

IMPERFECTIONS IN SOLIDS

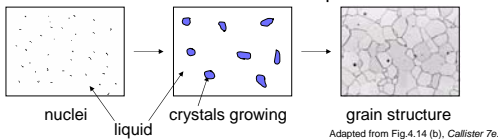
- What are the solidification mechanisms?
- What types of defects arise in solids?
- Can the number and type of defects be varied and controlled?
- How do defects affect material properties?
- Are defects undesirable?

Defects in crystals

- No crystal of significant size is perfect
 - Most crystals contain defects
 - » Point defects – missing atoms, substituted atoms, displaced atoms etc.
 - » Line defects – dislocations
 - » Planar defects – Stacking faults, twins, Crystallographic shear planes

Imperfections in Solids

- **Solidification**- result of casting of molten material
 - 2 steps:
 - Nuclei form
 - Nuclei grow to form crystals that grow into each other – grain structure
- Start with a molten material – all liquid

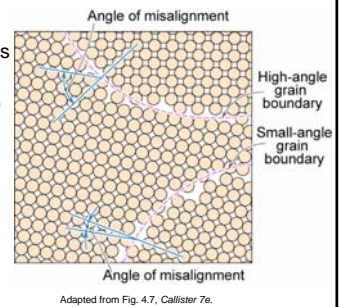


- Crystals grow until they meet each other

Polycrystalline Materials

Grain Boundaries

- regions between crystals
- transition from lattice of one region to that of the other
- slightly disordered
- low density in grain boundaries
 - high mobility
 - high diffusivity
 - high chemical reactivity

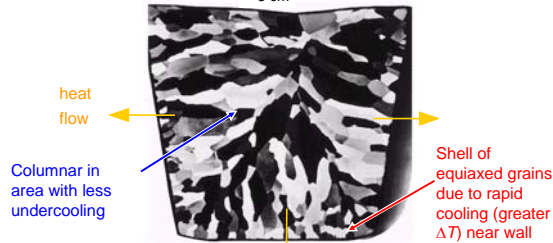


Solidification

Grains can be - equiaxed (roughly same size in all directions)

- columnar (elongated grains)

~ 8 cm



Grain Refiner - added to make smaller, more uniform, equiaxed grains.

Imperfections in Solids

All macroscopic crystals are non-perfect and have defects.

- What are these imperfections?
- Why are they important?

Many of the important properties of materials are due to the presence of imperfections.

3 Classes of Imperfections

- Vacancy atoms
- Interstitial atoms
- Substitutional atoms

Point defects

- Dislocations

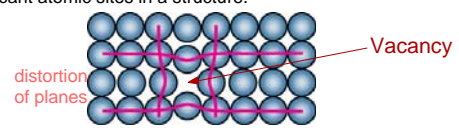
Line defects

- Grain Boundaries

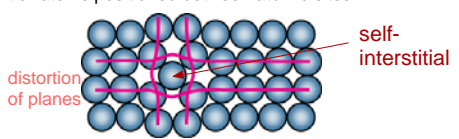
Area or Planar defects

Point Defects

- **Vacancies:**
-vacant atomic sites in a structure.

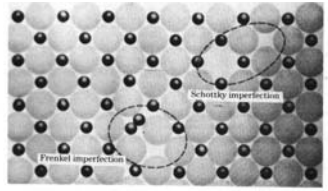


- **Self-Interstitials:**
-"extra" atoms positioned between atomic sites.



Types of point defects in solids

Defects are of paramount importance for the diffusion of ions and atoms in solids



Schottky defect: vacancy, missing ions moved to the surface (can be cations or anions)

Frenkel defect: vacancy, missing ions on interstitial positions (cations only)

Importance of point defects for solid properties

defects are **centers of reactivity**

defects can show either **self diffusion in a concentration gradient** or **diffusion under an external electric field (ionic conductivity)**

defects are responsible for **mass transport (diffusion)**

Fick's 1st law: mass transport J for a given point in a solid in the presence of a concentration gradient $\delta c/\delta x$

$$J = -D \cdot \delta c/\delta x \quad [\text{mol cm}^{-2} \text{ s}^{-1}]$$

J: mass transport; D: diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$)
 $\delta c/\delta x$: concentration gradient (change of concentration along a line in the solid)

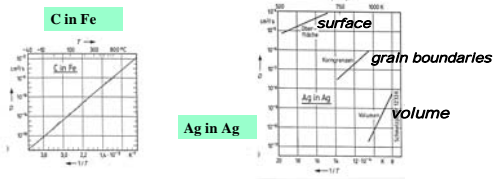
Temp. Dependence Of Diffusion Coefficient

Diffusion coefficients show an exponential temperature dependence (Arrhenius type):

$$D = D_0 \cdot e^{-Q/kT}$$

D_0 : D for $T \rightarrow \infty$,
 Q: activation energy of diffusion,
 k: Boltzmann factor

The logarithmic representation of $\lg D$ versus $1/T$ is linear, the slope corresponds to the activation energy and the intercept to D_0 .



Occurrence/Properties of Point Defects in Crystals

Alkali halides	Schottky (cations and anions)
Alkaline earth oxides	Schottky (cations and anions)
Silver halides	Frenkel (cations)
Alkaline earth fluorides	Frenkel (anions)

Typical activation energies for ion diffusion

Na ⁺ in NaCl	~ 0,7 eV
Cl ⁻ in NaCl	~ 1 eV
Schottky pair	~ 2,3 eV

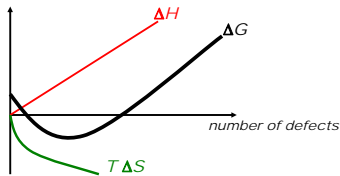
(1 eV/molecule = 96.49 kJ/mol)

Elementary Thermodynamics Of Defects

due to thermodynamic reasons defects are always present in a real crystal, up to a certain (low!) concentration the presence of defects give a reduction of the free enthalpy (ΔG) !!!

$$\Delta G = \Delta H - T \Delta S \quad (\Delta G \text{ neg.} \rightarrow \text{spontaneous formation})$$

ΔG : Free enthalpy of a crystal ; ΔH : enthalpy to create a defect
 ΔS : increase of entropy upon formation of a defect
 T: absolute temperature



Equilibrium Concentration: Point Defects

- Equilibrium concentration varies with temperature!

No. of defects $\rightarrow N_s = \exp\left(\frac{-Q_v}{kT}\right)$

No. of potential defect sites. $\rightarrow N$

Activation energy Q_v

Boltzmann's constant k

Temperature T

$(1.38 \times 10^{-23} \text{ J/atom-K})$
 $(8.62 \times 10^{-5} \text{ eV/atom-K})$

Each lattice site is a potential vacancy site

Elementary Thermodynamics Of Defects

Number of defects under equilibrium conditions:

$$\frac{N_s}{N} = \exp\left(\frac{-W}{kT}\right)$$

n_s : number of defects; N : number of lattice positions
 W: energy difference of defect vs. no defect
 k: Boltzmann constant; T : absolute temperature

some typical numbers for NaCl ($W = 188 \text{ kJ/mol}$):

T (K)	n_s/N	n_s/cm^3
0	-	-
298	3.1×10^{-17}	5×10^5
1073	2.5×10^{-5}	4×10^{17}

$\sim 1.6 \times 10^{22}$ ion pairs per cm^3 : one of 25,000 atomic positions is empty at 1073 K

Estimating Vacancy Concentration

- Find the equil. # of vacancies in 1 m^3 of Cu at 1273°C .

$$\rho = 8.4 \text{ g/cm}^3 \quad A_{\text{Cu}} = 63.5 \text{ g/mol}$$

$$Q_v = 0.9 \text{ eV/atom} \quad N_A = 6.02 \times 10^{23} \text{ atoms/mol}$$

$$\frac{N_s}{N} = \exp\left(\frac{-W}{kT}\right) = 2.7 \times 10^{-4}$$

$$\text{For } 1 \text{ m}^3, N = \rho \times \frac{N_A}{A_{\text{Cu}}} \times 1 \text{ m}^3 = 8.0 \times 10^{28} \text{ sites}$$

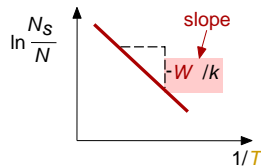
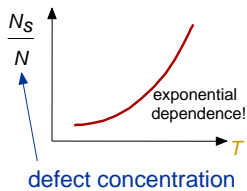
- Answer:

$$N_s = (2.7 \times 10^{-4})(8.0 \times 10^{28}) \text{ sites} = 2.2 \times 10^{25} \text{ vacancies}$$

Measuring Defect Energy

- We can measure W experimentally:

$$\frac{N_s}{N} = \exp\left(\frac{-W}{kT}\right)$$

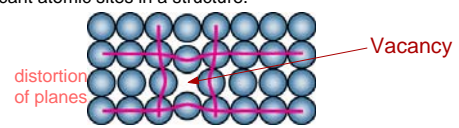


3 Classes of Imperfections

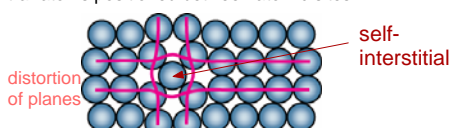
<ul style="list-style-type: none"> • Vacancy atoms • Interstitial atoms • Substitutional atoms 	Point defects
<ul style="list-style-type: none"> • Dislocations 	Line defects
<ul style="list-style-type: none"> • Grain Boundaries 	Area or Planar defects

Point Defects

- **Vacancies:**
-vacant atomic sites in a structure.

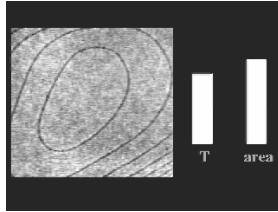


- **Self-Interstitials:**
-"extra" atoms positioned between atomic sites.

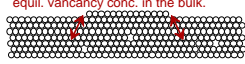


Observing Equilibrium Vacancy Conc.

- Low energy electron microscope view of a (110) surface of NiAl.
- Increasing T causes surface island of atoms to grow.
- Why? The equil. vacancy conc. increases via atom motion from the crystal to the surface, where they join the island.

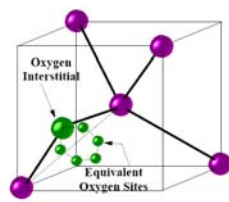


Island grows/shrinks to maintain equil. vacancy conc. in the bulk.



Interstitial Impurities

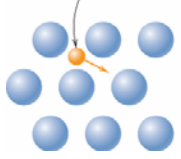
Atoms not residing on lattice sites are called interstitials. They can be foreign, unwanted impurities, intentionally introduced impurities, or "misplaced" host atoms. Dopant atoms diffuse through the semiconductor faster as interstitials, but we need to place them in substitutional sites to make use of them.



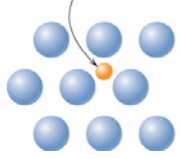
Diffusion Mechanisms

- **Interstitial diffusion** – smaller atoms can diffuse between atoms.

Position of interstitial atom before diffusion



Position of interstitial atom after diffusion




More rapid than vacancy diffusion

Point Defects in Alloys

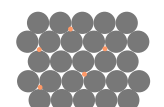
Two outcomes if impurity (B) added to host (A):

- **Solid solution of B in A** (i.e., random dist. of point defects)

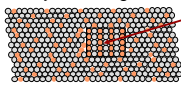


Substitutional solid soln.
(e.g., Cu in Ni)

OR



Interstitial solid soln.
(e.g., C in Fe)
- **Solid solution of B in A plus particles of a new phase** (usually for a larger amount of B)



Second phase particle
 --different **composition**
 --often different **structure**.

Imperfections in Solids

Conditions for substitutional solid solution (S.S.)

- Hume – Rothery rule

1. Δr (atomic radius) < 15%
2. Proximity in periodic table
i.e., similar electronegativities
3. Same crystal structure for pure metals
4. Valency
 - All else being equal, a metal will have a greater tendency to dissolve a metal of higher valency than one of lower valency

Imperfections in Solids

Application of Hume–Rothery rules – Solid Solutions

1. Would you predict more Al or Ag to dissolve in Zn?
2. More Zn or Al in Cu?

Element	Atomic Radius (nm)	Crystal Structure	Electro-negativity	Valence
Cu	0.1278	FCC	1.9	+2
C	0.071			
H	0.046			
O	0.060			
Ag	0.1445	FCC	1.9	+1
Al	0.1431	FCC	1.5	+3
Co	0.1253	HCP	1.8	+2
Cr	0.1249	BCC	1.6	+3
Fe	0.1241	BCC	1.8	+2
Ni	0.1246	FCC	1.8	+2
Pd	0.1376	FCC	2.2	+2
Zn	0.1332	HCP	1.6	+2

Table on p. 106, Callister 7e.

Imperfections in Solids

- Specification of composition

weight percent $C_1 = \frac{m_1}{m_1 + m_2} \times 100$

m_i = mass of component 1

atom percent $C_1 = \frac{n_{m1}}{n_{m1} + n_{m2}} \times 100$

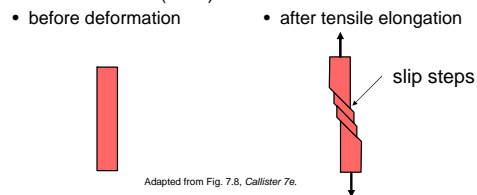
n_{m1} = number of moles of component 1

Line Defects

Dislocations:

- are line defects,
- slip between crystal planes result when dislocations move,
- produce permanent (plastic) deformation.

Schematic of Zinc (HCP):



Line Defects

A missing line or additional line of atoms is called a dislocation. Dislocations are either pure edge, pure screw or a combination of both type called mixed character.

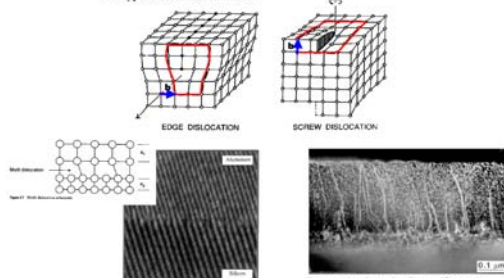


Figure 7.4 A TEM micrograph of the dislocations of Fig. 7.3. The dislocations are the (111) planes of aluminum edge dislocations and the (111) planes of the silicon substrate.

The term, "threading", describes specific cases in which the dislocation "breaks" through a growth layer (i.e. starts at or near the substrate and ends on the surface).

Imperfections in Solids

Linear Defects (Dislocations)

Are one-dimensional defects around which atoms are misaligned

- **Edge dislocation:**
extra half-plane of atoms inserted in a crystal structure
 $\mathbf{b} \perp$ to dislocation line
- **Screw dislocation:**
spiral planar ramp resulting from shear deformation
 $\mathbf{b} \parallel$ to dislocation line

Burger's vector, \mathbf{b} : measure of lattice distortion

Imperfections in Solids

Edge Dislocation

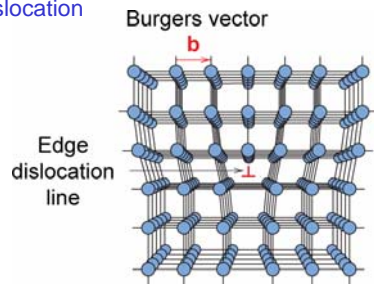
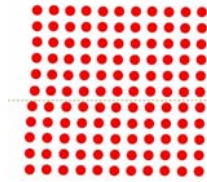


Fig. 4.3, Callister 7e.

Motion of Edge Dislocation

- Dislocation motion requires the successive bumping of a half plane of atoms (from left to right here).
- Bonds across the slipping planes are broken and remade in succession.

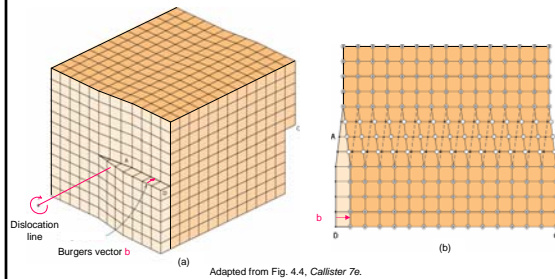


Atomic view of edge dislocation motion from left to right as a crystal is sheared.

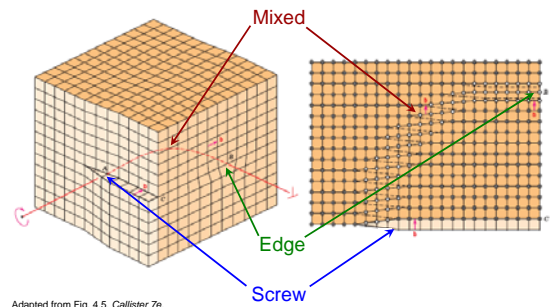
(Courtesy P.M. Anderson)

Imperfections in Solids

Screw Dislocation



Edge, Screw, and Mixed Dislocations



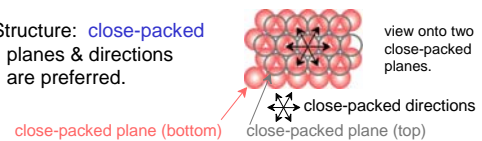
Imperfections in Solids

Dislocations are visible in electron micrographs



Dislocations & Crystal Structures

- Structure: **close-packed** planes & directions are preferred.

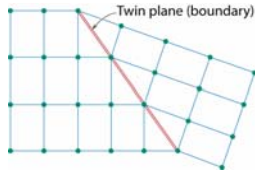


- Comparison among crystal structures:
 FCC: many close-packed planes/directions (ductile)
 HCP: only one plane, 3 directions
 BCC: none (hard but brittle)



Planar Defects in Solids

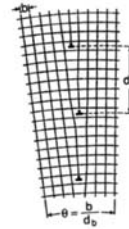
- One case is a **twin or grain boundary (plane)**
Essentially a reflection of atom positions across the **twin plane**.



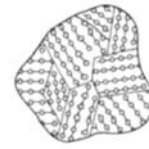
- Stacking faults**
For FCC metals an error in ABCABC packing sequence
Ex: ABCABABC

Planar Defects in Solids: Grain Boundary

A **grain boundary** is an array of dislocations that line up to form a plane that forms a boundary between two crystalline regions (grains) that are misoriented relative to one another.



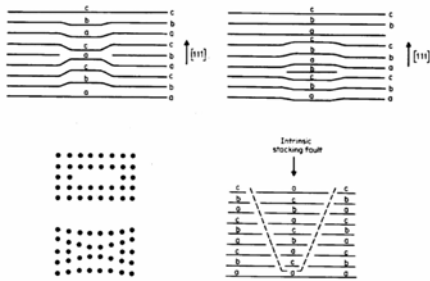
Low Angle Grain Boundary



High Angle Grain Boundaries

Planar Defects in Solids: Stacking Fault

A **stacking fault** is a disruption in the stacking of layers in the crystal.



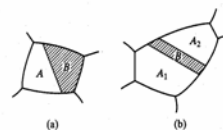
Twins

- Sometimes the regular internal structure of a crystal will be interrupted in such a way that two pieces of the "crystal" are related to one another by rotation about an axis or reflection in a mirror plane
 - We then have a rotation or a reflection twin
 - Twin because the two components of the twin are related to each other by a symmetry operation and have a plane of atoms in common (Composition plane)
 - Reflection plane is twin plane
 - Rotation axis is twin axis
 - In one piece of material this twinning process can occur multiple times leading to several components all with a well defined relative orientation

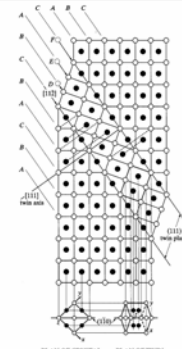
Twins in close packed metals

- Annealing twins often form in FCC metals such as Cu, Ni, α -brass, Al that have been cold worked and annealed
 - As the crystal regrows a stacking fault leads to the formation of twins
 - Components are related by 180° rotation around $\langle 111 \rangle$
- Deformation twins can occur in deformed HCP metals such as Zn, Mg, Be and BCC metals (α -Fe)
 - They are reflection twins

Appearance and structure of annealing twins



In (a) only two components are present in a crystal in (b) there are three components. B is twin band sandwiched between components A_1 and A_2 with same orientation as each other. The atomic structure of such as twin band in an FCC metal is shown on the right.



Stacking faults

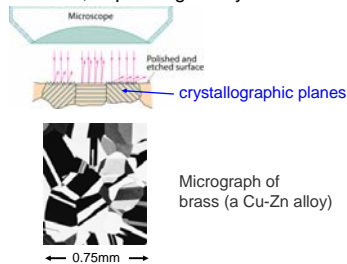
- Stacking faults occur in wide variety of materials not just simple metals
- Consider a structure to be built up from successive layers of atoms or other units, if the regular stacking of these units is interrupted we have a stacking fault
- Close packed metals provide simple examples
 - Perfect FCC has a ABCABCABCABC sequence
 - » A, B, C represent different close packed (111) layers
 - The sequence ABCABCBCABCABC has a stacking fault
 - Perfect HCP is ABABABABABAB
 - ABABABCABABABABAB has a stacking fault
 - Faults that put two of the same layers together AA BB or CC are unlikely due to their very high energy

Microscopic Examination

- Crystallites (grains) and grain boundaries vary considerably in size.
- Can be quite large
 - ex: Large single crystal of quartz or diamond or Si
 - ex: Aluminum garbage can - see the individual grains
- Can be quite small (mm to nm)
 - necessary to observe with a microscope, even a TEM. "microstructure", "nanostructure"

Optical Microscopy

- Useful up to 2000X magnification.
- Polishing removes surface features (e.g., scratches)
- Etching changes reflectance, depending on crystal orientation.



Optical Microscopy

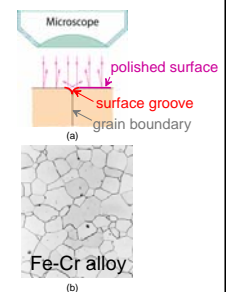
Grain boundaries...

- are imperfections,
- are more susceptible to etching,
- may be revealed as dark lines,
- change in crystal orientation across boundary = contrast.

Definition:
ASTM grain size number:

$$N = 2^{n-1}$$

number of grains/in²
at 100x magnification



ASTM International was formed in 1898 as the American Society for Testing and Materials.

Optical Microscopy

- Polarized light
 - metallographic scopes often use polarized light to increase contrast
 - Also used for transparent samples such as polymers

Microscopy

Optical resolution ca. 10^{-7} m = 0.1 μ m = 100 nm

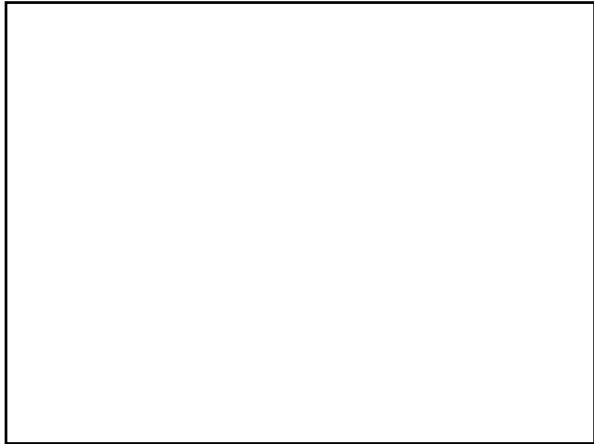
For higher resolution need higher frequency

X-Rays? Difficult to focus.

Electrons (SEM, TEM, STEM)

- wavelengths ca. 3 pm (0.003 nm)
(Magnification - 1,000,000X)
- Atomic resolution possible
- Electron beam focused by magnetic lenses.

Scanning Probe Microscopies (STM, AFM, ...)



Solid State Reactions: General Aspects

Classical solid state reaction:

The starting materials are finely grinded pressed to a pellet and heated to a temperature near the melting temperature. The reaction progress then depends on different parameters

1. Temperature

activation energy of diffusion is lowered with increasing temperature

empirical rule: $T_{\text{reaction}} > 2/3 T_{\text{melting temp.}} (T[K])$

2. Energetics

classical Solid State reactions are usually exothermic, "thermodynamically controlled"

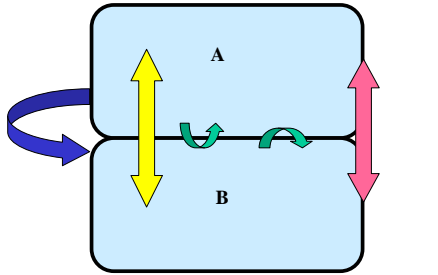
3. Yield

Products are formed with yields of ~100%

4. Grain Structure

Porosity, grain size distribution and contact planes between reacting grains are of paramount importance for the reaction rate

Possible reaction paths between two solid grains A and B



- █ gas phase diffusion
- █ volume diffusion
- █ interface diffusion
- █ surface diffusion

Importance Of Surface Area For Solid State Reactions

The common surface of reacting grains influences strongly the reaction rate:

$$\text{Surface area } S = 6 \text{ cm}^2 = 6 \times 10^{-4} \text{ m}^2 = 6 \times 10^6 \mu\text{m}^2$$



grinding
Typical 10 μm edge length

$$10 \mu\text{m} \rightarrow S = 6 \times 10^2 \mu\text{m}^2$$

Cube: 1 cm edge length (=10⁴ μm)

$$10^9 \text{ particles} \rightarrow S_{\text{total}} = 10^9 \times 6 \times 10^2 \mu\text{m}^2 = 6 \times 10^{11} \mu\text{m}^2$$

Grinding limited to ~10 micron powder.
Increase in surface area <10³.

MUCH bigger changes in nm range.

Container materials for solid state reactions

Depends on the maximum reaction temperature and the type of reacting material.
(e.g. quartz is an acidic solid unsuitable for basic reactants)

GLASSES:

Pyrex: 76% SiO₂, 16% B₂O₃ (+ BaO ...)

$T_{\text{max.}} \sim 400 \text{ }^\circ\text{C}$
 $T_{\text{max.}} \sim 1100 \text{ }^\circ\text{C}$

CERAMICS:

Al-silicates: $T_{\text{max.}} \sim 1700 \text{ }^\circ\text{C}$
MgO: $T_{\text{max.}} \sim 2200 \text{ }^\circ\text{C}$

Corundum (α-Al₂O₃): $T_{\text{max.}} \sim 1900 \text{ }^\circ\text{C}$
BN: $T_{\text{max.}} \sim 2900 \text{ }^\circ\text{C}$

METALS

Steel: $T_{\text{max.}} \sim 1400 \text{ }^\circ\text{C}$ (under inert gas)
Mo: $T_{\text{max.}} \sim 2000 \text{ }^\circ\text{C}$

Pt: $T_{\text{max.}} \sim 1600 \text{ }^\circ\text{C}$ (PtO↑)
Ta: $T_{\text{max.}} \sim 2500 \text{ }^\circ\text{C}$

Solid-Solid Reactions

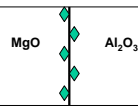
Model for a classical solid-solid reaction (below melting point !):

Interface between **two crystals or two grains of a powder**

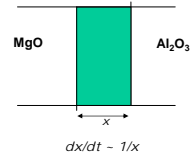
possible products: small crystallites ("powder"), single crystals ...



Phase 1:
formation of seeds



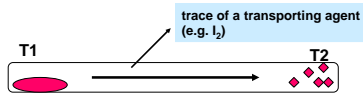
Phase 2:
growth of seeds



Chemical transport reaction

A solid is dissolved in the gas phase at one place ($T=T_1$) by reaction with a transporting agent (e.g. I_2). At another place ($T=T_2$) the solid is condensed again.

Whether $T_1 < T_2$ or $T_1 > T_2$ depends on the thermochemical balance of the reaction!
Transport can proceed from higher to lower or from lower to higher temperature



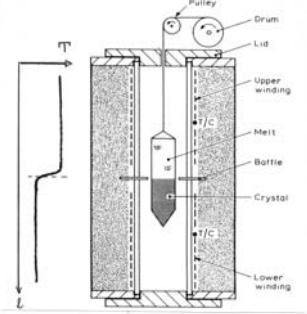
Main application: purification and crystallisation of solids

Growth of big single crystals (e.g. Si)



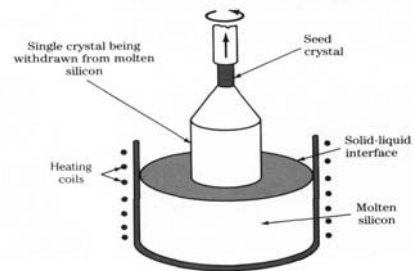
Abb. 1. Großer Monokristall mit einem Durchmesser von 10 cm und einer Länge von 100 cm. (Herstellung der Wafer-Technologie, hergestellt im Jahre 1958 für die IBM)

Growth of single crystals: Bridgman-Stockbarger-process (moving temperature gradient)



Czochralski process: Si (!)

- a rotating seed crystal is raised slowly from a melt with equal composition

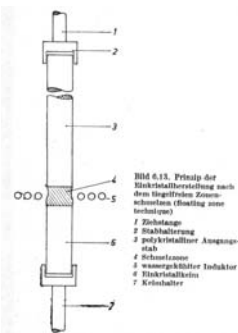


Zone melting

- a small slice of the sample is molten and moved continuously along the sample
- impurities normally dissolve preferably in the melt
(!! icebergs in salt water don't contain any salt !!)

- segregation coefficient k :
 $K = C_{\text{solid}}/C_{\text{liquid}}$
(c : concentration of an impurity)

only impurities with $k < 1$ can be removed by zone melting !!



Hydrothermal synthesis

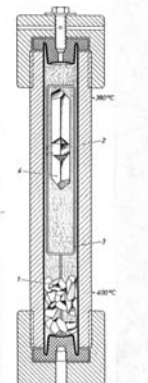
Chemical transport in supercritical aqueous solution (H_2O : $T_k=374\text{ °C}$, $p_k=217,7\text{ atm}$)

Autoclave for the growth of SiO_2 single crystals (\rightarrow quartz)

1500 bar, T- gradient 400 \rightarrow 380 $^{\circ}C$

- 1: nutrient (powder), 2: seed crystal,
- 3: mechanical fixing of crystal
- 4: product crystal

Lit.: Die Rolle der Hydrothermalsynthese in der präparativen Chemie, A. Rabenau, Angew. Chem. 97 (1985) 1017



Summary

- Point, Line, and Area defects exist in solids.
- The number and type of defects can be varied and controlled (e.g., T controls vacancy conc.)
- Defects affect material properties (e.g., grain boundaries control crystal slip).
- Defects may be desirable or undesirable (e.g., dislocations may be good or bad, depending on whether plastic deformation is desirable or not.)