Lecture on Materials Science - Microstructure of Materials

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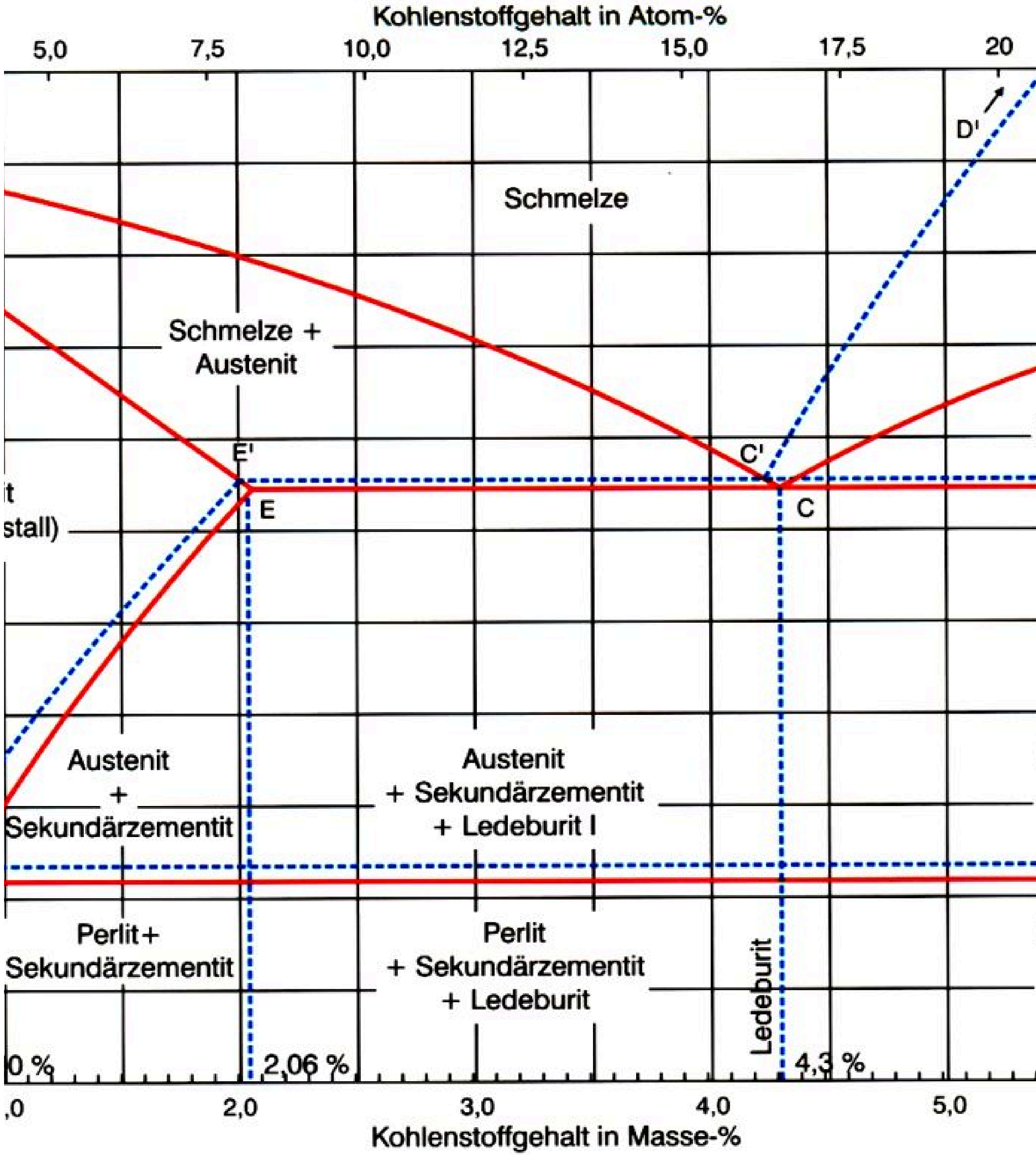
Parts of the script are adopted from Prof. Dr.-Ing. Jürgen Häberle



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Contents

- Basic Concepts
- Crystal Formation
- Phase Diagrams
- Microstructure

Topics

Terms

Alloy

- from "ligare" - to bind, join, unite
- Mixture of several atomic species (*components*) with *metallic character*
- Components
  - usually metallic (Cu, Ni)
  - non-metallic (C, P, S, N, O)
- Variations
  - which components
  - number of components
  - concentration of components

Chemical Composition or Concentration

Mass fraction, weight fraction, mass percent (synonyms)

$\frac{m_1}{\sum_i m_i} \cdot 100 = m_{1-rel}$ in [%]

Ex. $m_{Cu-rel} = \frac{m_{Cu}}{m_{Cu}+m_{Fe}} \cdot 100$

Masses m of components are different

Atomic fraction

$\frac{n_1}{\sum_i n_i} \cdot 100 = n_{1-rel}$ in [%]

Ex. $n_{Cu-rel} = \frac{n_{Cu}}{n_{Cu}+n_{Fe}} \cdot 100$

When the masses m of components are similar, then n_{rel} and m_{rel} are equal.

Exercise

1 kg alloy 25% Ni - 75% Cu.

How much mass does Cu and Ni have for the mass fraction and atomic fraction?

Solution

- Mass fraction
- Atomic fraction

Phase

- Known in relation to the state of matter (solid, liquid, gaseous, plasma)

General definition

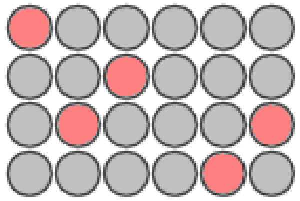
A phase is understood as a chemically and physically homogeneous component of an alloy or matter in general.

- Single-phase
- Two-phase
- Solid solution

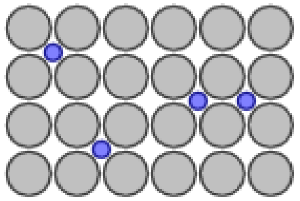
Types of Solid Solutions

Substitutional solid solution

- similar chemical character
- similar diameter
- same crystal lattice



Substitutionsmischkristalle



Einlagerungsmischkristalle

Interstitial solid solution

- smaller atoms
- placed in the gaps of the crystal lattice (interstitial or interstitial atoms)
- second component is dissolved

Both types are single-phase.

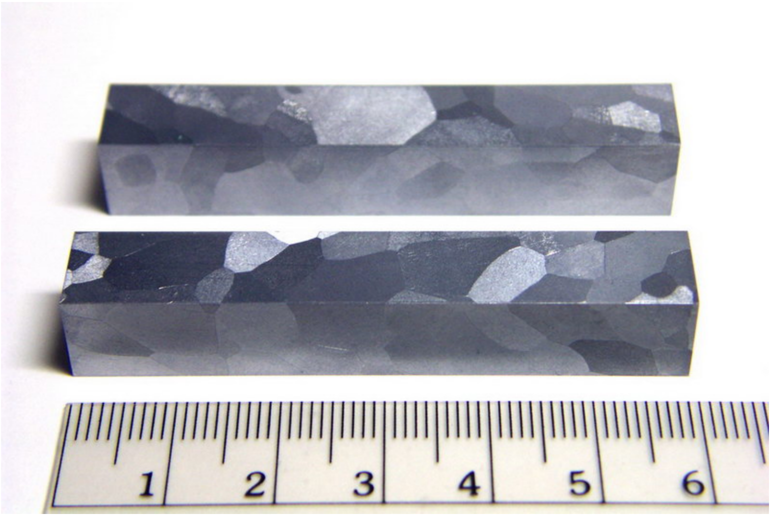
Intermetallic phase

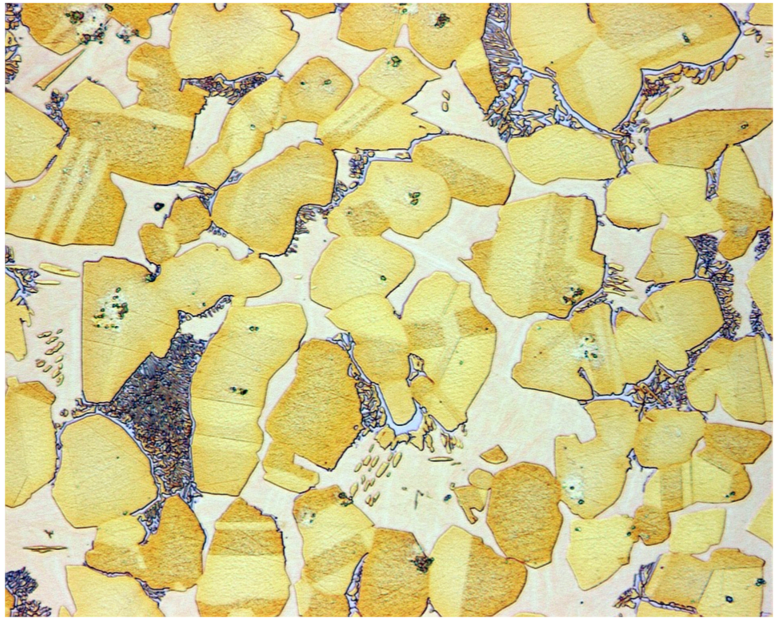
- mostly complex lattice structure, independent of the original lattices
- ordered interstitial structures
- not a compound in the chemical sense (law of constant and multiple proportions does not apply)
- predominant bond type: metallic bond, but with added atomic and ionic bond components

Characteristic: hard and very brittle

Microstructure of Materials

- characterized by the type, size, shape, orientation, and arrangement of individual components (phases), such as crystallites (grains), amorphous regions, reinforcements, or fillers





Formation of Microstructure

Melt → Cooling / Undercooling

↓

Nucleation (homogeneous + heterogeneous)

↓

Crystal growth → Crystallization

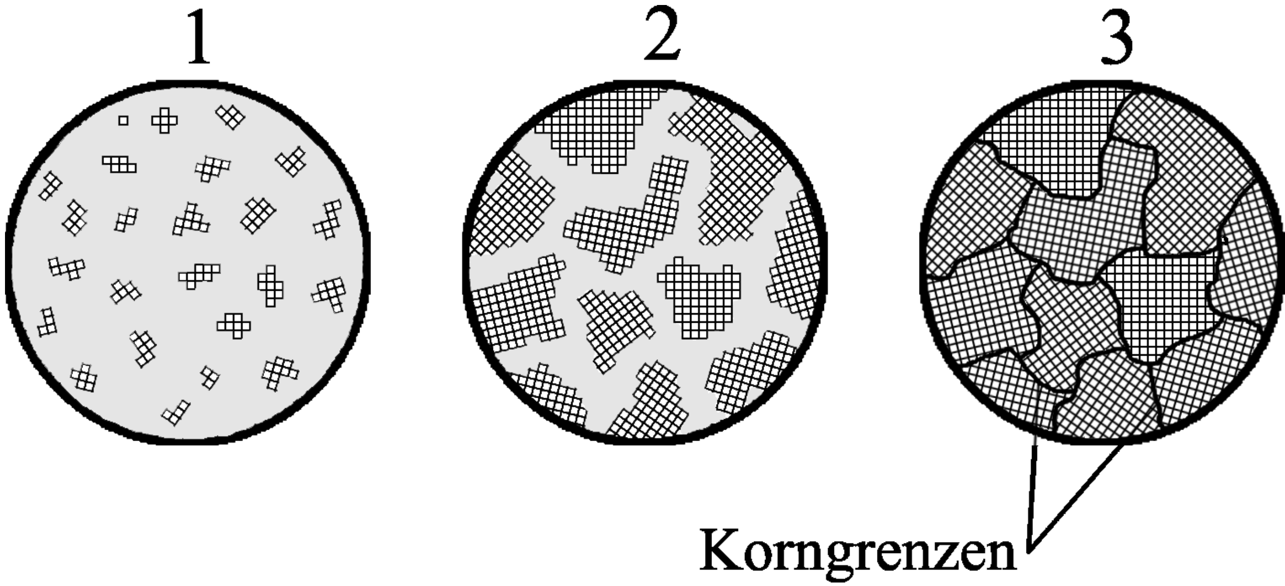
↓

Formation of crystallites (grain formation with grain boundaries)

↓

∑ of all grains and grain boundaries

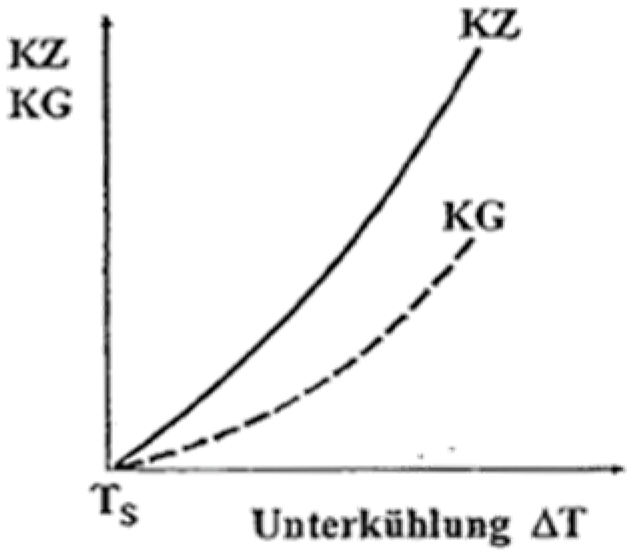
=> Microstructure

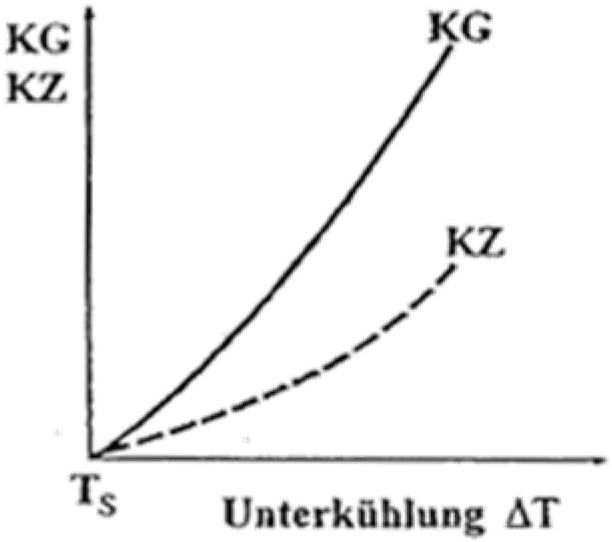


Nucleation

- Solidification does not occur uniformly -> formation of nuclei
- homogeneous (same type) or heterogeneous (different type)
- Growth of nuclei (crystal growth) until the entire melt has solidified
- There are relationships between the number of nuclei (NN) and the crystallization speed (CS) on one hand and the undercooling ΔT on the other.

Influencing Factors on Grain Size Formation





a) → fine-grained microstructure

b) → coarse-grained microstructure

- large number of nuclei -> fine-grained microstructure
- rapid crystal growth and low NN -> coarse-grained microstructure

Terms

Grain

- Nuclei have completed growth and touch each other
- Crystal orientation between adjacent grains is generally different
- Shape and size are determined by heat flow
    - uniform in all directions - *globular*
    - preferred direction of heat flow - *transcrystalline solidification*

Grain boundary

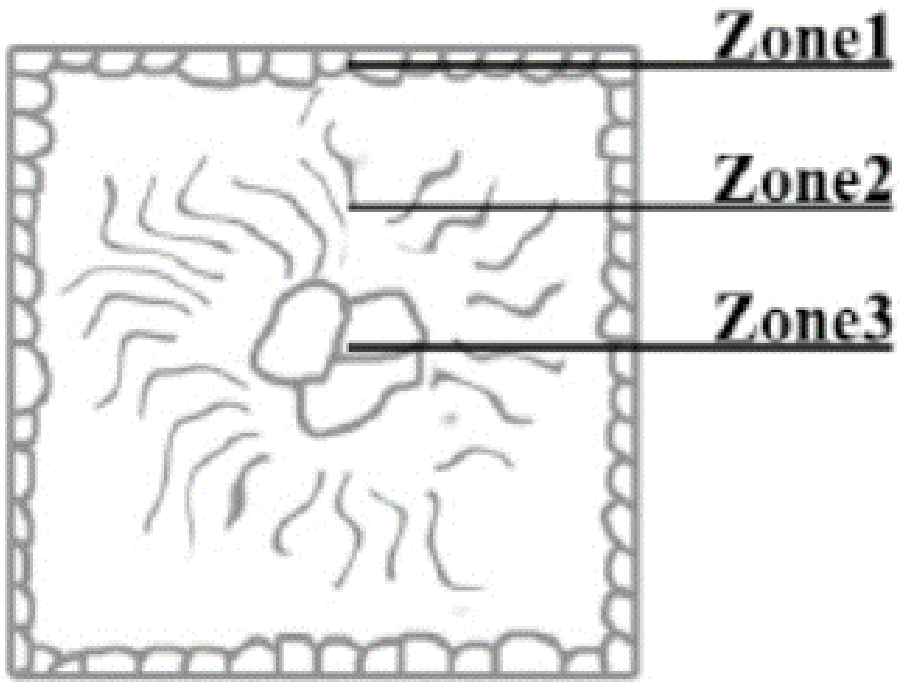
- Transition areas between grains

Casting or Continuous Casting

- During casting or continuous casting in a metal mold (ingot mold), a casting structure forms in three zones, usually with a clear demarcation between them:

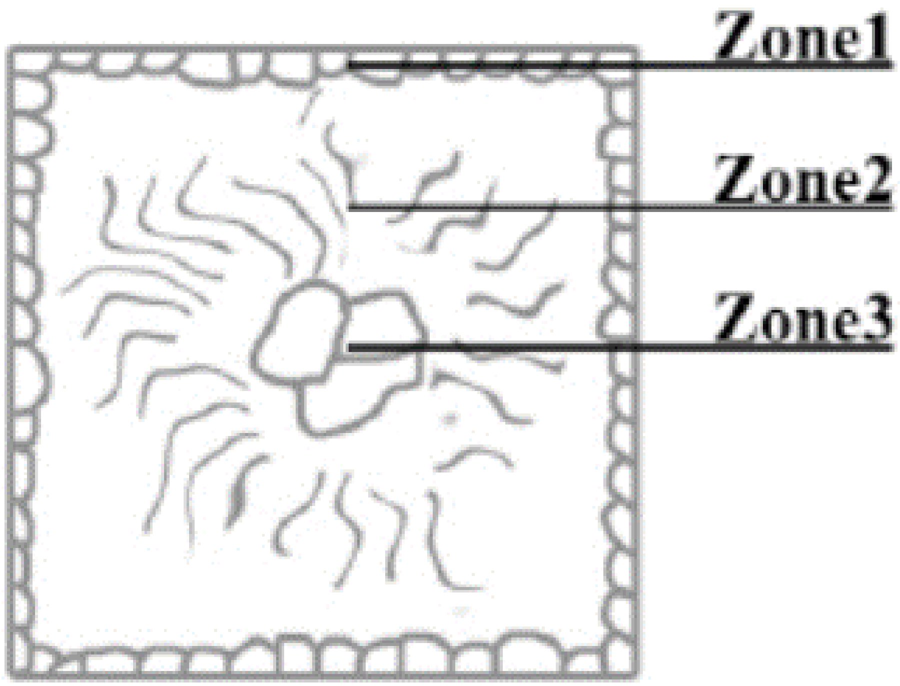
1. Fine-grained globular boundary zone

- strong undercooling of the melt at the mold wall
- formation of numerous crystal nuclei -> small, uniform crystallites



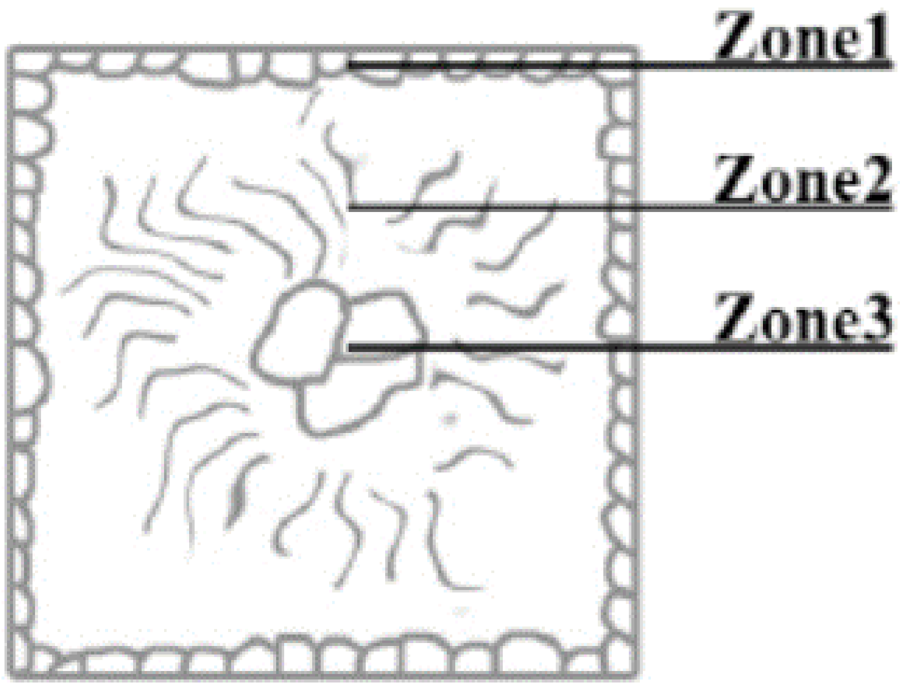
2. Transcrystallization zone with stem-like, very coarse crystallites

- directed growth of crystallites (stem crystals), where the crystallographic orientation aligns with the direction of the heat gradient;
- the orientation that arises from this => casting texture



3. Globular core zone

- impurities are pushed ahead by the stem crystals and accumulate in the core
- high number of different-type nuclei
- fine-grained globular core zone
- In very pure metals, however, a coarse-grained structure is found in the third zone



Microstructure Detection

- Generally, individual crystallites (grains) in a material are not visible to the naked eye.
- For materials science investigations, however, it is necessary to analyze the existing microstructure.
- Work steps:
    - targeted sample extraction
    - grinding and polishing the sample
    - etching the surface

Metallographic Sections

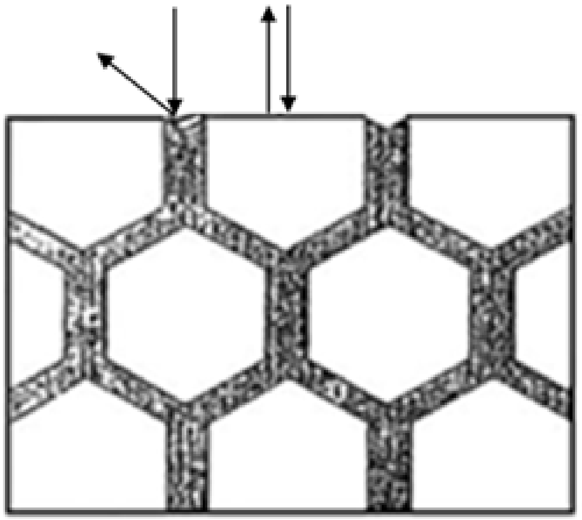
- A carefully prepared section can be viewed with a light or scanning electron microscope.
- The scanning electron microscope not only offers significantly higher resolution but also greater depth of field.

Etching

Etching for microstructure development can also be regarded as a corrosion process.

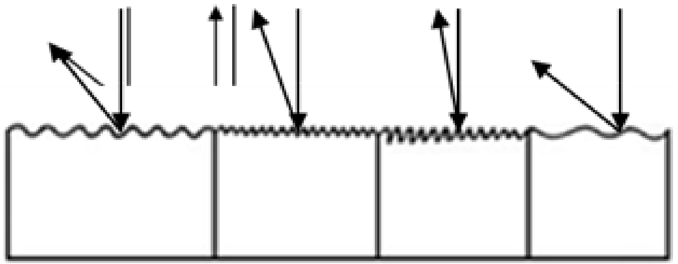
Grain boundary etching

- preferential dissolution of grain boundaries



Grain surface etching

- adjacent grain sections are roughened or covered with oxide layers to different extents
- grains reflect light differently



Macro Sections

Using macro etching, only those microstructural phenomena that are visible to the naked eye or under a magnifying glass can be studied. The following analyses are possible:

- Segregation and its localization: Heyn and Oberhoffer etching or Baumann print
- Quality of welds: Adler etching
- Development of force flow lines after plastic deformation: Fry etching

Terms for the Qualitative and Quantitative Description of Microstructures

Metallography - Metals

Ceramography - Ceramics

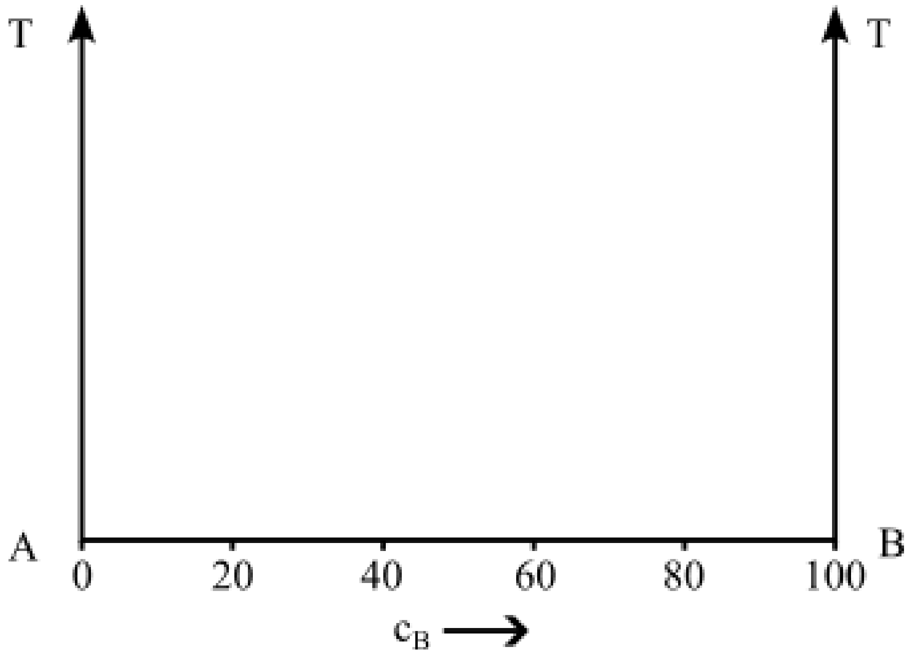
Plastography - Polymer materials

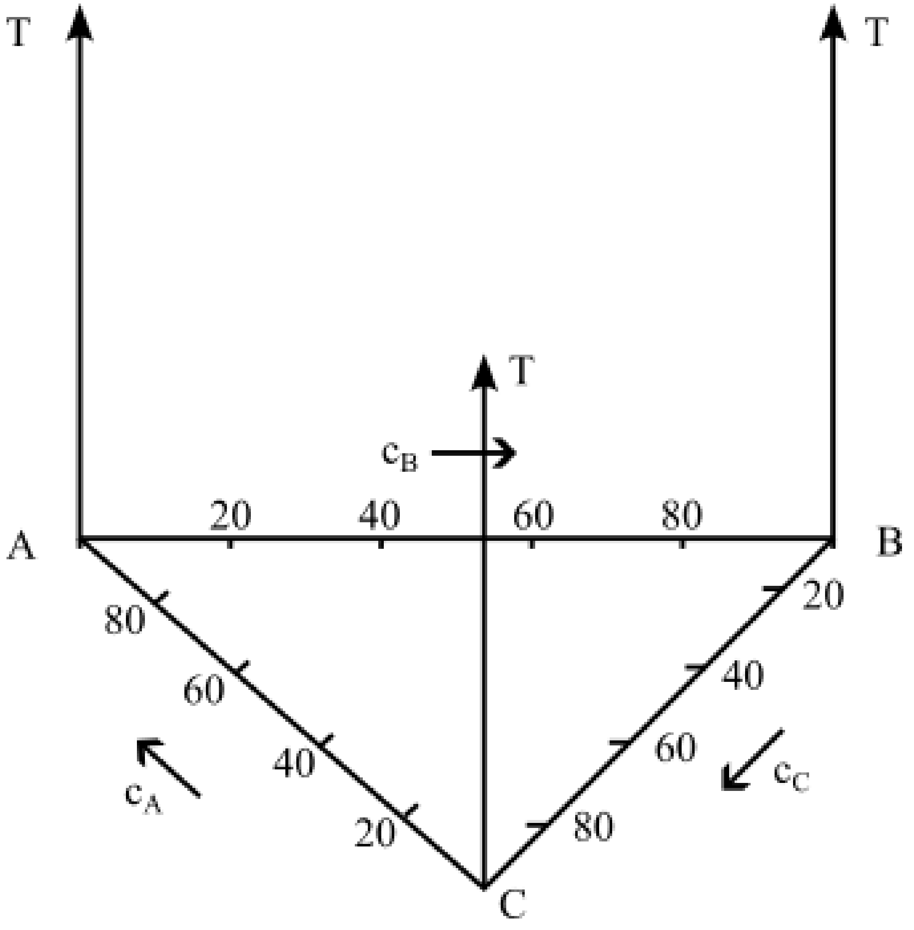
Phase Diagrams

- Also known as phase diagram
- Represents the state of alloys and material mixtures depending on chemical composition, temperature, and sometimes pressure
- The state refers to the phases present (all solid, liquid, gaseous)

Attention!

Phase diagrams are equilibrium diagrams. They are only valid for very slow cooling from the molten state to room temperature, where equilibrium between the phases (at or between phase boundaries) can be established.


T
T
A
B
0
20
40
60
80
100
c_B


T
T
T
c_B
20
40
60
80
A
B
80
60
40
20
20
40
60
80
c_A
c_C
C

Solubilities

- Insoluble
- Soluble

Example from Experience

- Oil film on water is insoluble and separates due to the difference in density
- Salt/sugar crystals in water dissolve completely and become invisible

Phase Diagrams (ZSD)

- Phases and phase boundaries can be represented as a phase diagram
- The number of phases in equilibrium is governed by the number of alloy components and the number of degrees of freedom according to the Gibbs Phase Rule
- A degree of freedom includes the possible change of state variables without changing the equilibrium (i.e., the number of phases)
- The number of freely selectable state variables is determined by the phase rule

Gibbs Phase Rule

$$F = n - P + 2$$

(for gases and liquids)

F = Degrees of freedom; n = Number of components; P = Number of phases

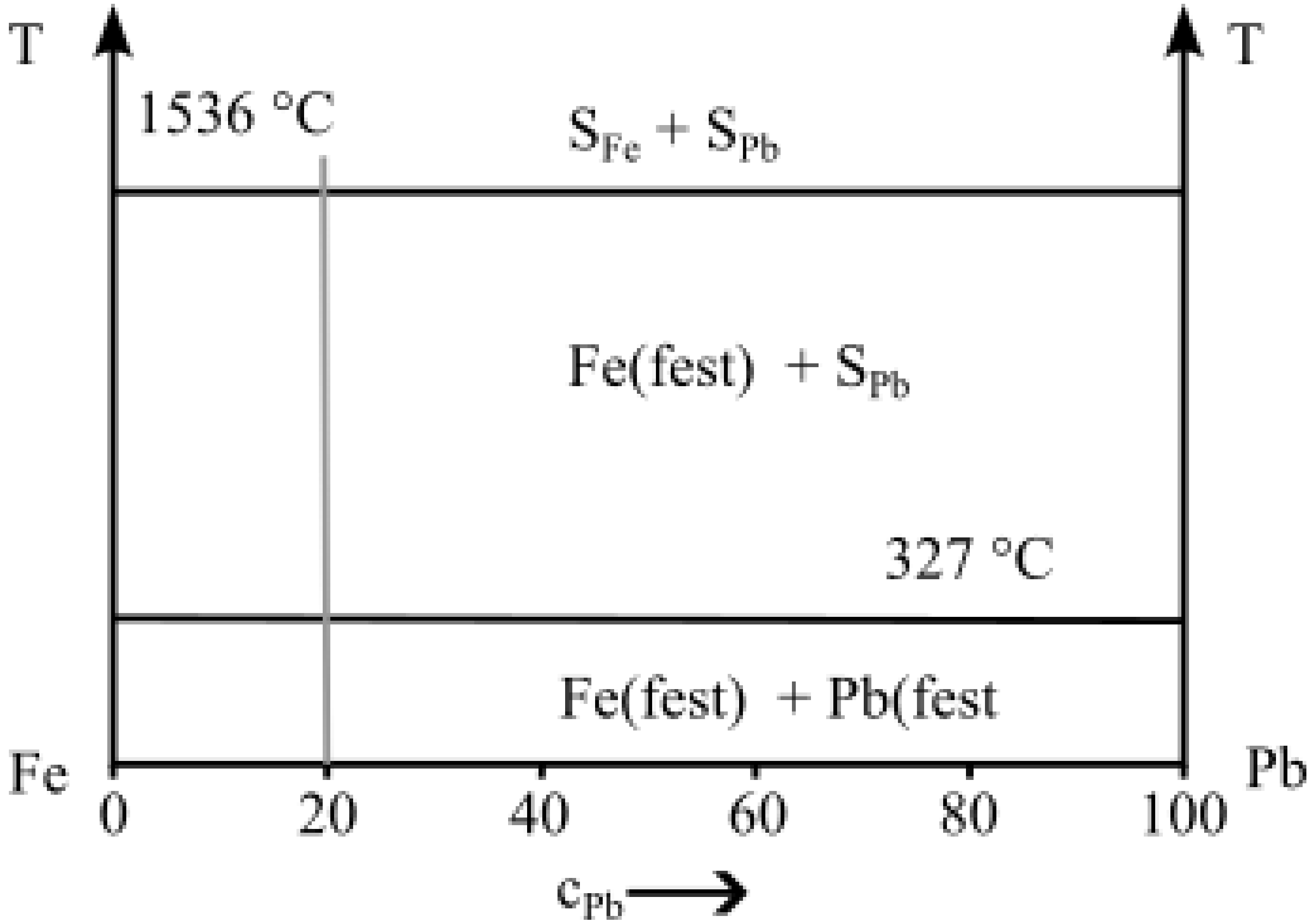
At constant pressure (solids):

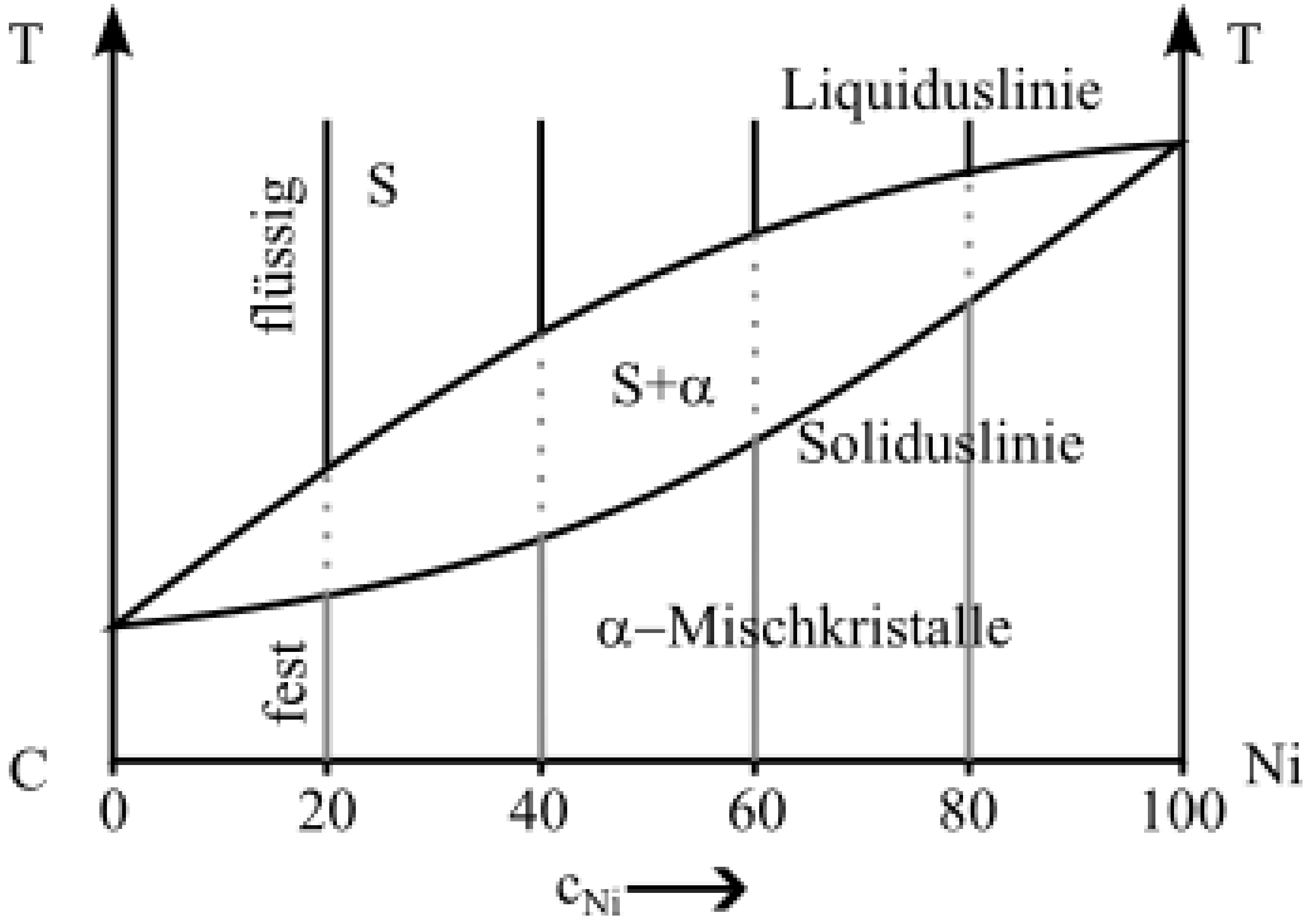
$$F = n - P + 1$$

Thus, for cooling and heating curves of metallic systems:

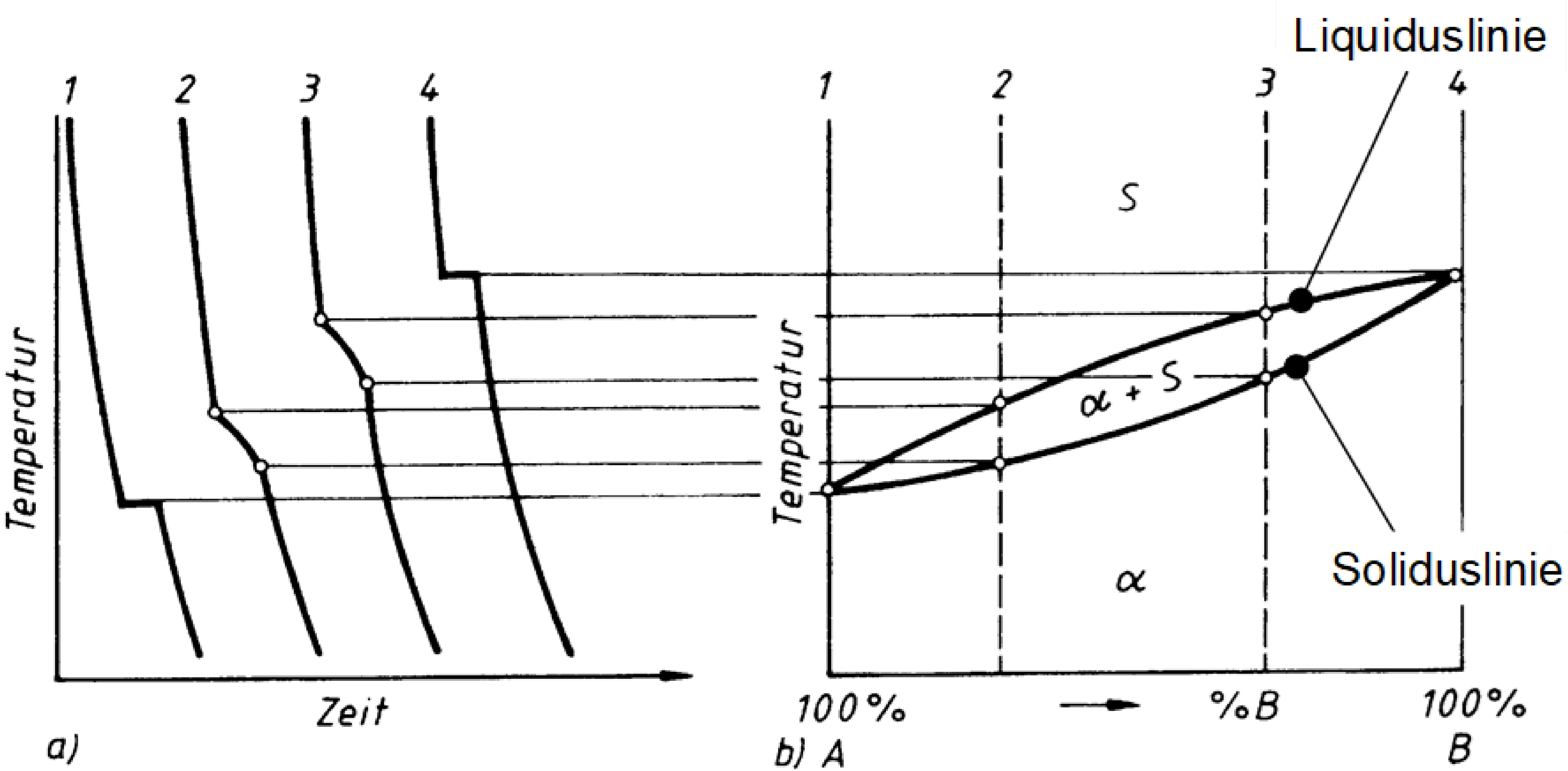
F = 0 → a hold point and

F = 1 → a break point.


T
T
1536 °C
S_Fe + S_Pb
Fe(fest) + S_Pb
327 °C
Fe(fest) + Pb(fest
Fe
Pb
0
20
40
60
80
100
c_Pb



T
T
Liquiduslinie
flüssig
S
S+α
Soliduslinie
α–Mischkristalle
fest
C
Ni
0
20
40
60
80
100
c_{Ni}


Liquiduslinie
1
2
3
4
Temperatur
Zeit
a)
1
2
3
4
S
α + S
α
Temperatur
100 %
% B
100 %
b) A
B
Soliduslinie

Eutectic Separation

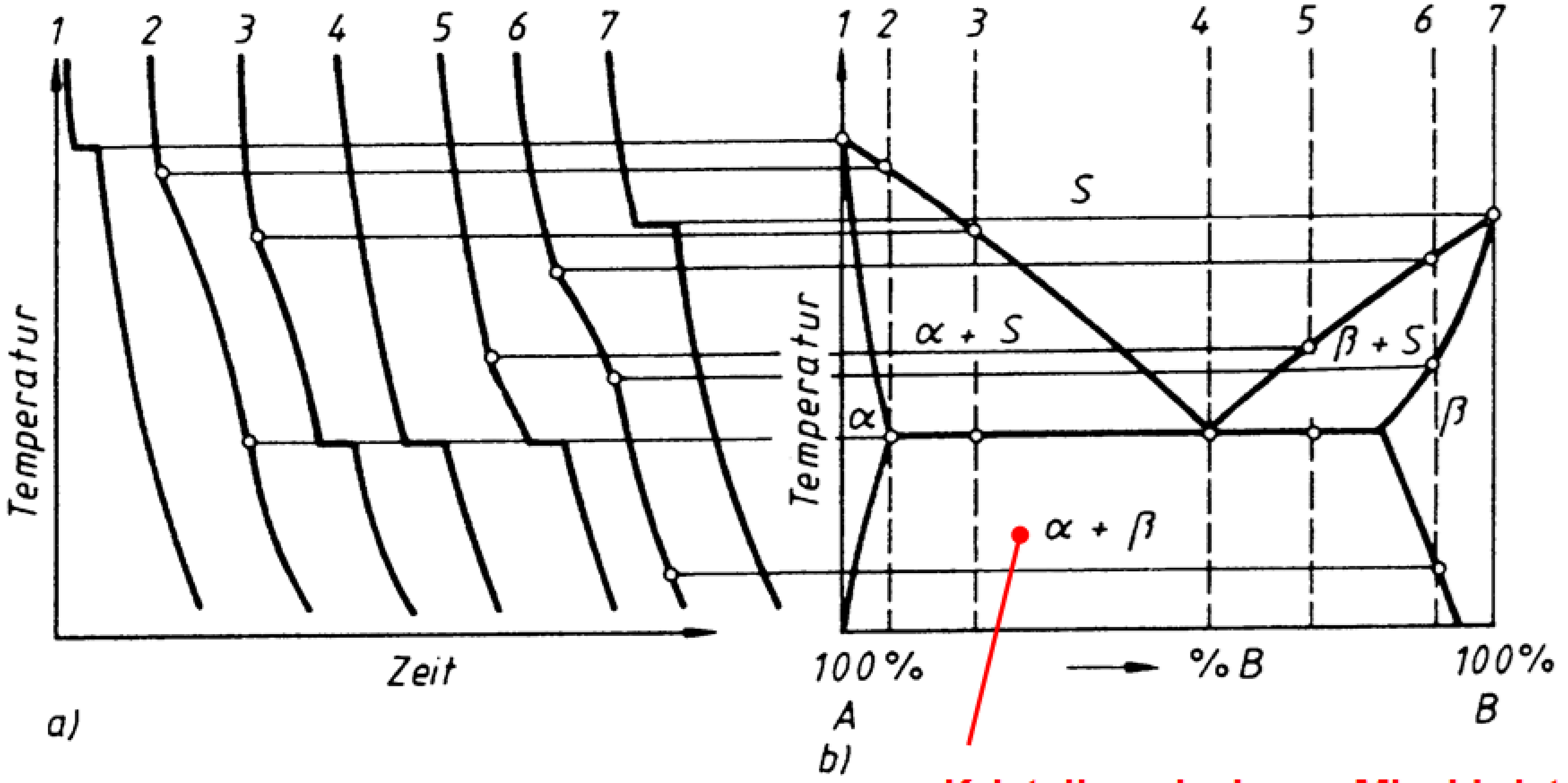
- Components are **soluble** in the liquid state
- Components are **insoluble** in the solid state

Eutectic Reaction

- At a particular concentration, S crystals of A and B solidify into a fine-grained crystal mixture (eutectic) at a constant temperature (eutectic line)
- Eutectic structure often has a layered or lamellar structure
- Alloys of other concentrations precipitate the predominant component (A or B crystals) before reaching the eutectic line, so the concentration of the remaining melt approaches the eutectic composition
- The eutectic line forms the solidus line of the entire system

Systems with Miscibility Gaps

- Components are **soluble** in the liquid state
- Components are **partially soluble** in the solid state



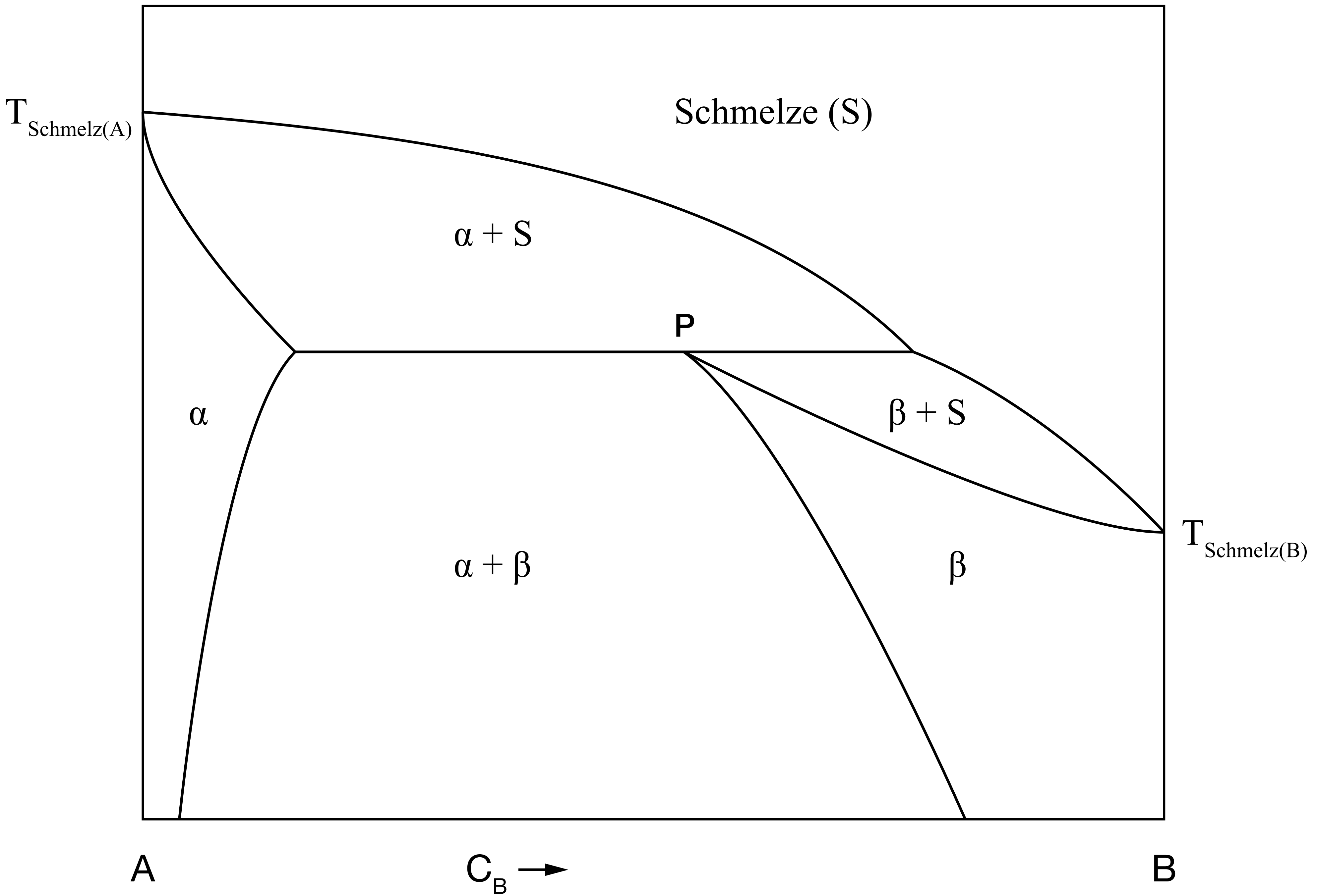
Kristallgemisch aus Mischkristallen

Solubility or saturation lines

- Lines separating single-phase regions (α, β) from the region of crystal mixtures ($\alpha + \beta$)
  Special case:
- A system of mixed crystals forms interstitial solid solutions
- The concentration axis ends with the saturation of component B in the lattice of component A
- The single-phase region of component B cannot exist.

Systems with Peritectics (Peritectic Separation)

- Significantly different melting/solidification temperatures of the components are characteristic
- On cooling from the melt, an α solid solution forms
- At constant temperature (peritectic line), α and the melt react to form a second solid solution, β
- In a peritectic reaction, β solid solutions form from the melt and already precipitated α solid solutions at constant temperature.



$T_{Schmelz(A)}$
Schmelze (S)
α + S
P
α
β + S
$T_{Schmelz(B)}$
α + β
β
A
C_B →
B

Real Diagrams

- Previous diagrams were ideal and do not occur in reality
- The iron-carbon diagram (EKD) is the most important real diagram
- Base metal is iron -> steel or cast iron
- The EKD consists of ideal diagrams - the peritectic, eutectic, and eutectoid subdiagrams

- Depending on the form of carbon, a distinction can be made between the stable system Fe-C, where carbon exists as graphite, and the metastable system Fe-Fe3C, where carbon is present as Fe3C (intermediate phase cementite)
- Stable means that carbon cannot be broken down further as graphite, but Fe3C decomposes into iron and temper carbon after long-term annealing
- The metastable system represents a relative minimum of the system's total energy. For technical purposes, it can be considered "sufficiently stable."

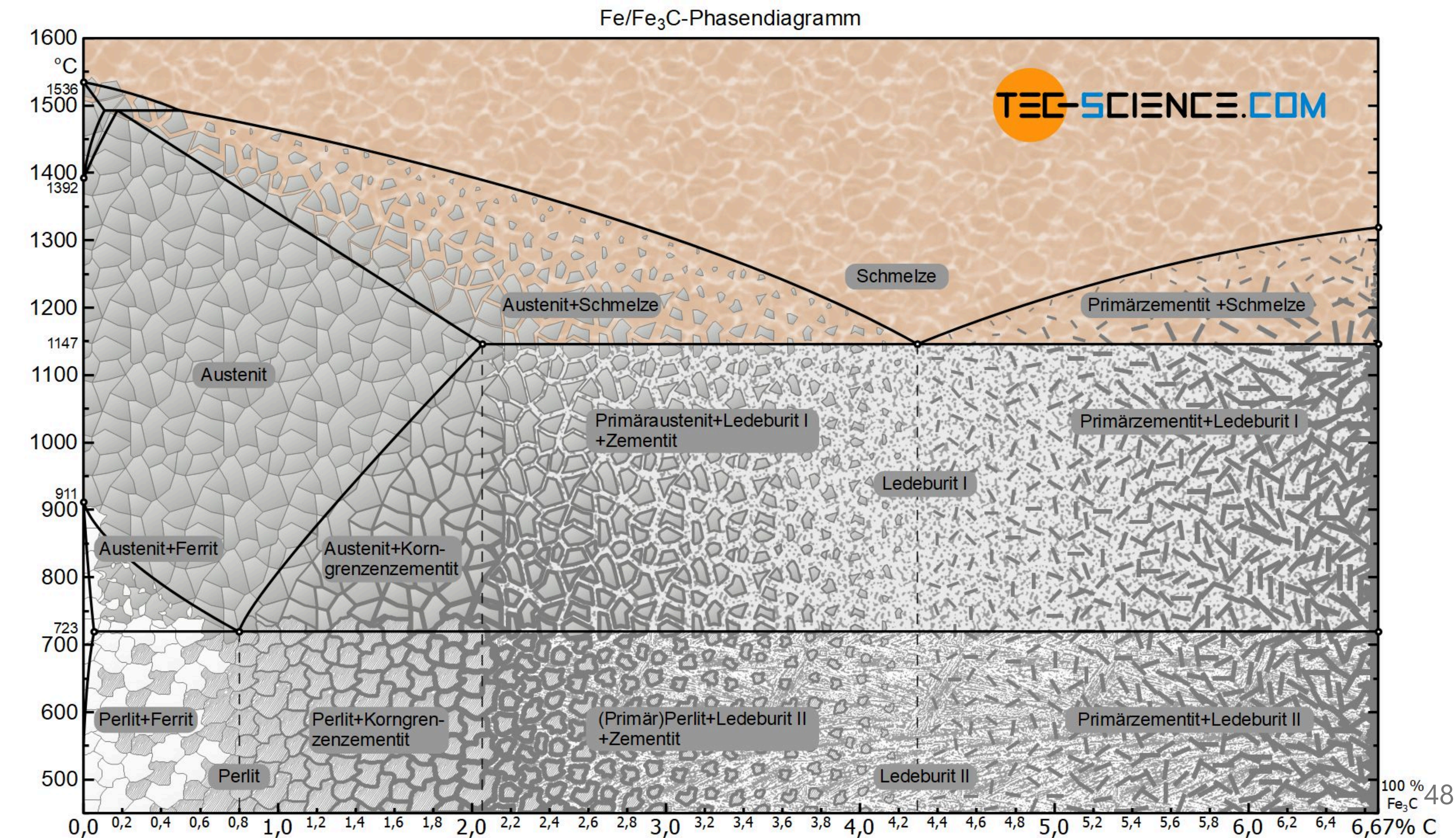
Iron-Carbon Diagram (EKD)

- Most important phase diagram
- Iron is the most important material in mechanical engineering.

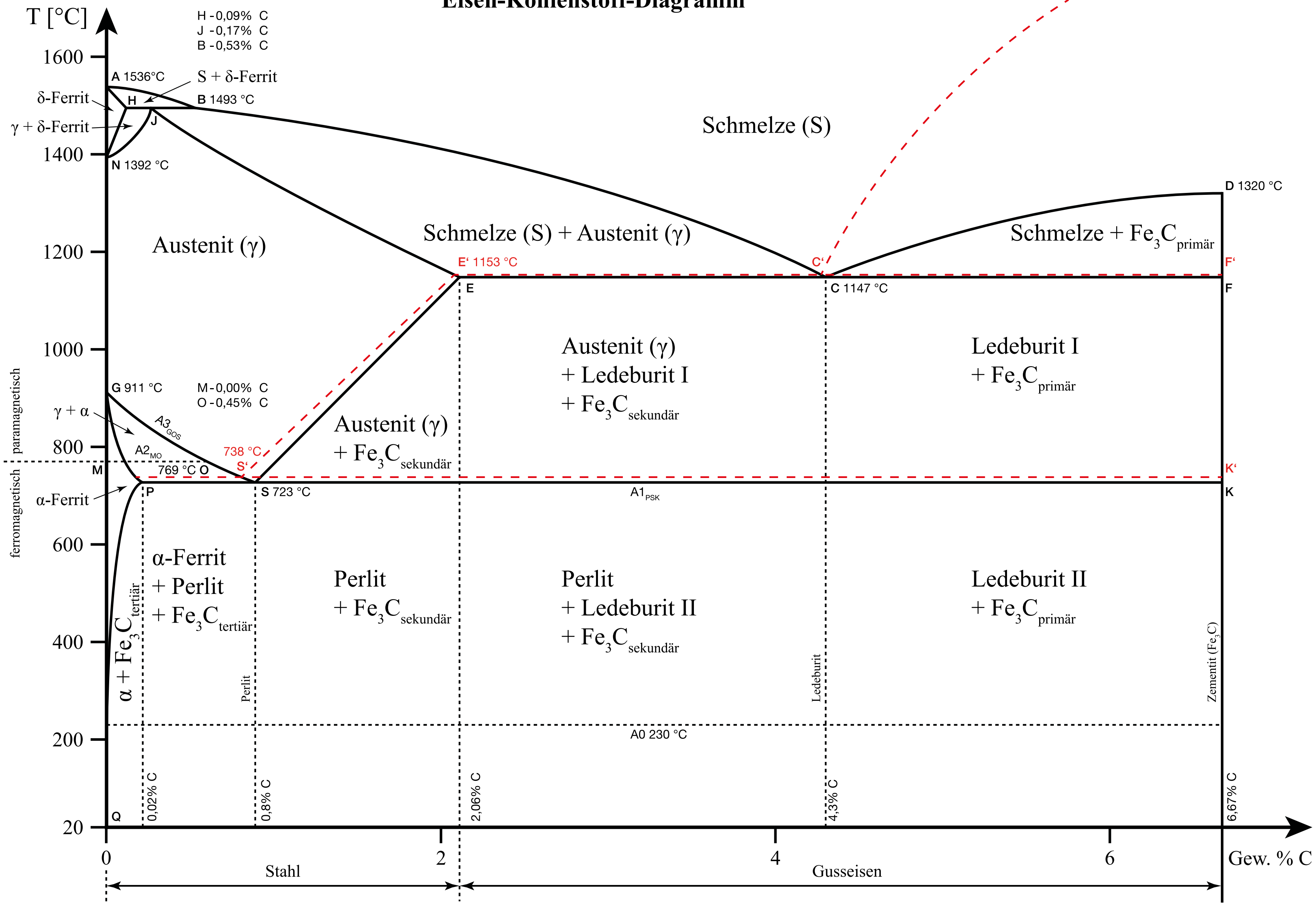
Reasons:

- Low cost
- High strength and elastic stiffness
- Variety of possible alloys
- Availability
- Castability, weldability, etc.

Explanation video for the Iron-Carbon Diagram


Fe/Fe3C-Phasendiagramm
1600
°C
1536
1500
1400
1392
1300
1200
1147
1100
1000
911
900
800
723
700
600
500
tec-science.com
Schmelze
Austenit+Schmelze
Primärzementit +Schmelze
Austenit
Primäraustenit+Ledeburit I
+Zementit
Primärzementit+Ledeburit I
Ledeburit I
Austenit+Ferrit
Austenit+Korn-
grenzenzementit
Perlit+Ferrit
Perlit+Korngren-
zenzementit
(Primär)Perlit+Ledeburit II
+Zementit
Primärzementit+Ledeburit II
Perlit
Ledeburit II
100 %
Fe3C
0,0 0,2 0,4 0,6 0,8 1,0 1,2 1,4 1,6 1,8 2,0 2,2 2,4 2,6 2,8 3,0 3,2 3,4 3,6 3,8 4,0 4,2 4,4 4,6 4,8 5,0 5,2 5,4 5,6 5,8 6,0 6,2 6,4 6,67% C

Eisen-Kohlenstoff-Diagramm



Important Equilibrium Lines

ABCD - Liquidus line

AHIECF - Solidus line

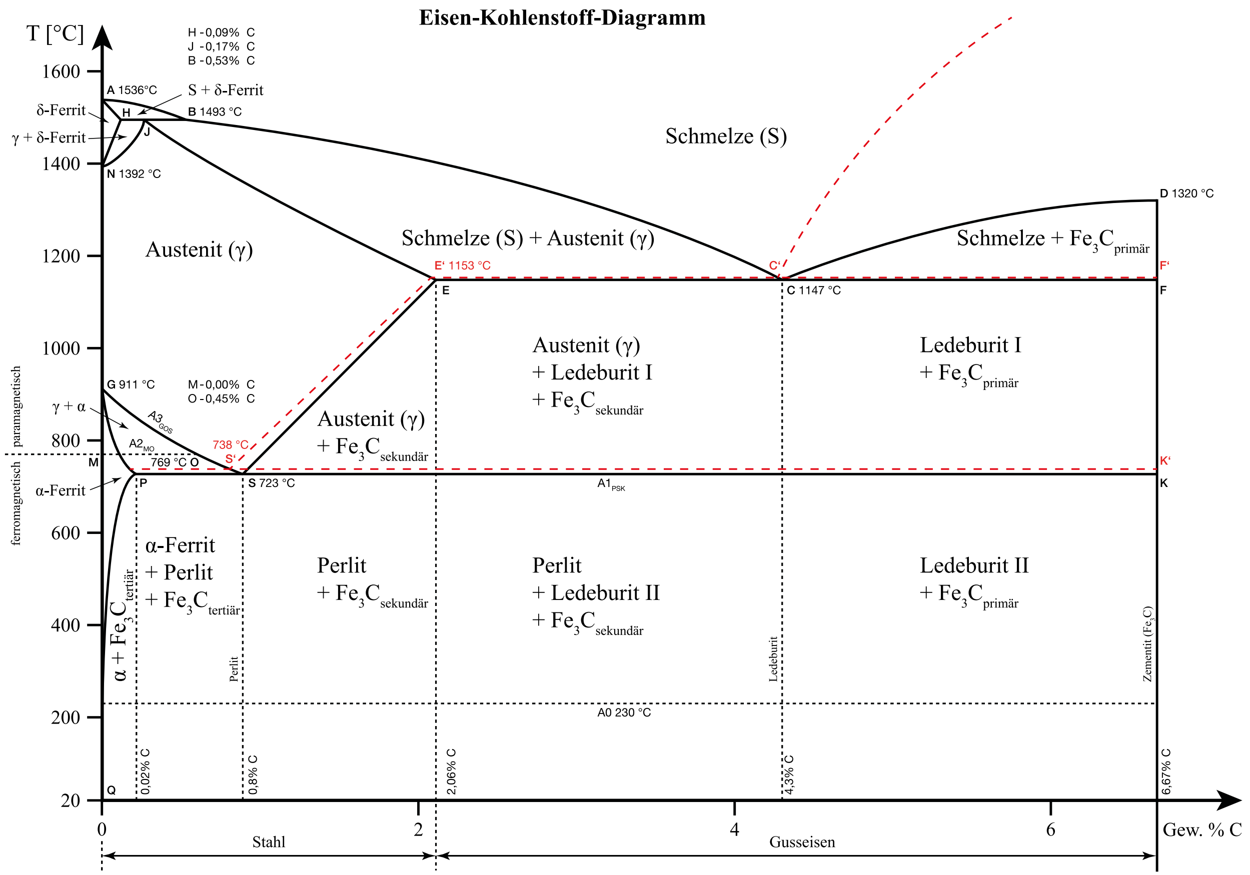
ECF - Eutectic line

PSK - Eutectoid

ES, PQ - Saturation lines

MOSK - Curie line

QPSECD - Formation/Dissolution of Fe3C



Points in the Phase Diagram

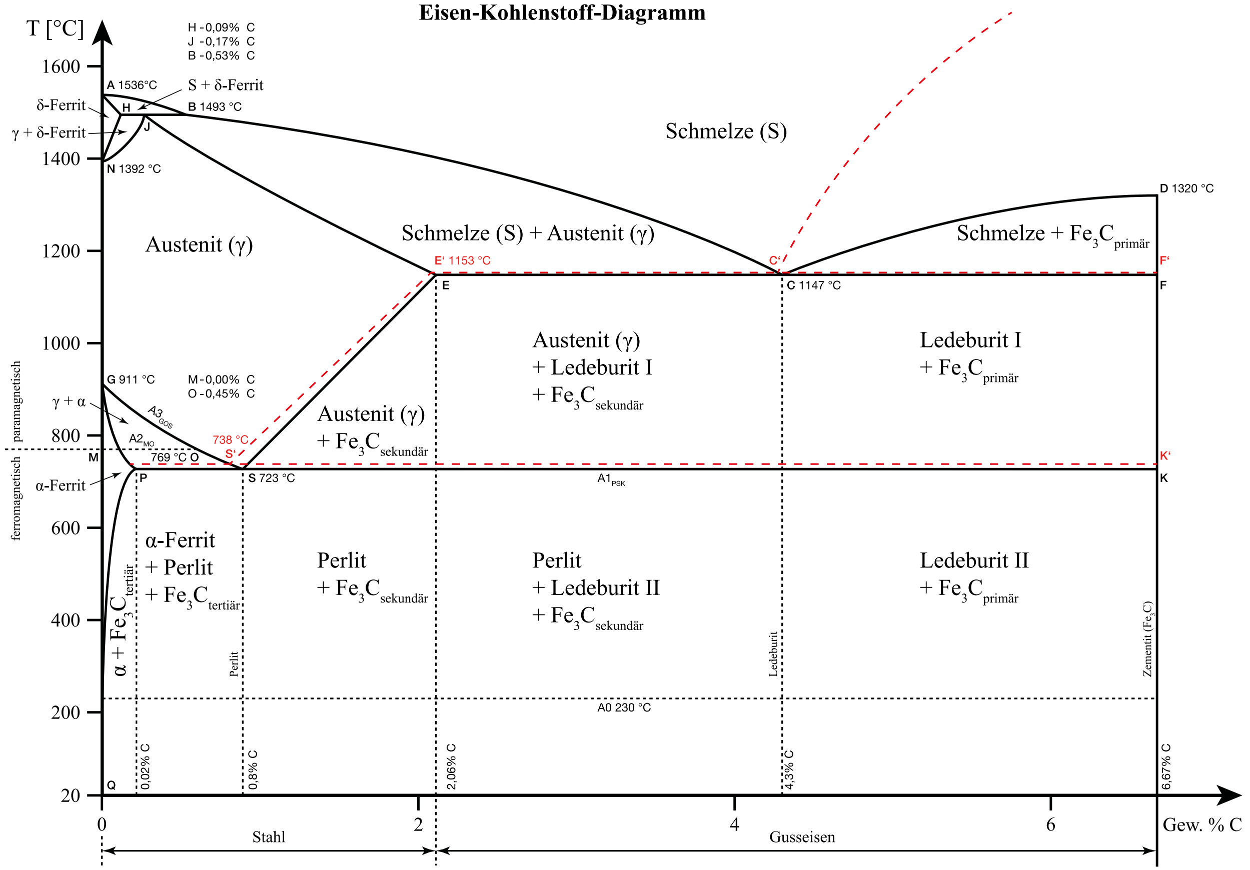
S - Eutectoid point

C - Eutectic point

G - α / γ transformation point of pure iron

E - Point of maximum C solubility in α-solid solution (MK)

P - Point of maximum C solubility in γ-solid solution (MK)



The following equilibrium temperatures (transformation temperatures) are used:

A - arreter (to stop)
r - refroidir (to cool)
c - chauffer (to heat)
e - équilibre (equilibrium)

- Ac1: 723°C
- Ac3: dependent on C content

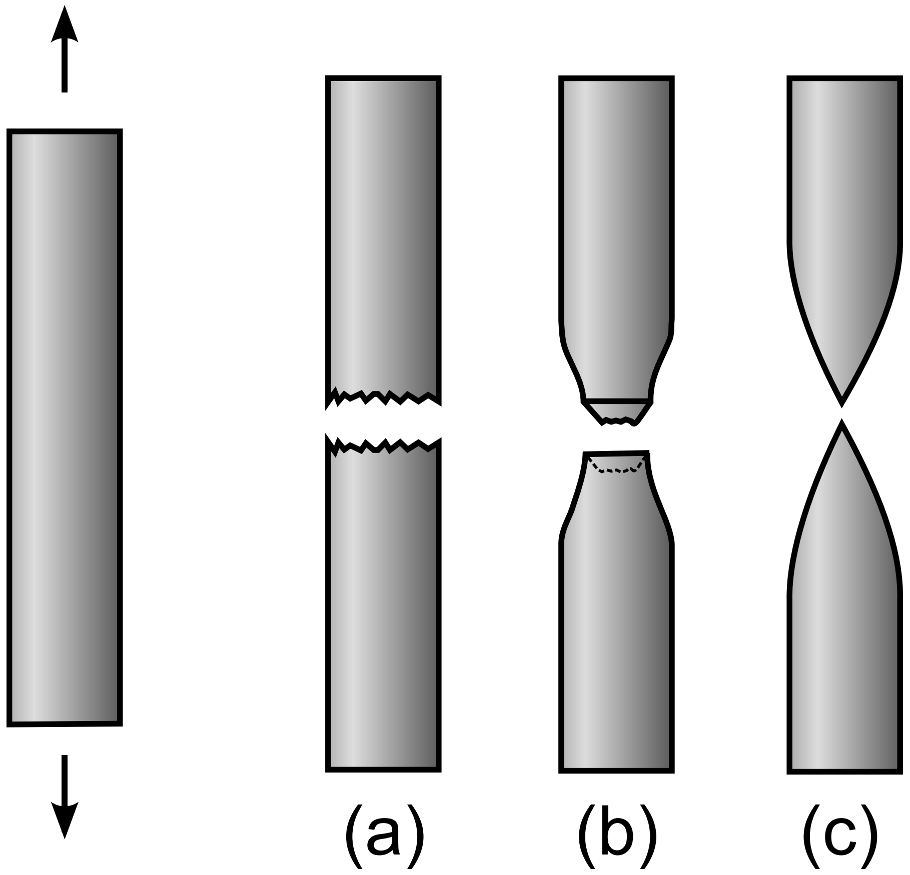
Grenzlinie im Fe-C-Diagramm	...begrenzt das Umwandlungs-geschehen	Bezeichnung der Grenzlinien-temperaturen, ermittelt im Gleichgewicht	beim Abkühlen	beim Erwärmen
PSK	$\alpha + Fe_3C \leftrightarrow \gamma$	A_{e1}	A_{r1}	A_{c1}
GS	$\alpha + \gamma \leftrightarrow \gamma$	A_{e3}	A_{r3}	A_{c3}
SE	$\gamma + Fe_3C \leftrightarrow \gamma$	$A_{e\,cm}$	$A_{r\,cm}$	$A_{c\,cm}$
NI	$\gamma + \delta \leftrightarrow \gamma$	A_{e4}	A_{r4}	A_{c4}

Phases and Microstructures in the Iron-Carbon System

Solid Solutions

α-Solid Solution (bcc)

- Structure called Ferrite (α-Ferrite)
- Pure ferritic structure has low hardness/strength but high ductility (toughness)
- Max. C solubility: only 0.02%



δ-Solid Solution (bcc)

- δ-Ferrite is only stable above 1392°C
- Technically of minor importance
- Max. C solubility: 0.12%

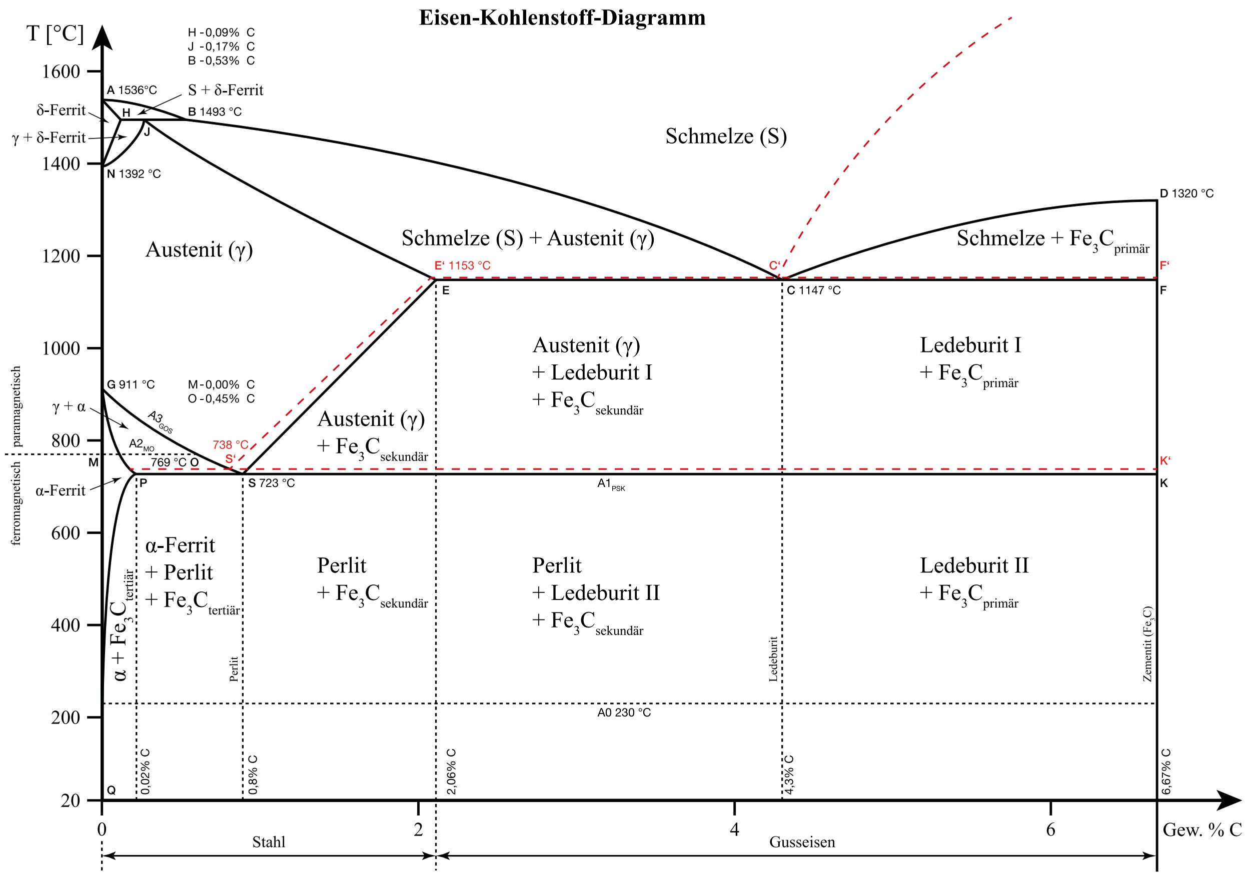
γ-Solid Solution (fcc)

- Structure called Austenite
- Forms above the G-S-E line
- Stable at room temperature by alloying with Ni, Mn, and quenching (austenitic steels)
- Non-magnetic, tough, and can be hardened by cold working
- Max. C solubility: 2.06%

Intermediary Phase

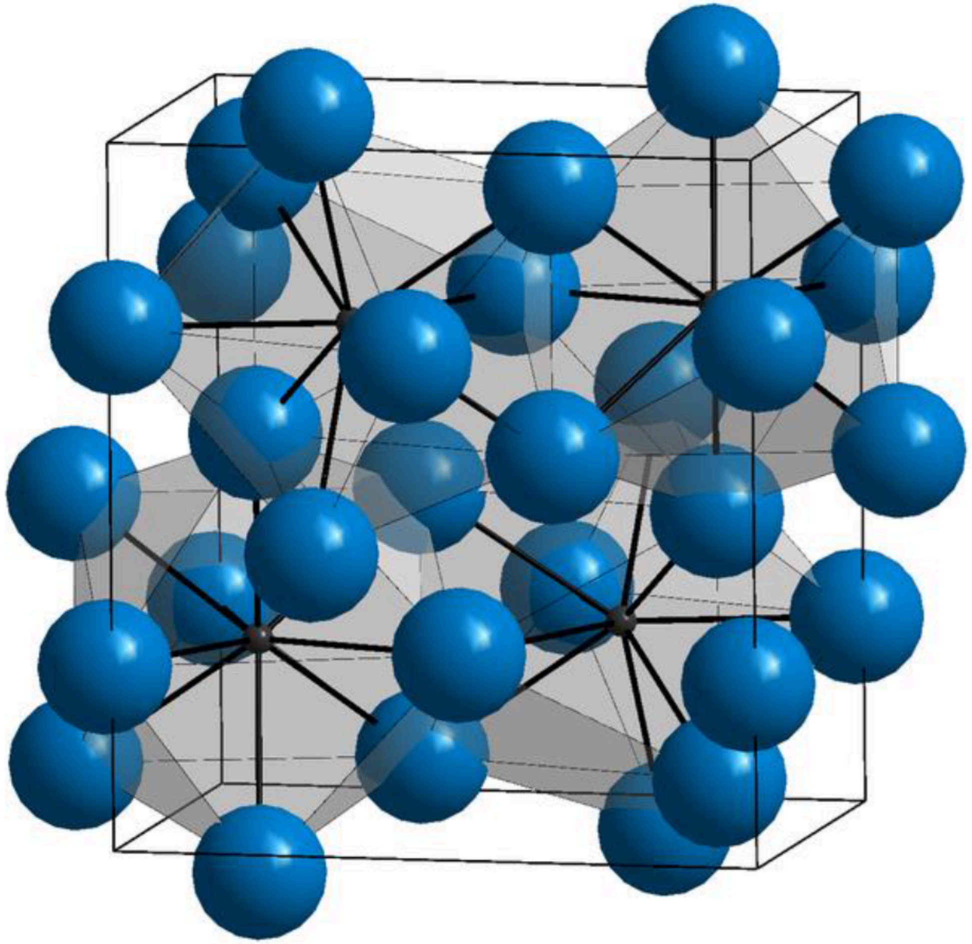
Cementite (Iron carbide Fe3C); 6.67 mass-% C content

- **Primary cementite**: primary crystallization from the melt (line CD)
- **Secondary cementite**: precipitated from austenite (line ES)
- **Tertiary cementite**: precipitated from ferrite (line PQ)



Crystal Structure of Cementite

- Orthorhombic unit cell
- Contains 12 iron and 4 carbon atoms
- Carbon atoms are irregularly surrounded by eight iron atoms in a distorted trigonal-prismatic arrangement



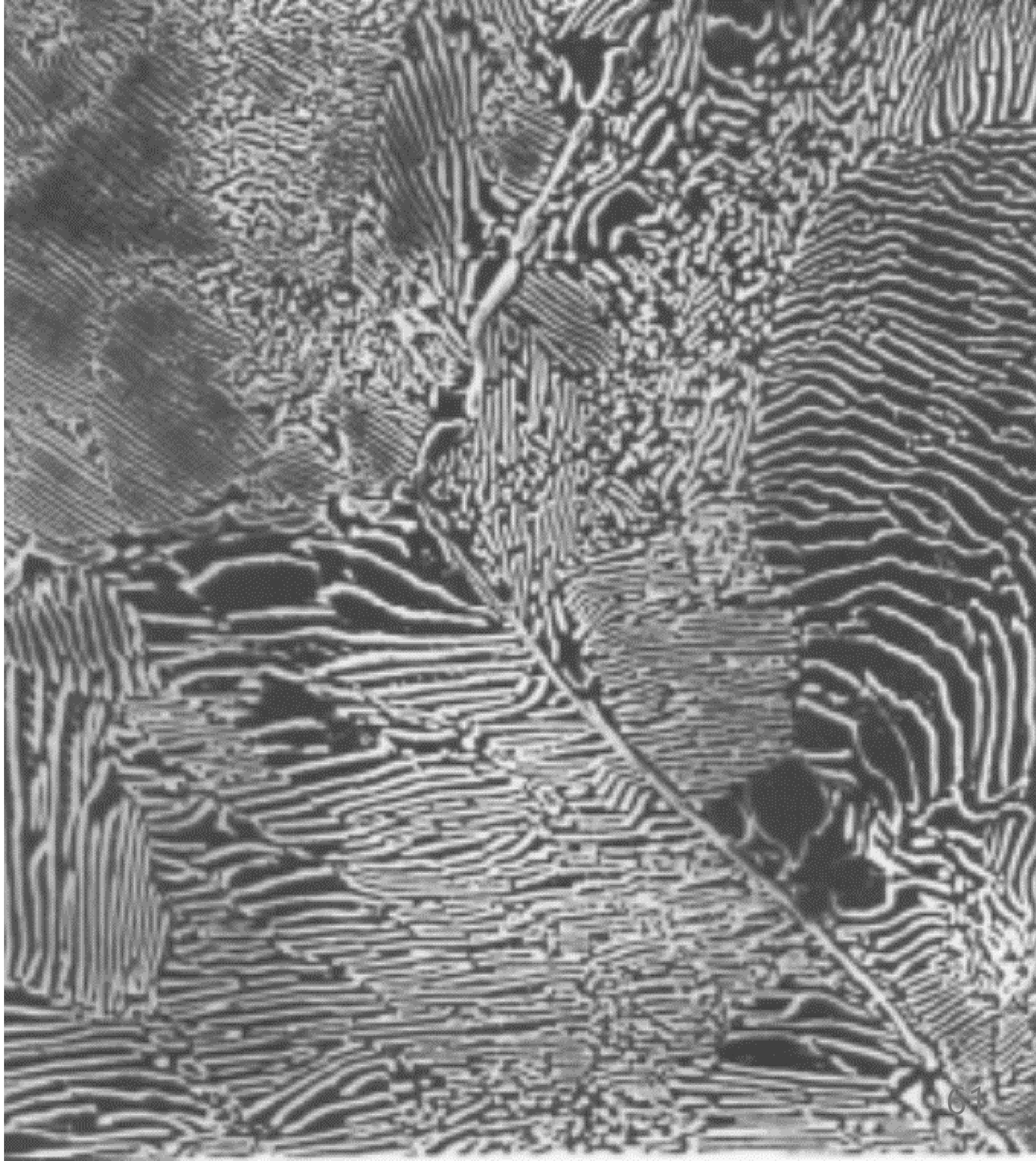
Cementite is hard and brittle. The majority of technical iron-carbon alloys solidify with the formation of cementite.

Phase Mixtures / Mixtures of Solid Solutions

Pearlite (Eutectoid)

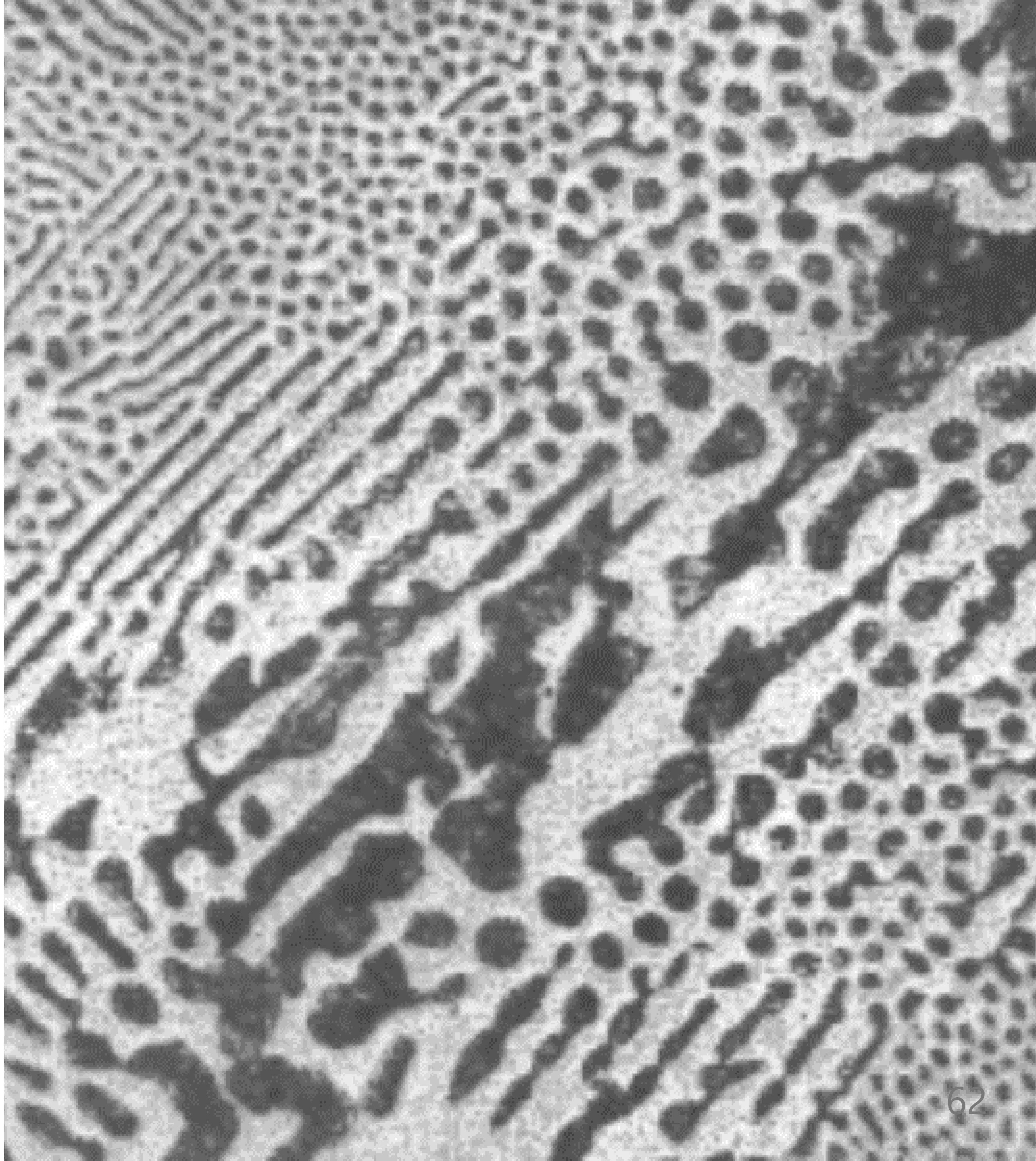
- Structure consisting of cementite and ferrite (phase mixture)
- Forms by the "eutectoid" decomposition of austenite (γ-solid solution) with 0.8% C at 723°C
- Eutectoid point S: 100% pearlite at this point
- Relatively high hardness, strength, poor formability, and low toughness

- Lamellar structure (layers of α-solid solution and Fe3C crystals)
- Often referred to as a "pearlite stage," subdivided into pearlite, fine-lamellar, and ultra-fine-lamellar pearlite based on lamellar spacing.



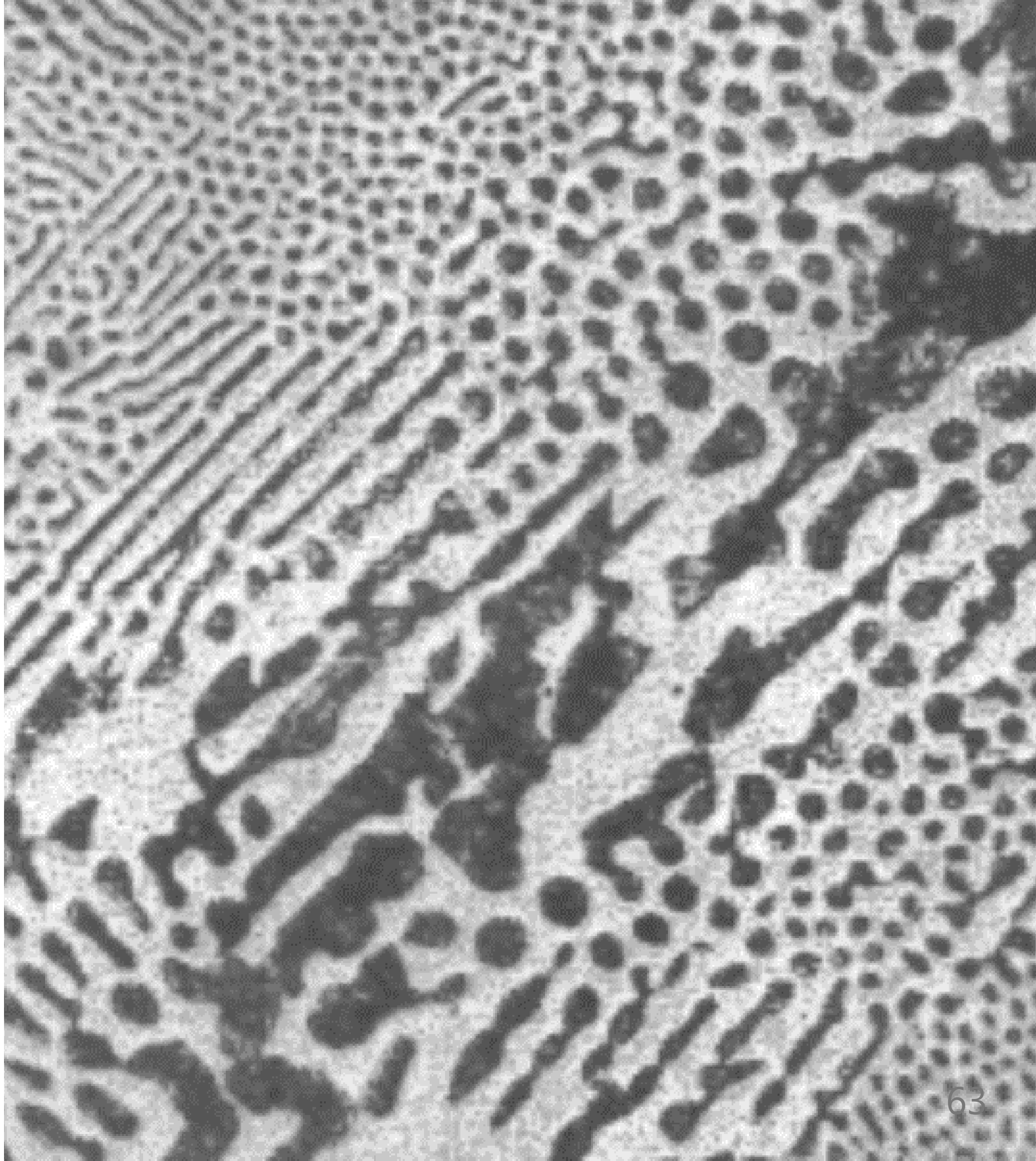
Ledeburite (Eutectic)

- Structure consisting of austenite and cementite or "decomposed" austenite and cementite (phase mixture), carbon content 4.3%, melting temperature 1147°C
- Eutectic point C: 100% ledeburite at this point
- Distinction between Ledeburite I (just below 1147°C), and Ledeburite II at room temperature.



Ledeburite (Eutectic)

- At room temperature, ledeburite appears as a fine mixture of Fe3C crystals and pearlite, visible under a light microscope as a characteristic "panther fur" structure.



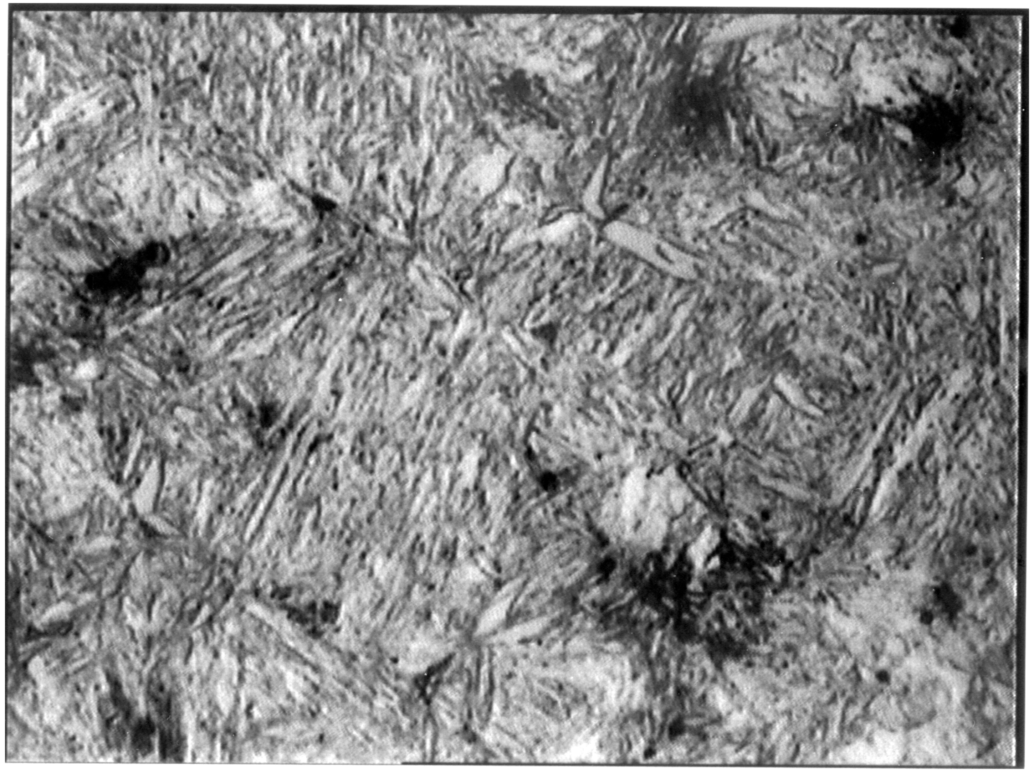
The properties of the alloy (e.g., steel, cast iron) are determined by the types of phases present (e.g., α-solid solution, Fe3C), their quantity (dependent on C content), and the distribution within the structure.

Phases and Microstructures in Non-equilibrium Conditions

- Equilibrium states are dominated by diffusion processes
- With faster temperature changes, carbon diffusion, which is necessary for the decomposition of austenite, is hindered
- This results in new microstructural components that no longer correspond to the equilibrium state
- Leads to "supersaturated" carbon

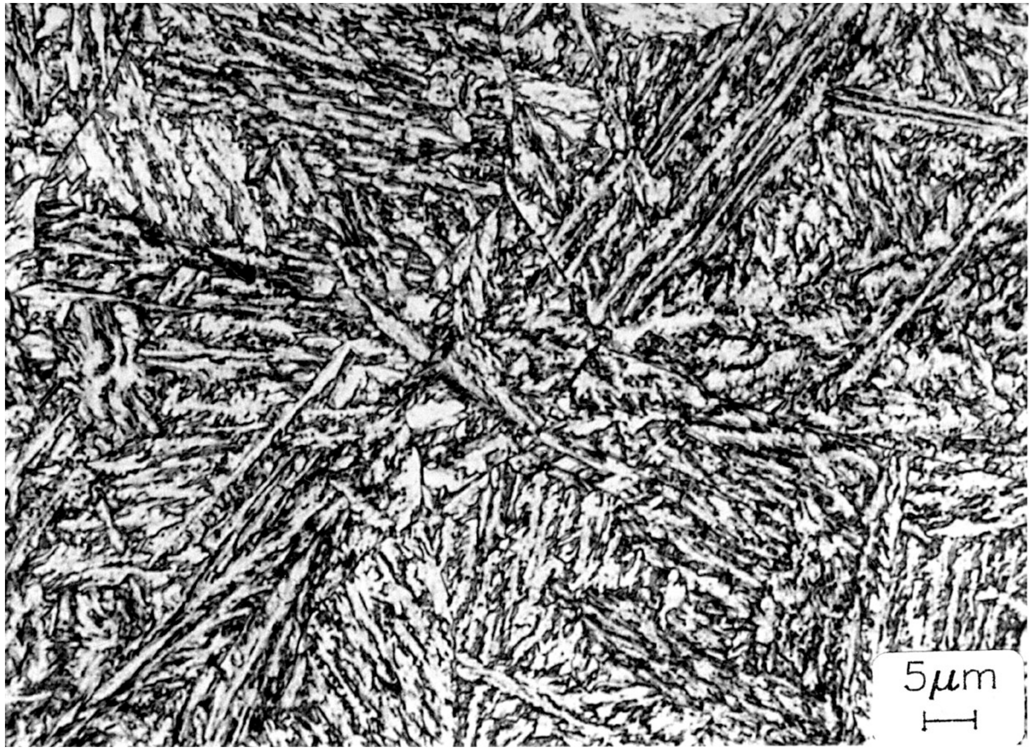
Martensite

- Body-centered tetragonal (BCT) lattice ("strained ferritic lattice")
- Mostly fine-needle-like, very hard, and brittle microstructure
- Carbon trapped in the BCC lattice of α-Fe distorts the lattice and expands it tetragonally ("diffusionless transformation")



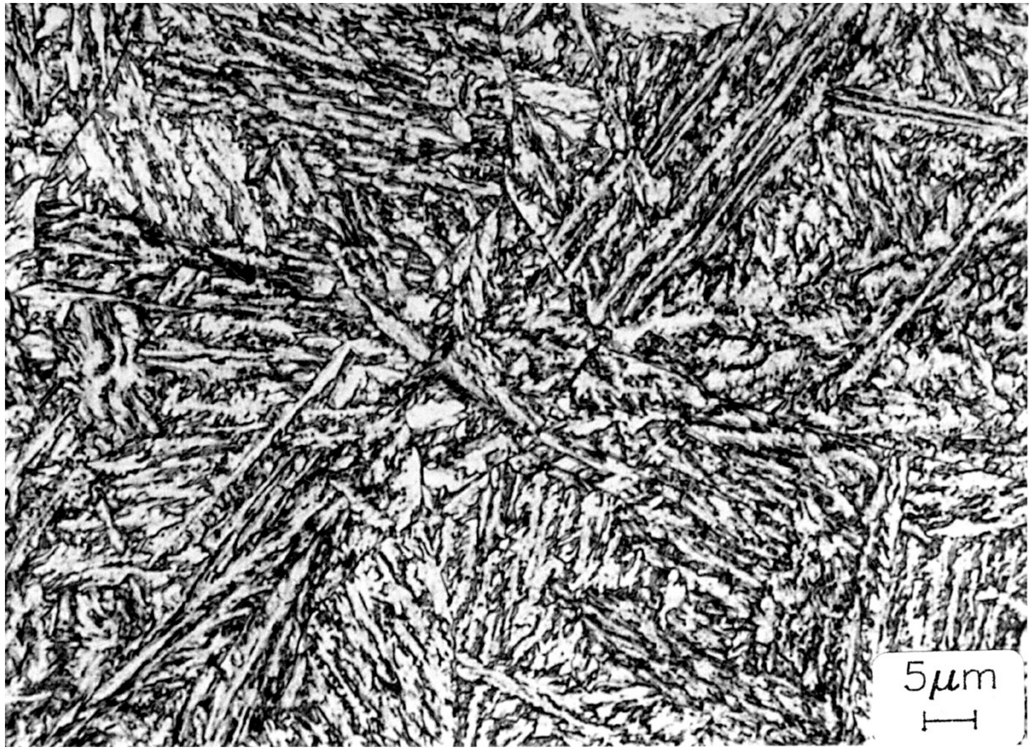
Bainite

- Unlike the formation of martensite, here the transformation in the crystal lattice is coupled with diffusion processes
- Forms in the temperature range between pearlite and martensite at cooling rates too low for martensite formation but too high for pearlite formation



Bainite

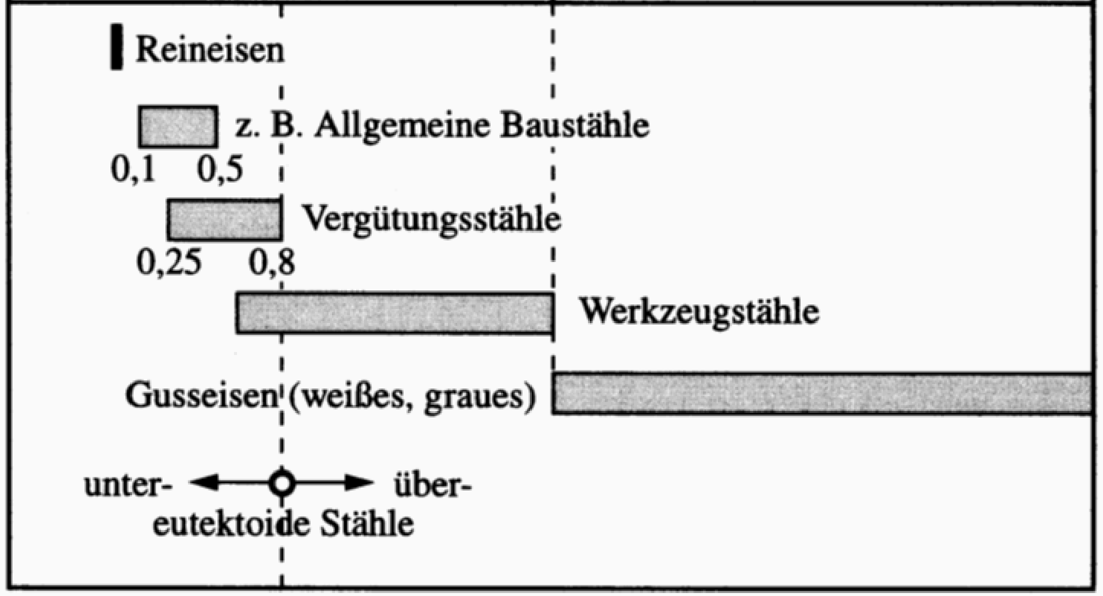
- Pure bainite can only be achieved through isothermal cooling, e.g., during austempering
- Advantageous where hardening and tempering may cause cracks
- It has excellent strength and toughness properties



Iron-Carbon Alloy Designations

Carbon Content (mass-%)	Designation	Type
0.02 < C < 0.8	(Carbon) steel	Hypoeutectoid steels
C = 0.8	(Carbon) steel	Eutectoid steels
0.8 < C < 2.06	(Carbon) steel	Hypereutectoid steels
2.06 < C < 4.3	Cast iron	Hypoeutectic cast iron
C = 4.3	Cast iron	Eutectic cast iron
4.3 < C < 6.67	Cast iron	Hypereutectic cast iron

Stähle		Gusseisen
Festigkeit nimmt zu, Verformbarkeit mäßig ab	hohe Festigkeit durch Härten und Vergüten, aber spröde und schlagempfindlich	mäßige Festigkeit (außer GGG und legiertem Gusseisen), sehr spröde, sehr schlagempfindlich
Bei geeigneter Wärmebehandlung sind Werkstoffe warm-, z. T. kaltverformbar, härt- und vergütbar		Ledeburit verhindert Warmformgebung



- Furthermore, a distinction is made between black cast iron (gray cast iron), in which the excess carbon appears as graphite, and white cast iron, where the carbon is in the form of cementite
- As the C content increases, the strength and hardenability of the steel increase, while its elongation, forgeability, weldability, and machinability (via cutting tools) decrease
- The corrosion resistance to water, acids, and hot gases is practically unaffected by the carbon content
- Steels with carbon content below 0.25 mass-% are well weldable

References

Rainer Schwab: Material Science and Material Testing for Dummies, 2019; ISBN-10 352771538X

Basics of Metallurgy