Hall–Petch relation and boundary strengthening

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Abstract

The Hall–Petch relation is discussed separately for the yield stress of undeformed polycrystalline metals and for the flow stress of deformed metals. Key structural parameters are the boundary spacing, between grain boundaries in the former case and between dislocation boundaries and high angle boundaries in the latter. An analysis of experimental data supports the Hall–Petch relation for undeformed metals over a grain size range from about 20 nm to hundreds of micrometers. For deformed metals, boundary strengthening is not a constant and the Hall–Petch relation must be modified.

Keywords: Yield stress; Flow stress; Grain size; Dislocation boundaries; Nanostructure

1. Introduction

Originally proposed at the beginning of the 50s for grain boundary strengthening in polycrystalline metals, the Hall–Petch relation [1,2] has later been expanded to cover also the strengthening effect of various types of boundaries introduced by plastic deformation [3]. Also the structural scale has been expanded from the micrometer scale to nanometer dimensions [4]. This very broad application of the Hall–Petch relation has raised questions, not only about its predictive capability, but also about the physical basis for the relation. These questions are briefly discussed in the present paper in connection with experimental findings.

2. Hall–Petch relation

In its first formulation the Hall–Petch relation expressed the dependency of the lower yield point or the fracture stress of iron on the grain size. It was later also suggested for the effect of the grain size on other mechanical properties of polycrystalline metals and alloys [5]. In the following the Hall–Petch relation will be discussed separately for the yield stress and for the flow stress. In both cases the influence of the grain size \( D_{GB} \) will be introduced by the parameter \( D_{GB}^{-1/2} \). Other values for the exponent have been discussed [3] but will not be considered here.

The yield stress \( \sigma_y \) is related to the grain size by the equation [1,2]:

\[
\sigma_y = \sigma_0 + k_1 D_{GB}^{-1/2}
\]

where \( \sigma_0 \) and \( k_1 \) are constants. \( \sigma_0 \) is a friction stress, which includes contributions from solutes and particles but not from dislocations, i.e. \( \sigma_0 \) is the flow stress of an undeformed single crystal oriented for multiple slip or approximately the yield stress of a very coarse-grained, untextured polycrystal.

The flow stress at a particular strain \( \sigma(\varepsilon) \) is related to the grain size by the equation [6]:

\[
\sigma(\varepsilon) = \sigma_0(\varepsilon) + k_1(\varepsilon) D_{GB}^{-1/2}
\]
where $\sigma_0(\varepsilon)$ and $k_1(\varepsilon)$ are constants at a given strain. With different constants Eq. (2) has also been applied to describe the effect of grain size on other strength parameters especially the hardness. As in the case of Eq. (1), single crystals or coarse-grained polycrystals are required to obtain $\sigma_0(\varepsilon)$.

In Eqs. (1) and (2) the stress is divided into two parts: one which is independent of the grain size and one which is grain-size dependent. For example in Eq. (2) $\sigma_0(\varepsilon)$ is the flow stress of the grain interior and $k_1(\varepsilon)D_{GB}^{-1/2}$ can be considered as a strength contribution due to the additional resistance to dislocation motion caused by the presence of grain boundaries.

The contribution of the grain interior, $\sigma_0(\varepsilon)$ is related to the density of dislocations accumulated in dislocation boundaries. Neglecting the contribution from redundant dislocations, which decrease significantly with increasing strain, the dislocation density for a mixed tilt/twist boundary can be approximated by $1.5 S_{\sqrt{\theta b}}$, where $S_{\sqrt{\theta b}}$ is the area of boundaries per unit volume, $\theta$ is the misorientation angle and $b$ is the Burgers vector. Dislocations are also present between the dislocation boundaries, but as only pure metals with medium to high stacking fault energy are considered the contribution from such unassociated dislocations is neglected. Eq. (2) can then be written:

$$\sigma(\varepsilon) = \sigma_0 + M\varepsilon G\sqrt{1.5bS_{\sqrt{\theta b}}} + k_1(\varepsilon)D_{GB}^{-1/2}$$

(3)

where $\sigma_0$ is the frictional stress (as in Eq. (1)), $M$ is the Taylor factor, $\varepsilon$ is a number and $G$ is the shear modulus.

At large strains, many of the dislocation boundaries or low angle boundaries LAB’s ($\theta < 15^\circ$) evolve into high angle boundaries HAB’s ($\theta > 15^\circ$), which are indistinguishable from the original grain boundaries. Based on an assumption of an identical strengthening effect of the two types of boundaries $D_{GB}$ is replaced by $D_{HAB}$ and the flow stress $\sigma_f$ can be expressed:

$$\sigma_f = \sigma_0 + M\varepsilon G\sqrt{1.5b(S_{\sqrt{\theta b}})} + k_1(\varepsilon)D_{HAB}^{-1/2}$$

(4)

As an alternative to Eq. (4) the flow stress of deformed metals has simply been related to the boundary spacing without taking into account if the boundaries are low angle dislocation boundaries or high angle boundaries [3]. In this case the relation between the flow stress and the average boundary spacing $D_B$ is:

$$\sigma_f = \sigma_0 + k_2D_B^{-1/2}$$

(5)

where $k_2$ is a constant. In this formulation as in Eq. (1) the boundary resistance is considered to be constant independent of the character of the boundary, for example Eq. (5) has been used to relate the flow stress of hot deformed metals to the subgrain size [3]. However, for such structures it has also been suggested [7] that $k_2$ is a variable, which for low angle boundaries increases with their angle.

3. Strength increase by structural refinement

The empirical validity of Eq. (1) has led to extensive research and development to increase the yield stress of polycrystalline metals and alloys by refining their grain size, which in today’s industrial materials can be 5–10 $\mu$m or even smaller. However, if Eq. (1) is valid there is still a large potential for yield strength improvement by reducing the grain size to the submicrometer range. In accordance with Eqs. (1) and (4), a structural refinement by plastic deformation should also be a promising route to increase the flow stress. Structural refinement by different processing routes has therefore been an active research area in the last 10–20 years. As a result nanocrystalline metals and alloys with a grain size as small as 10–20 nm can now be produced for example by inert gas condensation [8] or electrodeposition [4,9]. Such fine scale structures can also be obtained by plastic deformation to ultra high strains for example by friction or mechanical attrition [10]. It has been common practice to name such fine scale materials either nanocrystalline, nanostructured or ultrafine grained metals without taking structural differences into account. However, this will be done in the following: materials, where grain boundaries separate grains with little or no dislocation structure, are referred to as nanocrystalline, while materials with many low angle boundaries or a mixture of low and high angle boundaries are called nanostructured. It follows that nanocrystalline materials may be polycrystalline metals produced by deformation followed by recrystallization and by processes such as inert gas condensation or electrodeposition. Nanostructured materials are typically processed by plastic deformation. In both categories boundary spacings may reach from below 10 nm to hundreds of micrometers. In the following the yield stress of the former group and the flow stress of the latter will be discussed. In both cases the stress is determined at 0.2% offset.

4. Yield stress—polycrystalline metals

The relation between the yield stress and the grain size has been investigated for a number of metals and alloys and good agreement with Eq. (1) has been found [5,6]. The range of grain sizes is typically from about 10 $\mu$m to several hundred micrometers in samples, which have been recrystallized after deformation. In a few experiments on Cu [11] and Ni [12] it has been shown that the validity of Eq. (1) can be extended down to a recrystallized grain size of about 3–4 $\mu$m. Also fairly consistent values for the Hall–Petch slope $k_1$, have been found when taking into account especially the effect of solutes and of crystallographic texture [6,11].

The validity of Eq. (1) with an exponent of $-1/2$ in the micrometer range is the basis for examining whether...
Eq. (1) also describes the behaviour of nanocrystalline metals. However, a validation of the exponent is not possible at present because of a lack of data covering a range of grain sizes in high quality samples. Instead the predictive capability of Eq. (1) is tested for nanocrystalline metals, when applying values for \(\sigma_0\) and \(k_1\), obtained for recrystallized samples with grain sizes in the micrometer range. Such values have been obtained with good accuracy and nominal values for Al [13,14], Ni [15] and Cu [16,17] are given in Table 1. Note in this table that the strengthening effect of boundaries, \(k_1/Gb\), increases with decreasing stacking fault energy being the highest in Al and the lowest in Cu.

The nanocrystalline metals chosen for the test have been produced by inert gas condensation of Al, Ni and Cu [8]. These samples have a density of 97–99% of the theoretical density and to reach this density various compression and annealing processes have been applied. The Ni powders were compacted at room temperature and the Al and Cu powders were compacted at 100 and 150 °C, respectively. After compacting the Ni discs were annealed for 100 min at 300 °C (0.33 Tm) and the Cu discs for 240 min at 150 °C (0.33 Tm). The grain sizes were obtained by X-ray analysis for Cu and Ni and by transmission electron microscopy for Al, see Table 2. This table also contains values for the yield stress obtained by testing of miniature samples at room temperature [8]. A comparison between the experimental data and values calculated on the basis of the numbers in Tables 1 and 2 shows no systematic difference. For example lower experimental values, which could indicate a decrease in the magnitude of the grain boundary strengthening or higher experimental values, which could reflect a certain degree of plastic deformation during processing. Therefore the relatively good agreement between the experimental and calculated yield stress of Ni shows the good predictive capability of Eq. (1). Also the differences observed between the experimental and the calculated yield stress, can to a certain extent, be rationalized. For example in Cu it was observed [8] that highly twinned 1–5 \(\mu\)m grains were embedded in a structure of nanocrystalline grains, whereas the structure in Al and Ni is uniform. The number density of the large grains in Cu is relatively small but they may cause weakening. For Al where the experimental yield stress is significantly higher than that calculated a tentative suggestion is that powders might have been slightly oxidized during processing and that the high yield stress includes a contribution due to oxide dispersion strengthening.

As an alternative process to inert gas condensation nanocrystalline metals and alloys can be manufactured by electrodeposition. It is however, difficult by this process to control the chemical composition as impurities are introduced during processing and also the grain structure may be non-uniform [4,9,18]. It has however, been suggested [4,19] for nanocrystalline Ni that the yield stress–grain size relation agrees with Eq. (1). With good accuracy this agreement covers specimens with grain sizes down to about 20 nm [4,19]. For \(\sigma_0\) and \(k\) were found values 7 MPa and 0.18 MPa m\(^{1/2}\) [4], respectively in good agreement with the numbers in Table 1 for polycrystalline Ni. However, this comparison as well as the former must be taken with a certain caution not only because the number of samples is very limited, but also because structural and chemical effects unaccounted for, may affect the yield stress. A summary of the data [4,8,15,19] is given in Fig. 1.

<table>
<thead>
<tr>
<th>Material</th>
<th>(G) (MPa)</th>
<th>(b) (nm)</th>
<th>(k_1) (MPa m(^{1/2}))</th>
<th>(\frac{k_1}{Gb}) m(^{-1/2})×10(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>26,000</td>
<td>0.286</td>
<td>0.04</td>
<td>5.4</td>
</tr>
<tr>
<td>Nickel</td>
<td>79,000</td>
<td>0.249</td>
<td>0.16</td>
<td>8.1</td>
</tr>
<tr>
<td>Copper</td>
<td>45,000</td>
<td>0.256</td>
<td>0.14</td>
<td>12.2</td>
</tr>
</tbody>
</table>

\(\sigma_0\) is approximately 20 MPa for all three metals.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Grain size (nm)</th>
<th>Yield stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental(^a)</td>
<td>Calculated</td>
</tr>
<tr>
<td>Ufg.(^b)-Al</td>
<td>250</td>
<td>135</td>
</tr>
<tr>
<td>n(^c)-Ni</td>
<td>28</td>
<td>1.150</td>
</tr>
<tr>
<td>n(^c)-Cu</td>
<td>26</td>
<td>535</td>
</tr>
</tbody>
</table>

\(^a\) 0.2% offset.  
\(^b\) Ultrafine-grained.  
\(^c\) Nanocrystalline.
5. Flow stress—deformed metals

At low and medium strains the effect on grain size or the flow stress at a particular strain is described satisfactorily by Eq. (2). This has been shown empirically for a number of polycrystalline metals and alloys tested in tension at room temperature [5,6]. It has also been found that Eq. (2) covers a grain size range down to the smallest grain sizes examined about 3–4 µm [11]. For nanocrystalline metals it is consistently found that the strain hardening stage is so limited that a test Eq. (2) is not meaningful.

At large plastic strains Eq. (4) has been used in flow stress structural analysis of metals deformed monotonically by rolling or tension [20]. In such an analysis the boundaries subdividing the microstructure have been separated into incidental dislocation boundaries (IDB’s) and geometrically necessary boundaries (GNB’s). The IDB’s are suggested to be formed by mutual trapping of glide dislocations and the GNB’s are boundaries, whose angular misorientations are controlled by the difference in glide-induced lattice rotations in the adjoining volumes. These suggestions have led to flow stress–structural relations similar to Eq. (4) by assuming that IDB’s and GNB’s cause dislocation strengthening and high angle boundary strengthening, respectively. ($S_{LV}θ_{LAB}$) and $D_{HAB}$ are therefore replaced by ($S_{LV}θ_{IDB}$) and $D_{GNB}$, respectively [19]. Based on these changes Eq. (4) has been evaluated for Al [21] and for Ni [22] cold-rolled to large strains. A lamellar structure is formed and $D_{GNB}$ and $D_{IDB}$ are taken as the distance between the lamellar boundaries and the interconnecting (bamboo) boundaries, respectively, assuming the flow to take place in the regions between the lamellar boundaries. Based on quantitative characterisation of structural parameters, good agreement between calculated and experimental behaviour is observed both as regards the absolute flow stress values and hardening rates [21,22]. Similar good agreement has been obtained for the structural–flow stress relation in aluminium deformed to ultrahigh strains by cumulative roll bonding [23]. The structural scale in the different experiments is in the range 100 nm to 1 µm. Finer scale structures in the range 10–100 nm have been obtained by deformation processes such as high pressure torsion, mechanical attrition and friction. It is a general observation that the flow stress increases as the microstructure is refined but quantitative structural data are not yet available to test flow stress–structural relations, as for example Eq. (4).

The deformation microstructures obtained by monotonic deformation to large strains are lamellar structures, where an investigation by transmission electron microscopy allows a distinction between IDB’s and GNB’s. However, after strain path changes e.g. in cyclic deformation the structure may become more equiaxed and subdivided by a mixture of low and high angle boundaries. Introducing the density of high angle boundaries as $f$, Eq. (4) can be rewritten:

$$\sigma_f = \sigma_0 + M\alpha G\sqrt{1.5bS_{V}\theta_{LAB}(1 - f)} + k_1\sqrt{S_V f}$$  \hspace{1cm} (6)

where $S_V$ is the total boundary area per unit volume and $θ_{LAB}$ is the average angle of low angle boundaries. Based on a structural characterization by electron back scattered diffraction analysis Eq. (5) has satisfactorily explained the observed flow stress–structure relationship in an Al–0.13 Mg alloy [24] deformed by equal channel angular extrusion to a von Mises strain of 10 and annealed at temperatures in the range 100–400 °C after deformation.

The analysis above illustrates the importance of both dislocation strengthening and high angle boundary strengthening. However, frequently the flow stress structural analysis of deformed metals is based on one structural parameter, the boundary spacing $D_B$ and Eq. (5) is applied. Good agreement with experimental data can be observed, however, with values for $k_2$ in Eq. (5) much higher than found for $k_1$ in Eq. (1) and also in many cases with a negative value for $σ_0$ [3,25]. The high $k_2$ values can be rationalized by taking $S_V$ equal to $2/D_B$ where $D_B$ is the boundary spacing measured along random lines. Eq. (5) is then:

$$\sigma_f = \sigma_0 + \left[M\alpha G\sqrt{3b\theta_{LAB}(1 - f)} + k_1\sqrt{f}\right]D_B^{1/2}$$

$$= \sigma_0 + k_2D_B^{-1/2}$$  \hspace{1cm} (7)

This equation gives a very high value for the slope for example for hypothetical values $f = 0.5$ and $θ = 5^o$, $k_2$ for aluminium is approximately 0.14 MPam$^{1/2}$ to be compared with $k_1 = 0.04$ MPam$^{1/2}$ for recrystallized aluminium (Table 1). According to Eq. (7) a gradual decrease in boundary spacing may be followed by a gradual increase in $k_2$. Therefore a plot of experimental
data, where \( \sigma_0 \) and \( k_2 \) are taken to be constants may be considered to be a relatively coarse approximation, not reflecting the change in boundary characteristics as \( D_B \) decreases with increasing plastic strain. An example of a plot according to Eq. (5) is given in Fig. 2 for Ni, cold-rolled over a large strain range [22]. Illustrating that a high slope and a negative volume of \( \sigma_0 \) and a high angle boundary show the same orientation angle, and above which a dislocation boundary and a high angle boundary show the same resistance? Also the strengthening effect of grain boundaries and deformation-induced high angle boundaries embedded in a deformation microstructure has at present not been quantified. To do so will require testing of specimens with well-characterized structural parameters and in parallel detailed characterization preferably by high resolution electron microscopy of boundary structures [29]. Such studies are important not only to analyse strengthening mechanisms but also to give guidelines for future optimisation of structural and mechanical properties by changing processing conditions and by changing the response of materials to plastic deformation for example by alloying [30].

A final point to be addressed is the stress–structural relationship based only on one parameter, the grain size in Eq. (1) and the boundary spacing in Eq. (5). As \( k_2 > k_1 \) an extrapolation of the flow stress obtained for deformed structures, where \( D_B \) typically is larger than 100 nm to nanocrystalline metals with \( D_{GB} \) smaller than about 100 nm will indicate a decrease in boundary strengthening. Such a decrease is suggested as a general phenomenon [31] but it may simply reflect that boundary strengthening depends on the boundary characteristics, which again depends on the method of synthesis.

7. Conclusions

The predictive capability of the Hall–Petch relation Eq. (1) for the yield stress of recrystallized metals with grain sizes in the micrometer range has been demonstrated for nanocrystalline metals produced by inert gas condensation and electrodeposition with grain sizes in the range 20–100 nm.

Physically based models are still in demand to underpin the Hall–Petch relation (Eq. (1)). The mechanisms underlying these models may change with the structural scale, but observations show that dislocation-based mechanisms are operative at all length scales.

The Hall–Petch relation for the flow stress of deformed metals is applicable if the strength contribution form boundaries is introduced as a variable parameter and not as a constant as in Eq. (1). By adding strength contributions linearly from dislocation boundaries and high angle boundaries (Eq. (4)) good agreement is obtained between structural-based models and experiments for deformed metals with boundary spacings above 100 nm.

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