Advanced Mechanical Properties and Deformation Mechanisms of Bulk Nanostructured Materials

Dr. Khayati

Imperfections or Crystalline defect:

Is generally used to describe any deviation from an orderly array of lattice pointes.

Point defects:

Vacancies, Interstitial atoms (C,H,O,N), and Substitutional atoms (Other alloying element)

Introduce compressive or tensile strain fields that disturb the atomic arrangements in the surrounding crystal.

Line defect:

Dislocation: Edge dislocation & Screw dislocation

Surface defect:

Grain boundaries, Low angle and High angle grain boundary, staking fault, surface of materials
Point Defects

VACANCIES AND SELF-INTERSTITIALS

Vacancy

One normally occupied from which an atom is missing

It is **not possible** to create such a material that is free of these defects.
Point Defects

Vacancy

The equilibrium number of vacancies for a given quantity of material depends on temperature and increases with temperature according to:

\[ N_v = N \exp \left( -\frac{Q_v}{kT} \right) \]

- **N**: The total number of atomic sites,
- **Q_v**: The energy required for the formation of a vacancy,
- **T**: The absolute temperature in kelvins,
- **k**: The gas or Boltzmann’s constant (1.38 \( 10^{-23} \) J/atom-K, 8.31 J/mol K, 1.98 cal/mol.K)

For most metals, the fraction of vacancies (\( N_v/N \)) just below the melting temperature is on the order of \( 10^{-4} \)!
Point Defects

Self-interstitial

An atom from the crystal that is crowded into an interstitial site, a small void space that under ordinary circumstances is not occupied.

Relatively large distortions in the surrounding lattice because:

- The atom is substantially larger than the interstitial position in which it is situated.
- The formation of this defect is not highly probable.
- It exists in very small concentrations, which are significantly lower than for vacancies.
For interstitial solid solutions, impurity atoms fill the voids or interstices among the host atoms.

- The atomic diameter of an interstitial impurity must be substantially smaller than that of the host atoms.

- Normally, the maximum allowable concentration of interstitial impurity atoms is low (less than 10%).

- Even very small impurity atoms are ordinarily larger than the interstitial sites, and as a consequence they introduce some lattice strains on the adjacent host atoms.

Example

Carbon forms an interstitial solid solution when added to iron; the maximum concentration of carbon is about 2%. 

$C, H, N, O$
Compressive or tensile strain fields on the vicinity of point defects

Regions of compression
Regions of tension
Regions of compression
Regions of tension

vacancy (a)
Interstitial atom (b)
Small substitutional atom (c)
Large substitution atom (d)
LINEAR DEFECTS

DISLOCATIONS

A linear or one-dimensional defect around which some of the atoms are misaligned.

**Edge dislocation**

The magnitude of this distortion decreases with distance away from the dislocation line; at positions far removed, the crystal lattice is virtually perfect.
A Burgers vector $b$ is required to close a loop of equal atom spacing's around the edge dislocation.
LINEAR DEFECTS

Screw dislocation

Exists, which may be thought of as being formed by a shear stress that is applied to produce the distortion.

The atomic distortion associated with a screw dislocation is also linear and along a dislocation line, line ab.
A Burgers vector $\mathbf{b}$ is required to close a loop of equal atom spacing around the screw dislocation.
LINEAR DEFECTS

Mixed dislocation

Have both edge and screw components, with a transition region between them. The Burgers vector, however, remains the same for all portions of the mixed dislocation.

The lattice distortion that is produced away from the two faces is mixed, having varying degrees of screw and edge character.

!Neither pure edge nor pure screw!
LINEAR DEFECTS

Burgers vector

The magnitude and direction of the lattice distortion associated with a dislocation is expressed in terms of a Burgers vector.

For a screw, Burgers vector perpendicular to the dislocation line are parallel

Whereas

For an edge, Burgers vector are perpendicular to the dislocation line.
Burgers vector

All positions of the curved dislocation in this figure will have the Burgers vector shown.

Where is the position of Burgers vector in crystal?
LINEAR DEFECTS

The Burgers vector and the plane are helpful in explaining how materials deform.

Schematic of slip line, slip plane, and slip vector, Burgers vector
The speed with which dislocations move in materials is close to or greater than the speed of sound!
LINEAR DEFECTS

Slip: A dislocation motion and causes a metallic material to deform: Plastic deformation.

**Edge dislocation**

- Direction of motion $\parallel$ Burgers vector;
- The slip direction $\perp$ Dislocation line;
- Burgers vector $\parallel$ Dislocation line;
- The dislocation line motion $\parallel$ the direction of $\mathbf{T}$;

**Screw dislocation**

- Direction of motion $\perp$ Burgers vector;
- The slip direction $\parallel$ Dislocation line;
- Burgers vector $\parallel$ Dislocation line;
- The dislocation line motion $\parallel$ the direction of $\mathbf{T}$;
Bulk nanostructured (NS) materials

Bulk NS materials are single or multi-phase polycrystals with nanoscale grain size and usually can be classified into nanocrystalline (NC, < 100 nm) and ultrafine grain (UFG, < 1000 nm) materials.

As we know, the grain size of conventional structural polycrystalline materials typically falls in what is widely described as the coarse grained (CG) regime (≥1μ m) which may include the fine grained sub-regime (1-10μ m). By extending the grain size down to the nanometer regime, NS materials provide us, not only with an excellent opportunity to study fundamental structure-property relationships and deformation mechanisms in polycrystalline materials, but also present us with an attractive potential for technological applications with their novel properties.
Bulk nanostructured (NS) materials

Due to the small grain size, bulk NS materials are structurally characterized by a large volume fraction of grain boundaries (GBs, 50% for 5 nm grains, 30% for 10 nm grains), which may significantly alter their physical, mechanical, and chemical properties in comparison with conventional CG materials.

For instance, with the validity of extending the Hall-Petch relationship down to at least a small threshold grain size value of about 10-20 nm, the strength of UFG materials is typically 5-10 times that of conventional CG material of similar composition, and thus offers interesting possibilities related to structural applications.
Hall-Petch relationship

- By **reducing the grain size**, we increase the number of grains and, hence, increase the amount of grain boundary area.
- Dislocation moves only a short distance before encountering a grain boundary and being stopped, and the strength of the metallic material is increased.

\[
\sigma_y = \sigma_0 + Kd^{-1/2}
\]

Where \(d\) is the average diameter of the grains, and \(\sigma_0\) and \(K\) are constants for the metal, \(\sigma_y\): yield strength.
Bulk nanostructured (NS) materials

Fig. 1 Grain size regimes of nanocrystalline, fine grained, ultrafine grained and coarse grained materials.

[Diagram showing grain size regimes]
Syntheses

Bulk NS materials usually can be synthesized via a variety of techniques which can generally grouped into two broad categories:

“two-step” approach, in which individual nano particles, agglomerates or clusters is first produced (by inert-gas condensation, mechanical attrition, etc.) and then consolidated using cold/hot isostatic pressing (CIP/HIP), quasi-isostatic Ceracon forging and spark plasma sintering (SPS),
or a “one-step” approach such as electrodeposition and severe plastic deformation ( SPD).

Despite encouraging results it is evident that bulk NS materials produced by the “two-step” approach frequently have extraneous defects, such as porosity, insufficient bonding and impurities.

SPD refines grains of CG materials to produce nanostructures.
Hot isostatic pressing (HIP) Process

- HIP = high-temperature pressing (hot consolidation) of encapsulated powders or sintered high-density (density >92% of theoretical) compacts.
- Pressure: 100...300 MPa
- Time: 2...6 hours
- HIP-low strain rate process because stress rise in slow
Hot isostatic pressing (HIP)

Preparative steps of HIP:

1. Encapsulation:
   - container production
   - leak testing
   - filling

2. Degassing (evacuation of absorbed gases and moisture) and crimping of the can
Typical HIP cycles

I HIP in unit with internal heating zone

II HIP of externally heated encapsulated part

Examples of two typical HIP cycles
Hot isostatic pressing (HIP)

A cross section view of the HIP vessel
Hot isostatic pressing (HIP)

Recent developments of HIP equipment:

1. Increased Cooling HIP systems (providing productivity and decrease in cost)

2. Ultra High Pressure and Temperature Systems
   - Pressures up to 1000 MPa
   - Temperatures up to 3000°C

3. Duplex systems for HIP, WIP, CIP (hot isostatic pressing, warm isostatic pressing, cold isostatic pressing)
**Advantages of HIP:**

1. **Materials/products of higher performance**

2. **Cost savings because of**
   - Lower lifecycle cost (of higher performance materials)
   - The HIP near-net shape process
   - Lower unit costs of large parts and production volumes of small-weight parts
Disadvantages of HIP:

- Little shear on the particle surfaces (because of consolidation by hydrostatic stress). Therefore:

  1) It is necessary (in some applications) to subject HIP-compact to post-consolidation deformation or

  2) The microstructural defects can be minimized by use of powders atomized with rapid solidification rate and clean handling in inert gas
Hot isostatic pressing (HIP)
Mechanism of consolidation

- Full density is achieved more easily under the conditions of higher packing density.
- Packing density of commercial spherical powders vary from 0.62...0.72.
- Mostly pre-alloyed powders are used.

<table>
<thead>
<tr>
<th>Type of Packing</th>
<th>Diagram</th>
<th>Comments</th>
<th>Number of Contact Points</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubical</td>
<td><img src="chart.png" alt="Cubical Diagram" /></td>
<td>Second layer placed directly over first</td>
<td>6</td>
<td>48</td>
</tr>
<tr>
<td>Single Stagger</td>
<td><img src="chart.png" alt="Single Stagger Diagram" /></td>
<td>Second layer placed directly over first</td>
<td>8</td>
<td>40</td>
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<tr>
<td>Double Stagger</td>
<td><img src="chart.png" alt="Double Stagger Diagram" /></td>
<td></td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>Pyramidal</td>
<td><img src="chart.png" alt="Pyramidal Diagram" /></td>
<td>Equivalent to ocp in crystallography</td>
<td>12</td>
<td>26</td>
</tr>
<tr>
<td>Tetrahedral</td>
<td><img src="chart.png" alt="Tetrahedral Diagram" /></td>
<td>Equivalent to hcp in crystallography</td>
<td>12</td>
<td>26</td>
</tr>
</tbody>
</table>

Five examples of ordered packing arrangements of mono-sized spheres and their resulting pore volumes. Courtesy of Adam Hilger, Hot Isostatic Pressing.
Two models of the HIP process

1. **Microscopic model**: calculates density as a function of the process variables: time, pressure, temperature, initial packing density, material properties. Model predicts density.

2. **Macroscopic model**: shape change under pressure is analyzed utilizing plastic theory of porous metals. Macroscopic models are tools to predict the size and shape change (important in production of net-shape parts).
Hot isostatic pressing (HIP)

Microscopic model: three stages of consolidation process

0) stage of packing density
1) stage of connected porosity
2) stage of closed porosity

Powder packed in a container which will be exposed to high pressure and temperature.

Three stages of the consolidation process
**Microscopic model:**

- HIP maps (density vs temperature maps) at constant pressure and initial packing density
- Two mechanisms of HIP densification:
  1. Plastic yielding
  2. Power-law creep (the dominant mechanism of densification)
Hot isostatic pressing (HIP)

Macroscopic model:

A comparison of the predicted shape change for axisymmetric product to the actual shape change after HIP
Hot isostatic pressing (HIP)

Other application fields:

1. P/M tool steels:
   - High speed steels
   - Cold work tool steels (0.8...3.9% C)
   - Wear and corrosion resistant steels (1.7...3.7% C)
   - HIP/clad products (see section 7.10)

2. Ni-base superalloys

3. Corrosion resistant Ni- and Fe-based alloys

4. Titanium and titanium aluminide

5. Metal matrix composites - MMC

6. Hardmetals and cermets etc.
Quasi-isostatic Ceracon forging
Plasma activated sintering (PAS);
field activated sintering technique (FAST),
spark-plasma sintering.

Plasma activated sintering = pressure-assisted sintering activated by electrical discharges between powder particles
Plasma activated sintering (PAS)

Time-temperature-pressure cycle for the PAS-process:

1) Application of pressure

2) Initiation of pulsed discharges resulting in formation of pulse plasma between particles (to activate powder surface)

3) Resistance heating (for densification)

4) Lowering of pressure and temperature
Plasma activated sintering (PAS)

Technological parameters:

- Pressure: 10-65 MPa
- Total time: <10 minutes
- Pulse on-state duration: 30...60 sek

Application:

- ceramic materials
- metallic materials
- ceramic-metallic composites (hardmetals, cermets) etc.
Two of the mostly used SPD techniques are;

Equal-channel angular pressing (ECAP) \hspace{1cm} \text{High pressure torsion (HPT)}.

Since the first pioneering works in the 90th demonstrated the capability of SPD to produce bulk NS billets, there has been a rapidly growing interest in investigation and applications of this innovative technique because of several advantages:

- Potential industrial realization,
- 100% dense with artifacts free,
- Contamination-free,
- Large enough for practical structural parts.
Deformation Mechanisms

When the grain size falls in the nanometer regime (say < 10 nm), a transition of the dominant deformation mechanisms from the usual dislocation-mediated plasticity to grain boundary-mediated processes takes place which corresponds to a transition in the slope of Hall-Petch relationship.

The deformation mechanisms of a face centered cubic polycrystals with medium and high stacking fault energy as a function of grain size.
Surface Defects

Stacking Faults (Deformation fault in FCC)

The formation of a stacking fault in an FCC metal is equivalent to the formation of a thin HCP region.

Stacking faults interfere with the slip process.
Surface Defects

**Stacking Faults** *(Deformation fault in HCP)*

A stacking fault in an HCP metal is equivalent to the formation of a thin FCC region.

**Stacking Faults** *(Deformation fault in BCC)*

It is more difficult to form stacking faults in a bcc lattice than in the close packed FCC and HCP structures.

**Comparison the staking fault between FCC, HCP &BCC**

Stacking faults occur most readily in fcc metals,
Surface Defects

Stacking faults occur most readily in FCC metals

A stacking fault in an FCC metal can be considered to be an extended dislocation consisting of a thin hexagonal region bounded by partial dislocations.

The nearly parallel dislocations tend to repel each other.

The surface tension of the stacking fault pulling them together.

Cross slip is more difficult in metals with wide stacking fault ribbons.
It is well established that solid solution alloying favors twinning in fcc and bcc metals.
Stacking faults are found in FCC metals when there is an interruption in the ABCABCABC \ldots stacking sequence of close-packed planes.
The greater the width of the stacking fault (SF)

Or

The lower the stacking fault energy (SFE)

SF $\uparrow$ SFE $\downarrow$ Cross slip $\downarrow$ $n$ (work hardening exponent) $\uparrow$
Cross-Slip

The process whereby a screw dislocation glides into another slip plane having a slip direction in common with the original slip plane.

Cross-slip is possible in both FCC and BCC metals because a number of intersecting slip systems are present. Consequently, cross-slip helps maintain ductility in these metals.

In many HCP $c/a=1.633$ metals, no cross-slip can occur because the slip planes are parallel (i.e., not intersecting). Therefore, polycrystalline HCP metals tend to be brittle. Fortunately, additional slip systems become active when HCP metals are alloyed or heated, thus improving ductility.
Planar slip

When the dislocations tend to stay in planar array with a difficult cross slip, low stacking fault energy, the presence of coherent precipitate, low temperature and small strain.

Wavy slip

When the dislocation are uniformly distributed in that matrix, cross slip is easy, high stacking fault energy, incoherent precipitate, large strain and at temperature greater than 0.4 Tm.
By alloying or heating to elevated temperatures, additional slip systems are active in HCP metals, permitting cross-slip to occur and thereby improving ductility.
Influence of Crystal Structure

<table>
<thead>
<tr>
<th>Structure and material</th>
<th>Slip plane</th>
<th>Slip direction</th>
<th>Number of slip systems</th>
<th>$\tau_{CRSS}$ (MPa)</th>
<th>Slip geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCC</td>
<td>{111}</td>
<td>(110)</td>
<td>{4} $\times$ (3) = 12</td>
<td>0.58</td>
<td></td>
</tr>
<tr>
<td>Ag (99.99%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu (99.999%)</td>
<td></td>
<td></td>
<td></td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>Ni (99.8%)</td>
<td></td>
<td></td>
<td></td>
<td>5.7</td>
<td></td>
</tr>
<tr>
<td>Diamond cubic Si, Ge</td>
<td>{111}</td>
<td>(110)</td>
<td>{4} $\times$ (3) = 12</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A closed thompson tetrahedron

An opened out Thompson tetrahedron
Slip takes place on the \{101\bar{0}\} prism planes at room temperature and on the \{101\bar{1}\} pyramidal planes at higher temperatures.
Significance of Dislocations

Plastic deformation: A result of dislocation motion;

Elastic deformation: A result of stretching of interatomic bonds;

1. Slip explains why the strength of metals is much lower than the value predicted from the metallic bond.

2. Slip provides ductility in metals. If no dislocations were present, an iron bar would be brittle and the metal could not be shaped by metalworking processes, such as forging, into useful shapes.

3. We control the mechanical properties of a metal or alloy by interfering with the movement of dislocations.

4. Dislocation densities of $E6 \text{ cm/cm}^3$ are typical of the softest metals, while densities up to $E12 \text{ cm/cm}^3$ can be achieved by deforming the material.

Amorphous materials such as silicate glasses do not have a periodic arrangement of ions and hence do not contain dislocations.
Deformation Mechanisms

The grain boundary-mediated processes include grain boundary sliding, migration and grain rotation. The macroscopic plastic deformation capability of nanocrystalline materials with grain boundary-mediated processes is usually very limited under conventional deformation conditions, unless under some specific conditions such as:

- Dynamic loading,
- Miniature sample geometries,
- Deformed at elevated temperature which promote the activation of boundary process.
In contrast, when the grain size falls in the micrometer regime (>1μm), intragranular dislocation activity plays a dominant role in plastic deformation. Micrometer sized grains generally provide sufficient space for dislocation activity, such as nucleation, dislocation tangling, cutting and propagation and as a consequence, the associated strain hardening results in a high tensile ductility. When the grain size is smaller than 1μm and larger than about 10 nm, GBs act as both dislocation sources and sinks, and they lead to the absorption of dislocations by grain boundaries as soon as the dislocations are emitted from the opposite boundaries.
Since very few dislocations can accumulate within ultrafine grains, the resultant strain hardening is very low, resulting in limited tensile ductility.

In related studies, it was experimentally shown that, under the right conditions, such as at a very low strain rate of 10^-5 s^-1 or elevated temperatures, GB sliding can be activated in UFG materials with a mean grain size larger than 100 nm.
Deformation Mechanisms

However, under normal deformation conditions, grain boundary sliding is limited and hence does not contribute to the poor ductility of UFG materials.

When the grain size is smaller than about 50 nm, deformation twinning has been frequently reported even in materials with medium to high stacking fault energies such as Cu and Ni, and this was led to the suggestion that twinning is a major plastic deformation mechanism in UFG materials.

Systematic high resolution transmission electron microscopy studies revealed that the deformation twinning in UFG materials was formed by the emission of Shockley partial dislocations from GB.

A more recent study indicates that further decreasing the grain size of UFG materials actually impedes twinning (i.e., inverse grain size effect), which was explained using generalized planar fault energies and grain-size effects on the emission of partial dislocations.
Dislocations in the FCC (Glissile dislocation)

Slip by this two-stage process creates a stacking fault ABCA’CABC in the stacking sequence.

Shockley Partialss
Glissile

A part of the crystal which has undergone slip intermediate between full slip and no slip.
Dislocations in the FCC (Glissile dislocation)

- The surface tension of the stacking fault tends to pull them together.
- The partial dislocations will settle at an equilibrium separation determined primarily by the energy per unit area of the fault.

\[
F = \frac{G b_2 b_3 \cos 60}{2\pi d} = \gamma \implies d = \left( \frac{G b_2 b_3 \cos 60}{2\pi \gamma} \right) = \left( \frac{G a}{\sqrt{6}} \frac{a}{\sqrt{6}} \frac{1}{2} \right) = \frac{Ga^2}{24\pi\gamma}
\]

\( \gamma : \text{J/m}^2 \) is the energy per unit area of the fault
Mechanical Properties

In the case of structural materials, strength, ductility, fracture and creep under static loading, deformation and properties under dynamic impact and cyclic loading are some of the most important mechanical properties.

A structure must support load, thus mechanical strength is an obvious requirement and quite often it is among the most important criteria of any materials selection decision.

In addition, good ductility is essential to avoid catastrophic failure in load-bearing applications and for many shaping and forming operations without tearing or fracturing. The dynamic behavior of materials is important in oil and gas industry and demolition as well as military. Moreover, dynamic deformation of materials is one of the seminal aspects in studying and improving the crashworthiness of transportation systems. The structural materials are often supporting cyclic load which makes it important to investigate the fatigue behavior. Obviously, these mechanical properties of bulk NS materials should be known before their industrial applications.
Ductility

The ductility of materials is usually defined as the extent to which a material can be deformed plastically. Usually, ductility is measured in uniaxial tension. It is desirable that structural materials have both high strength and high ductility. However, the strength and ductility usually are trade-off with each other, i.e. increasing the strength sacrifices the ductility, and elevating the ductility typically lowers the strength. This strength-ductility dilemma also applies to CG and NS/UFG metals and alloys: the former have good ductility but low strength, while the latter have high strength but low ductility.