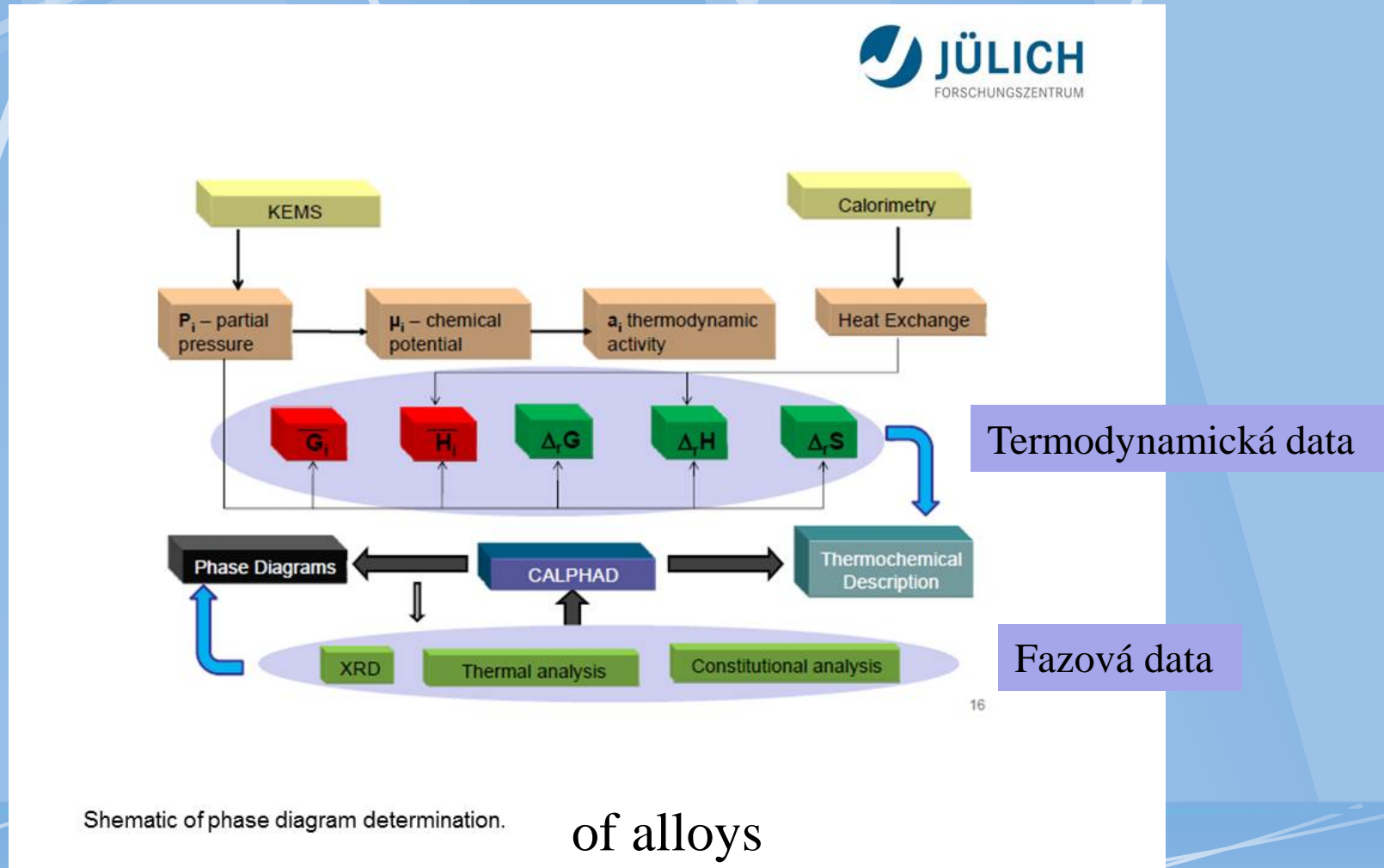


Experimentální metody studia FR

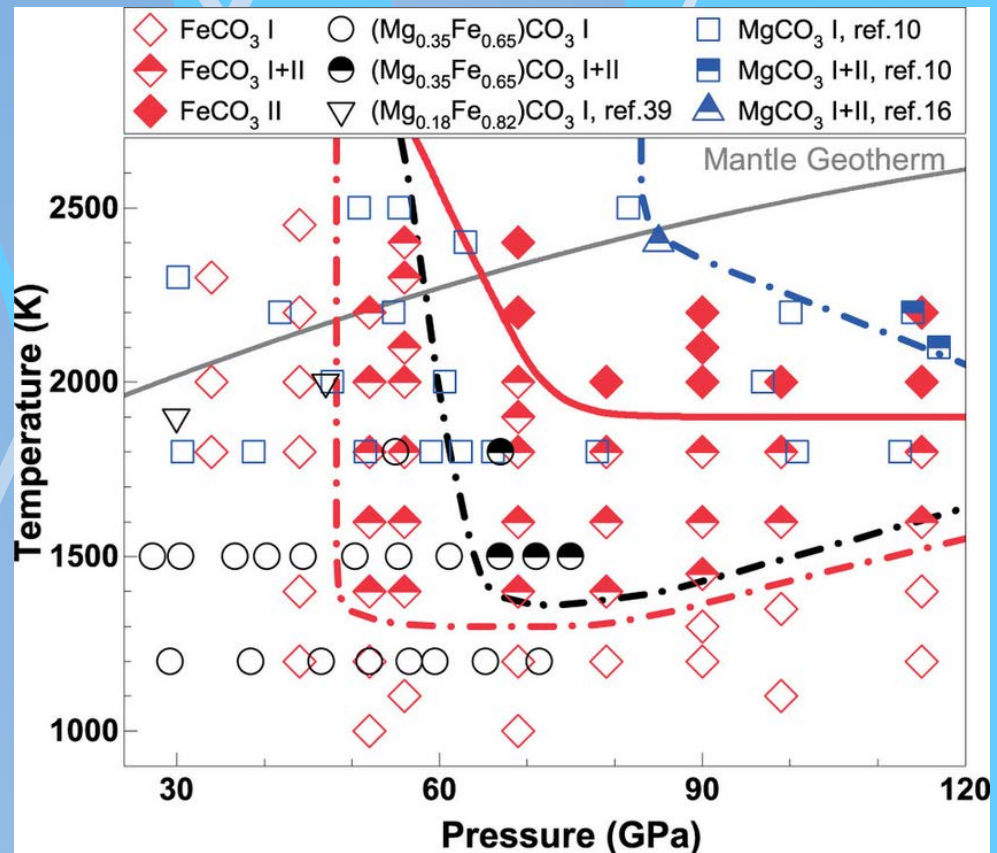


Experiment

Měření fázových dat

Měření termodynamických dat

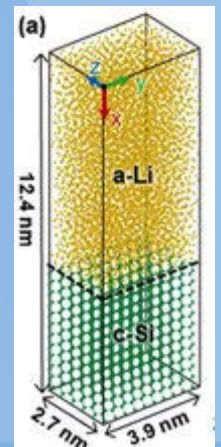
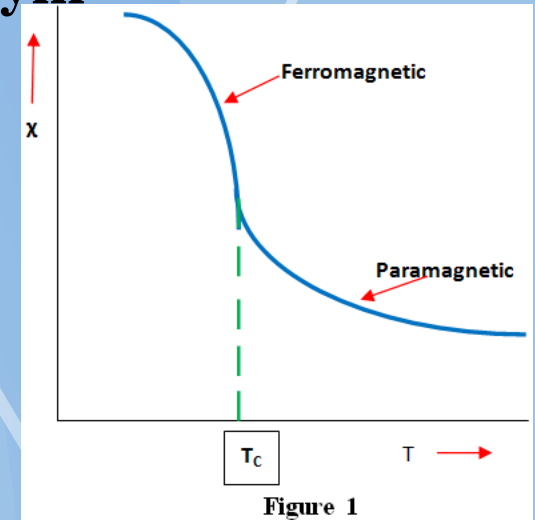
Viz data získaná řešením
fázové rovnováhy v
uzavřené soustavě
nacházející se v
termodynamické
rovnováze



Při experimentu měníme teplotu, (tlak), složení.

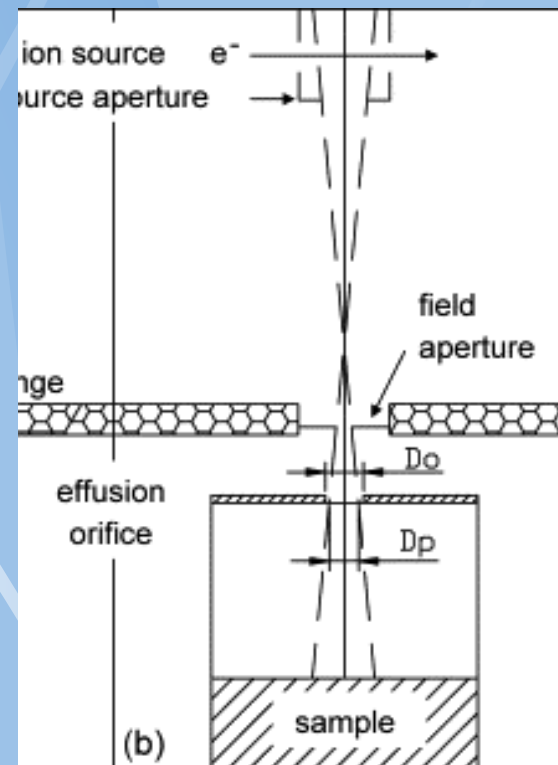
Měření fázových dat

- **Neisotermální metody (pro soustavy s rychlým ustavením termodynamické rovnováhy)**
 - Termická analýza (TA, DSC, DTA,...)
 - Měření chemických potenciálů
 - Měření magnetické susceptibility
 - Měření vodivosti
 - Dilatometrie
- **Isotermické metody (Equilibration)**
 - Metalografie , difrakce (XRD) – fázové podíly
 - Mikroanalytické metody (WDX, EDX, Laserová ablace, ...) – složení koexistujících fází
 - Studium difúzních párů a multivrstev
 - **Aplikace analytické chemie na anorganické, organické, či polymerní směsi** (destilace na koloně, extrakce,

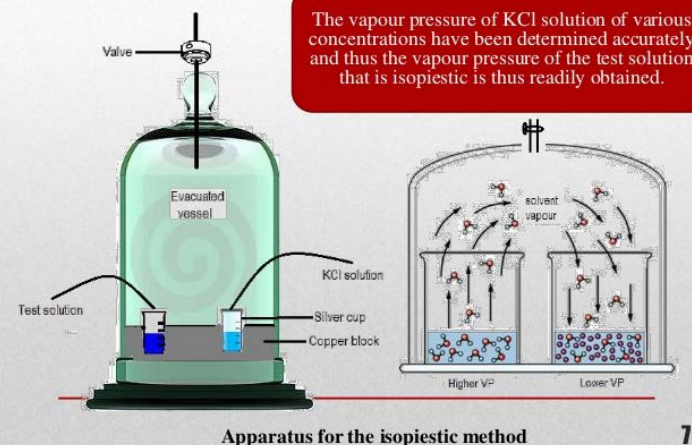


Měření termodynamických dat

- **Kalorimetrické metody**
 - Měření entalpií a tepelných kapacit
 - Měření entalpii fázových transformací
- **Temperace s plynnou fází**
 - Statické metody měření tenzí par (aktivity složek)
 - Kondenzační metody a neisotermické isopiestické metody
 - Knudsenova efúzní metoda
- **Měření elektromotorických napětí (ΔG)**



Isopiestic method is used for precise determination of vapour pressures.



Apparatus for the isopiestic method

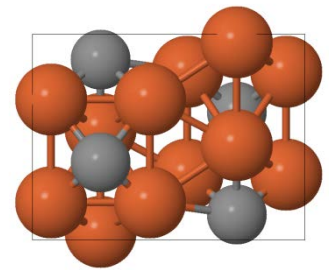
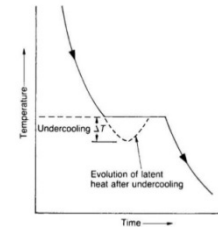
Role of phase Transformation Kinetics

Nucleation effects (undercooling)

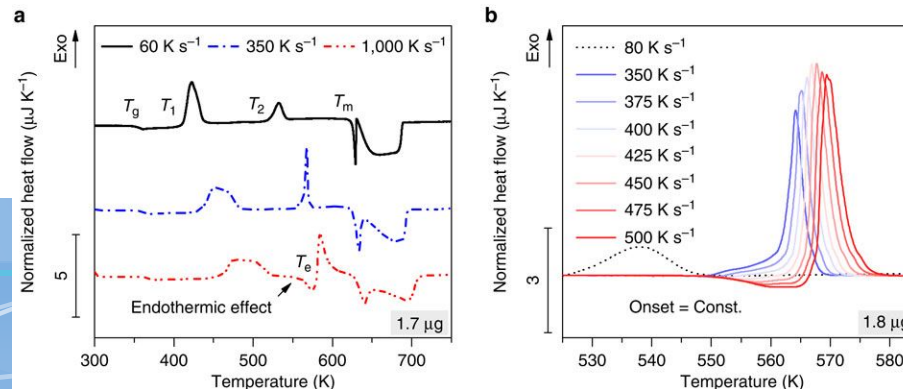
Formation of metastable phases

Shifting of Transformation-Start Temperature with Heating Rate

Cooling curve for a pure metal showing possible undercooling.

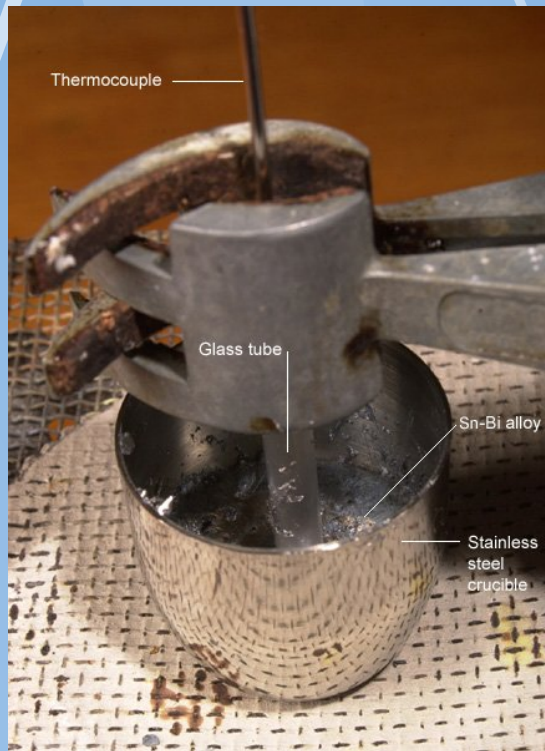


Cementite vs. graphite

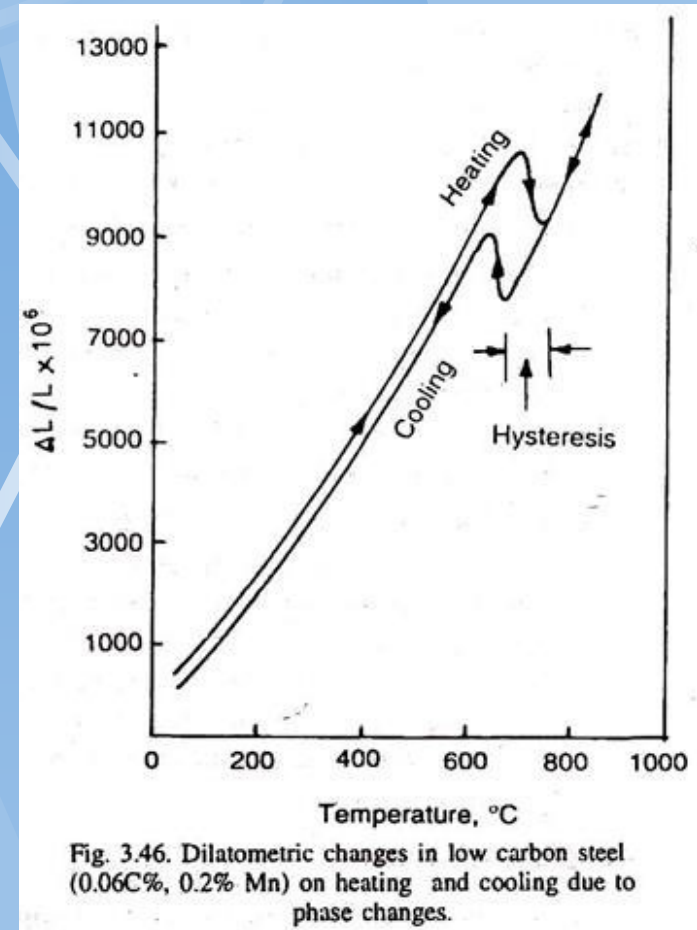
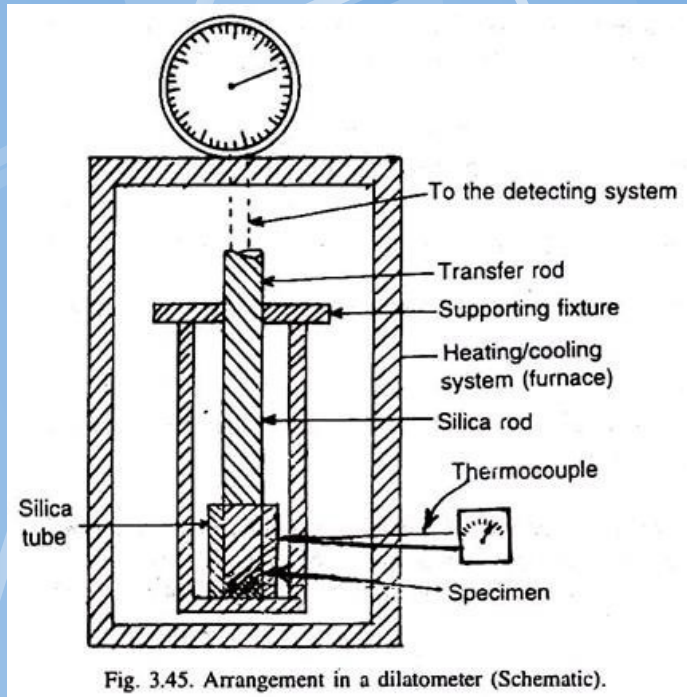


Heating of Au₇₀Cu_{5.5}Ag_{7.5}Si₁₇.

Thermal analysis (viz samostatná lekce)



Dilatometry

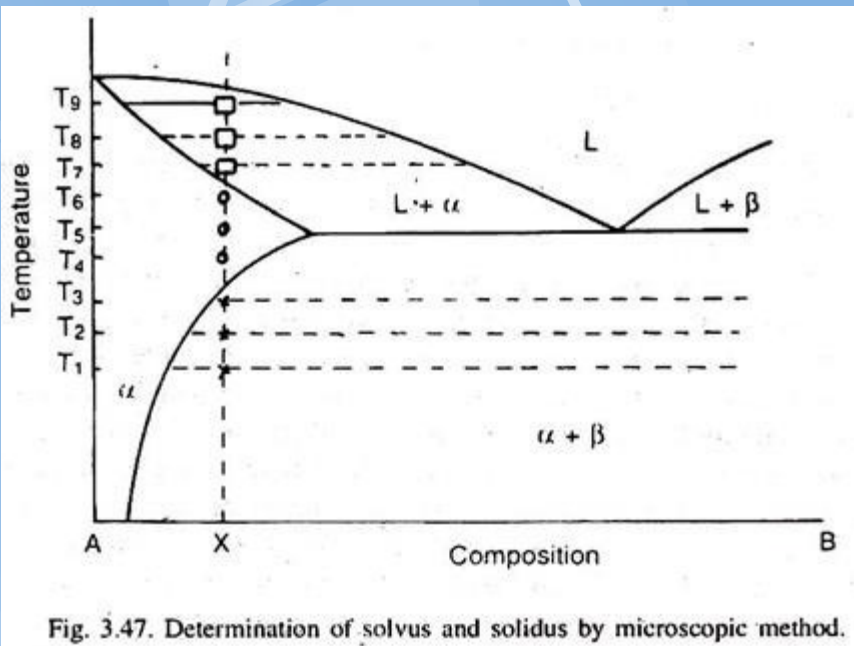


Dilatometry is based on the volume (length) change associated with most phase changes. Fig. 3.45 schematically shows the main features of a dilatometer. The temperature and dilation (change in length) of the sample are simultaneously monitored as a function of time. The simplest dilatometer usually consists of a silica tube with one end closed and provision for the sample to rest firmly upon the closed end inside the tube.

Microscopic Methods

Rapid quenching:
method for conservation
of chemical composition

Light microscopy = history

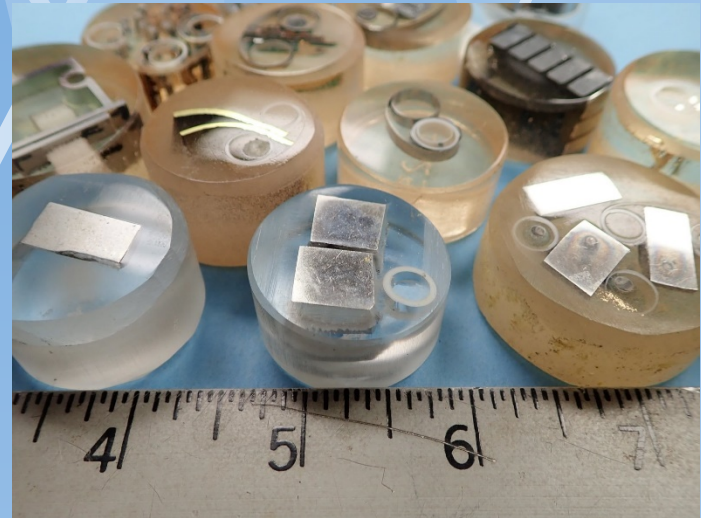


There are various methods using microscopic techniques in determining the phase diagrams. Moreover, microscopic techniques are also used to verify the phase diagrams determined by other methods, where microscopic examination of cast and heat-treated alloys at small composition intervals across the system is done. It is a worth-while but laborious work.

Metallography

Sample preparation:

- **Cutting**
- **Grinding**
- **Polishing**
- **Etching**
- **Microscopy**



[\(10\) Metallography Part I -
Macroscopic Techniques - YouTube](#)

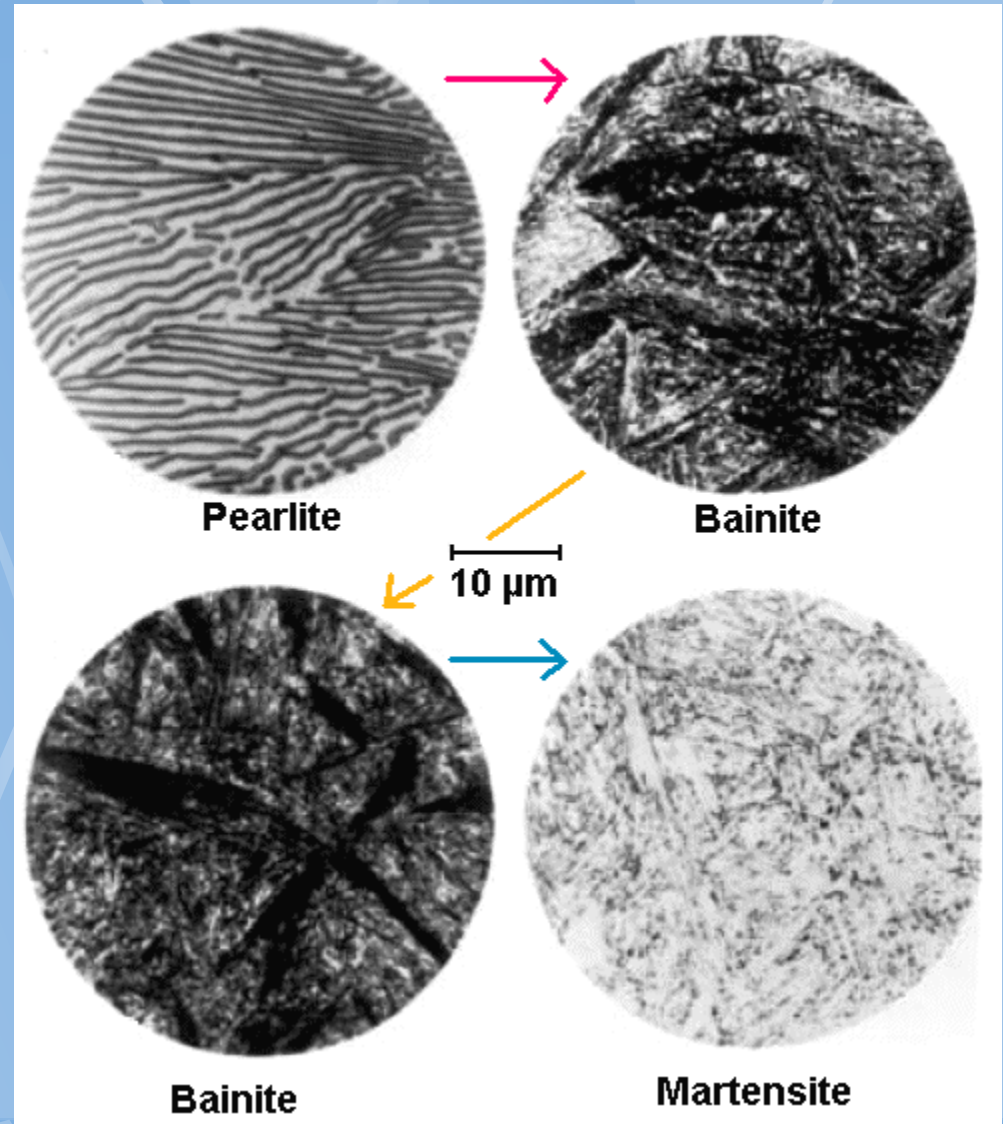
[\(10\) Metallography Part II -
Microscopic Techniques - YouTube](#)

Microstructure

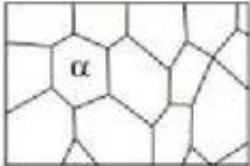
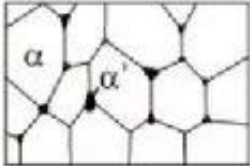

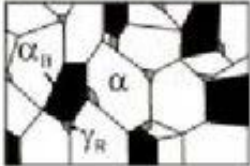


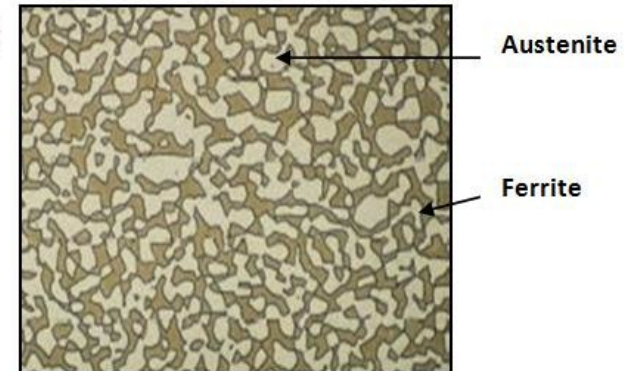
A micrograph of bronze revealing a cast dendritic structure

[Metallography - Wikipedia](#)

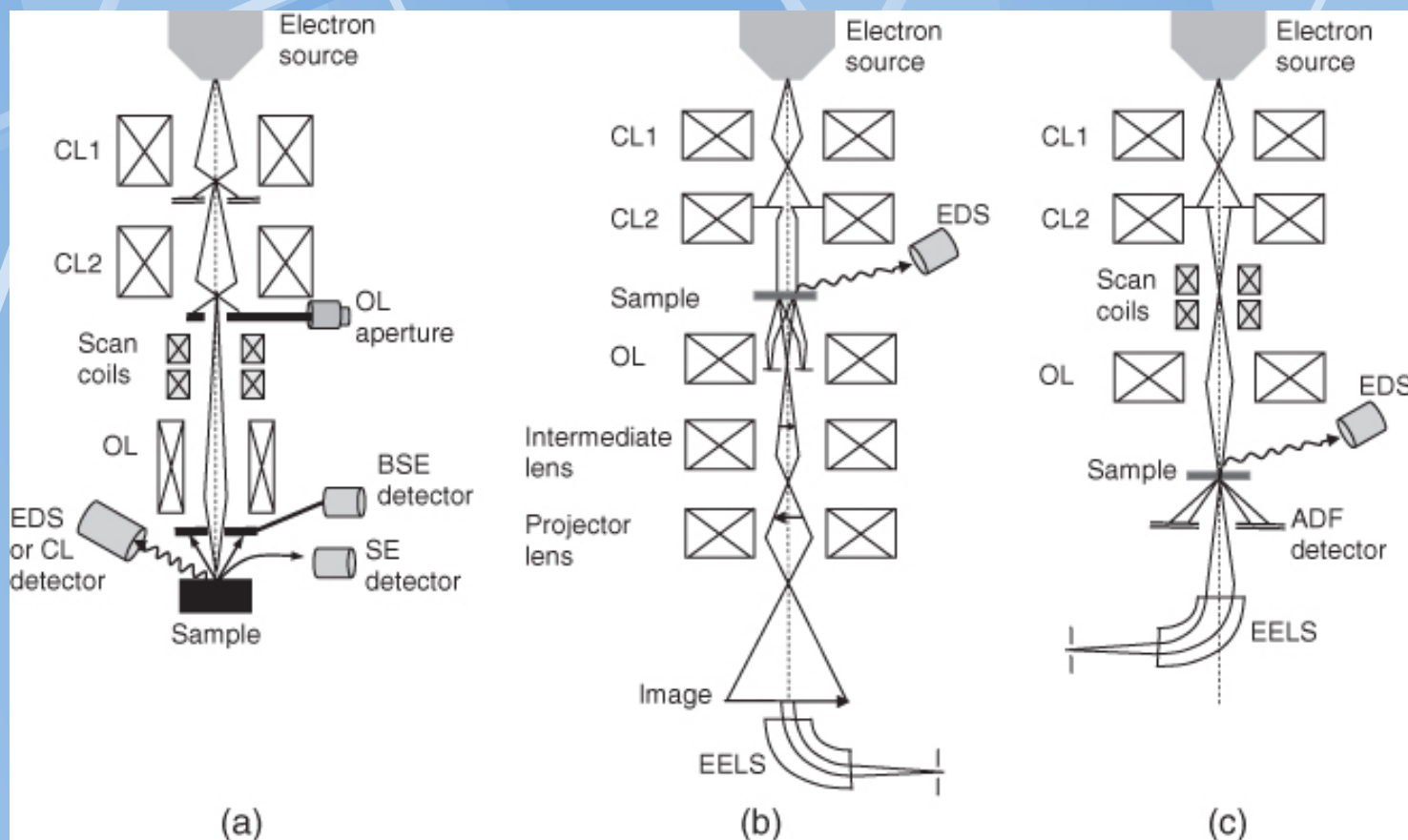


Microstructure phase analysis

Steel type		Parameters	Phases
Single phase (Mild steel)		<ul style="list-style-type: none"> - Grain size - Grain shape 	α = ferrite
Two phase (Dual Phase steel)		<ul style="list-style-type: none"> - Grain size - Volume fraction - Local chemical composition 	α = ferrite α' = martensite
Two phase (Duplex steel)		<ul style="list-style-type: none"> - Grain size - Volume fraction - Local chemical composition 	α = ferrite γ = austenite
Multi phase (TRIP steel)		<ul style="list-style-type: none"> - Grain size - Volume fraction - Local chemical composition - Phase stability 	α = ferrite $\alpha_{\bar{}}$ = bainite γ_R = retained austenite

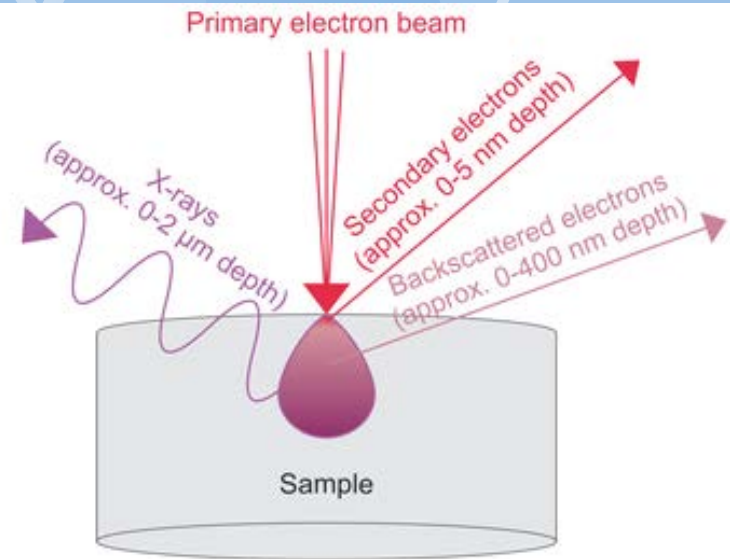
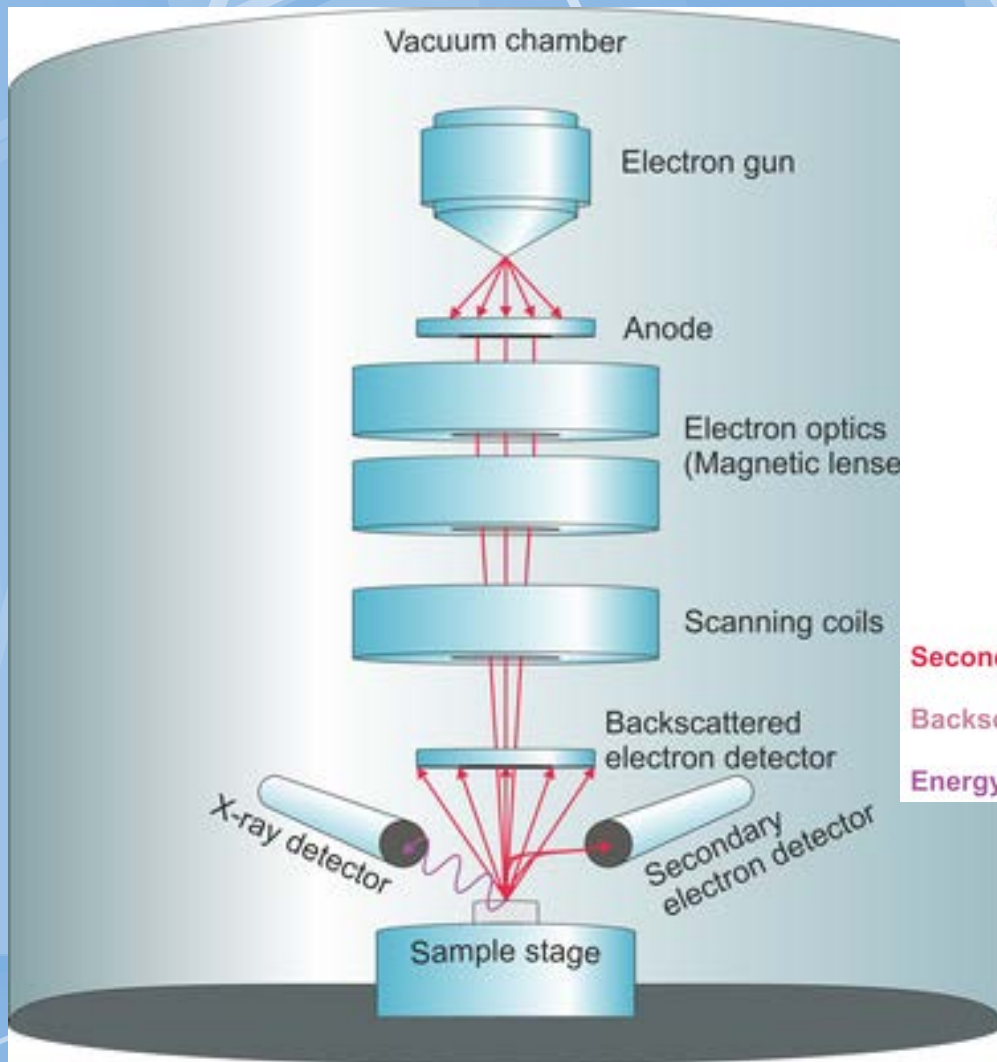


Metody elektronová mikroskopie



Simplified schematic cross-sections of an (a) SEM, (b) TEM and (c) STEM instrument.

Detectors



Secondary electron imaging (SEI): mainly topography contrast

Backscattered electron imaging (BEI): mainly material contrast

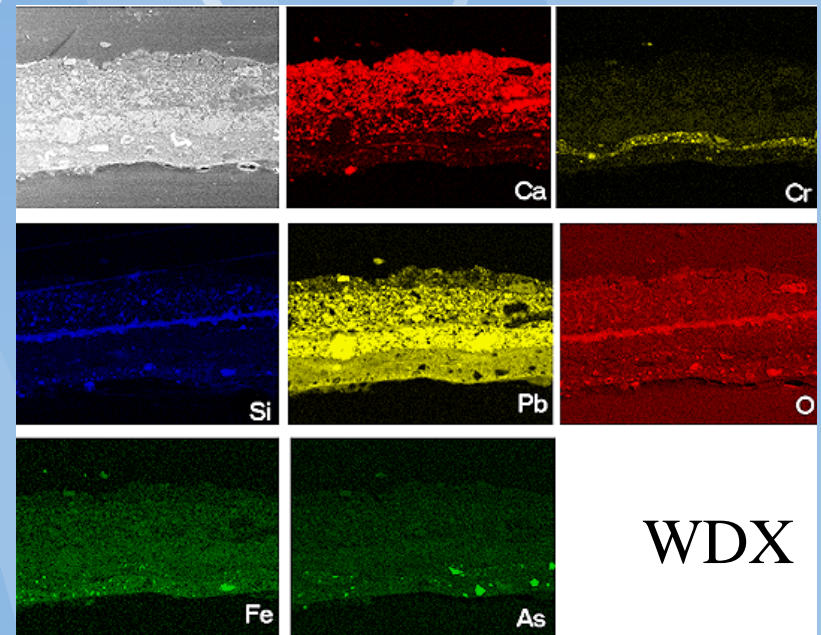
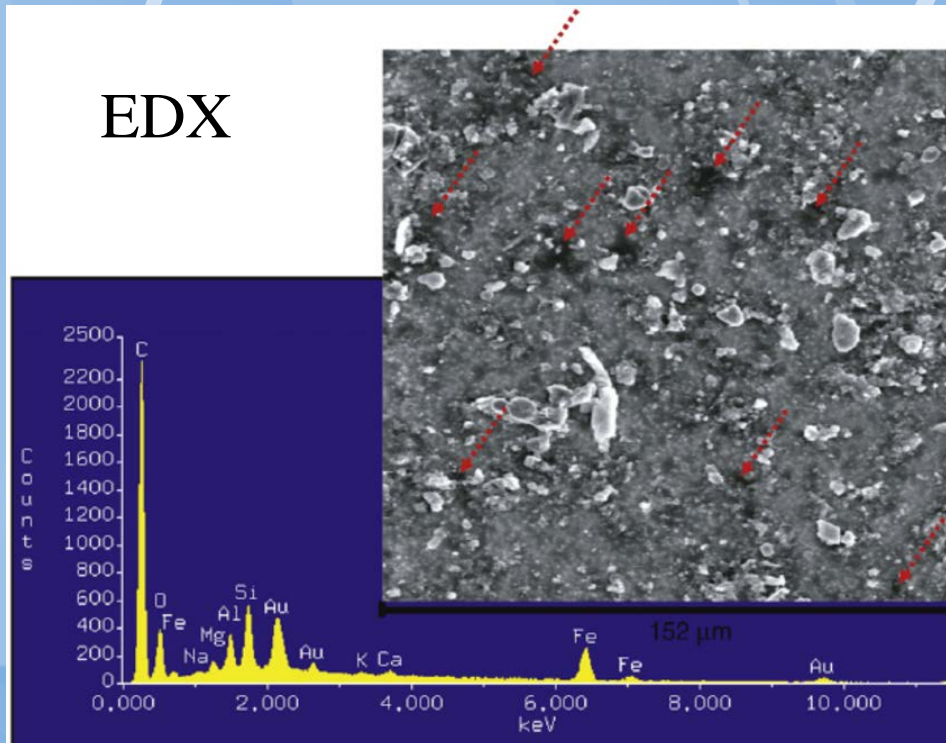
Energy-dispersive X-ray spectroscopy (EDX): elemental analysis

SEM

Scanning electron microscopy

Analýza chemického složení koexistujících fází:

- -Energy-dispersive X-ray spectroscopy
- -Wavelength-dispersive X-ray spectroscopy (x-rays within a small wavelength range)

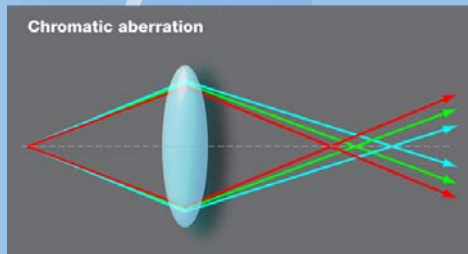
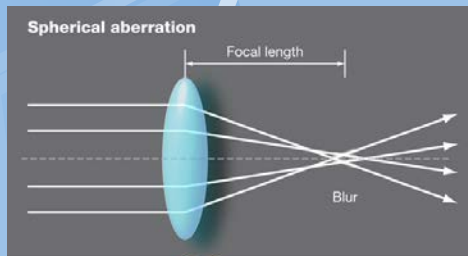


Mapping of elements

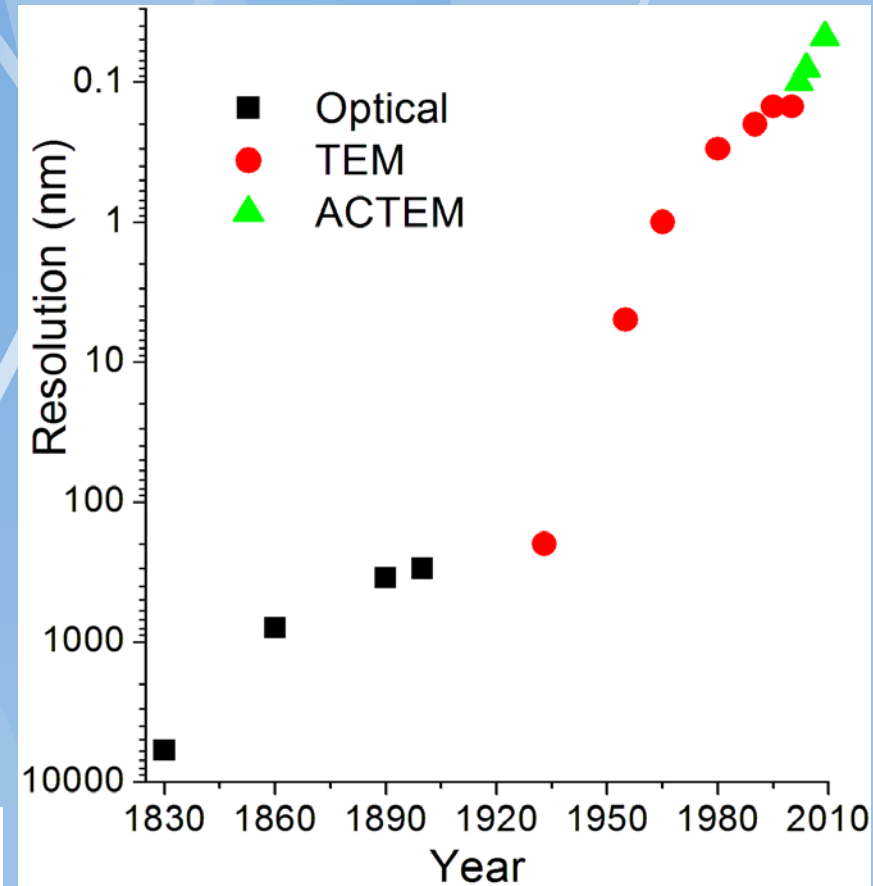
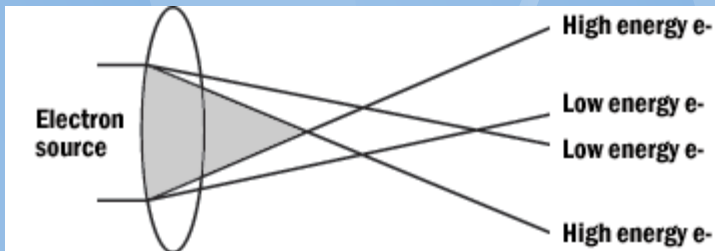
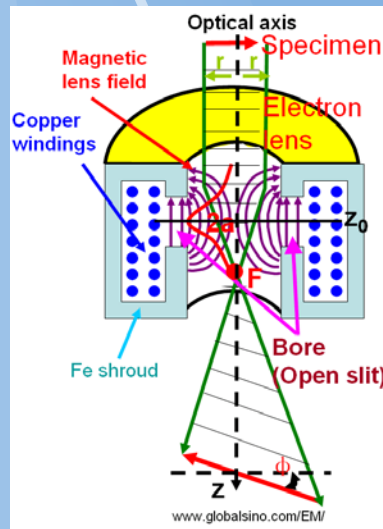
HRTEM

(aberration corrected TEM)

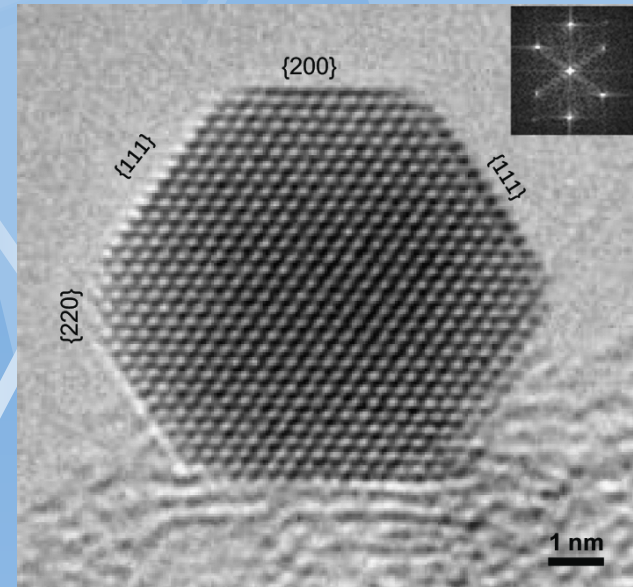
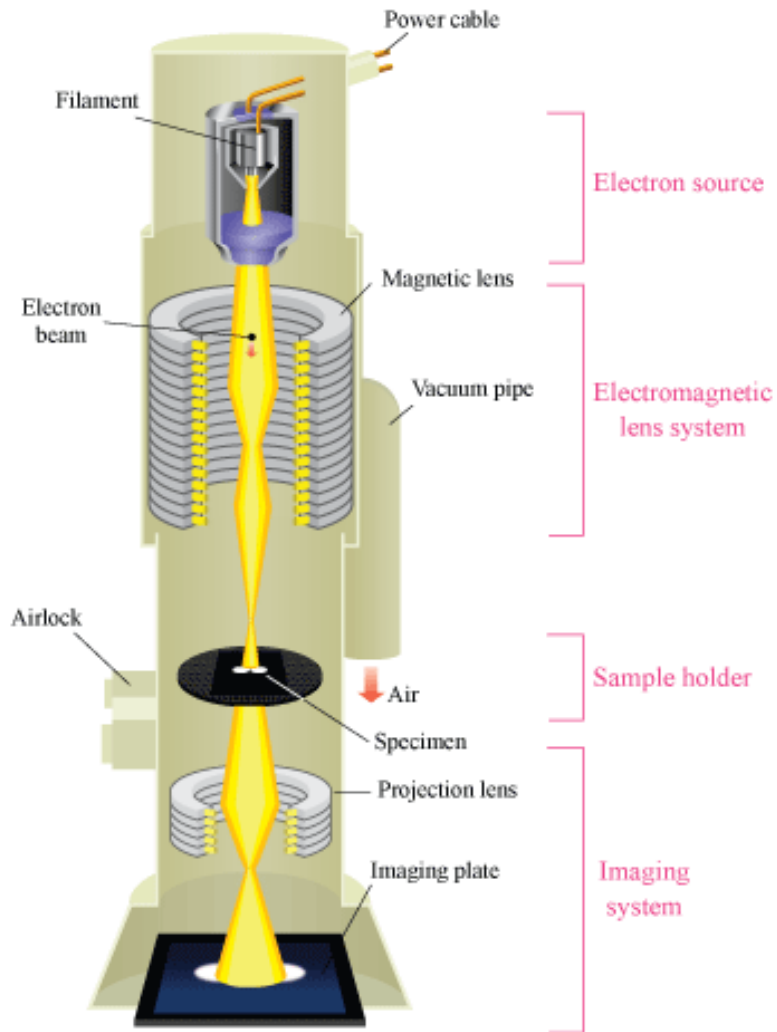
Light beam



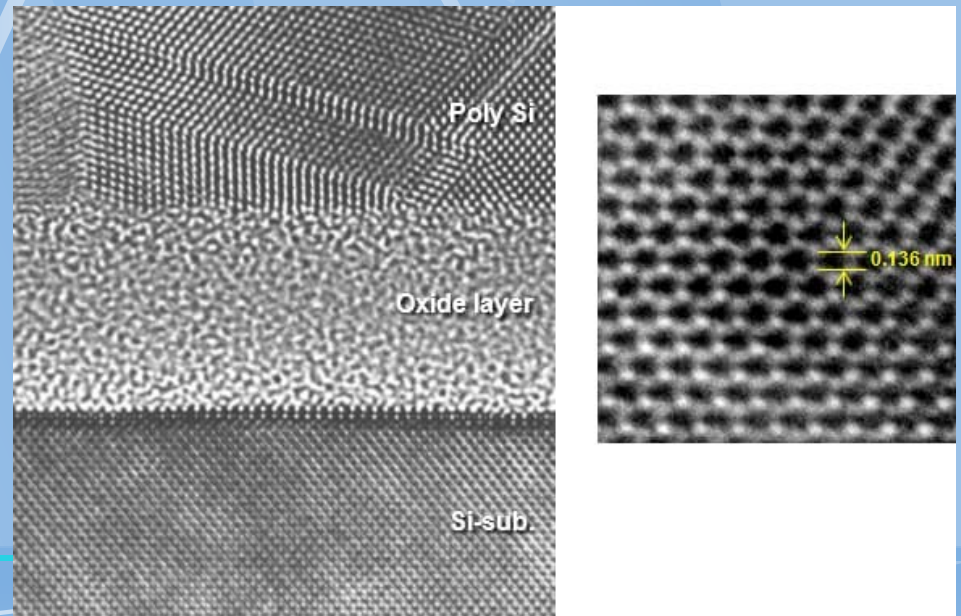
Electron beam



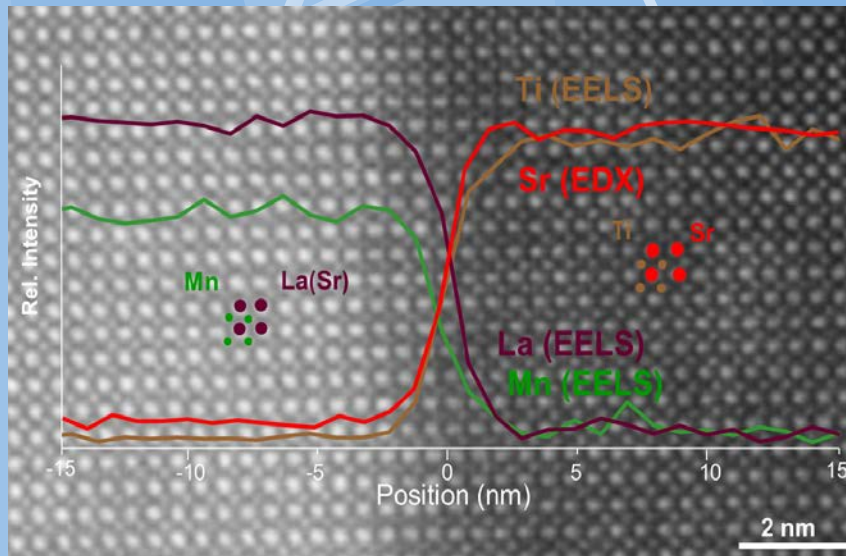
HRTEM



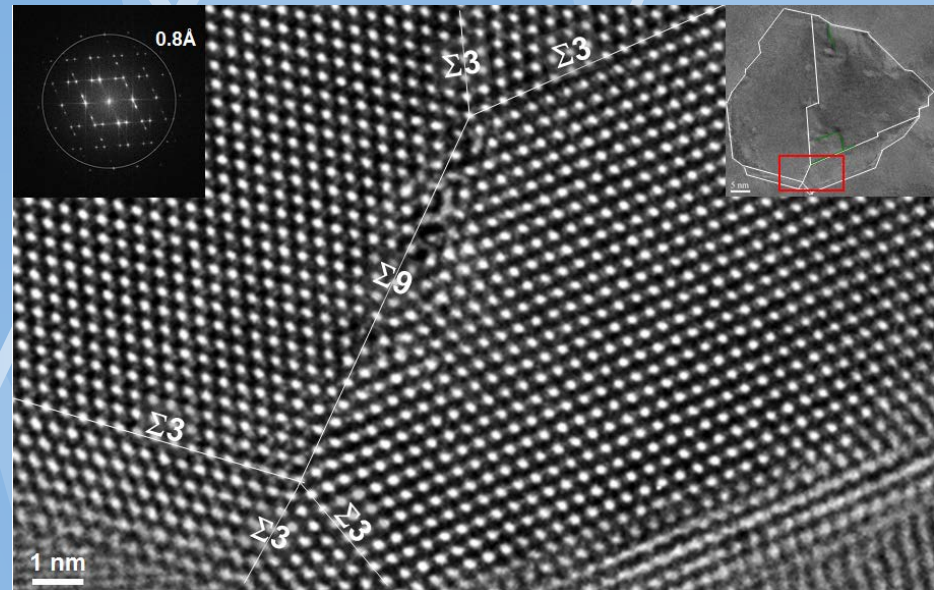
https://www.researchgate.net/figure/High-resolution-TEM-image-of-an-AgI-nanoparticle-recorded-parallel-to-the-01104-zone_fig21_278072402



Examples (FEI Titan 80–300)



*HAADF-STEM image (filtered by NAD) of a $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3/\text{SrTiO}_3$ interface with the individual atomic columns well resolved across the interface. Overlaid is an EELS/EDX intensity profile across this interface. P.M. Leufke and D. Wang et al., *Thin solid films*, 2012, 520, 5521-5527.*



*Fig. 2: Atomic resolution TEM image of a triple and a quadruple line at the interface between $\Sigma 3$ boundaries and a $\Sigma 9$ boundary in nanocrystalline palladium. H. Rösner and C. Kübel et al., *Acta Mat.*, 2011, 59, 7380-7387.*

X-Ray Diffraction Methods

X-rays are used while alloys are in solid-state to:

- (i) Identify composition of a phase
- (ii) Crystal structure of the phase
- (iii) Lattice parameter of the crystal structure.

And, thus, are used to locate the solvus lines in phase diagrams.

The method of lattice parameter measurement depends on the fact that crystal dimensions, i.e., lattice parameter increases with the increase of the solute content in the solid solutions, till it gets saturated.

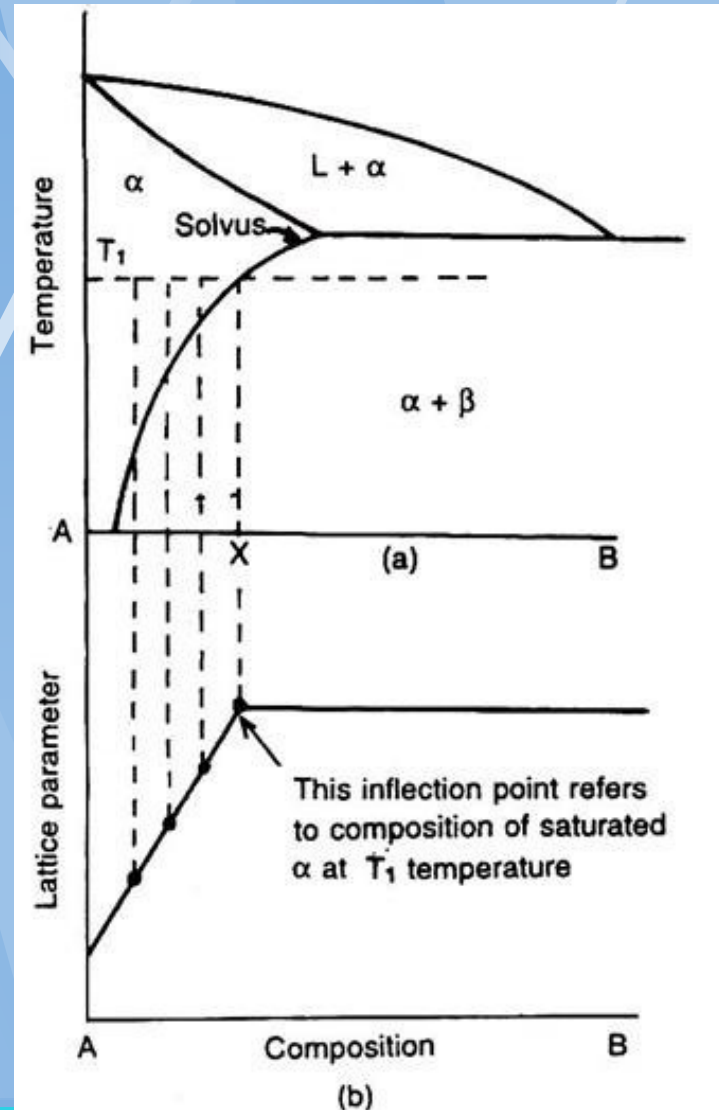
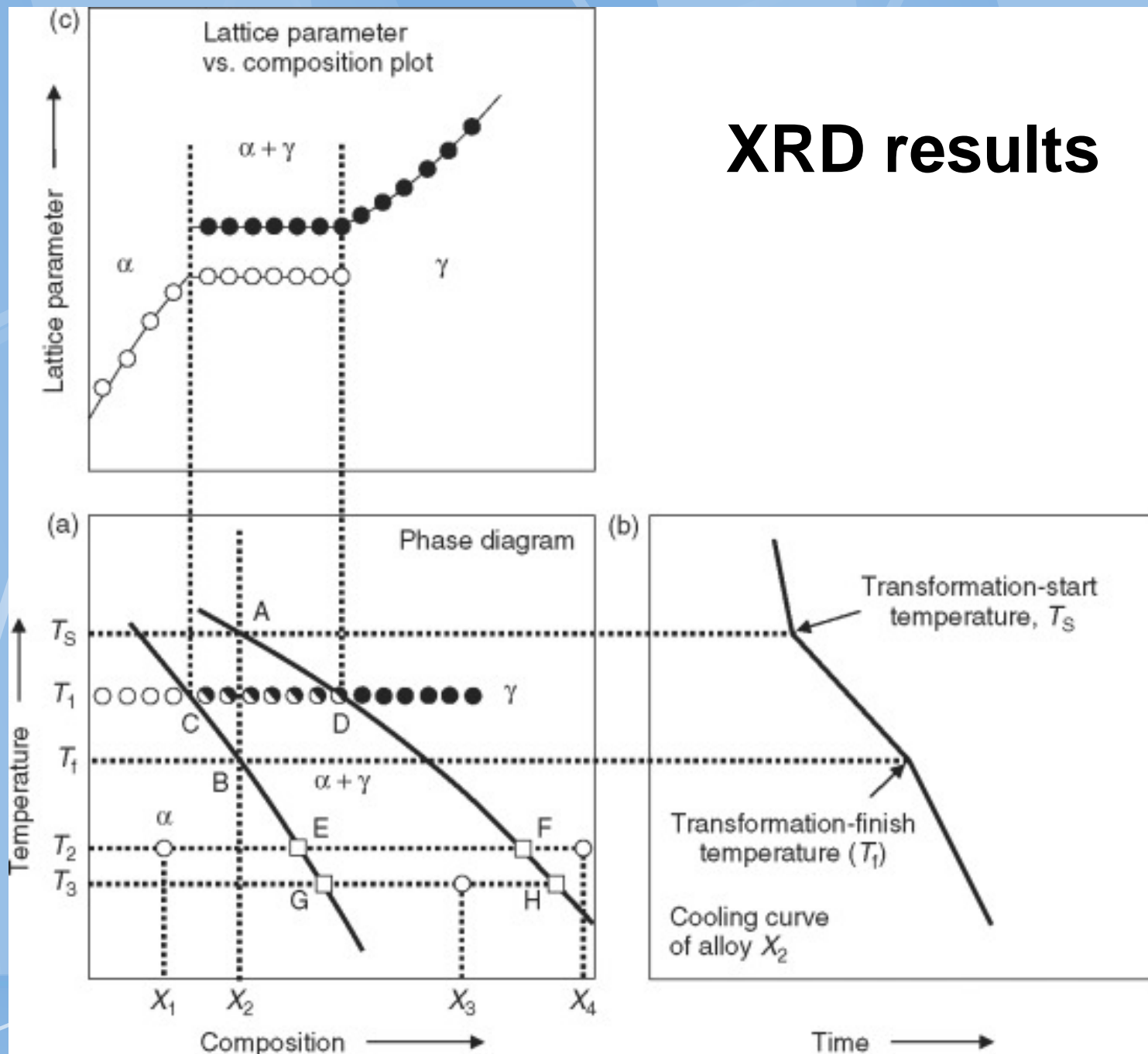


Fig. 3.48. Solvus point determination by use of x-ray diffraction measurement of lattice parameter.

XRD results



Electrical Resistivity Method

The technique of measurement of electrical resistivity is often used to locate the solvus and horizontal isotherms in the solid state of the alloys.

The electrical resistivity of a solid solution changes nonlinearly with the increase in concentration of the solute. But the electrical resistivity of a phase-mixture is not characteristic of any one of the conjugate phases, but changes linearly with the volume fraction of the phases, Fig. 3.49 (b). The sudden change in the slope of the graph indicates the location of the phase boundary (solvus).

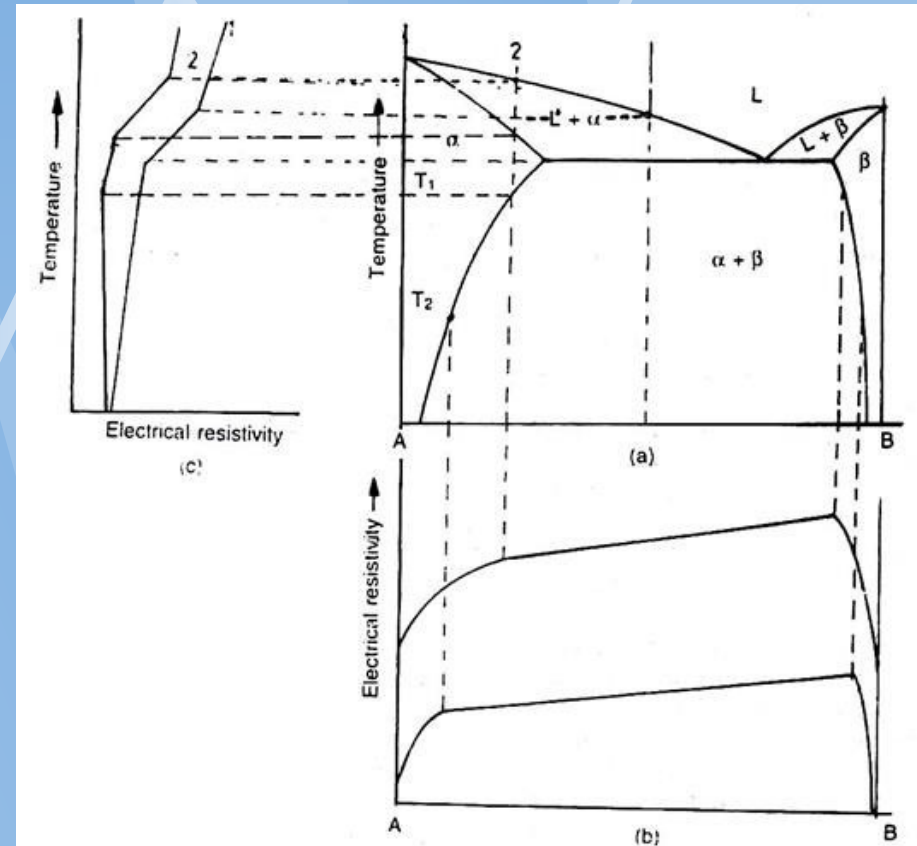
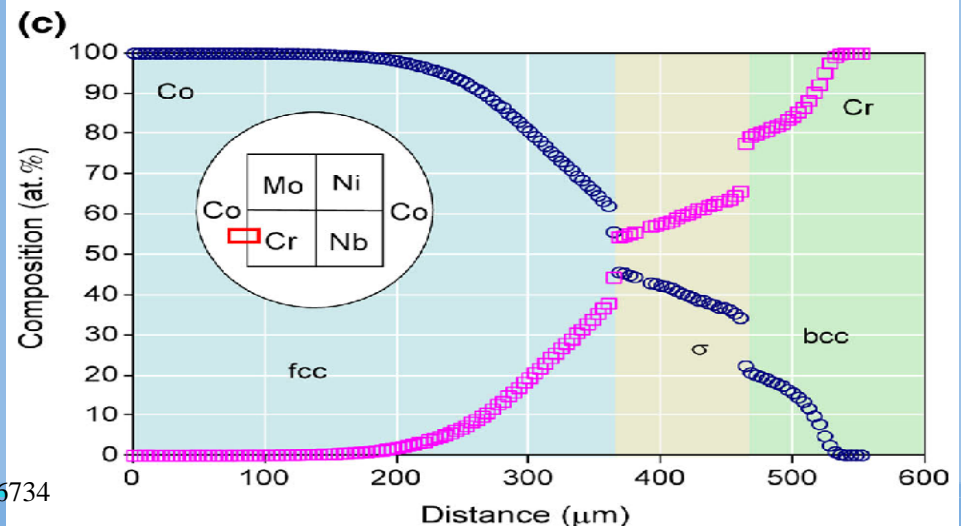
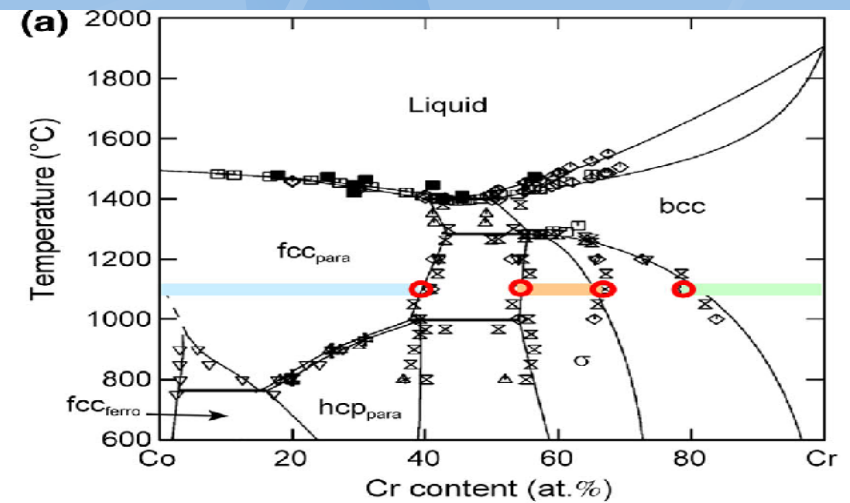


Fig. 3.49 Electrical resistivity as a means to locate the points of solvus.

Diffusion couples

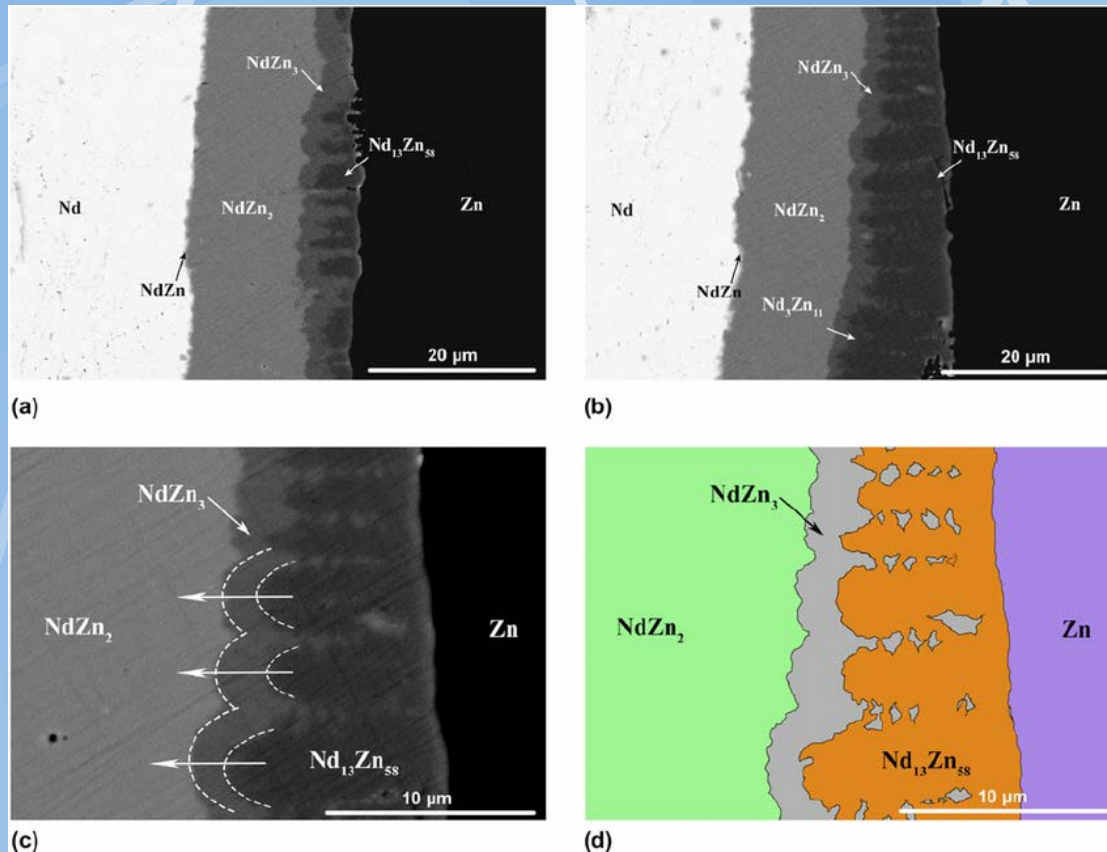
The use of **diffusion couples** in **phase diagram** studies is based on the assumption of local equilibria in the **diffusion** zone. The latter implies that each infinitely thin layer of such a **diffusion** zone is in thermodynamic **equilibrium** with the neighbouring layers.



Studium difúzních párů

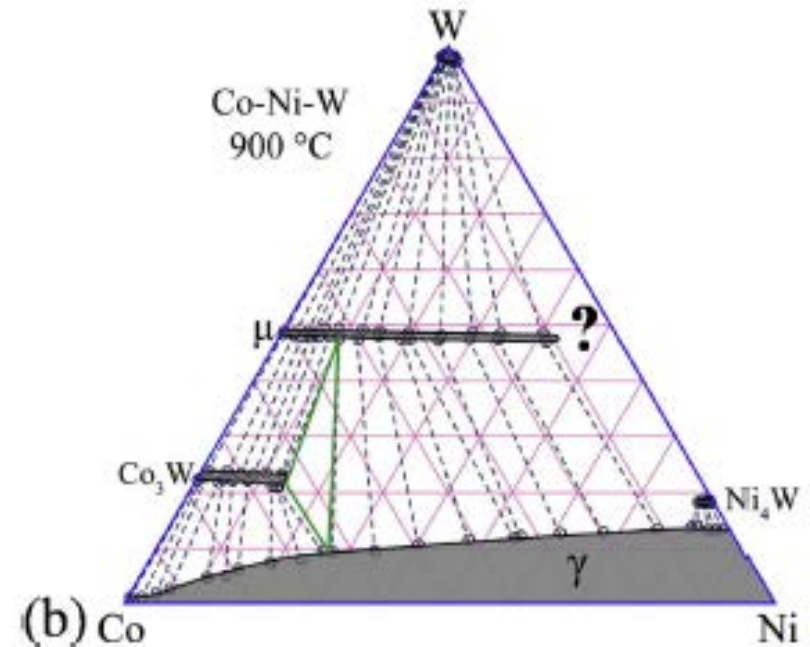
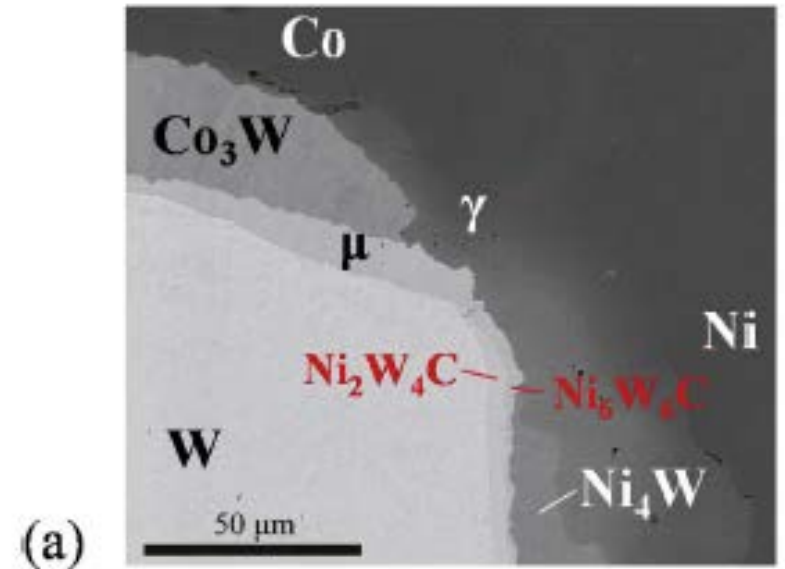
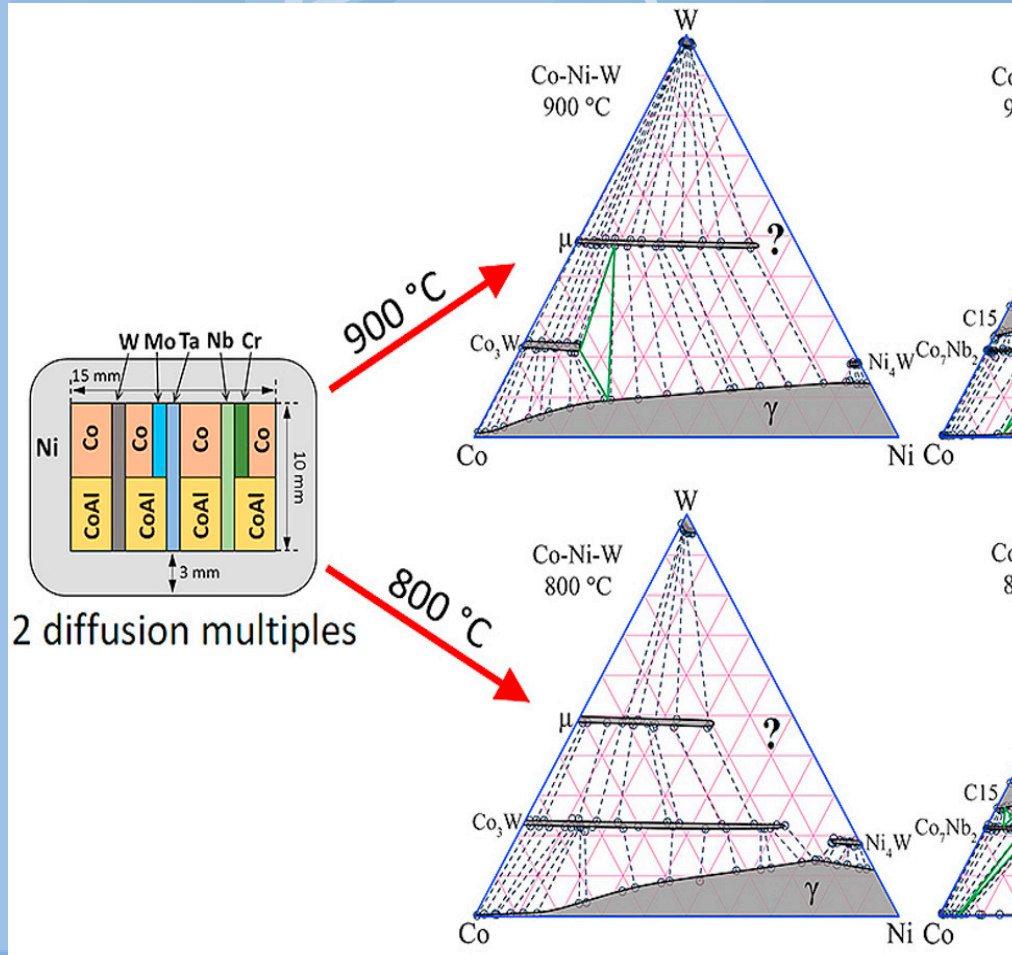
Problems:

- nucleation
- diffusion
- local stress
- Kirkendal effect



https://www.researchgate.net/figure/267028713_fig7_FIG-14-Evolution-of-phase-growth-in-the-Nd-Zn-diffusion-couple-annealed-at-300-C-for

Diffusion multiples



Problem of reactive or volatile elements

High vapour tensions: alkali metals, Zn, Cd, Mg, Ga,..., Se, Te, ...Hg, In, As, Sb, Bi ,

Reactive elements: S, P,

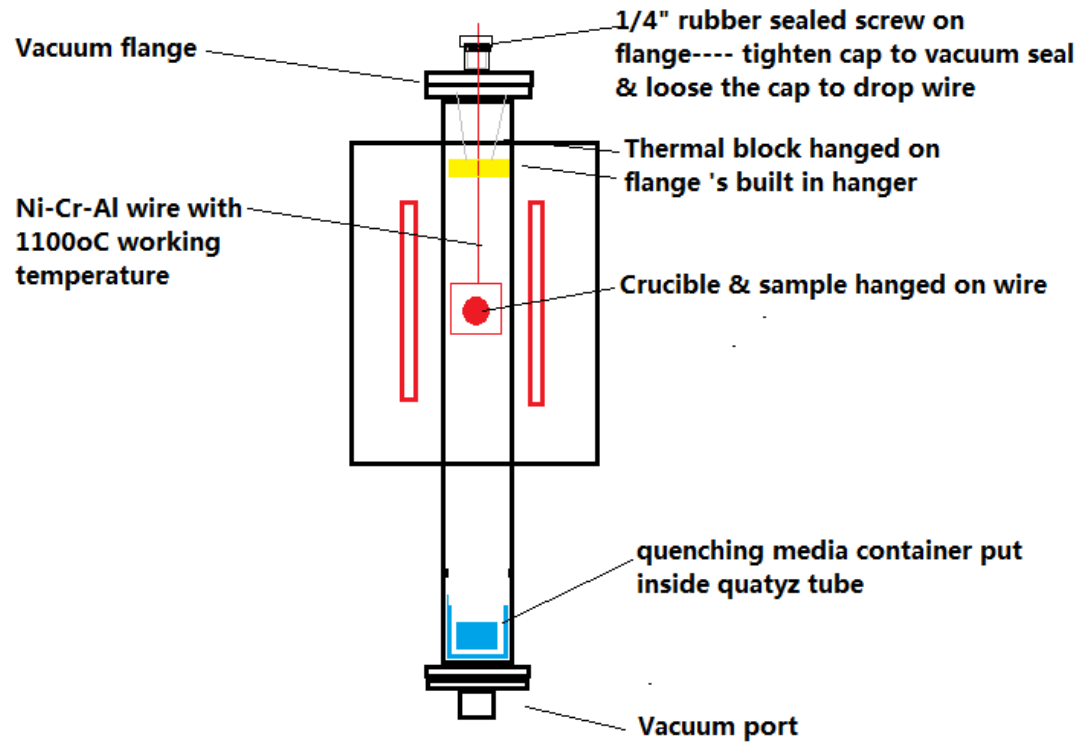
Special container materials: stable oxides, Al_2O_3 , Y_2O_3 , ..., SiC, graphite, quartz, Teflon,, Mo, W

Special atmospheres or vacuum

Advantages: activity measurements, galvanic cells, weight loss measurements, MS apply, Analysis of gases above samples,.....

Ceramic Systems

Quenching sample in Vacuum

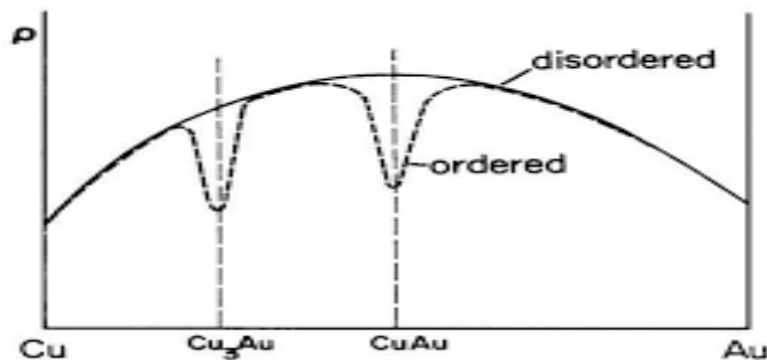
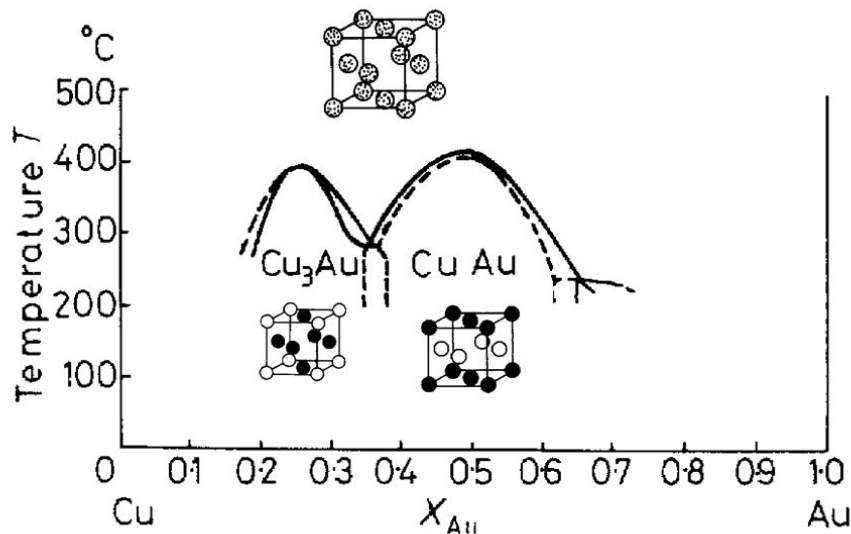


Problems:

- No suitable container material
- high temperature experiment

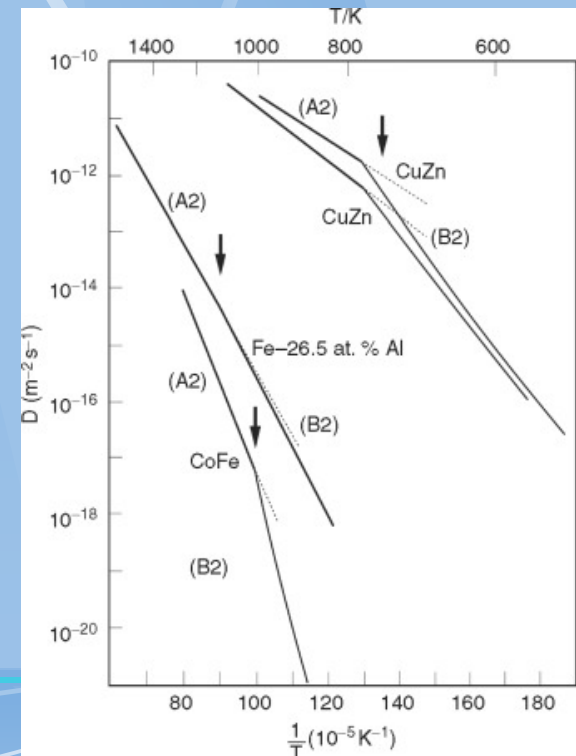
Order – disorder systems

A Phase Diagram Which Includes a Typical Disorder to Order Transformation



Methods:

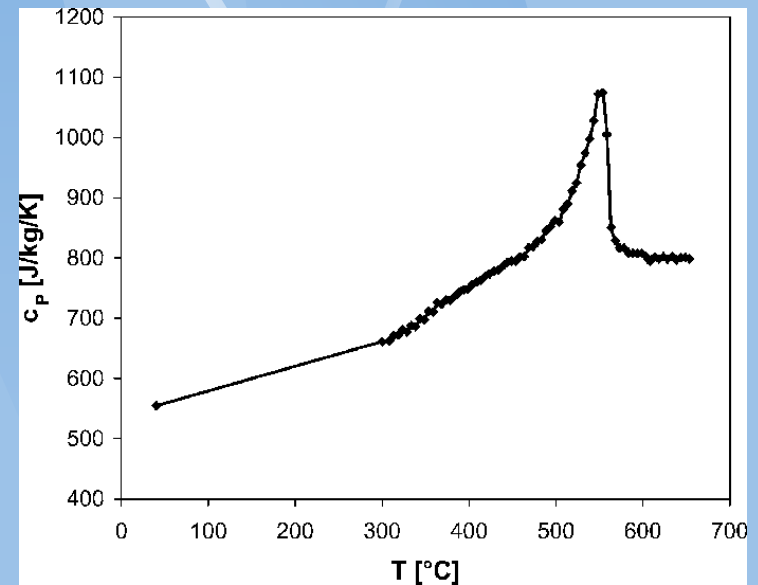
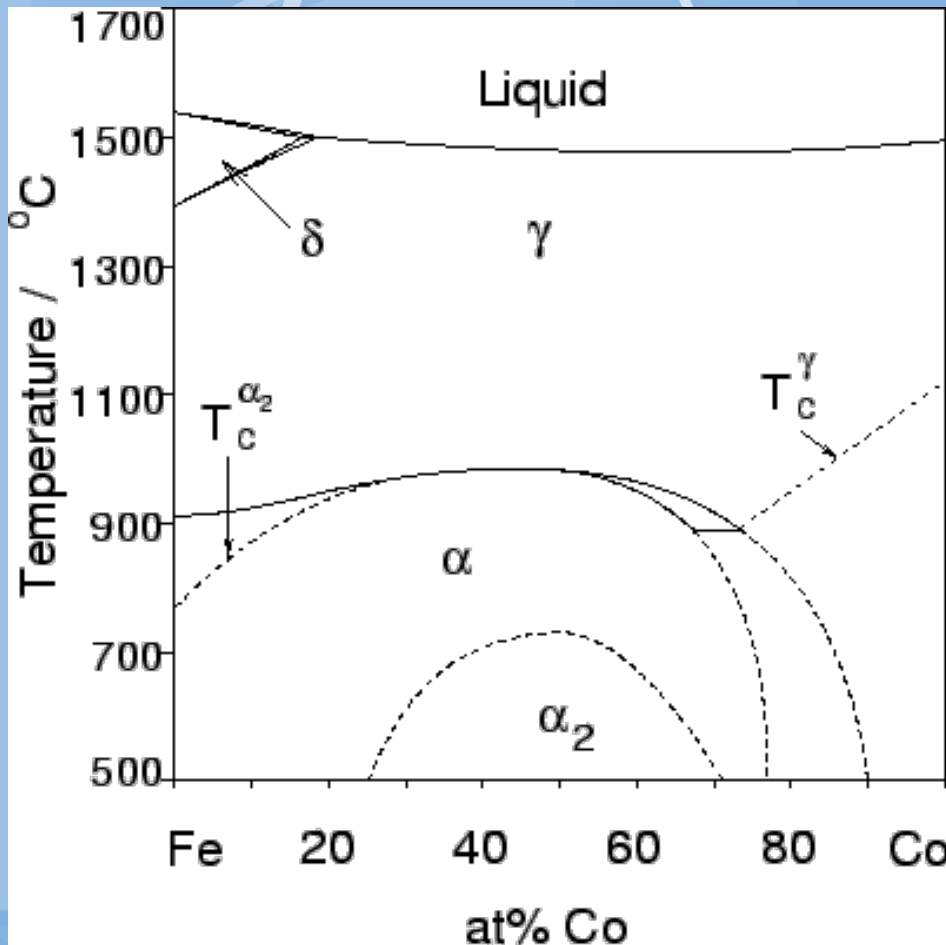
- Electric resistivity
- Thermal analysis
- Singular point methods:



Magnetic transformation

Methods:

- Measurement of magnetism
- Thermal analysis - TGA



The temperature dependence of the heat capacity of the Fe 3 Al-5 at.% Cr

Pressure Dependent Phase Diagrams

Pumps, detonators, ...

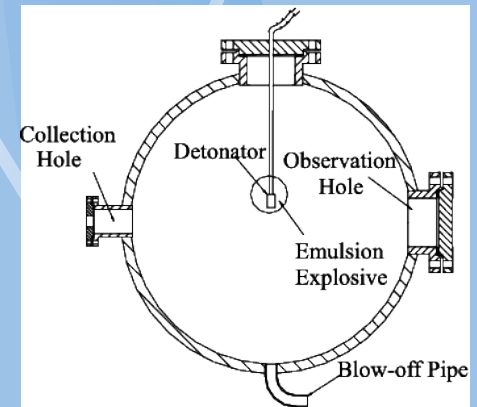
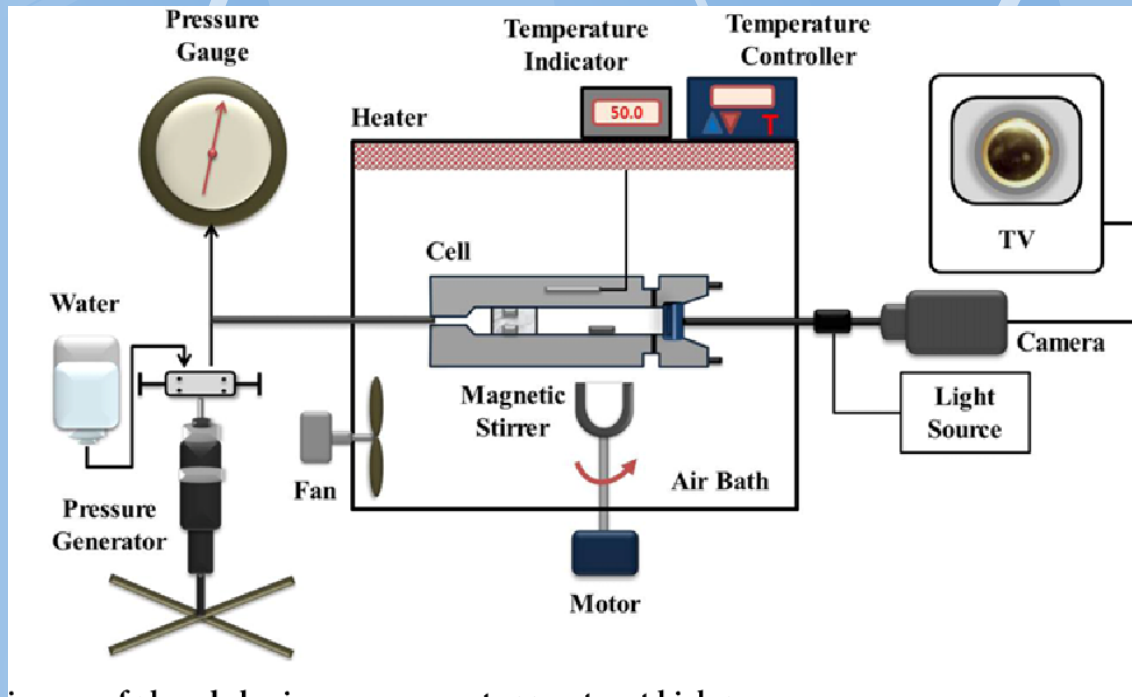


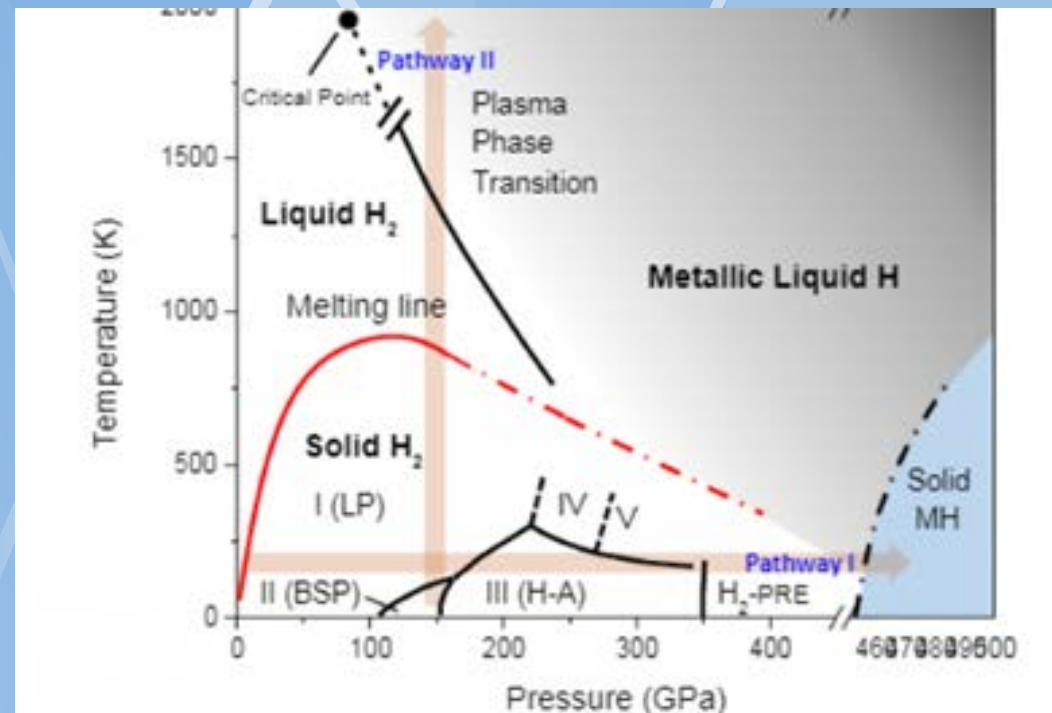
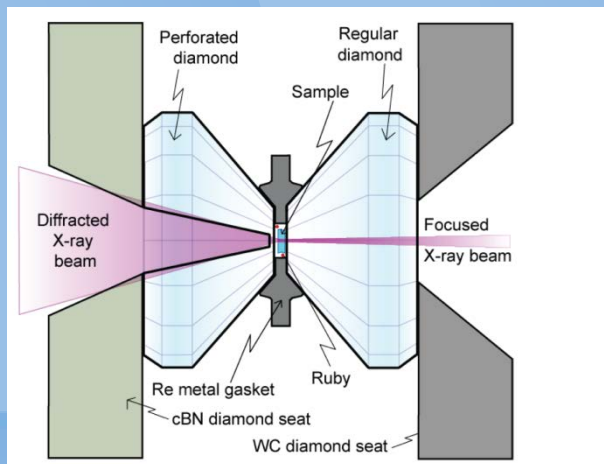
Diagram of phase behavior measurement apparatus at high pressure

[https://www.semanticscholar.org/paper/Phase-behavior-for-the-poly\(2-methoxyethyl-mixture-Jang-Choi/0807df69cc920c2c6c8315e83f321fbbd9b8302b/figure/6](https://www.semanticscholar.org/paper/Phase-behavior-for-the-poly(2-methoxyethyl-mixture-Jang-Choi/0807df69cc920c2c6c8315e83f321fbbd9b8302b/figure/6)

Diamond – anvil –Cell

Techniques:

Diamond – anvil –Cells
is transparent for VIS,
UV, gama X-rays, IR,



<https://www.nextbigfuture.com/2016/11/preparation-of-diamonds-for-diamond.html>

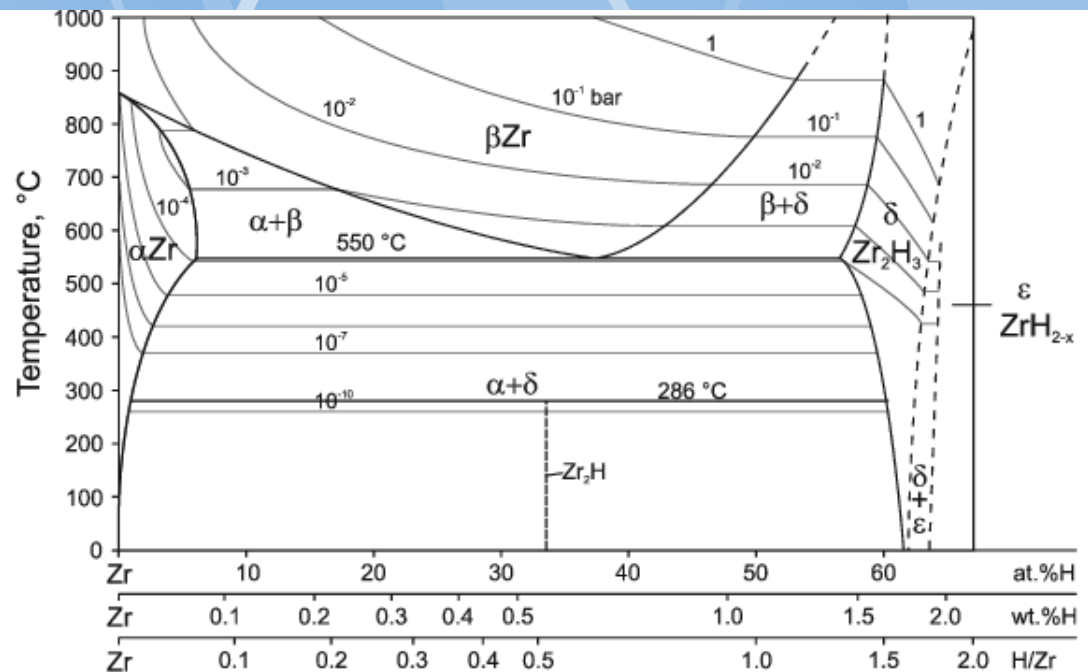
Podobně i pro Fe a další

Hydrogen Containing Systems

Techniques:

- General H pressure measurements

Nuclear power industry:
material design



Diskuse

