. The excursions were observed for a total of nine measurements located within 0.74 µm of the boundary, and only when one side of the indenter was facing the boundary. Although most of these indents crossed over the boundary at maximum indentation depth, it is readily concluded from the load-displacement data that the indenter was still well away from the boundary at the instant of the excursion, at distances ranging from 0.11 to 0.34 µm. In six of the nine indentations, the material yielded in one displacement burst at constant load, as shown in Figure 3.9a; the other three curves show two bursts, which are separated by a loading portion, as in Figure 3.9b. A summary of the indentation parameters at the yield excursions is given in Table 3.2.

As discussed in Section 2.3.5, initial yield phenomena have been attributed to the nucleation or multiplication of dislocations, and alternatively to the escape of piled-up dislocations to the free surface upon the fracture of the native oxide. While the present results cannot rule out any particular mechanism,
it is clear that the observed yielding at higher loads is strongly related to the presence of the grain boundary and can therefore not be explained by these concepts. It is proposed that these yield excursions are due to transmission of piled-up dislocations across the boundary, as schematically shown in Figure 3.10. The purpose of the following section is to justify this assumption from energy considerations.

Figure 3.9: Indentation response near the Fe-Si grain boundary showing (a) one yield excursion, and (b) two yield excursions (marked with arrows). The dashed line represents the bulk response, which was calculated by averaging six load-displacement curves of indentations in the grain interior.
### Table 3.2
Indentation data for observed yield excursions (bursts) at the boundary in the Fe-Si bicrystal; “1st” and “2nd” entries denote indentations that showed two separate bursts. The numbering of the lines corresponds to their order in Figure 3.8.

<table>
<thead>
<tr>
<th>Line</th>
<th>Indent to boundary</th>
<th>Initial distance to boundary</th>
<th>Distance to boundary at onset of burst</th>
<th>Load at onset of burst</th>
<th>Depth at onset of burst</th>
<th>Length of burst</th>
<th>CSM hardness before burst</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$d_{center}$ (nm)</td>
<td>$d_{burst}$ (nm)</td>
<td>$P$ (mN)</td>
<td>$h$ (nm)</td>
<td>$\Delta h$ (nm)</td>
<td>$H$ (GPa)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>493</td>
<td>210</td>
<td>1.24</td>
<td>130</td>
<td>11</td>
<td>3.20</td>
</tr>
<tr>
<td>2</td>
<td>370</td>
<td></td>
<td>131</td>
<td>1.02</td>
<td>110</td>
<td>16</td>
<td>3.70</td>
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<tr>
<td>2</td>
<td>1</td>
<td>665</td>
<td>335</td>
<td>1.67</td>
<td>152</td>
<td>10</td>
<td>3.17</td>
</tr>
<tr>
<td>2</td>
<td>1st 517</td>
<td>223</td>
<td>1.39</td>
<td>135</td>
<td>4</td>
<td>3.33</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2nd 189</td>
<td></td>
<td>1.79</td>
<td>151</td>
<td>20</td>
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<tr>
<td>3</td>
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<td>2.83</td>
<td>197</td>
<td>19</td>
<td>3.20</td>
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<tr>
<td>2</td>
<td>463</td>
<td>1st 146</td>
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<td>146</td>
<td>4</td>
<td>3.17</td>
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<tr>
<td></td>
<td>2nd 109</td>
<td></td>
<td>1.88</td>
<td>163</td>
<td>13</td>
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<tr>
<td>3</td>
<td>330</td>
<td>1st 106</td>
<td>1.01</td>
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<td>4.25</td>
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<tr>
<td></td>
<td>2nd 78</td>
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<td>116</td>
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<td>196</td>
<td>1.91</td>
<td>165</td>
<td>12</td>
<td>2.88</td>
<td></td>
</tr>
</tbody>
</table>

![Figure 3.10](image-url)

Figure 3.10: Illustration of the proposed mechanism accounting for the observed yield excursions during indentation near a grain boundary: (a) dislocation pile-up and (b) dislocation transmission.
3.4.2 Analysis of the stored elastic energy

Comparing the curve showing a yield excursion to the bulk response in Figure 3.9a, it is readily found that there is quite an amount of extra elastic energy stored near the boundary prior to the excursion. The excess of stored energy $W_{GB}$ is given by the area between both curves up to the onset of the excursion (cf. Eq. (2.24)) as illustrated in Figure 3.11. For the particular indentation shown here, this energy is computed to be $9 \cdot 10^{-12}$ J.

Let us assume that a single dislocation pile-up experiences an applied shear stress due to the indenter as given by the experiments. Assuming Schmid behavior and taking into account the geometry of the experiment, which is addressed in Section 3.6.1, it is readily found that the applied shear stress at the excursion resolved on the pile-up slip plane is approximately half of the applied stress, which is by definition equal to the recorded hardness of approximately 3 GPa. This leads to an applied shear stress value of $\tau_a = 1.5$ GPa. From Table 3.2, the distance from the indenter to the grain boundary at the onset of the burst is estimated to be of the order of 200 nm. Eq. (2.5) subsequently gives the number of dislocations in the pile-up to be approximately 40. The stress fields of a stressed pile-up of 40 dislocations can be calculated from linear elasticity. Under an applied shear stress of $\tau_a$, the positions of the edge dislocations in the pile-up with the first dislocation locked at $x = 0$ are given by [20,21]:

![Figure 3.11: Graphic representation of the additional elastic energy stored prior to a yield excursion.](image)
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\[
\sum_{i=1}^{N-1} \frac{\mu b}{2\pi(1-\nu)} \frac{1}{x_j - x_i} + \tau_n = 0 \quad (3.4)
\]

It can be shown that the positions \(x_i\) of the dislocations are given by the zeros of the polynomial

\[
g(x) = \prod_{i=1}^{N-1} (x - x_i) \quad (3.5)
\]

where \(g(x)\) is the first derivative of the \(N\)-th Laguerre polynomial

\[
g(x) = L'_N \left( \frac{4\pi(1-\nu)\tau x}{\mu b} \right) \quad (3.6)
\]

The calculations provide the position of each of the 40 dislocations with respect to each other, which can be used to compute the total energy of the dislocation burst, i.e. the excursion in Figure 3.9a. The theoretical prediction of the length of the burst is equal to \(nb = 10\) nm, which is of the same order of magnitude as experimentally observed (see Table 3.2).

Because the positions of the dislocations in the stressed pile-up are known, the elastic energy stored in the 40 dislocation loops near the spearhead of the pile-up can be predicted from

\[
E_i = \sum_i E_{\text{self}} + \sum_p \sum_q E^I(r_{pq}) \quad (3.7)
\]

It turns out that the self energy \(E_{\text{self}}\) of the leading dislocation loops of radius 200 nm is far less than the interaction energy \(E^I\) among the loops, i.e. \(1.7 \times 10^{-13}\) J and \(6.9 \times 10^{-12}\) J, respectively. Similar values have been found for indentation of thin films [22]. Comparison with the experimentally determined value for \(W_{\text{GB}}\) of \(9 \times 10^{-12}\) J leads to the conclusion that there is a fair agreement with \(E_i\) and that the excursions observed in the load-displacement curves can be attributed to the release of dislocations from the pile-up at the boundary.

### 3.4.3 Transmission mechanisms

Before the excursion, the dislocation pile-up between the indenter and the grain boundary leads to hardening, corresponding to an increased curvature of the loading curve. When the first dislocation is transmitted across the boundary, this dislocation may act as a nucleation site (e.g. a Frank-Read source) so that the stress required to transmit subsequent dislocations is reduced. The pile-up is thus released as a sudden dislocation burst into the adjacent grain. After the excursion,
significant pile-ups can no longer be sustained at the boundary due to the availability of dislocation sources in the adjacent grain, and consequently the measured indentation response returns to bulk behavior.

In the release of the pile-up into the adjacent grain, several mechanisms may be active as discussed in Chapter 2. In the light of our observation of two separate excursions for some of the indentations, the mechanism of absorption and re-emission (Figure 2.6d) is believed to be predominant. At the first excursion, dislocations are absorbed into the grain boundary and pile up at a boundary step. With increasing load, this pile-up produces a stress high enough to nucleate dislocations in the adjacent grain, thereby causing a second yield excursion. Since the extent of dislocation absorption by the boundary depends on the local density of grain boundary dislocations and steps, the corresponding burst may vary in size or be absent altogether, as for the indentations showing only one excursion. The possible presence of segregated impurities may provide additional obstacles to grain boundary dislocations or easy sites for nucleation in the adjacent grain. However, this is not expected to change the observed behavior in a qualitative sense. An alternative explanation of the two separate excursions may be given by multiple slip, i.e. subsequent slip on two different slip planes or slip systems. However, considering Schmid factors as a first approximation as detailed in Section 3.6, and given the fact that both single and double bursts are observed while the crystallography remains the same, this explanation appears to be less likely.

The proposed mechanism of dislocation absorption and re-emission is supported by in situ transmission electron microscopy studies of slip propagation across boundaries in bcc metals [23-25]. In some cases, dislocations were found to stop at a short distance from the grain boundary and cross-slip into a plane nearly parallel to the boundary [26]. Because of the non-planar core structure of screw dislocations [27], non-Schmid behavior is observed [28] and dislocation pile-ups rarely occur during macroscopic deformation. In the present case however, the movement of dislocations is confined to a small volume and it can therefore be assumed that some extent of pile-up exists.

3.5 Grain boundary hardness measurements

Hardness profiles across the grain boundaries may be calculated using hardness values from the continuous stiffness measurement averaged over a portion of the loading curve. The values then represent the hardness experienced by the indenter
over this entire range, rather than at the maximum indentation depth. This allows the contribution from the observed nonlinearities in the indentation response to be included in the hardness analysis. Due the indentation size effect, the CSM hardness decreases continuously with increasing indentation depth, and an additional depth dependence of the hardness may be presented by the work hardening introduced by mechanical polishing. Since neither of these depth dependences is expected to be correlated to the presence of a grain boundary, the hardness values of indentations with the same indentation depth can be used to construct a hardness profile. In the present analysis, the CSM hardness has been averaged from 80 to 200 nm indentation depth. For both materials under investigation, the hardness at 80 nm indentation depth had come within approx. 15% of the hardness measured at 200 nm.

Figure 3.12 shows the hardness profiles of the investigated boundaries. All three bicrystals showed a significant hardness peak within 1 µm of the boundary. The peak hardness in both Mo bicrystals coincides with the position of the boundary. In the Fe-Si bicrystal however, the maximum hardness was attained around 0.3 µm from the boundary and only to the side where the yield excursions were observed. Immediately following the peak, a local minimum of the hardness is observed on both sides of the Fe-Si and Mo Σ3 boundaries and on one side of the Mo Σ11 boundary. The hardness on the other side of the Mo Σ11 boundary decreased more gradually to the grain interior value.

The hardness peaks show that significant dislocation pile-ups are formed at all three grain boundaries. For the indentations on Mo, the absence of detectable slip transfer suggests that the shear stress at the spearhead of the pile-up is not sufficient to initiate emission into the adjacent grain. This perception will be further substantiated in the next section. Following the hardening regime, significant softening with respect to the grain interior appears between roughly 0.5 and 1.0 µm from the boundary. This may be explained by the elastic interaction between induced lattice dislocations and the grain boundary [29,30], which may be either attractive or repulsive; an attractive force on the outer dislocation loops around the indenter may lead to apparent softening in the indentation response.

The indentation measurements on the Fe-Si bicrystal show a marked dependence on the azimuthal orientation of the indenter with respect to the boundary. Both the characteristic yield excursions and the increased hardness are observed only when one side of the indenter is facing the boundary. This was verified by an additional measurement with the indenter rotated 180° to eliminate
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Figure 3.12: CSM hardness profiles across (a) Mo $\Sigma 3$, (b) Mo $\Sigma 11$ and (c) Fe-Si grain boundary. The data points represent a moving average over 5 measurements of both hardness and distance. A positive distance to the boundary corresponds to an orientation where one side of the indenter impression faces the grain boundary; for negative distances, an apex of the impression points towards the boundary.
the possibility that this observation is due to the crystallographic asymmetry across the boundary. The orientation dependence can be understood by approximating the stress field by uniaxial pressure components perpendicular to the faces of the indenter, and recognizing that the resolved shear stress at the grain boundary is a maximum when one side is facing the boundary.

In contrast to the presently found short-range hardening within less than 1 µm from the boundary, some authors (e.g. Lee et al. [31]) have reported long-range hardening over several tens of micrometers and attributed this to intrinsic grain boundary hardening. In these and other experiments in literature, Ngan and Chiu [32] found a Hall-Petch type dependence of the hardness on the distance to the grain boundary, from which they calculated the Hall-Petch slope \( k_y \) as a measure of the resistance to slip transfer across the particular boundary. This approach is however disputed, as further indentation measurements on similar grain boundaries showed no appreciable hardening [3]. The marginality of the hardening effect observed in the present experiments indeed suggests that reported calculations of grain boundary properties solely based on hardening should be viewed with caution. Instead, the observed yield excursions allow for a more direct calculation of slip transmission properties, as will be shown in the next section.

3.6 Slip transmission: a Hall-Petch approach

3.6.1 Activated slip systems

Since the transmission of dislocations depends on the relative orientation of the active slip systems on either side of the boundary [33], the geometry of the indentation experiments on the Fe-Si bicrystal needs to be known in order for a complete analysis to be conducted. Using the EBSD information, we can calculate the favored slip systems on both sides of the boundary. In the indented grain, we assume a uniaxial compressive stress perpendicular to the faces of the Berkovich indenter as discussed before, and calculate the resolved shear stress for all possible slip systems on \{110\} and \{112\} planes based on Schmid behavior as a first approximation. Table 3.3 shows the five most favored slip systems and their respective Schmid factors for an applied stress component along \{0.004 -0.119 -0.993\}, which is the normal to the indenter face closest to the grain boundary. For each slip system, the angle \( \theta \) between the slip direction and the grain boundary normal vector \{-0.752 0.558 0.352\} is given as a measure for the
pump-up distance. Accordingly, the highest pile-up shear stress is established on the \((1\overline{1}2)\{1\overline{1}1\}\) slip system, having the largest Schmid factor and the shortest pile-up distance.

To predict the activated slip systems in the adjacent grain, we use the geometric criterion defined by Eq. (2.8). The factor \(M\) is a maximum for the favored slip system, i.e. the angle \(\alpha\) between the intersection lines of the slip planes with the boundary plane, and the angle \(\beta\) between the slip directions are to be minimized. The results of this optimization are summarized in Table 3.4. Assuming a dislocation pile-up in the indented grain on the \((1\overline{1}2)\{1\overline{1}1\}\) slip system as obtained above, we find that slip is transmitted most easily to the \((101)\{1\overline{1}1\}\) system in the adjacent grain with \(M = 0.82\), \(\alpha = 16^\circ\) and \(\beta = 32^\circ\). The relative orientation of these slip systems to the boundary plane is schematically shown in Figure 3.13.

![Figure 3.13: Relative orientation of the predicted slip systems, the grain boundary plane and the indenter.](image)
3.6.2 Calculation of the Hall-Petch slope

The dislocation pile-up at hand is confined to a small distance $d$ by the grain boundary on the one side and the indenter on the other side. Slip transmission occurs when the shear stress at the spearhead of the pile-up reaches a critical value $\tau^*$ given by [34,35]:

$$\tau^* = (\tau_a - \tau_0)\sqrt{\frac{d}{4r}}$$ \hspace{1cm} (3.8)

where $\tau_a$ is the applied resolved shear stress, $\tau_0$ is the intrinsic frictional shear stress resisting dislocation motion in the lattice and $r$ is the distance from the front of the pile-up to the dislocation source in the adjacent grain. Rewriting Eq. (3.8) gives the Hall-Petch type equation

$$\tau_a = \tau_0 + \frac{k_y}{\sqrt{d}}$$ \hspace{1cm} (3.9)

where the Hall-Petch slope is defined as

$$k_y = 2\tau^* \sqrt{r}$$ \hspace{1cm} (3.10)

Note that this definition is based on shear stress and differs in that respect from the definition in Eq. (2.10) based on yield stress. Consequently, it yields a different Hall-Petch slope value $k_y$. In this section, we will consistently use the shear-stress-based definition given in Eqs. (3.9)-(3.10).

We assume again a uniaxial compressive stress perpendicular to the surface of the indenter. Since the hardness $H$ defined by Eq. (2.23) is equal to the applied average stress, the applied resolved shear stress $\tau_a = \sigma \cos \phi \cos \lambda$, with the Schmid factor $\cos \phi \cos \lambda$ close to 0.5 as shown in Table 3.3, can be approximated at any time during the indentation as half of the measured hardness, $\tau_a = H / 2$. The CSM data are used to evaluate this hardness at the instant of the excursion; the values for each excursion are shown in Table 3.2. A good measure for the pile-up delimiting distance $d$ at the onset of the excursion is given by the distance across the surface from the indenter to the boundary, which is easily obtained from the geometry of the indenter, the initial distance to the boundary and the indentation depth at which the excursion occurs. Using these values for $\tau_a$ and $d$, and assuming that the frictional shear stress is equal to 200 MPa as for $\alpha$-Fe [36], the Hall-Petch slope for the Fe-Si boundary is found to be $k_y = 0.63$ MNm$^{-3/2}$ with a standard deviation of 0.09 MNm$^{-3/2}$. Following Eq. (3.9), Figure 3.14 shows a plot of the applied shear stress versus the inverse square root of the
distance to the boundary for the observed yield events. Although the distances at which slip transmission was observed do not span such a large range as to conclusively validate the $d^{1/2}$ dependence of the shear stress, the results appear to be in general agreement with the proposed Hall-Petch type relation. Moreover, the resulting Hall-Petch slope $k_y = 0.63$ MNm$^{-3/2}$ compares well to the macroscopic value for α-Fe, $k_y = 0.583$ MNm$^{-3/2}$ [37,38].

3.6.3 Predictive criteria for slip transmission

The fact that slip is transferred across the Fe-Si boundary during indentation whereas Mo, having a higher Hall-Petch slope, does not show this behavior under identical conditions, allows us to set up some predictive criteria for slip transmission to occur. For completeness, the results from a recent paper by Wang et al. [39] are included, in which strain bursts during similar indentation experiments on grain boundaries in coarse-grained niobium polycrystals are reported. Table 3.5 lists the relevant properties of the investigated grain boundaries. The macroscopic Hall-Petch slope values $k_y$ are consistent with the observations of slip transfer. In molybdenum, having the highest $k_y$ value and thus the highest resistance to slip transfer, dislocations piled up at the grain boundary.
as evidenced by the observed hardening; however, no transmission of dislocations to the adjacent grain was detected. The Hall-Petch slope for Fe-Si is lower; in this case, the boundary only yielded when faced by one side of the indenter. In the experiments by Wang et al. on niobium, having the lowest \( k_y \) value, slip transmission was observed irrespective of the azimuthal orientation of the indenter, which they did not take into account.

Besides the intrinsic resistance to slip transfer as quantified by the macroscopic value of the Hall-Petch slope, the ease of slip transfer is largely determined by the geometry of the experiment and the relative orientation of the slip systems. Wang et al. found that in niobium, strain bursts are observed for boundaries with \( m > 0.9 \), where \( m \) is given by

\[
m = \cos \theta_A \cos \theta_B
\]  

(3.11)

and \( \theta_A \) and \( \theta_B \) are respectively the angles between the closest slip planes on opposite sides of the boundary and the closest slip directions on these planes. However, this approach does not take the orientation of the grain boundary plane into account. Moreover, the closest available slip systems are not necessarily those activated during deformation, since slip, at least in the Schmid approximation, proceeds mainly on systems for which the resolved shear stress is highest. A more complete description of the misorientation is therefore given by the criteria presented in Section 3.6.1, leading to a misorientation factor \( M \). For example, the coherent Mo \( \Sigma 3 \) boundary has two perfectly aligned slip systems on either side \( (m = 1) \); however, these are not the slip systems that are active during indentation. In fact, slip transfer from the active slip plane in the indented grain is relatively difficult \( (M = 0.78) \) as shown in Table 3.5. This difficulty in slip propagation has been confirmed by in situ straining of \( \Sigma 3 \) symmetric tilt

### Table 3.5
Relevant parameters for the occurrence of slip transmission during indentation.

<table>
<thead>
<tr>
<th>Material</th>
<th>H-P slope ( k_y ) (MNm(^{-3/2}))</th>
<th>Closest slip system orientation ( m )</th>
<th>Activated slip system orientation ( M )</th>
<th>Slip transmission observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>0.78 [40]</td>
<td>1.00 (( \Sigma 3 ))</td>
<td>0.78 (( \Sigma 3 ))</td>
<td>No</td>
</tr>
<tr>
<td>Fe-Si</td>
<td>0.58 [38]</td>
<td>0.93</td>
<td>0.82</td>
<td>Yes, depending on indenter orientation</td>
</tr>
<tr>
<td>Nb [39]</td>
<td>0.19</td>
<td>0.90 - 0.99</td>
<td>-</td>
<td>Yes, regardless of indenter orientation</td>
</tr>
</tbody>
</table>
boundaries [23,24], which showed that the dislocation – grain boundary interaction strongly depends on the orientation of the tensile axis with respect to the boundary plane.

The combined results of Mo, Fe-Si and Nb as summarized in Table 3.5 suggest that the Hall-Petch slope $k_y$ is the primary parameter predicting the occurrence of slip transfer during Berkovich indentation. Boundaries with $k_y << 0.6$ show slip transfer regardless of the orientation of the indenter, whereas boundaries with $k_y >> 0.6$ do not allow slip to be transferred under similar conditions. In the transition range with $k_y \approx 0.6$, the azimuthal orientation of the indenter with respect to the boundary appears to play an important role, as illustrated by the results on Fe-Si. Clearly, the misorientation of the slip systems through the boundary also affects the transmission properties to a considerable extent; however, more results from a wider range of misorientations are needed to analyze this aspect quantitatively.

3.7 Slip transmission: a gradient plasticity approach

3.7.1 Size effects on the interfacial yield stress

The strain gradients in sharp indentation experiments of submicrometer length scale are appreciable and may produce size effects, such as the well-known indentation size effect (Section 2.3.3) or effects of dimensional constraints [41], which are not adequately explained by classical theories of plasticity. In the present experiments on Fe-Si, the applied shear stress needed to initiate slip transmission increases significantly as the distance to the boundary decreases. This has been rationalized in the previous section by a Hall-Petch type analysis, but alternatively it may be regarded as a new type of size effect: the boundary appears to be stronger when the probed volume becomes dimensionally constrained. In a recently developed framework of one-dimensional gradient plasticity theory [8,42-44], the effect of interfaces on the yield strength of materials has been considered by incorporating an interfacial energy. The plastic strain gradients are assumed to be discontinuous across the interfaces, and the interfaces are allowed to follow their own yield behavior.

The analytical expressions for the yield stress, as derived in reference [44], predict that the interfacial yield stress increases as the specimen size decreases. In the indentation experiments, the interfacial yield stress may be considered physically as the stress required to initiate dislocation transmission to
the adjoining grain, and the specimen size as the distance $d$ between the indenter and the boundary. The interfacial yield (shear) stress $\tau_c$ can subsequently be expressed as

$$
\tau_c = \frac{\gamma}{2\ell} \coth \left( \frac{d}{\ell} \right)
$$

where $\gamma$ is an interfacial energy-like term and $\ell$ is an internal length scale. Although derived for a one-dimensional problem without explicitly considering the specific stress fields during sharp indentation, this expression provides a good fit to the experimental results, as shown in Figure 3.15. The resulting values for the fitting parameters are $\gamma = 349$ N/m and $\ell = 120$ nm. The internal length scale may be thought of as a characteristic distance in which a fixed proportion of the piled-up dislocations is positioned. In a stressed dislocation pile-up of 200 nm length under an applied shear stress of 1.5 GPa as described by Eqs. (3.4)-(3.6), 34 of the 40 dislocations are located within a distance of 120 nm from the boundary.

### 3.7.2 Comparison with the Hall-Petch description

Figure 3.15 shows plots of the Hall-Petch relation and the expression derived from one-dimensional gradient plasticity compared with the experimental results.

![Figure 3.15: Hall-Petch relation (dashed line) and analytical relation obtained through gradient plasticity (solid line) fitted to the experimental data points.](image)

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Both relations clearly show the trend of increasing interfacial yield stress with decreasing distance to the boundary and provide a reasonable fit to the data points with $R^2$ values of 0.48 and 0.76, respectively. In the limit of large distances to the boundary, the functions converge to different values; the Hall-Petch relation converges to $\tau_0 = 200$ MPa, while the gradient plasticity relation approaches $\gamma / 2\ell = 1.45$ GPa. This may be due to the fact that the one-dimensional theory presents a better description of the experimental situation at small distances than it does at larger distances, where the three-dimensional properties of the setup become more relevant, e.g. through cross-slip of dislocations and the geometry of the indenter. Physically however, the yield stress of the boundary in this limit has little meaning, since it cannot be measured at large distances from the boundary with the present technique.

3.8 Conclusions

We have characterized the mechanical response to nanoindentation of three bcc bicrystals as a function of the distance to the grain boundary. Dislocation pile-up at grain boundaries was evidenced in all bicrystals by significant hardening within 1 µm of the boundaries. The indentations on molybdenum showed extensive staircase yielding due to nucleation and multiplication of dislocations under the indenter. These yield excursions were found to be significantly attenuated close to the grain boundaries due to preferential dislocation nucleation at the boundary. From the interaction range of 0.3 µm, which is of the same order as the tip radius, the nucleation shear stress at the boundary is estimated to be 1.8 GPa.

Indentations close to the boundary in the Fe-Si bicrystal showed a characteristic yield excursion, which is attributed to slip transmission. This is supported by a comparison between the energy released during the excursion and the calculated interaction energy of the piled-up dislocations. The boundary resistance to slip transfer can be quantitatively related to the yield excursions by a Hall-Petch type calculation. By regarding the distance between the indenter and the boundary at the onset of slip transmission as representative for the slip pile-up, a Hall-Petch slope $k_y$ can be obtained that corresponds well to macroscopically determined values. Accordingly, it is shown that materials with higher $k_y$ values exhibit increasing difficulty in slip transmission across boundaries. The Hall-Petch slope is therefore considered the most important parameter predicting the occurrence of the observed yield excursions. For
materials with $k_y >> 0.6 \text{MNm}^{3/2}$, slip transmission is not expected under Berkovich indentation.

Alternatively, the yield events may be described by strain gradient plasticity theory in which the presence of grain boundaries is accounted for by incorporating an interfacial energy term. The fact that the critical shear stress for slip transmission increases with decreasing distance to the boundary may in this view be regarded as a new type of size effect related to the large strain gradients at hand. Fitting the analytical expression for the yield stress of the interface gives an internal length scale of 120 nm, which can be physically rationalized in terms of the dislocation pile-up length.

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