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Materials Science Lecture - Alloy Formation - Basics

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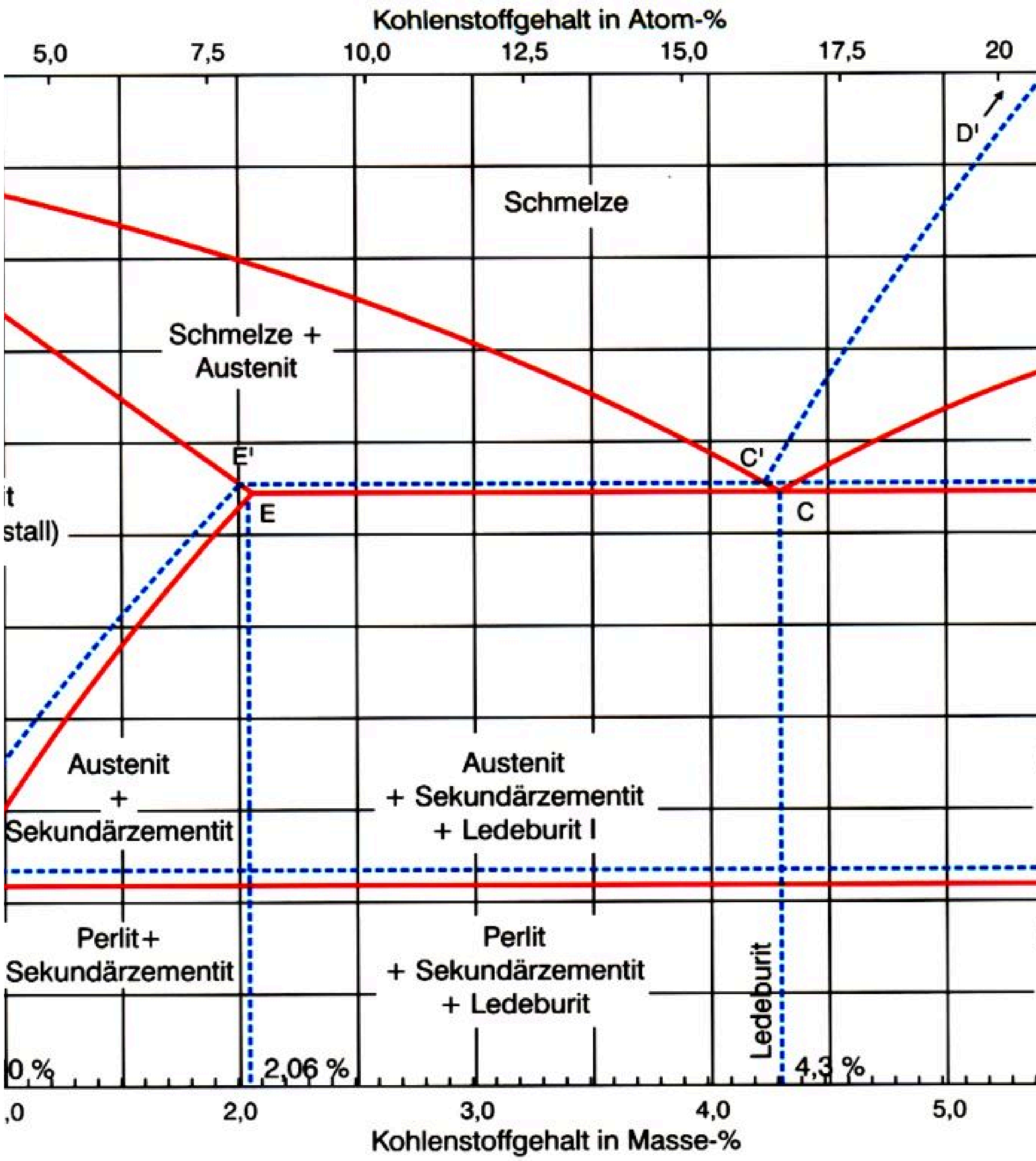
Parts of the script are adopted from Prof. Dr.-Ing. Jürgen Häberle



Contents

- **Basic concepts** of alloy formation
- **Crystal formation** and microstructure development
- **Phase diagrams** and phases
- **Diffusion** and mass transport

What is an Alloy?

Alloy

- **Origin:** from Latin "ligare" = to bind together, connect, unite
- **Definition:** Mixture of multiple atom types (*components*) with *metallic character*

Components can be:

- **Metallic:** Cu (Copper), Ni (Nickel), Fe (Iron), Al (Aluminum)
- **Non-metallic:** C (Carbon), P (Phosphorus), S (Sulfur), N (Nitrogen), O (Oxygen)

Why Alloys?

Advantages over pure metals:

- Higher strength
- Better corrosion resistance
- Improved processing properties
- Adjustable mechanical properties
- Economic efficiency

Everyday examples:

- Steel (Fe + C)
- Bronze (Cu + Sn)
- Brass (Cu + Zn)

Concentration and Composition

1. Mass fraction (Weight percent)

$$m_{rel} = \frac{m_1}{\sum_i m_i} \cdot 100 \; [\%]$$

2. Atomic fraction (Atomic percent)

$$n_{rel} = \frac{n_1}{\sum_i n_i} \cdot 100 \; [\%]$$

When are both specifications equal?

Note:

- When atomic masses are **similar** → $m_{rel} \approx n_{rel}$
- When atomic masses are **different** → $m_{rel} \neq n_{rel}$

Example:

- Cu (63.54 u) and Ni (58.69 u) → similar masses
- Fe (55.85 u) and C (12.01 u) → very different masses!

Exercise

An alloy with 1 kg total mass contains:

- **25 atomic-% Ni**
- **75 atomic-% Cu**

Questions:

1. What is the mass of Ni and Cu for the **atomic fraction**?
2. What would the mass be for a **mass fraction** of 25% Ni and 75% Cu?

Given:

- $A_{Cu} = 63.54$ u; $A_{Ni} = 58.69$ u; $u = 1.66 \times 10^{-27}$ kg

Solution - Part 1: Mass Fraction

▶ Show solution

▶ Show solution

Diffusion - The Foundation

Definition: Temperature and time-dependent mass transport

1st Fick's Law:

$$dm_A = -D \frac{dc_A}{dx} S \, dt$$

$$D = D_0 \exp\left(-\frac{Q_A}{RT}\right)$$

Parameters:

- dm_A = diffused amount of component A
- D = diffusion coefficient
- c_A = concentration of component A
- x = spatial coordinate

Diffusion

Important for:

- Steel hardening (case hardening, nitriding)
- Galvanizing
- Annealing
- Welding
- Soldering

Also outside metallurgy:

- Gas diffusion from tanks
- Diffusion of gases through membranes
- Corrosion

What is a Phase?

General definition:

> A phase is a chemically and physically **uniform homogeneous constituent** of an alloy or matter in general.

Known from states of matter:

- Solid (s)
- Liquid (l)
- Gaseous (g)
- Plasma (p)

But: In alloys, there are more than just states of matter!

Phase Examples

Single-phase

- Pure aluminum
- Pure iron
- Liquid water
- Water vapor

Two-phase

- Fog (water + air)
- Ice in water
- Supersaturated solutions
- Many technical alloys

Phase Changes

1. Transformations

- Unstable lattice modifications transform into stable ones
- Below an **equilibrium temperature**
- Example: γ-Fe → α-Fe upon cooling below 911°C
- In alloys: Change in solid solution configuration

2. Precipitations

- **Solubility** decreases (usually due to temperature change)
- Phases precipitate from the solid solution
- Requires **mass transport** (diffusion)
- Needs **heat** and **time**

Solid Solutions

Definition:

> A solid solution is a chemically homogeneous, uniform crystal built from **multiple atom types**.

Properties:

- At least 2 atom types
- **Homogeneous** on macroscopic level
- Heterogeneity only visible at atomic level
- English: "solid solution"
- Leads to "strains" in the lattice

Types of Solid Solutions

1. Substitutional Solid Solution

- Similar chemical character
- Similar atomic diameter (< 15% difference)
- Same crystal lattice

Examples:

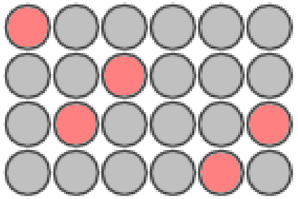
- Cu-Ni (completely miscible)
- Cu-Zn (brass)

Image source

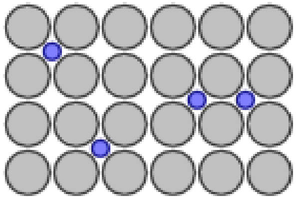
Types of Solid Solutions

2. Interstitial Solid Solution

- **Smaller** atoms
- Diameter ratio: $f = \frac{d}{D} \leq 0.41$
- Atoms in gaps (interstitial sites)



Substitutionsmischkristalle



Einlagerungsmischkristalle

Examples:

- C in Fe (steel!)
- N in Fe (nitriding)

Important: Both types are **single-phase**!

Image source

Intermetallic Phases

Characteristics:

- Complex lattice structure (several hundred atoms)
- Independent of parent lattices
- **Strong attractive forces** between atom types
- Bonding type: metallic + covalent + ionic
  - → **Intermediate** between metallic and chemical

Properties:

- Very **hard**
- Very **brittle**
- In technical alloys usually < 10%

Important Intermetallic Phases

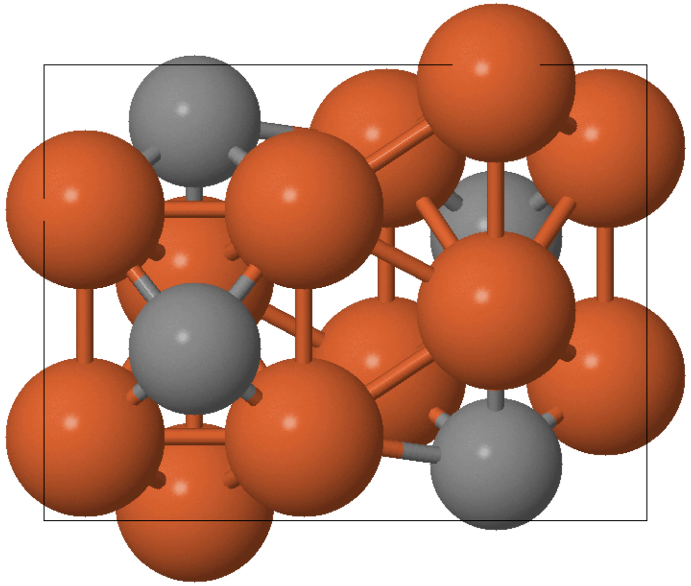
Interstitial Phases (Insertion Structures)

Carbides:

- Fe_3C (cementite) in steel
- $Cr_{23}C_6$ in stainless steels
- WC in hard metals

Others:

- Nitrides (e.g., Fe_4N)
- Borides (e.g., Fe_2B)



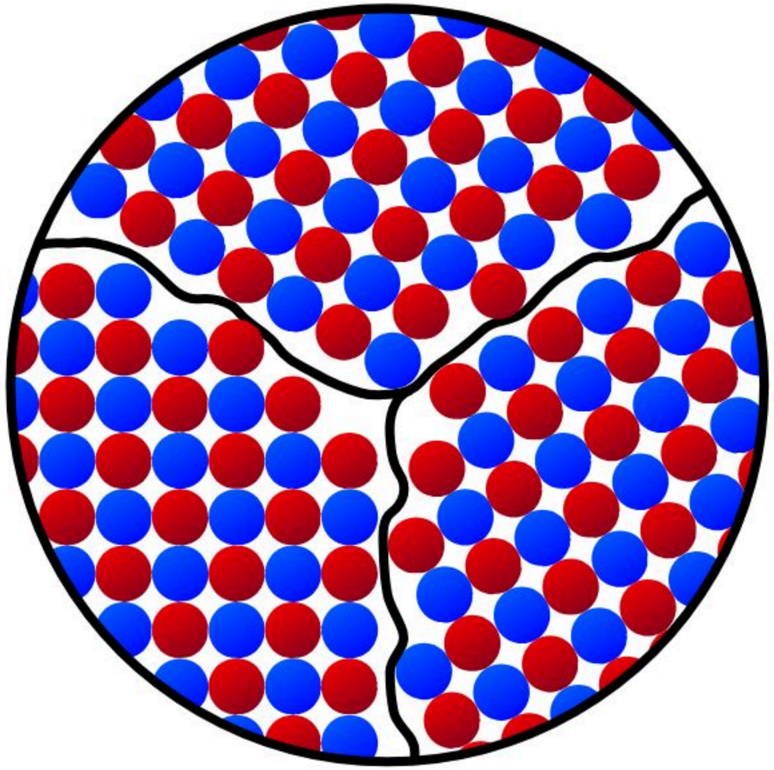
Applications:

- Tool steels
- Heat-resistant steels
- Wear-resistant coatings

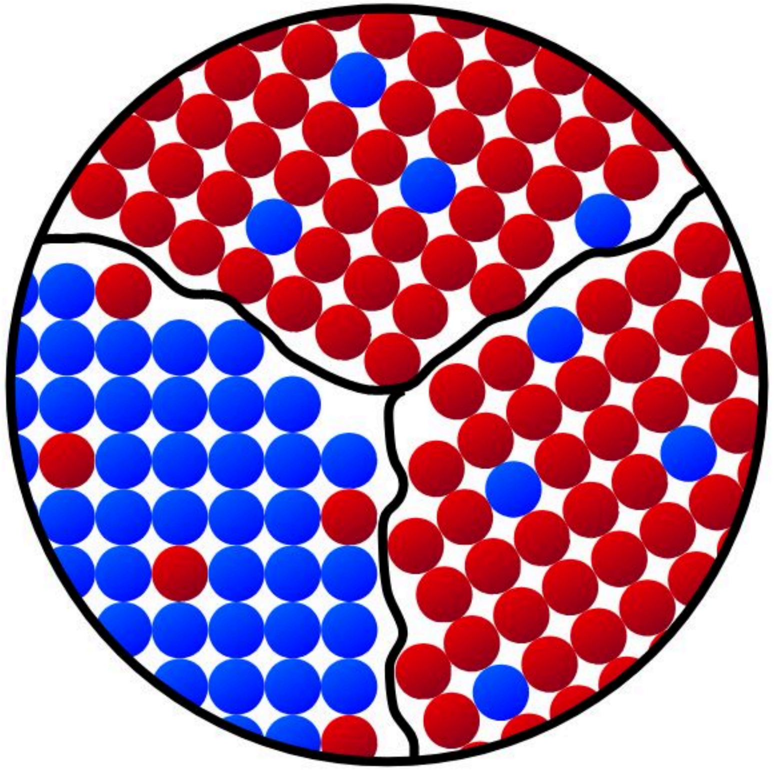
Legierungstypen

Die Komponenten der Legierung sind im festen Zustand ineinander ...

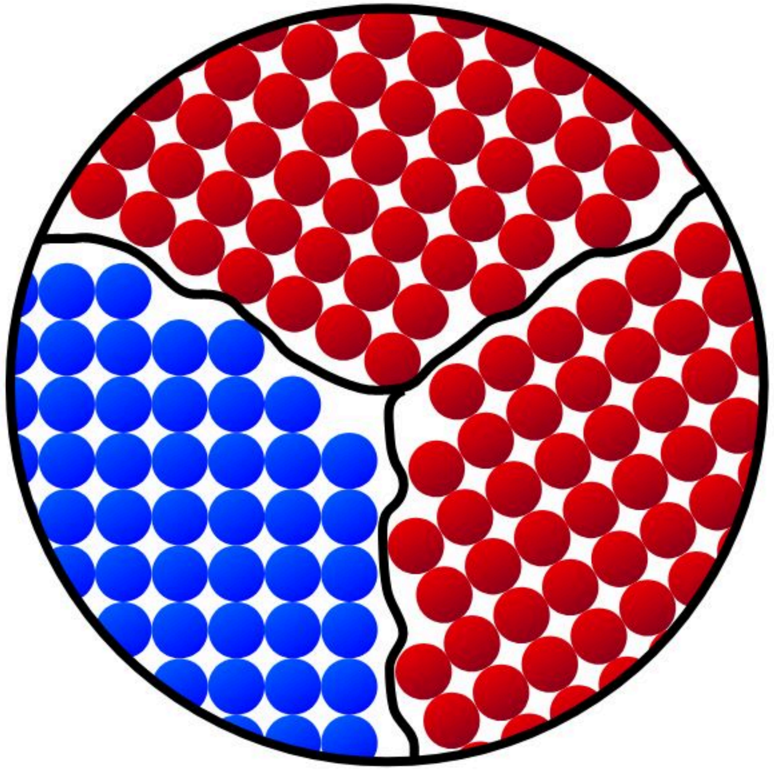
vollkommen löslich | **begrenzt löslich** | **vollkommen unlöslich**



Mischkristall



Kristallgemsich aus Mischkristallen



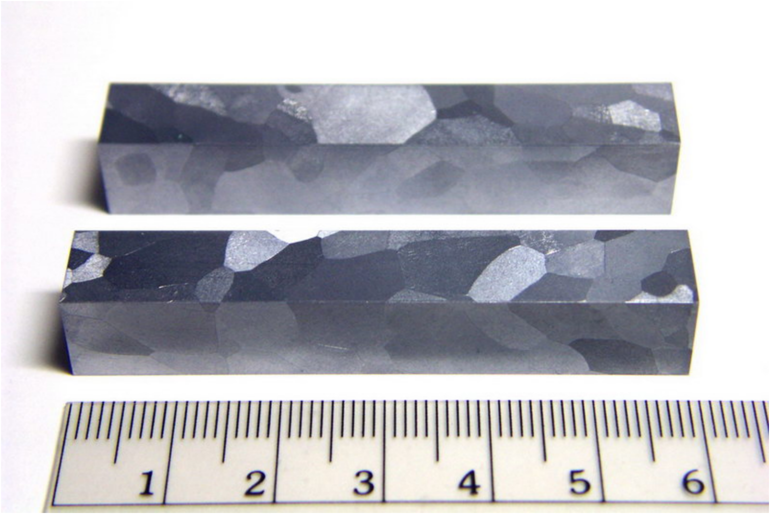
Kristallgemisch

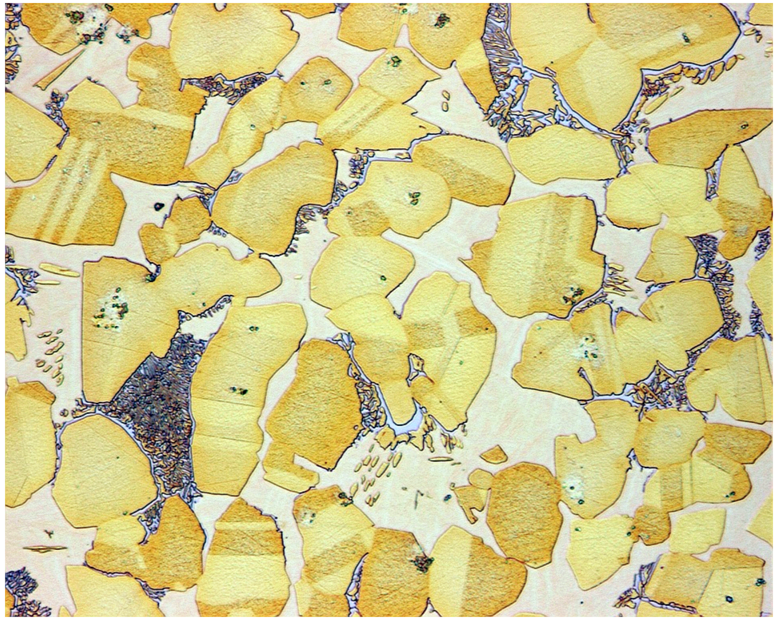
Microstructure of Materials

Definition:

Characterized by **type, size, shape, orientation, and arrangement** of individual constituents (phases):

- Crystallites (grains)
- Amorphous regions
- Reinforcements
- Fillers

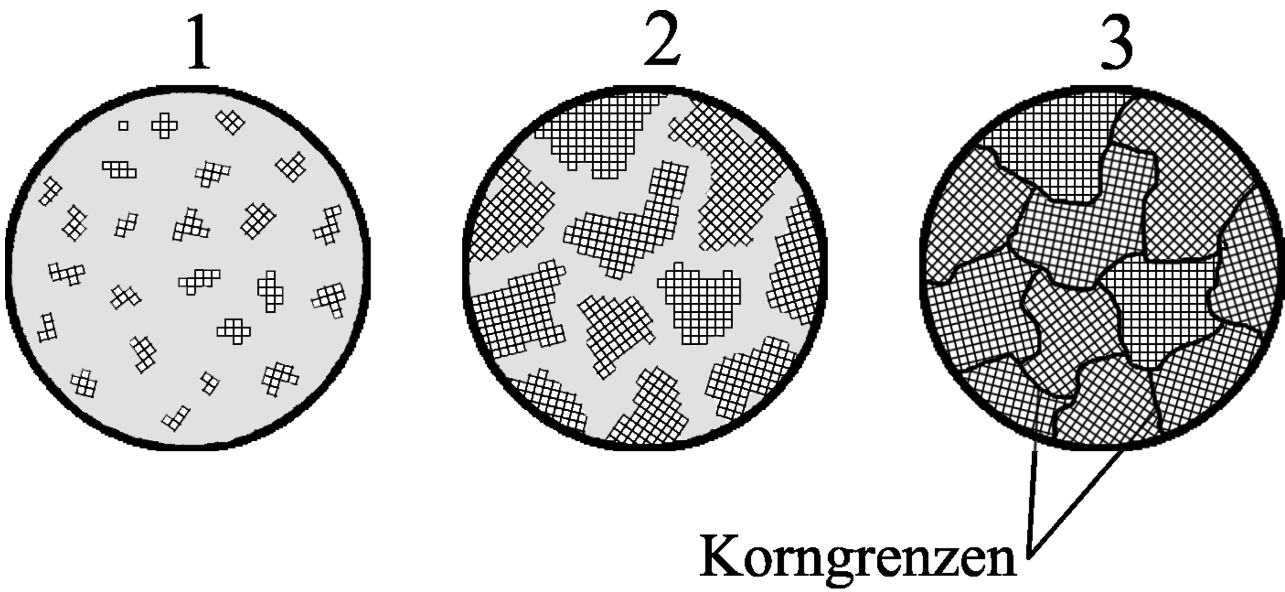




Microstructure Formation - Process

```
A[Melt] --> B[Cooling / Undercooling]
B --> C[Nucleation homogeneous + heterogeneous]
C --> D[Nucleus growth]
D --> E[Crystallization]
E --> F[Crystallite formationGrains + grain boundaries]
F --> G[Microstructure]
```

🎬 Video on crystal growth



Nucleation

Two Types:

Homogeneous Nucleation

- **Native** nuclei
- Fluctuations in the melt
- Higher undercooling required
- Rarer in practice

Heterogeneous Nucleation

- **Foreign** nuclei (impurities, mold wall)
- Lower undercooling required
- Most common form in practice
- Can be used purposefully (inoculation)

Crystal Growth

Relationships:

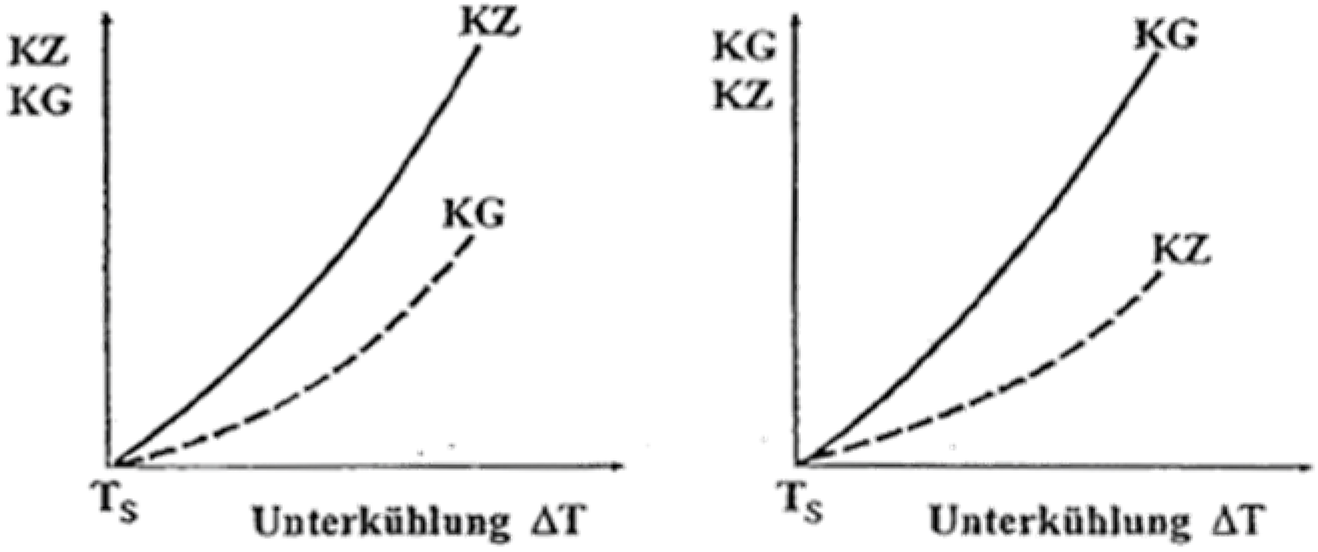
- **Number of nuclei (KZ)** depends on undercooling
- **Crystallization rate (KG)** depends on undercooling

Effect on Grain Size:

Condition	Result
Many nuclei + slow growth	Fine-grained
Few nuclei + fast growth	Coarse-grained

Note: Fast cooling → many nuclei → fine-grained!

Effect of Grain Size



a) Fine-grained Microstructure

- Many nuclei
- Fast cooling
- **Advantages:**
  - Higher strength
  - Better toughness
  - More uniform properties

b) Coarse-grained Microstructure

- Few nuclei
- Slow cooling
- **Disadvantages:**
  - Lower strength
  - More brittle
  - Anisotropic properties

Terms: Grain and Grain Boundary

Grain (Crystallite)

- Nuclei have completed growth
- Grains meet each other
- **Crystal orientation** between grains is different

Shape determined by heat flow:

- Uniform in all directions → **globular** (spherical)
- Preferred direction → **transcrystalline** solidification (columnar)

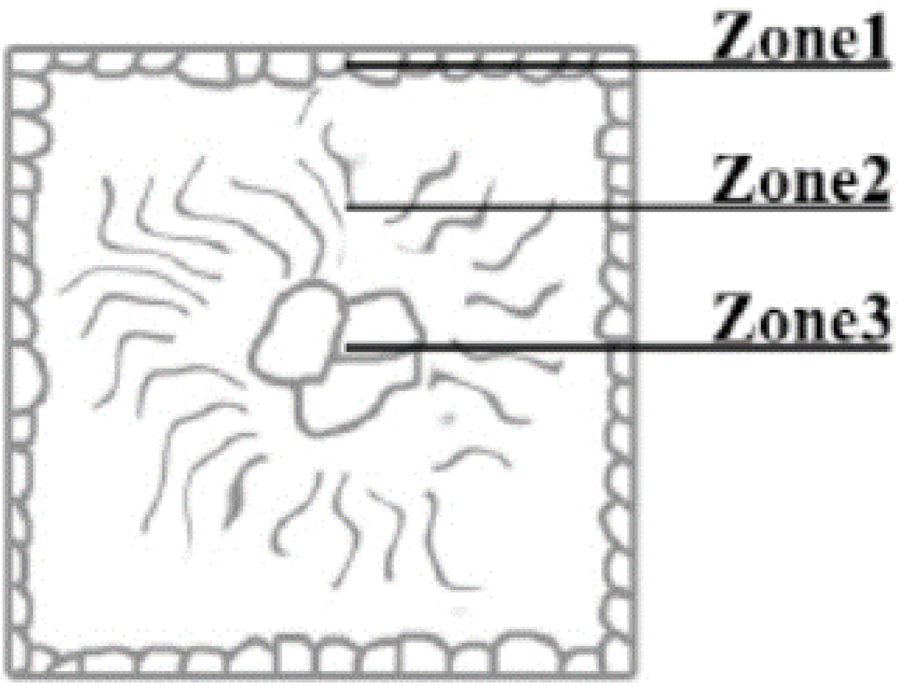
Grain Boundary

- Transition surfaces between grains
- Disturbed lattice structure
- Important for mechanical properties!

Casting and Continuous Casting - Three Zones

When casting into a metal mold (chill), **three characteristic zones** form:

1. **Fine-grained outer zone**
2. **Transcrystalline zone**
3. **Globular core zone**



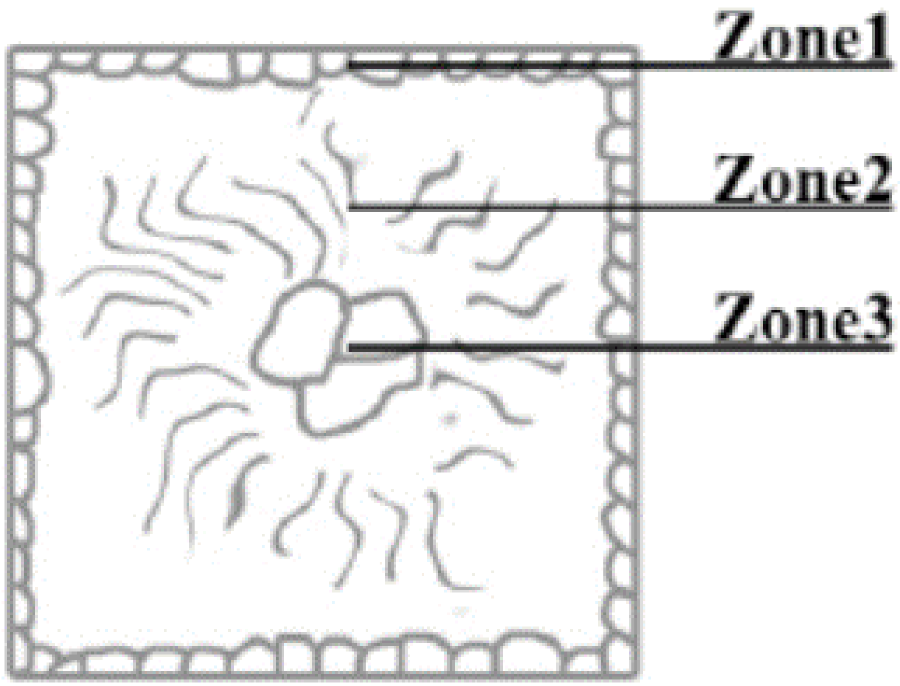
Zone 1: Fine-grained Outer Zone

Formation:

- Strong **undercooling** at mold wall
- Many crystal nuclei form simultaneously
- Rapid solidification

Result:

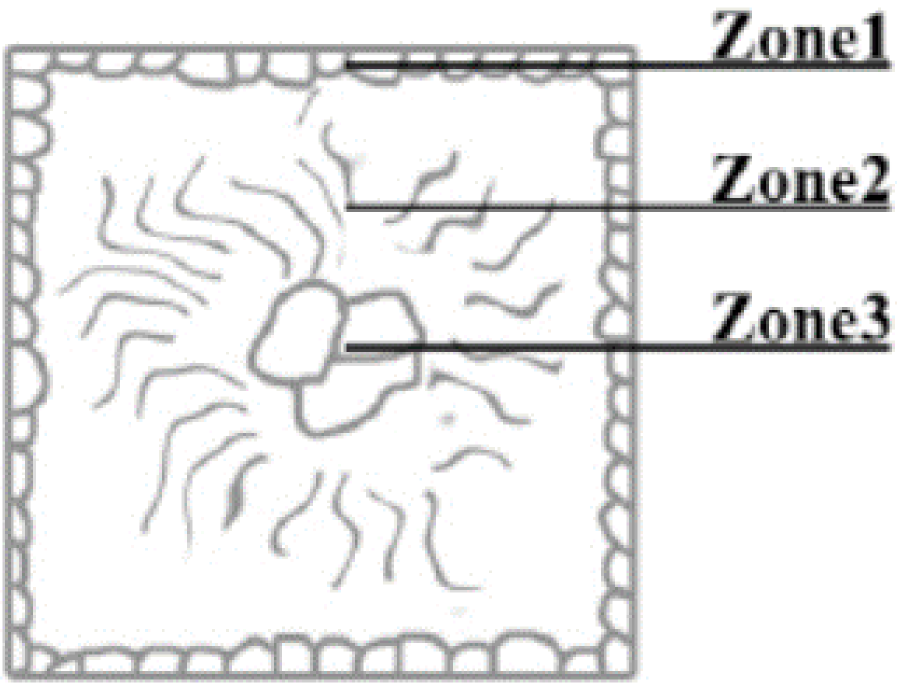
- Small, uniform crystallites
- Globular shape
- Fine-grained microstructure



Zone 2: Transcrystalline Zone

Formation:

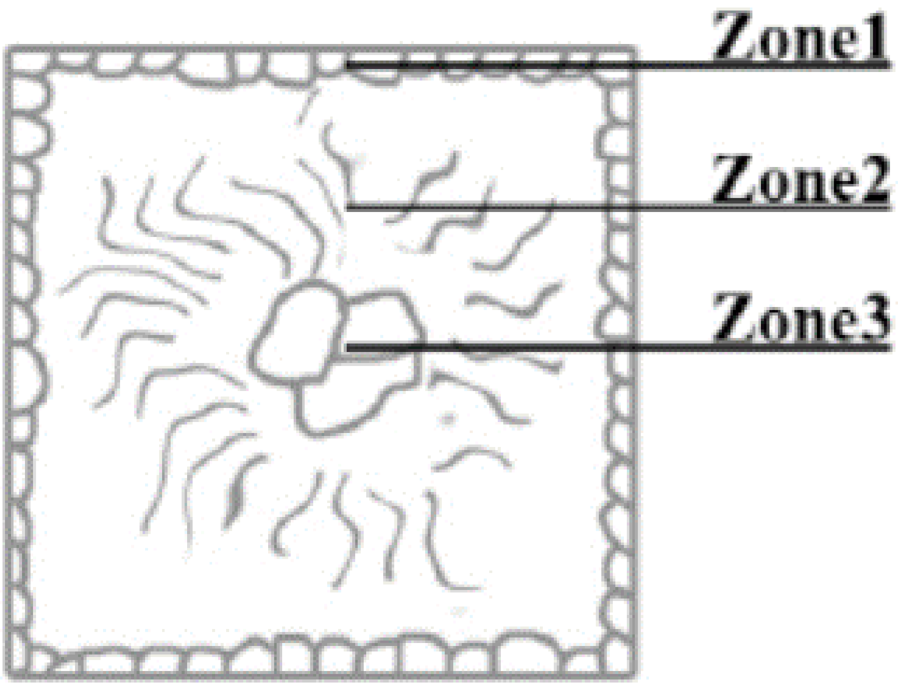
- **Directional** growth of crystallites
- Growth opposite to heat flow
- Crystallographic orientation parallel to temperature gradient



Zone 2: Transcrystalline Zone

Result:

- **Columnar crystals** (very coarse)
- Pronounced preferred orientation
- → **Cast texture** develops
- **Anisotropic** properties



Zone 3: Globular Core Zone

Formation:

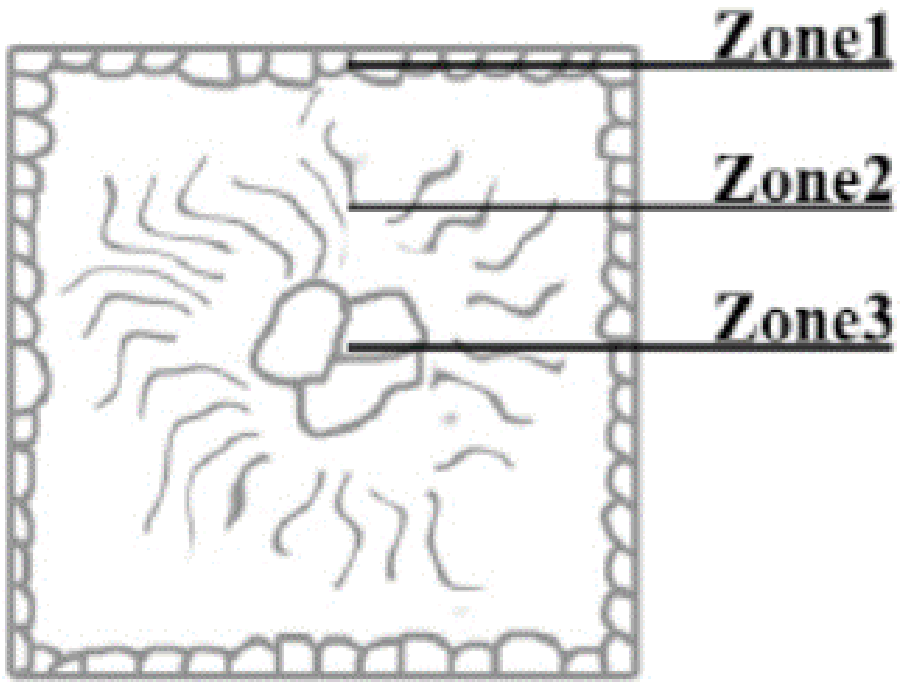
- Impurities are "pushed ahead" by columnar crystals
- Enrichment in core (**segregation**)
- Many **foreign nuclei**

Result in normal metals:

- Globular, fine-grained structure

In very pure metals:

- Coarse-grained microstructure



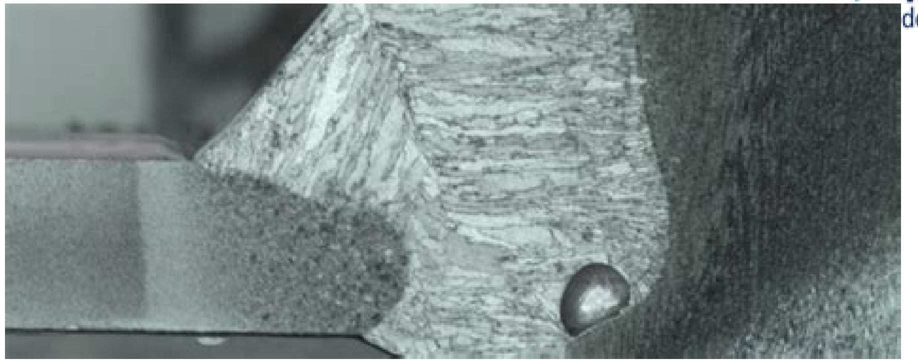
Welding - Microstructure Formation

Similar zones as in casting:

- Heat-affected zone (HAZ)
- Fusion zone with solidification microstructure
- Transition zone

Special features:

- Very fast cooling possible
- Fine-grained microstructure
- But: Risk of hardening



Microstructure Analysis - Why?

Problem:

- Crystallites are normally **not visible**
- Materials science investigations require visualization

Goal:

- Analyze microstructure
- Determine grain size
- Examine phase distribution
- Detect defects

Microstructure Analysis - Work Steps

Sample Preparation:

1. **Targeted sample extraction**
    - Select representative location
    - Gentle separation (avoiding microstructure influence)
2. **Grinding**
    - Various grits (coarse → fine)
    - Create plane surface
3. **Polishing**
    - Diamond suspension or oxide polishing
    - Mirror smooth surface

Microsections

Investigation methods:

Light microscope

- Up to approx. 1000× magnification
- Simple handling
- Sufficient for many applications

Scanning electron microscope (SEM)

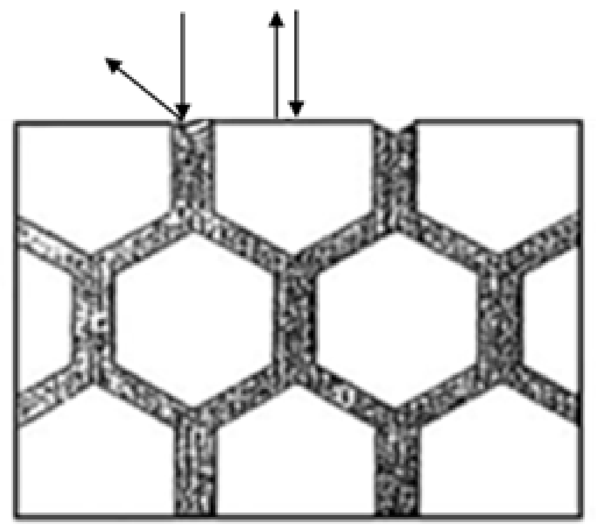
- Up to > 100,000× magnification
- **Higher resolution**
- **Greater depth of field**
- Elemental analysis possible (EDX)

Etching Methods

Etching = controlled corrosion process

1. Grain Boundary Etching

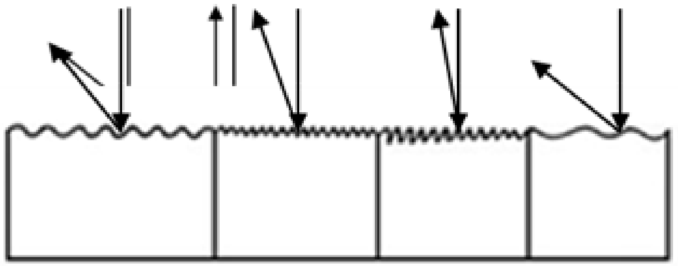
- Preferential dissolution of **grain boundaries**
- Grain boundaries appear as dark lines
- Grains become visible



Etching Methods

2. Grain Surface Etching

- Grain sections are roughened differently
- Or: different oxide layer thicknesses
- Grains reflect light with **different intensities**
- → Contrast formation through various gray tones



Macrosections

Definition: Microstructure examination with naked eye or magnifying glass

Applications:

1. **Detect and localize segregations**
    - Etching according to Heyn and Oberhoffer
    - Baumann print (for sulfur)
2. **Quality of welded joints**
    - Adler etching
3. **Lines of force** after plastic deformation
    - Etching according to Fry
    - Visualize fiber flow

Technical Terms for Microstructure Description

Scientific Disciplines:

Material	Field
Metals	**Metallography**
Ceramics	**Ceramography**
Polymers	**Plastography**

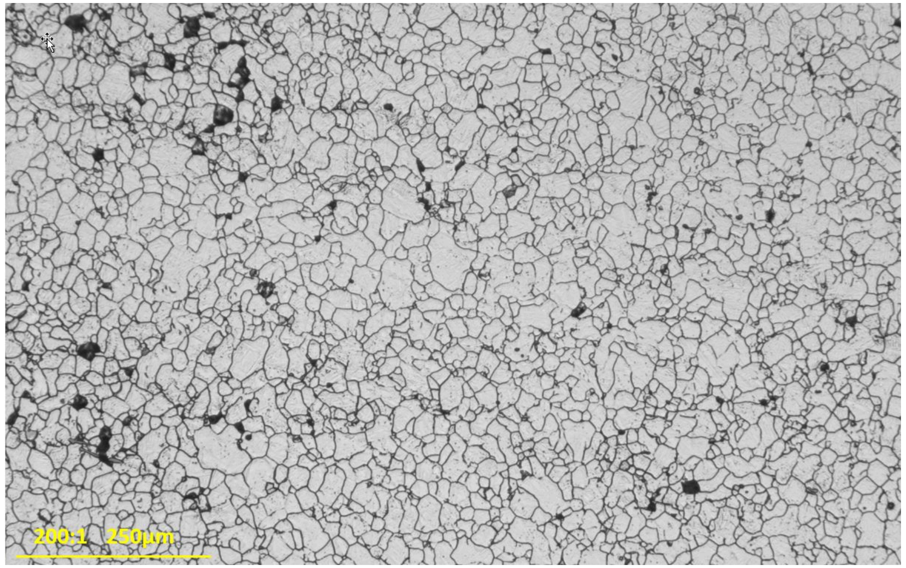
Qualitative description: Microstructure shape, phase distribution

Quantitative description: Grain size, phase fractions, grain size distribution

Grain Boundaries in Detail

Important effect:

- Insoluble constituents and impurities are **pushed ahead** by crystal fronts
- Enrichment at grain boundaries
- → **Grain boundary substances**



Influence of Grain Boundary Substances

Case 1: Deformable Grain Boundary Substance

- Material behavior is dominated by **grains**
- Good ductility
- Example: Pure metals with low impurities

Case 2: Brittle Grain Boundary Substance

- Material behavior is dominated by **grain boundaries**
- Intergranular fractures
- → **Embrittlement** of material!
- Example: Phosphorus segregation in steel

Important for: Weldability, hot forming, toughness

Summary

Key points of this lecture:

✓ Alloys = multi-component systems with metallic character

✓ Concentration: mass fraction ≠ atomic fraction (except for similar atomic masses)

✓ Phases = homogeneous regions with uniform properties

✓ Diffusion = temperature and time-dependent mass transport

✓ Solid solutions: substitutional and interstitial

✓ Microstructure develops through nucleation and crystal growth

✓ Grain size significantly influences mechanical properties

✓ Microstructure analysis through sectioning and etching

Outlook - Next Lecture

Phase Diagrams:

- How do we read phase diagrams?
- Lever rule
- Eutectic and eutectoid
- Practical application: Iron-carbon diagram

Preparation:

- Review: phases, concentration, solubility
- Practice problems on alloy compositions

References

Textbooks:

- Rainer Schwab: *Werkstoffkunde und Werkstoffprüfung für Dummies*, 2019; ISBN-10: 352771538X

Online Resources:

- Fundamentals of Metallurgy

Thank You for Your Attention!

Questions?

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🔗 ORCID

Next Lecture:

Phase Diagrams and Phase Equilibria