Microstructure-Properties: I
The Effect of Grain Size on Strength Creep Resistance

27-301
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Bibliography

- Llewellyn, DT & Hudd, RC, *Steels, Metallurgy and Applications*, Butterworths-Heinemann
- http://www.steeluniversity.org/content/html
Objective

• This lecture and the following one are concerned with the effects of grain size on properties.

• Two examples are given:
  – The effect of grain size on mechanical properties as in the Hall-Petch effect.
  – The effect of grain size on mechanical properties as in Nabarro-Herring creep.
Questions and Answers

1. What is the equation that describes the Hall-Petch effect on strength? Yield varies as inverse square root of grain size.

2. Based on the dislocation pile-up model, derive the H-P Eq. See the slides for the derivation, which is based on standard analysis of forces between dislocations.

3. What do we know about variations in the magnitude of the H-P effect? The H-P effect is strongest in metals with solutes and in planar slip materials.

4. Which other property does Hall-Petch apply to? Toughness.

5. What happens to the H-P effect at the nanoscale? The H-P effect tends to saturate.

6. Explain the practical significance of grain refinement. In many structural materials used at low homologous temperature, grain refinement is applied to increase strength and toughness.

7. Describe the basic characteristics of stress-strain and strain-time curves at low and high temperature. Testing at low T results in strain hardening; testing at high (homologous) T results in a saturation of flow stress (constant creep rate).

8. Why are Ni alloys (“superalloys”) the standard material for the hot zone of gas turbine engines? Explain why gamma-prime is so effective for strengthening superalloys. Superalloys are precipitation hardened and the hardening persists to a very high fraction of their melting point because of the behavior of partial dislocations.

9. Why are Coble and N-H Creep interesting from a grain size perspective? Because the creep rate depends directly on the grain size.

10. Explain the main features of a deformation mechanism map. Deformation maps display the variation in strain rate (via contours) as a function of temperature and stress (relative to the shear modulus).

11. Explain (qualitatively) how Nabarro-Herring creep works. The applied stress sets up a difference in chemical potential for vacancies between the “top” and “sides” of each grain; the resulting flow of vacancies is mass transport that allows strain to develop.

12. Derive the equation that describes NH creep and discuss the temperature and grain size dependence. See the slides.
Key Concepts

- Grain boundaries (effectively) have properties that differ from the matrix.
- Properties of polycrystal depend on the content of planar defects, i.e. grain boundaries, i.e. grain size.
- Grain boundaries in semiconductors used to make varistors have a one-way voltage barrier.
- The Hall-Petch effect quantifies the trend of increasing strength and toughness with decreasing grain size. That is to say, fine grain size strengthens the material.
- Creep rates (Coble creep) increase with increasing grain boundary area (per unit volume), hence decreasing grain size. Therefore grain size has the opposite effect at high temperatures where fine grain size weakens the material.
- Low temperature service optimized by fine grain size, but high temperature service optimized by use of single crystals.
Notation

- $\sigma_y$: yield strength
- $\sigma_0$: friction stress
- $K$ or $k$: Hall-Petch coefficient
- $d$: grain size
- $n$: number of dislocations in a pile-up
- $\nu$: Poisson’s ratio
- $G$: shear modulus
- $\tau$: shear stress
- $J$: vacancy flux
- $D$: diffusion coefficient
- $T$: (absolute) temperature
- $T_m$: melt $T$
- $\Omega$: atomic volume
- $\sigma$: stress
- $N$: concentration of vacancies
- $Q_m$: Activation energy for migration
- $Q_{\text{Vacancy}}$: Activation energy for vacancy formation
- $kT$: Boltzmann’s constant multiplied by temperature
- $A_{NH}$: numerical pre-factor for Nabarro-Herring creep
The Hall-Petch effect is remarkably simple to express but still difficult to explain in fundamental terms.

At ambient conditions (no creep), yield strength rises as the grain size decreases.

The variation in strength can be described by a power-law relationship:

$$\sigma_y = \sigma_0 + kd^{-1/2}$$

Dislocation Pile-ups

• The central idea is that dislocations are forced to pile up at grain boundaries, either because there is a barrier to crossing over into the next grain, or because a source must be activated in the next grain.
Dislocation Pile-up at a Boundary

- The classical explanation for the Hall-Petch effect is that some stress concentration in a given grain is required to initiate slip in its neighboring grain. That stress concentration is most plausibly obtained through a dislocation pile-up, see figure 5.5. The essence of the argument is that stress is higher as the number of dislocations increases.

- Thus the larger the grain size, the more quickly (in terms of macroscopic strain) is the critical stress reached at which slip is initiated in the neighboring grain.

- The form of the equation describing the pile-up stress contains a term in $\sqrt{d/r}$ where $d$ is the grain diameter and $r$ is the (average) distance to the source in the neighboring grain from the boundary.

Number of (edge) dislocations in pile-up:

$$n = \frac{(1 - \nu)\pi \tau d}{4Gb}$$

Stress at the head of the pile-up:

$$\tau_c = n\tau = \frac{(1 - \nu)\pi \tau^2 d}{4Gb}$$

Now invert the relationship to find the shear stress to overcome the critical breaking stress of the grain boundary and insert a friction stress (e.g. solutes):

$$\tau_{applied} = \tau_i + \frac{4Gb\tau_c}{(1 - \nu)\pi d} = \tau_i + kd^{-1/2}$$
Material Dependence

- The Hall-Petch constant, $k$ in the equation, varies considerably amongst materials. This in itself raises some questions about the mechanism(s) underlying the effect. The explanation given is purely geometrical and although the material dependence could be explained through the ratio $d/r$, it is not clear why this should be so!

- Solutes tend to enhance the magnitude of the Hall-Petch effect.

<table>
<thead>
<tr>
<th>Material</th>
<th>Crystal structure</th>
<th>$k_p$(MN/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low-carbon steel</td>
<td>bcc</td>
<td>0.307</td>
</tr>
<tr>
<td>Armco iron</td>
<td>bcc</td>
<td>0.583</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>bcc</td>
<td>1.768</td>
</tr>
<tr>
<td>Zinc</td>
<td>hcp</td>
<td>0.220</td>
</tr>
<tr>
<td>Magnesium</td>
<td>hcp</td>
<td>0.279</td>
</tr>
<tr>
<td>Titanium</td>
<td>hcp</td>
<td>0.403</td>
</tr>
<tr>
<td>Copper</td>
<td>fcc</td>
<td>0.112</td>
</tr>
<tr>
<td>Aluminum</td>
<td>fcc</td>
<td>0.068</td>
</tr>
</tbody>
</table>


Table 5.1
Values of $k_p$ for several materials
Grain Size and Fracture

- Grain size also has a marked effect on fracture, which was, in fact, part of Petch’s original contribution.

Fig. 17.14. Dependence of the brittle fracture stress on grain size at 77°C. (Petch, 1953. Courtesy of British Iron and Steel Institute.)

[McClintock & Argon]
Nanocrystalline materials

• All this suggests that remarkably strong materials can be generated if very small grain sizes can be achieved. This, of course, is one aim of nanocrystalline materials in which grain sizes are obtained that are well less than one micron. The processing (in metals) relies on either compaction of fine powders (which requires second phase particles in order to maintain the small grain sizes at sintering temperatures) or heavy deformations allied with recrystallization. This is an exciting area and is a lively area of research and development.

• How to make nanocrystalline material? Powders, ball milling, equal-angle channel extrusion, thin film deposition (chemical vapor deposition, physical vapor deposition, laser ablation).

• Question: what limit on strength exists for nanocrystalline materials? Does the Hall-Petch equation apply all the way down to 1nm grain size, for example?
**Inverse Hall-Petch**

- It has long been theorized that there is a lower limit to the grain size for the Hall-Petch effect. Below this grain size, dislocations cannot bow out between obstacles without touching a boundary, and there is not enough space for pile-ups to form.

- This lower limit is almost found in plots where the flow stress no longer increases once very small grain sizes are reached.


Grain refinement

- A crucial engineering consequence of the Hall-Petch effect is that there is a large industry around grain refinement.
- Many metals are used as castings, i.e. in the as-solidified state, so their grain size is important for their strength and toughness.
- Grain refiners are known for most systems, but are almost invariably used in casting aluminum alloys (typically TiB$_2$ which remains solid during casting because of its high melting point relative to Al).

![Macro-structures of Base Alloy and Boron Grain Refined Yellow Brass, 5x.](http://www.afsinc.org/Research/Chapter02.html)
Creep

• An important property of materials is their resistance to creep.
• Creep is irreversible (plastic) flow at low rates under low stresses.
• We will return to this issue in later lectures because of its importance.
• Creep is highly sensitive to temperature because thermal activation makes the largest contribution to plastic flow when the stress is too small to overcome mechanical barriers to dislocation motion.
• We shall derive the Nabarro-Herring creep equation because it provides a quantitative illustration of the direct influence of grain size on high temperature strength.
**Homologous Temperature**

- Therefore it is common to use *homologous temperature* as a measure of relative temperature:

  \[ T' = \frac{T}{T_{melt}} \]

- Therefore we expect materials tested at the same homologous temperature to show similar behavior.
- Materials will tend to creep at high homologous temperatures because diffusion allows changes in shape.
Creep: general characteristics

- Low temperature deformation is characterized by work hardening: high temperature by a short transient hardening, followed by steady-state flow.

- Similarly, constant load leads to steady-state flow at high T, but cessation of flow at low T (after a transient strain).
Creep Resistance: Superalloys

- Nickel-based “superalloys” originated with the Ni-Cr alloys used for heating elements in furnaces. In these, and the subsequent superalloys, their oxidation resistance is critical. *Very few materials possess ductility, oxidation resistance and strength at high temperatures.*

- The term superalloy refers - loosely - to the use of this alloy class at unusually high homologous temperatures.

- They are based on the Ni-Cr-Al ternary system but have many other alloy additions.

- The key to their success is the presence of a second phase, close to Ni$_3$Al (“gamma-prime”) that is coherent with the matrix and whose strength *increases* with temperature.
# Refractory Materials (Engines)

<table>
<thead>
<tr>
<th>Material</th>
<th>Melting Point (K)</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>3800</td>
<td>oxidizes</td>
</tr>
<tr>
<td>Tungsten</td>
<td>3650</td>
<td>oxidizes</td>
</tr>
<tr>
<td>MgO</td>
<td>3100</td>
<td>brittle (room T)</td>
</tr>
<tr>
<td>SiC</td>
<td>3000</td>
<td>brittle (room T)</td>
</tr>
<tr>
<td>Mo</td>
<td>2880</td>
<td>oxidizes</td>
</tr>
<tr>
<td>Nb</td>
<td>2740</td>
<td>oxidizes</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>2290</td>
<td>brittle (room T)</td>
</tr>
<tr>
<td>Cr</td>
<td>2160</td>
<td>brittle</td>
</tr>
<tr>
<td>Zr</td>
<td>2125</td>
<td>expensive</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(used for nuclear fuel cladding)</td>
</tr>
<tr>
<td>Pt</td>
<td>2042</td>
<td>expensive (crucibles)</td>
</tr>
<tr>
<td>Fe</td>
<td>1808</td>
<td>oxidizes</td>
</tr>
<tr>
<td>Co</td>
<td>1495</td>
<td>L12 intermetallic recently found, possibility</td>
</tr>
<tr>
<td>Ni</td>
<td>1726</td>
<td>V</td>
</tr>
</tbody>
</table>

This is a good example of the requirement for multiple properties to be satisfied: here we have creep strength, oxidation resistance, ductility and cost.
Superalloys: Temperature of Use

Why is temperature important? The efficiency of the engine is very sensitive to hot zone temperature. Therefore even small increases in the temperature to which turbine blades can be exposed produces significant gains in engine efficiency.

Fig. 1. Advances in temperature capability of turbine materials and processes since 1960.[1]
Grain Size effect on creep rate

Fig. 16. Influence of varying grain size on minimum creep rate of Ni-20-Cr-Ti-Al alloys. Alloy A: 3Ti, 2.2Al. Alloy B: 2.6Ti-1.58Al. Alloy C: 1.63Ti - 0.85Al. Alloy D: 1.06Ti, 0.65Al. [75]

[Microstructure and Properties of Materials: Stoloff]
Ni-Al phase diagram

Note the use of high Al contents in order to obtain very high volume fractions (>50%) of the Ni₃Al phase (gamma-prime) that exhibits INCREASING hardness/strength with increasing temperature (alloy d, Fig. 2.67, right). The ordered crystal structure of the Ni₃Al γ’ provides some of the enhanced strength.

Fig. 2. Ni-Al Phase Diagram.

Microstructure and Properties of Materials: Stoloff
Superalloy strengthening

• The coherent interface between the γ’ and the matrix is important because it means that the precipitate does not coarsen.

• The increasing strength with temperature (of the γ’) is critical: most materials soften with temperature. This effect is not completely understood and is likely the result of dislocation-dislocation interactions.

• The phase relationships allow a very large volume fraction of cuboidal γ’ to be precipitated in the matrix: this is a very effective barrier to dislocation creep.
Dislocations

fcc

\[ b = [110]/2 \]

2 partials!
Dislocations in $L1_2$

$L1_2$

$b = [110]$

4 partials!
Contemporary Issues

• An example of a contemporary issue is the effort being made by the manufacturers of gas turbine engines to transfer the technology for single crystal turbine blades from aircraft engines over to land-based gas turbines (for power generation).

• What’s the issue? Hot stage turbine blades for an aircraft engine are comparatively small - a few centimeters long. The equivalent component for a land-based turbine is an order of magnitude large - 30-70 cm long! Making these depends on control of directional solidification: faults give rise to new orientations and grain boundaries which weaken the material.

• Solution? Either much improved furnaces for directional solidification (very expensive and perhaps not feasible) or fabricate the single crystal from smaller pieces.
**Bonded “Single” Crystals**

- The approach adopted by one manufacturer is to grow thin single crystal pieces (slabs) of the nickel superalloy using standard directional solidification. Control of the crystal solidification direction is still feasible because of the thinness. Then two pieces, chosen for similar orientation, are bonded together.

- The bonding process relies on a boron-rich bonding alloy (braze) that produces transient melting.

- See, for example: Canadian Patents Database Patent 2307230: Turbine Blades Made From Multiple Single Crystal Cast Superalloy Segments
Creep Mechanisms

- **Dislocation Glide.** This is self-explanatory: dislocations move (conservatively) in response to shear stresses.
- **Nabarro-Herring Creep.** Creep can occur by mass transport, i.e. diffusion of atoms from regions of lower (algebraically) stress to regions of higher (more tensile) stress. This is equally effective in amorphous materials as in crystalline.
- **Coble Creep.** Mass transport can occur either in the bulk (leading to N-H Creep) or along interfaces such as grain boundaries. In the latter case it is known as Coble creep. Both of these mechanisms result in a significant grain size dependence.
- **Solute Drag Creep.** For dislocations gliding at high T, not only do the solute atoms interact with the dislocations but they can also move sufficiently rapidly for the drag effect to be significant.
- **Dislocation Climb-Glide Creep.** In between the (low) temperatures at which only dislocation glide is important, and the (high) temperatures at which diffusion dominates (at low stresses), a combination of glide and climb controls creep. That is to say, dislocation motion carries most of the strain but the dislocations circumvent obstacles by climb.
- **Grain Boundary Sliding** accommodated by diffusional flow. In superplasticity especially, sliding of one grain relative to another is very important.
- **Grain Boundary Sliding** accommodated by Dislocation Flow. This is the same mechanism of g.b. sliding but the accommodation is achieved by dislocation glide. Clearly one expects this to dominate over diffusion at lower temperatures.
- **We focus on Coble and Nabarro-Herring Creep because these are the creep mechanisms that are sensitive to grain size (by contrast to dislocation creep).**
Deformation Mechanism Maps

Deformation maps provide a convenient graphical view of the different regimes of deformation behavior as a function of temperature and stress.

Note that the location of the various region boundaries depends on the grain size.

More sophisticated versions of these maps have contours of equal strain rate. In general, the boundaries shift to lower temperatures and stresses with decreasing strain rate.

Figure 7.15
Deformation mechanism maps for several metals (Al and W) and nonmetals (Ge and MgO), all with a grain size of 32 μm. Nonmetals are somewhat more resistant to dislocation glide than metals. The covalent solid, Ge, is quite resistant to both dislocation and diffusional creep. (From M. F. Ashby, “A First Report on Deformation Mechanism Maps,” Acta Metall., 20, 857, Copyright 1972, with permission from Elsevier Science.)
Grain Size and NH Creep

- Smaller grain sizes expand the range over which Nabarro-Herring (and Coble) creep are observed.
- Alternatively, the map can be drawn in the space of stress (normalized by modulus) and grain size (normalized by Burgers vector). In this map, the temperature is fixed.
- Recall the discussion of Orowan bowing stress to understand why normalizing stress by modulus is reasonable.
Creep Mechanisms: diffusion

• For the purposes of this lecture, we will consider just one creep mechanism: self-diffusion between grain boundaries (Nabarro-Herring Creep).

• Assumption: grain boundaries are perfect sources and sinks of vacancies.

• Therefore a tensile stress (for example) on a polycrystalline body sets up a driving force for vacancy motion because the stress biases the vacancy concentration to be higher where the tensile stress is higher.

[Courtney 7.5]
Nabarro-Herring Creep

- The creep mechanism involving diffusion to/from grain boundaries through the bulk lattice is known as Nabarro-Herring creep for the scientists who identified it.

- The reason for the grain size dependence is simple: the diffusion path length is proportional to the grain size:
  - since the vacancy concentration at the boundaries is fixed by the stress and the path length is proportional to the grain size, the concentration gradient is inversely proportional to the grain size.
  - the creep rate (i.e. the strain rate) is proportional to the vacancy flux and is thus inversely proportional to the grain size.
Nabarro-Herring Creep: grain size dependence

• The creep rate in Nabarro-Herring creep is inversely proportional to the square of the grain size.

• The quadratic dependence of creep rate on grain size arises from distributing the vacancy flux over the (average) area of a grain facet.

• Bottom line: small grain size lowers creep resistance, and large grain size increases creep resistance.

• Ideal microstructure (w.r.t. grain structure) is a single crystal.
**N-H Creep: derivation: 1**

- Difference in vacancy concentration, $N_v$, (which provides the driving force). The activation energies are modified from the unstressed values by

\[ \exp\{\pm \text{stress} \times \text{atomic volume}\} = \exp\{-\frac{\sigma \Omega}{kT}\}. \]

Compression decreases the concentration (slightly) and tension raises it.

\[ \begin{align*}
N_{\text{vacancy}}^{\text{tension}} & \approx \exp \left\{ -\frac{Q_{\text{vacancy}}}{kT} \right\} \exp \left(\frac{\sigma \Omega}{kT}\right) \\
N_{\text{vacancy}}^{\text{compression}} & \approx \exp \left\{ -\frac{Q_{\text{vacancy}}}{kT} \right\} \exp \left(-\frac{\sigma \Omega}{kT}\right)
\end{align*} \]

- Given small stresses (1-50 MPa) and high temperatures, $\Omega \sim 10^{-29} \text{m}^3$, $kT \sim 1.4 \times 10^{-20} \text{J}$, $\sigma \Omega / kT \sim 0.02 \ll 1$. This permits us to linearize the driving force.
N-H Creep: derivation: 2

- Given small stresses (1-50 MPa), $\Omega \sim 10^{-29} \text{m}^3$, $kT \sim 1.4 \cdot 10^{-20} \text{J}$, $\sigma \Omega / kT \sim 0.02 \ll 1$. This permits us to linearize the driving force.
  \[ \Delta N_V \sim \frac{\sigma \Omega}{kT} \exp\left\{-\frac{Q_{\text{vacancy}}}{kT}\right\}. \]

- The vacancy flux is given by Fick’s first law:
  \[ J_V = D_V \frac{dN_V}{dx} \]

- The distance over which the diffusion occurs is approximated by the grain diameter, $d$:
  \[ J_V = D_V \left( \frac{\sigma \Omega}{kT} \right) \exp\left\{-\frac{Q_{\text{vacancy}}}{kT}\right\} \left(\frac{1}{d}\right). \]
N-H Creep: derivation: 3

- If we multiply the flux by the area over which diffusion takes place, which we approximate by the area of a grain boundary facet, $d^2$, we obtain the rate of change of volume. We can also include the diffusion coefficient in the expression, where $Q_m$ is the activation energy for vacancy motion;

\[ D_V = D_{0V} \exp\left\{-\frac{Q_m}{kT}\right\}. \]

\[ \frac{dV}{dt} = J_V d^2 \]

\[ \frac{dV}{dt} = d^2 D_{0V} \exp\left\{-\frac{Q_m + Q_{Vacancy}}{kT}\right\} \left(\frac{\sigma \Omega}{kT}\right) \left(\frac{1}{d}\right). \]
N-H Creep: derivation: 4

- Rate of change in length = volume rate \((\delta V/\delta t)\) / area; area \(\sim d^2\).

\[
\frac{\delta d}{\delta t} = D_0 V \exp\left\{-\frac{Q_m + Q_{\text{vacancy}}}{kT}\right\} \left(\frac{\sigma \Omega}{kT}\right) \left(\frac{1}{d}\right).
\]

- Strain = Change in length / length = \(\delta d/d\).
  therefore, the strain rate is the rate of change of strain:

\[
\frac{d\varepsilon}{dt} = D_0 V \exp\left\{-\frac{Q_m + Q_{\text{vacancy}}}{kT}\right\} \left(\frac{\sigma \Omega}{kT}\right) \left(\frac{1}{d^2}\right).
\]

- Collecting terms:

\[
\dot{\varepsilon} = A_{NH} \left(\frac{D_{\text{bulk}}}{d^2}\right) \left(\frac{\sigma \Omega}{kT}\right)
\]

Note the grain size dependence!
Experimental Evidence

The effect of grain size on the minimum creep rate for a series of Ni-based alloys tested at 800 °C. Based on: V. LUPINC and T. B. GIBBONS, "High Temperature Alloys for Gas Turbines", ed. Coutsouradis et al. (Applied Science, 1978) p. 335. Caution: the data shows that there is an optimum grain size for minimizing the creep rate (hinted at in this graph).
Diffusion

• *Creep* is therefore a phenomenon associated with *high temperatures*.
• High temperature is a relative term: one contribution that thermal activation makes is by increasing diffusion rates.
• Diffusion coefficients ($D = D_0 \exp\{-Q/RT\}$) are strongly (exponentially!) dependent on temperature.
• The activation energy (enthalpy, strictly speaking) is approximately proportional to the melting point of the material.
• At the same temperature, a higher melting point material will exhibit slower diffusion than a lower melting point material.
Diffusivity, Activation Energy

Porter & Easterling: diffusivity at the melting point is constant for a given class of material.

Similarly, the activation energy normalized by $RT_m$ is constant for a given class of material.

Fig. 2.13 (a) Melting point diffusivities and (b) normalised activation energies for various classes of materials. (After A.M. Brown and M.F. Ashby, *Acta Metallurgica* 28 (1980) 1085.)
Summary

- Grain size is a critically important aspect of polycrystalline materials.
- In the case of the Hall-Petch effect, in most materials, both the strength and the toughness increase as the grain size is reduced. This effect can be explained by the resistance of the boundaries to plastic flow (in the case of strength) and/or the decreased microcrack size in the case of fracture.
- Grain size can play a major role in controlling creep resistance. Grain size has the opposite effect at high temperatures than at ambient conditions. Larger grain size increases creep resistance - hence the use of single crystals where feasible, especially for superalloys.