

Vznik nové fáze

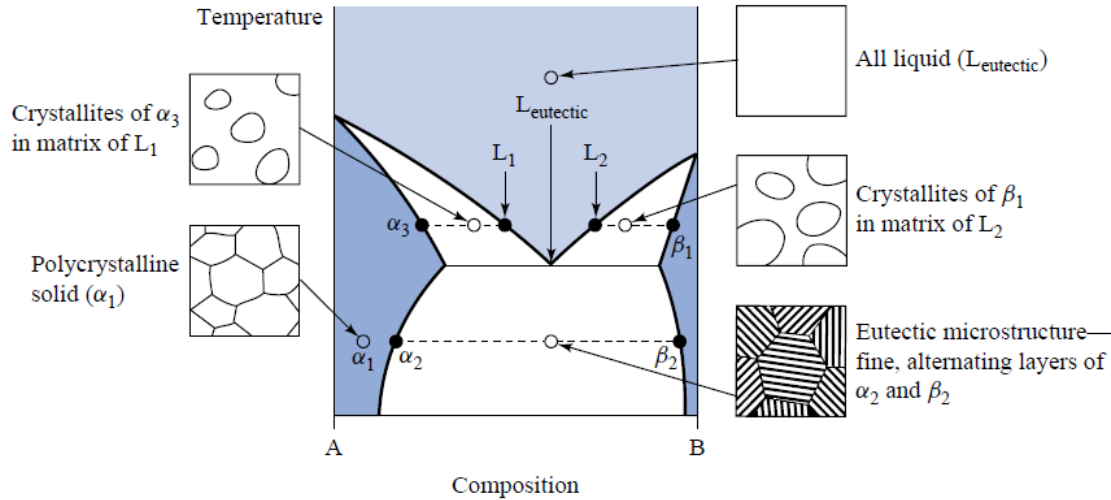
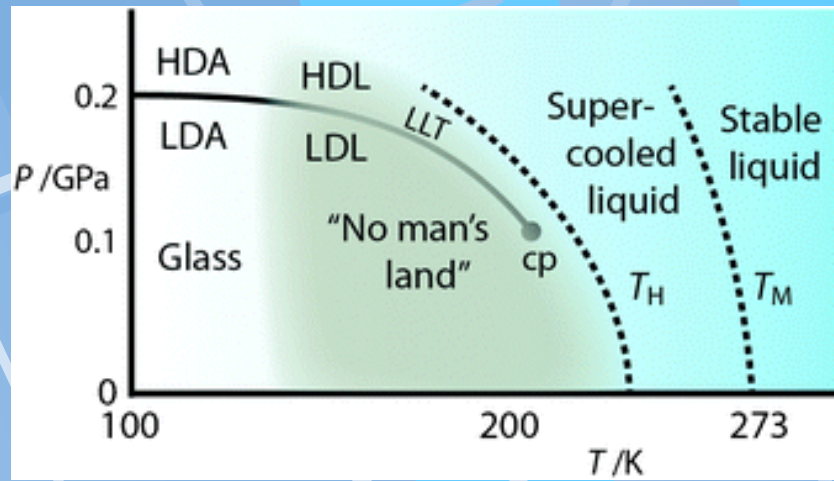


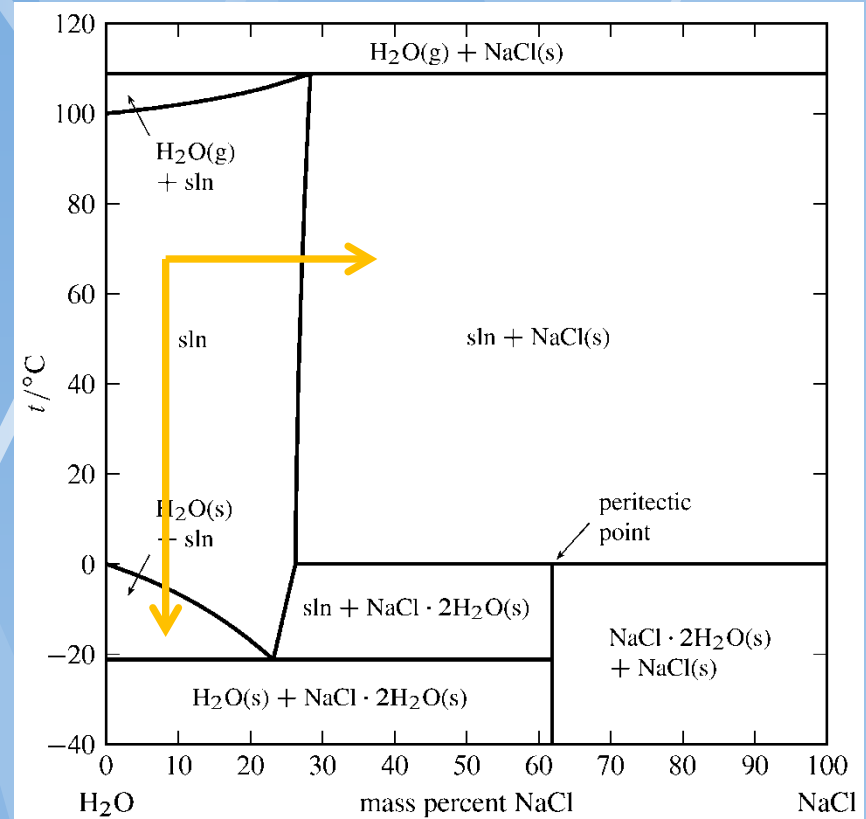
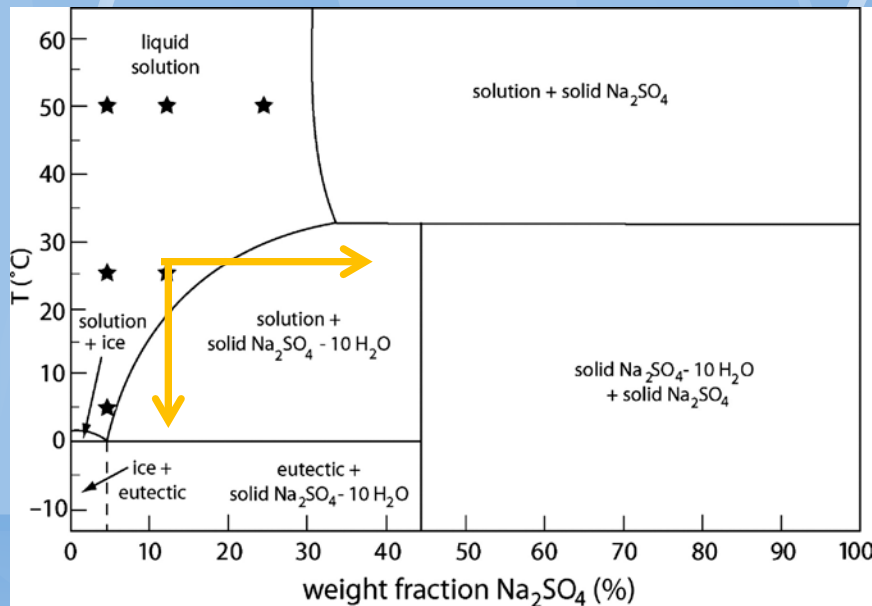
FIGURE 5-12



Vznik nové fáze

Je způsoben posuvem reprezentativního bodu celkového složení, tlaku a teploty soustavy ve fázovém diagramu.

Soustava se tak dostává do nerovnovážného stavu, který řeší fázovou přeměnou do stavu stabilnějšího.



Krystalizace solí v důsledků přesycení

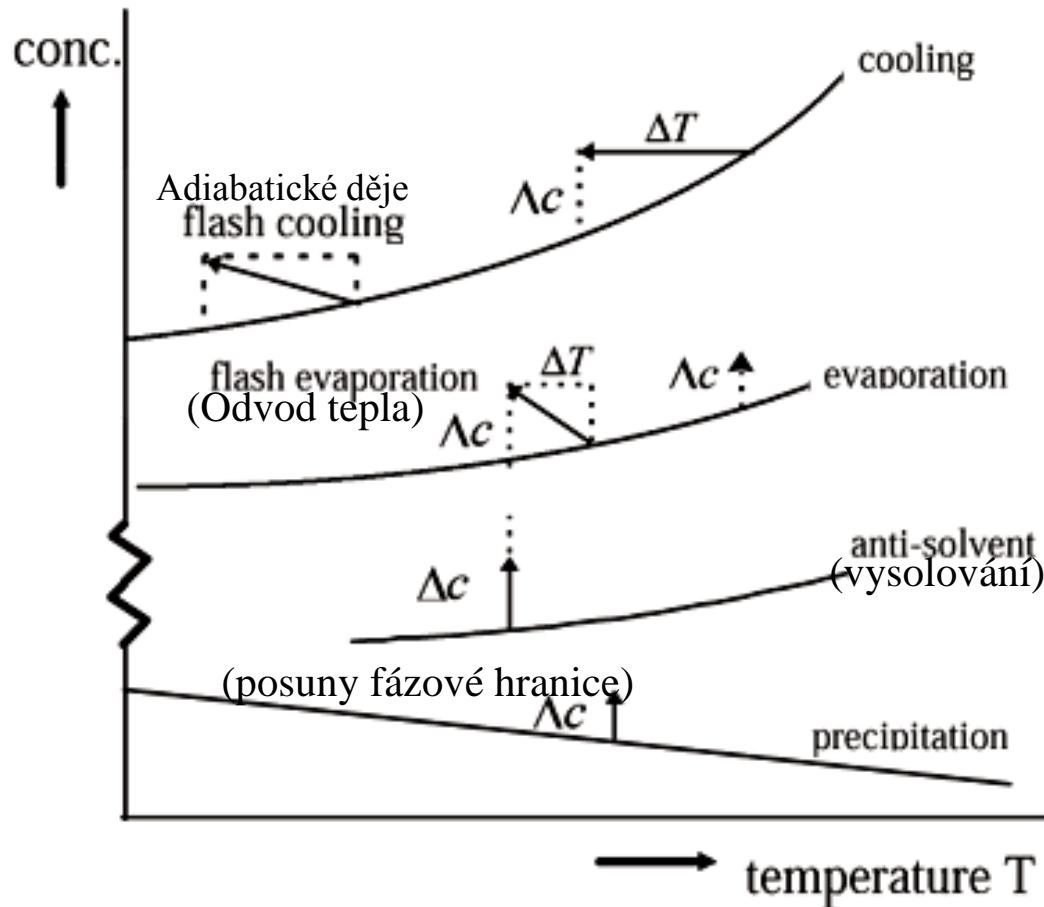
Rozlišujeme fázové přeměny v uzavřené (p , T změna) a otevřené soustavě (změna celkového složení).

Metody vytvoření přesycení roztoku

http://www.scielo.br/scielo.php?script=sci_arttext&pid=S0104-66322001000400007

$$\Delta c = c - c^*$$

c^* ... fázová hranice (rozpustnost)



Stupeň přesycení
 $S = c/c^*$

Relativní přesycení
 $\sigma = S - 1 = c/c^* - 1 = \Delta c / c^*$

Figure 2: Methods for creation of supersaturation in crystallization from solutions

Rel. přesycení lze určit i v %₃

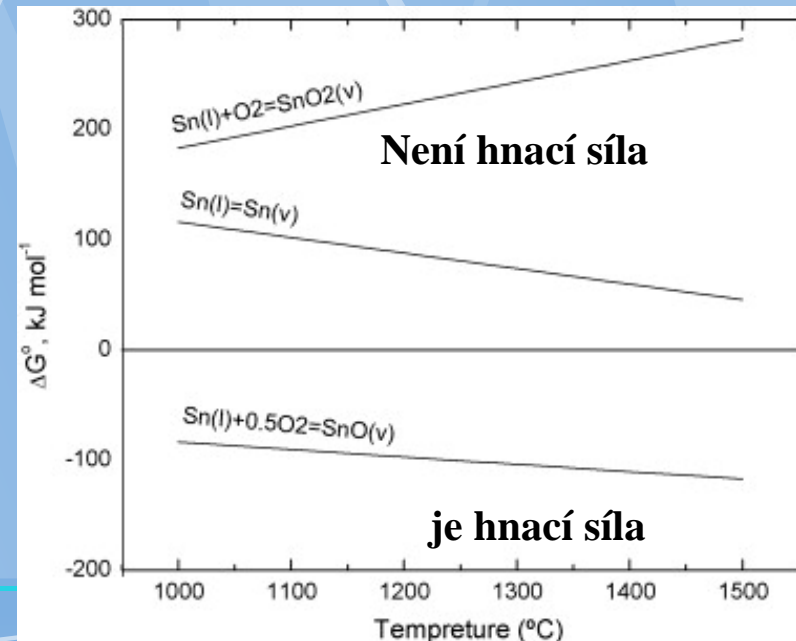
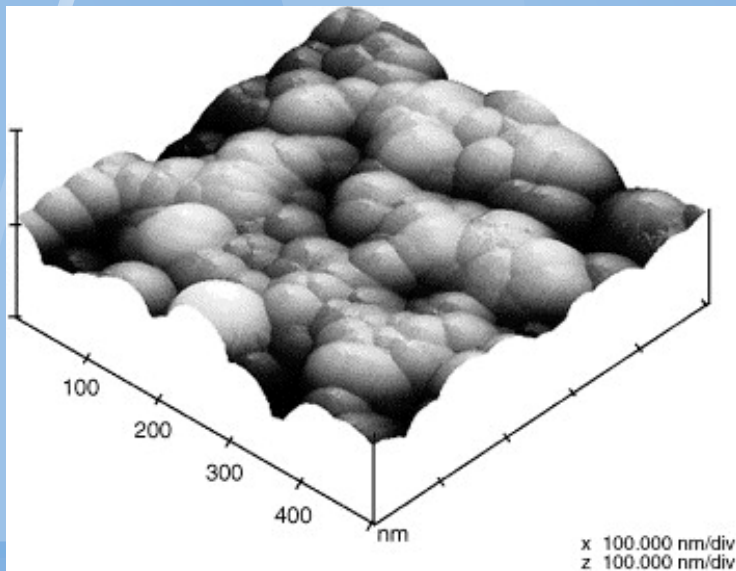
Hnací síly vzniku nové fáze

Přesycení
(fázová přeměna)

Kondenzace na
chladném substrátu

Reakční energie (chemická
reakce)

Změna reakční Gibbsovy
energie



Termodynamika vzniku nové fáze

Hnací síla transformace:

$$\Delta G^{th.} = nG^{mTD} + \Delta G^S \quad [J/mol]$$

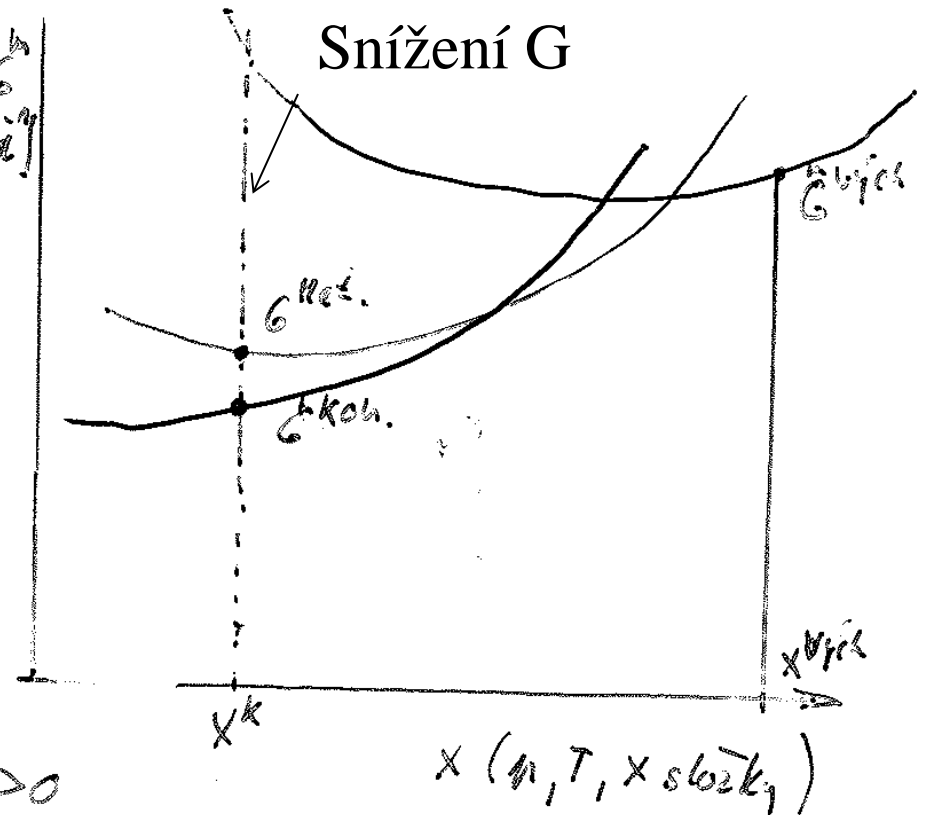
Termod. povrch.

ΔG^{mTD} lze spočítat z rovnou.
podmínek výchozí a konečné
fázové struktury

$$\Delta G^{mTD} = G^{m.kon.} - G^{m.vých.}$$

pro povrchový člen:

$$\Delta G^S = S \cdot \Delta A \text{ e. mezipovrch. energie } = A^2 - A^1 > 0$$



Povrchová energie kulovitého precipitátu

Pro 1 složkovou soustavu a kulovitou částici nové fáze platí:

$$\Delta G^{th.} = \frac{m}{M_L} \cdot \Delta G^{mTD} + 4\pi r^2 \cdot \Delta A = \frac{\rho}{M_L} \cdot \frac{4}{3}\pi r^3 \cdot \Delta G^{mTD} + 4\pi r^2 \cdot \Delta A$$

$$= 4\pi r^2 \cdot \left(\frac{r \cdot \rho}{3M_L} \cdot \Delta G^{mTD} + \Delta A \right)$$

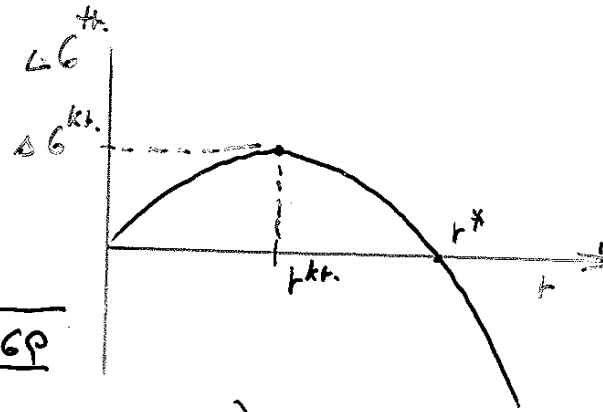
Char: body závislosti:

$$r^* = \frac{-\Delta A \cdot 3M_L}{\rho \Delta G^{TR}}$$

pro extrém:

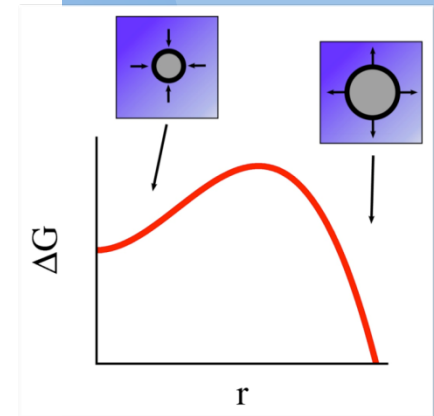
$$0 = \frac{\partial \Delta G^{th.}}{\partial r} = \frac{4}{3}\pi \frac{\Delta G \rho}{M_L} \cdot 3r^2 \Rightarrow r^{kt.} = \sqrt{\frac{4\pi \Delta G \rho}{M_L}}$$

$$\Delta G^{kt.} = \frac{16\pi^2 \Delta G^{TR} \rho}{M_L} \cdot \left(\frac{\Delta G \cdot \rho}{3M_L} \cdot \sqrt{\frac{4\pi \Delta G^{TR} \rho}{M_L}} + \Delta A \right)$$



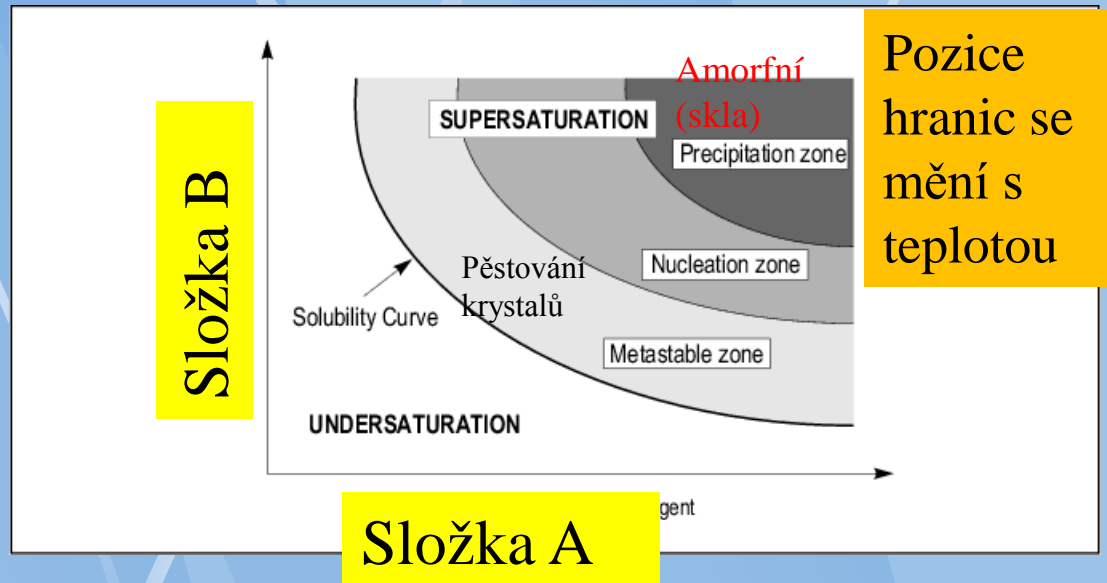
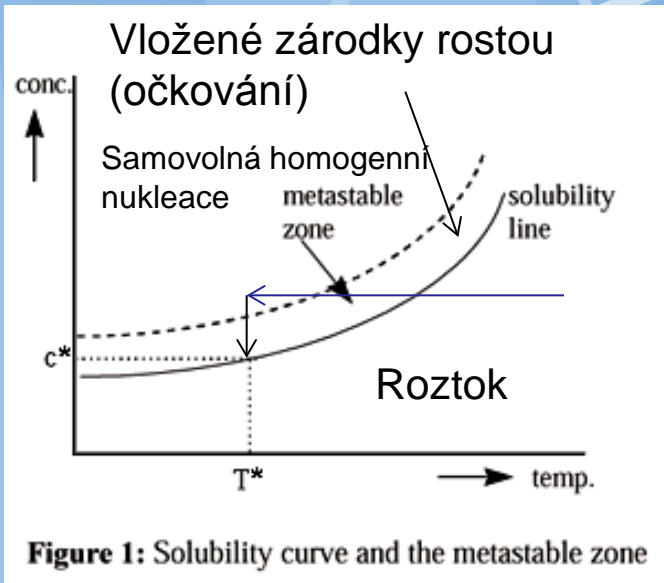
Podmínky pro vznik a růst nové fáze:

- $\Delta G^{mTR} < 0$
- jeli $\Delta A > 0$ pak zárodek nové fáze nesmí být izolovanou soustavou
- pokud je $\Delta G^{kt.}$ příliš vysoká může vzniknout metastabilní nová fáze s nižší $\Delta G^{kt.}$

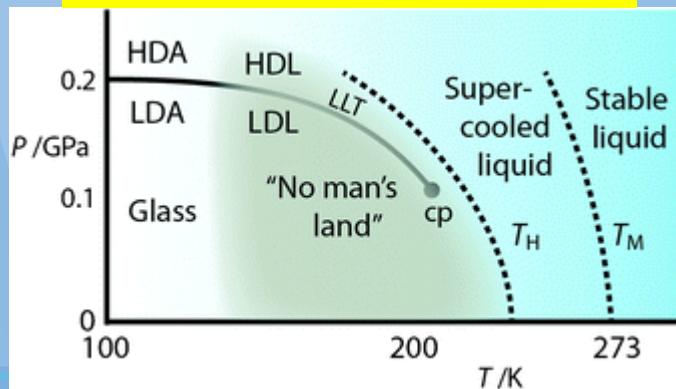


Nukleační a růstová zóna

(pro homogenní nukleaci)

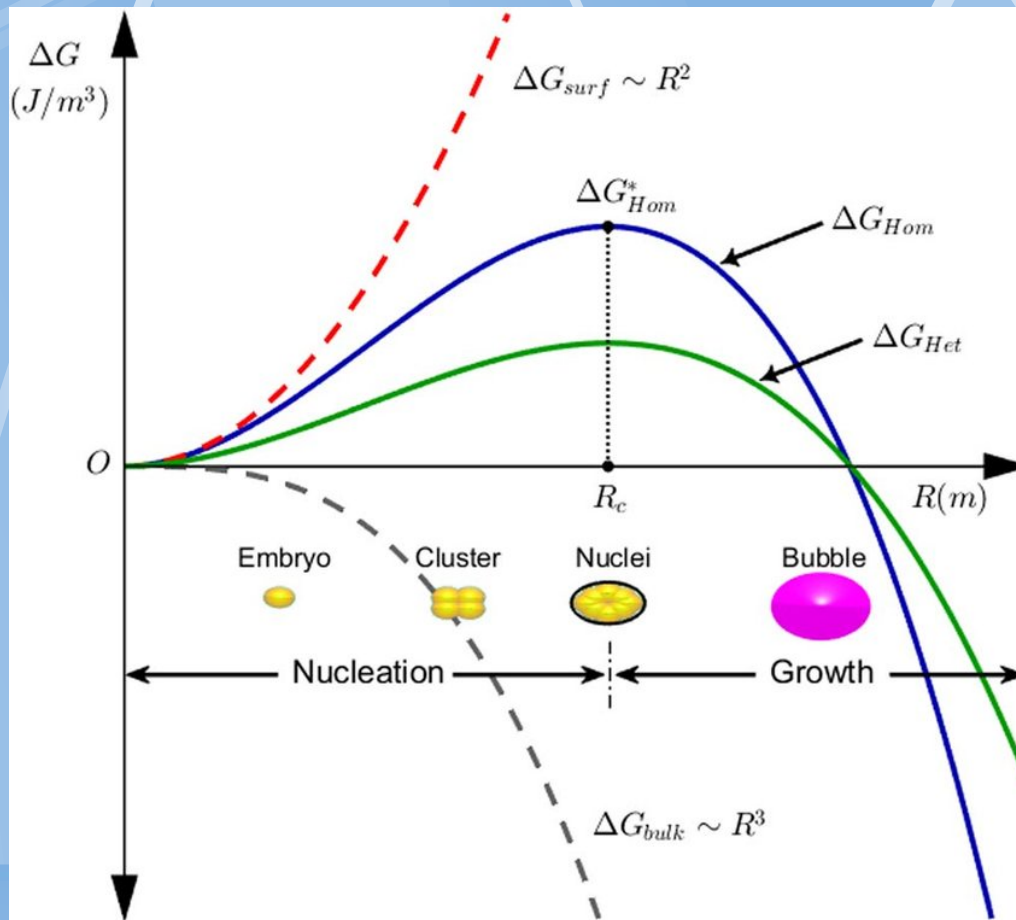


Extrémní nukl. batiéra

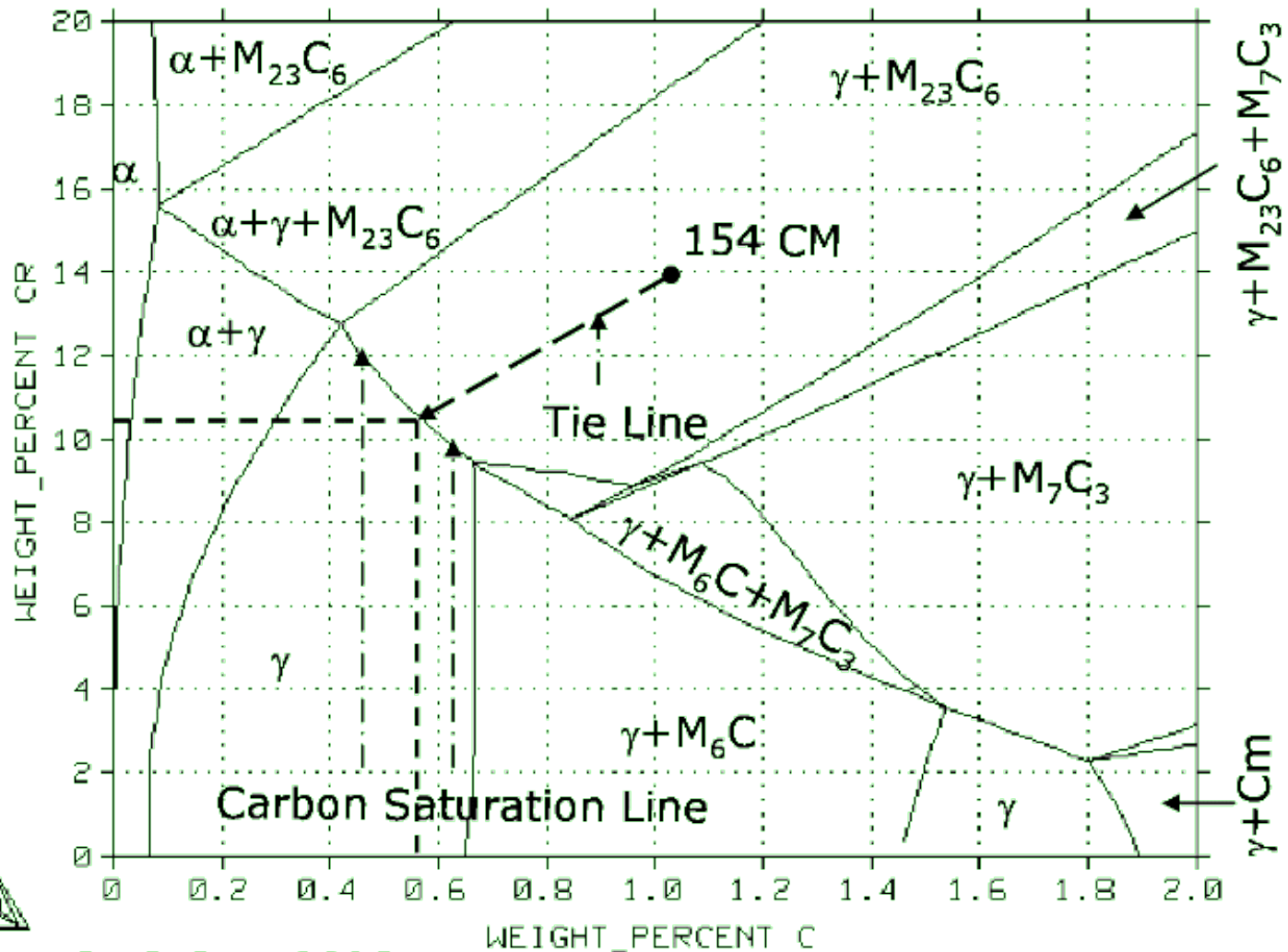



Viz pěstování monokrystalů např. CuSO4

Gibbs energy of nucleation (overview)

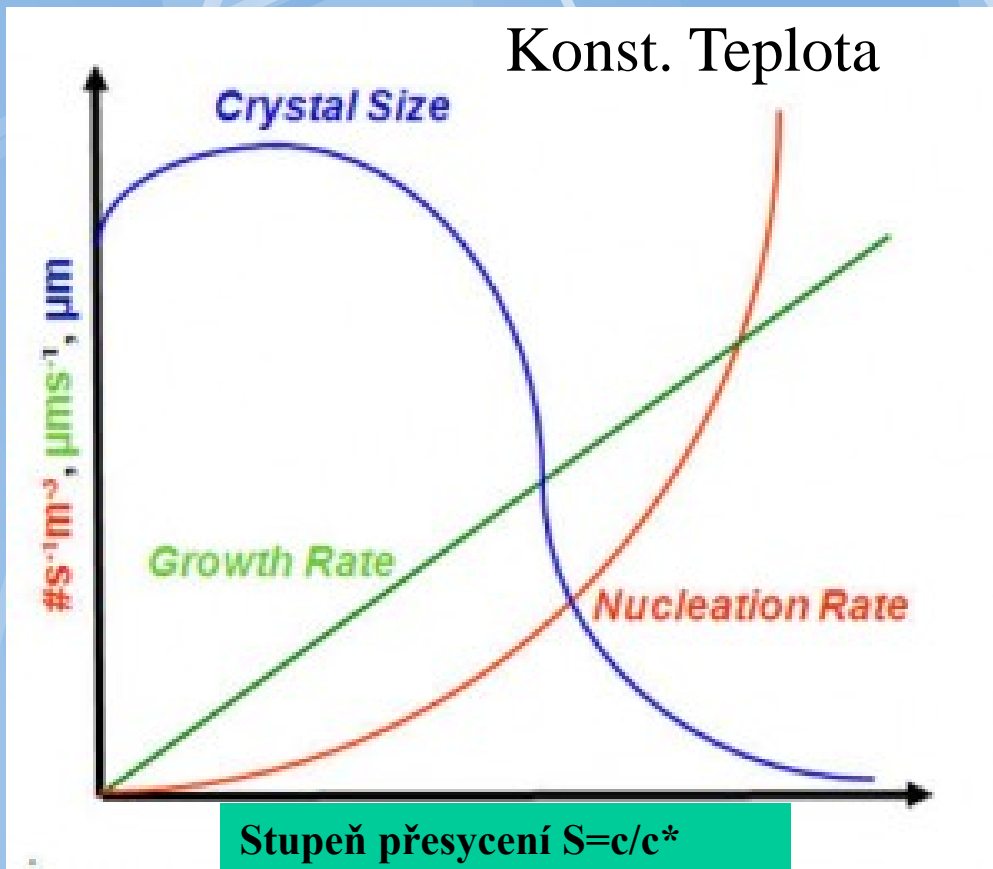


Alloys – saturation lines



 Fe-4Mo-Cr-C @ 1100°C

Rychlost růstu a rychlost nukleace



$$G = k_g \Delta C^g$$

$$B = k_b \Delta C^b$$

Kontrolováno difúzí (Dn) nebo růstem rozhraní (Rn)

Kontrolováno exponenciálně (distribuce lokální energie).

G = Growth Rate

k_g = growth constant

g = growth order

B = Nucleation Rate

k_b = nucleation constant

b = nucleation order > 1

ΔC = supersaturation

(Teplota má vliv na G a B, tím i na velikost krystalů)

Nukleace a růst

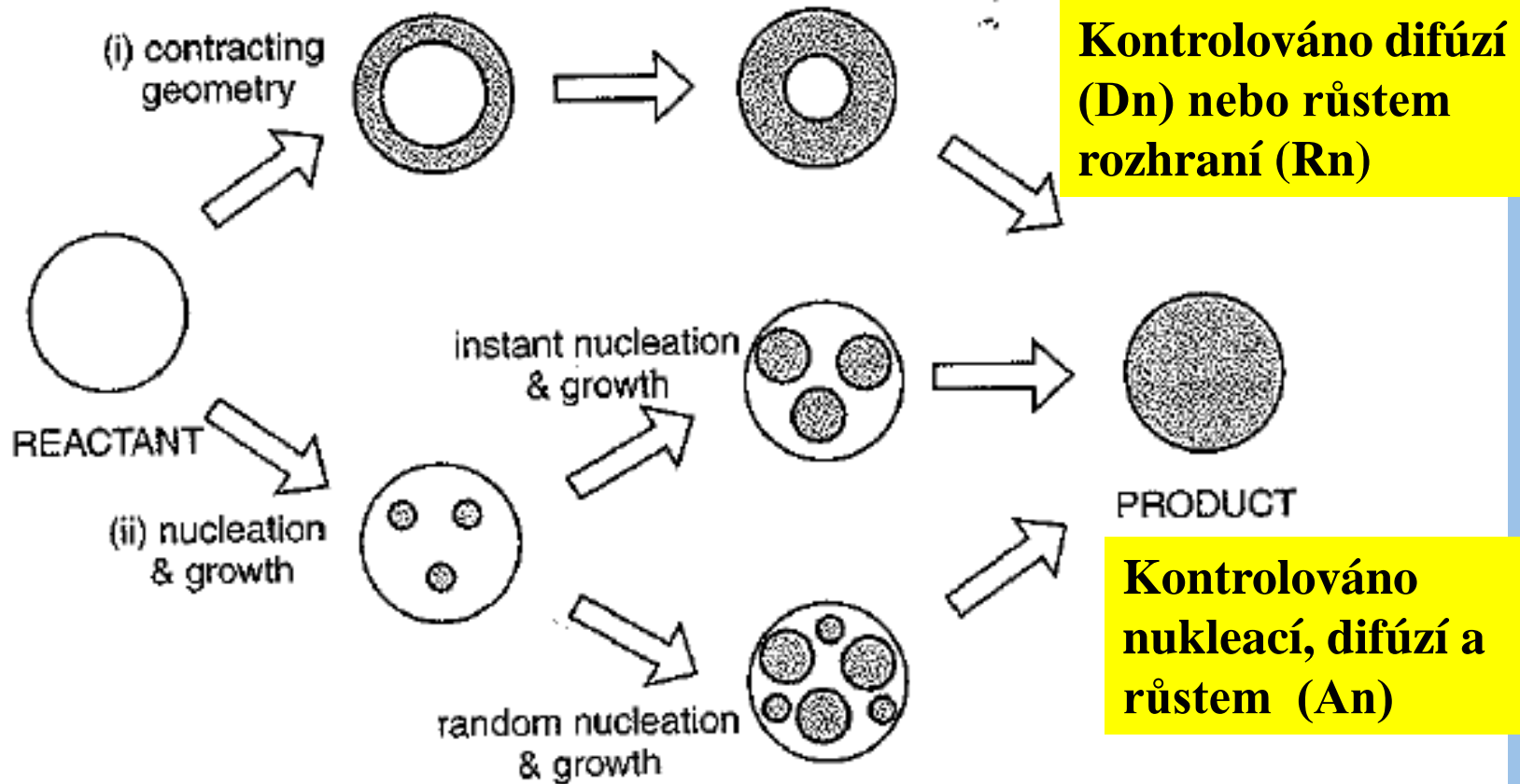
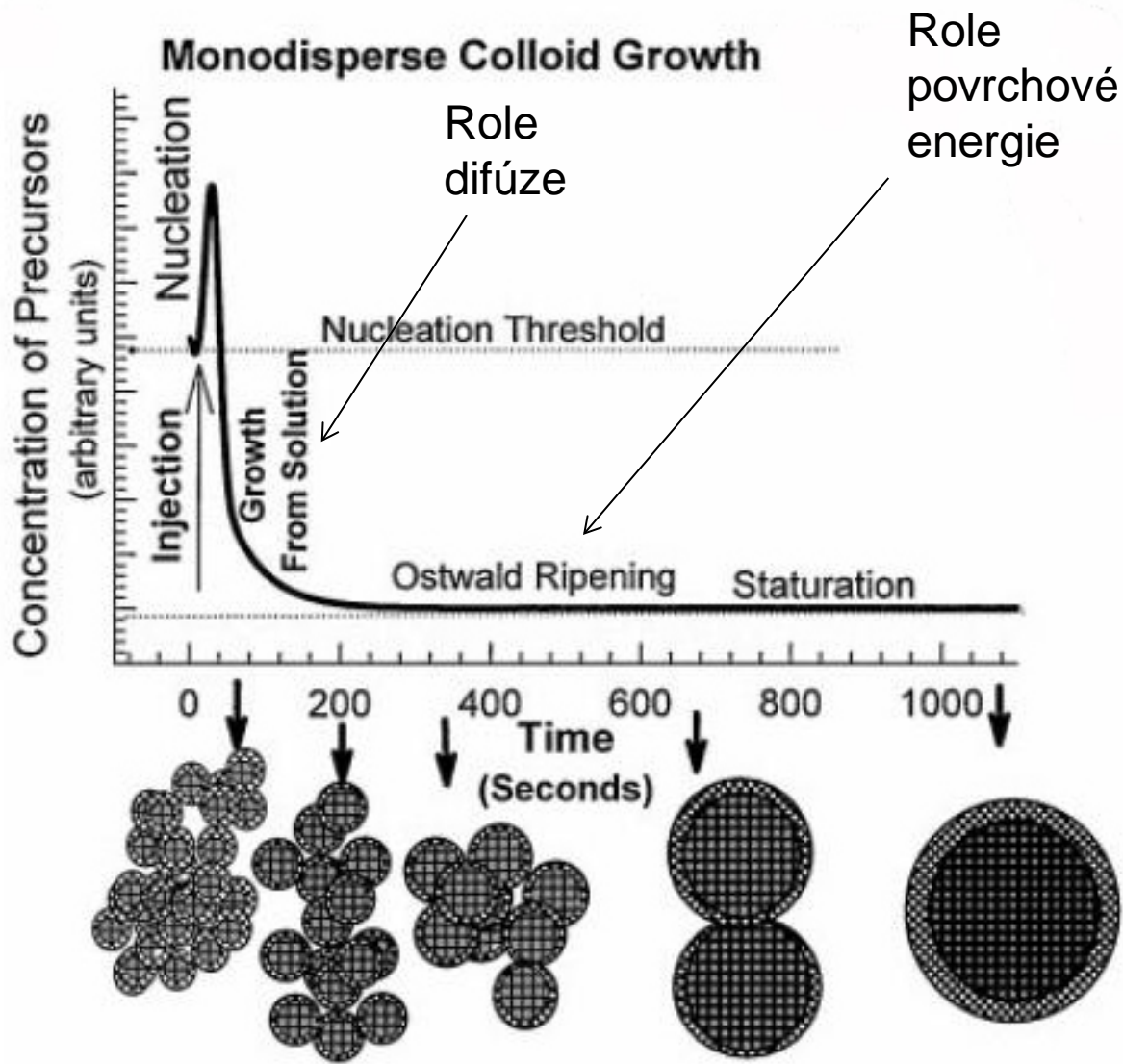


Figure 1 Schematic representation of the contracting geometry and nucleation–growth models

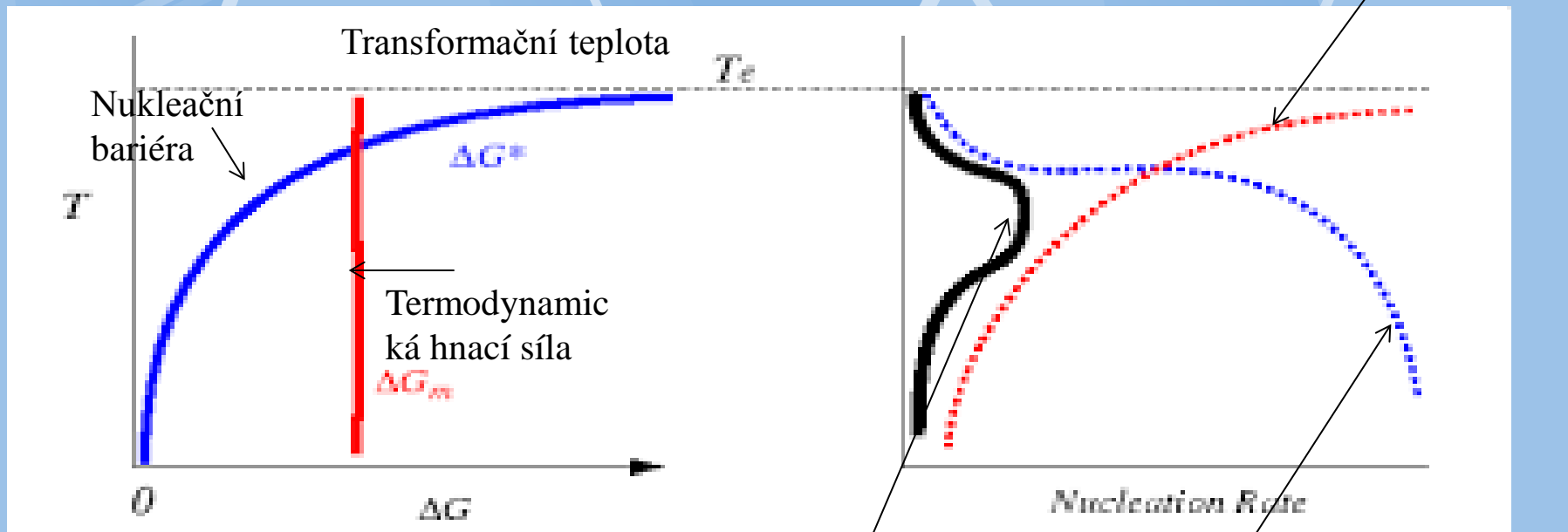
Cesta A: např. oxidace povrchových vrstev,
cesta B např. vznik hydridů v Zr slitinách

Kinetika vzniku tuhé fáze (krystalů) z přesyceného roztoku



- Příprava nasyceného roztoku při vyšší teplotě.
- Rychlé ochlazení
- Počátek a konec homogenní nukleace.
- Růst až do dosažení hranice rozpustnosti.
- Hrubnutí a sintrace

Rychlost transformace = rychlost difúze + rychlost nukleace

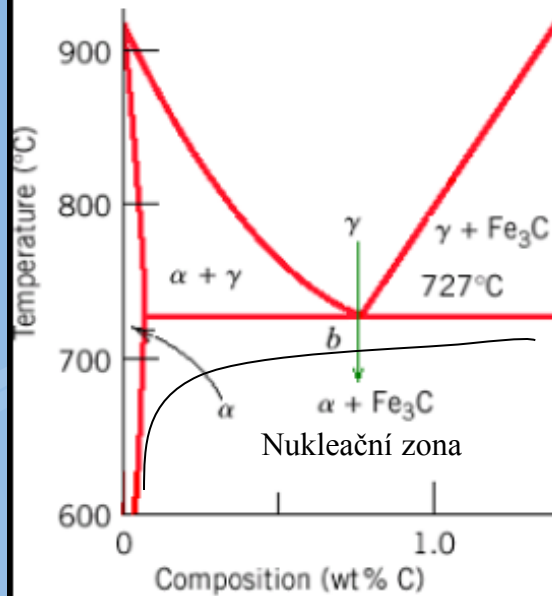


rychlost difúze

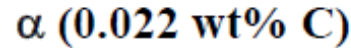
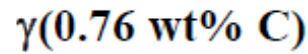
Rychlost fázové transformace

rychlost nukleace
Nehomogenní
+homogenní

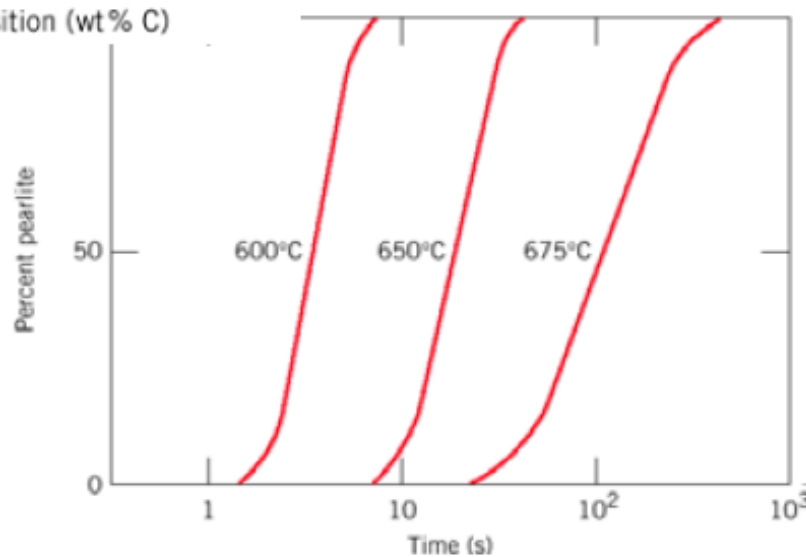
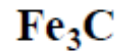
Let us consider eutectoid reaction as an example



eutectoid reaction:

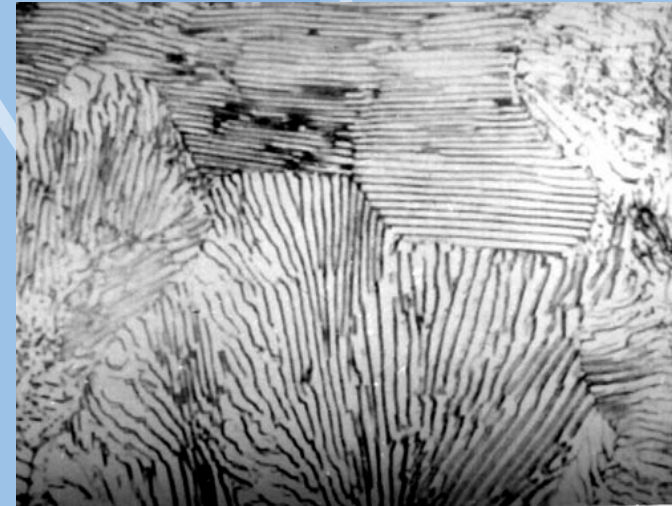


+



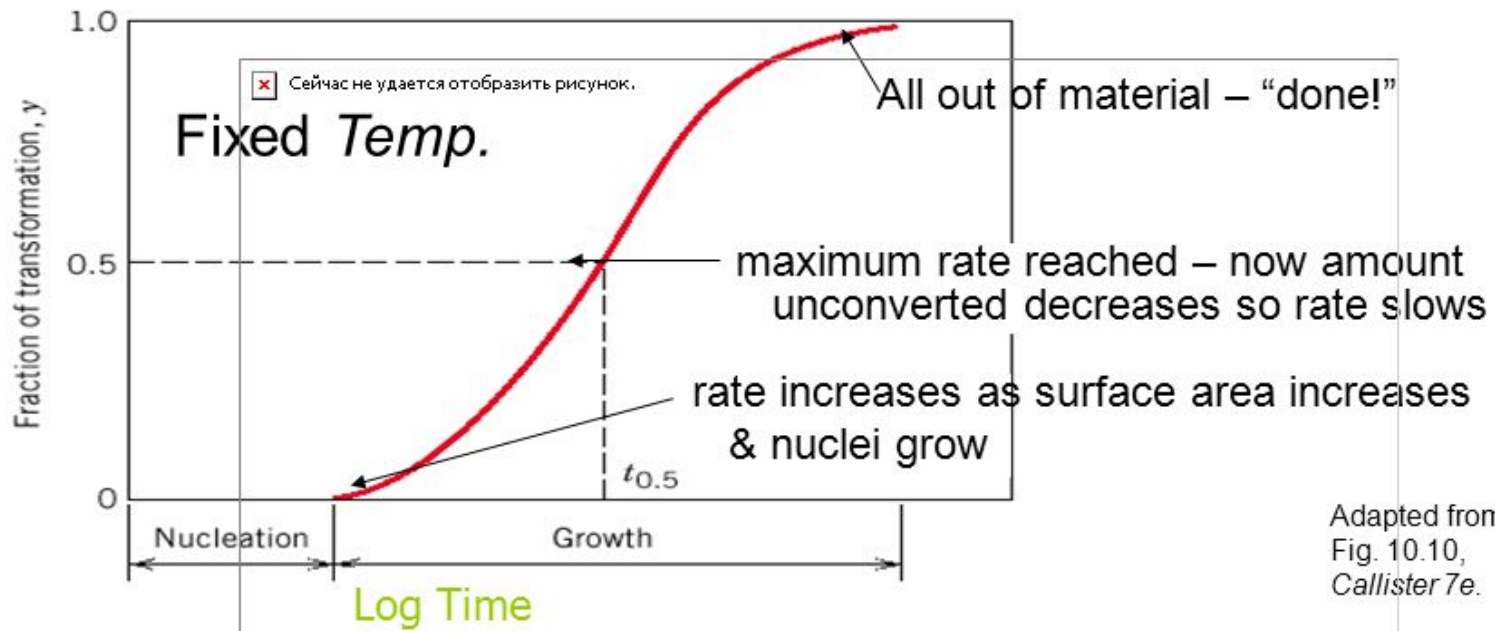
The S-shaped curves are shifted to longer times at higher T showing that the transformation is dominated by nucleation (nucleation rate increases with supercooling) and not by diffusion (which occurs faster at higher T).

Perlit: lamely cementitu a feritu



Perlit (eutektoidní ocel)

Rate of Phase Transformation



– Modeled by the Avrami Rate Equation:

$$y = 1 - e^{-kt^n}$$

Rate of transformation can be defined as reciprocal of time for transformation to proceed halfway to completion:

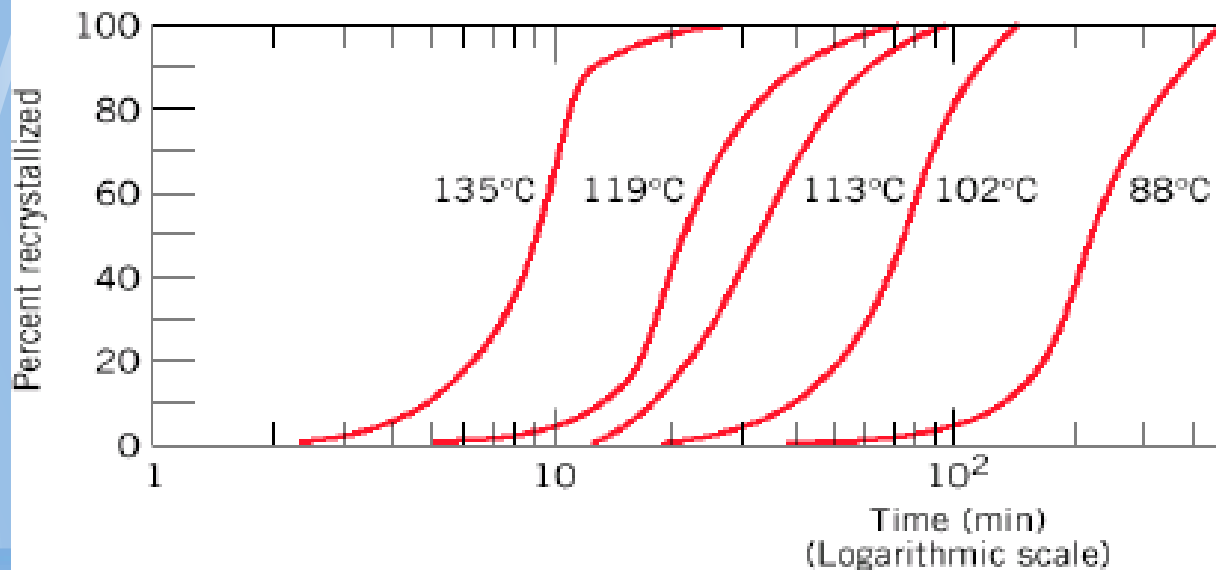
$$r = 1 / t_{0.5}$$

Rate increases with temperature according to Arrhenius equation, characteristic for thermally activated processes:

$$r = A \exp(-Q_A/kT) = A \exp(-Q_m/RT)$$

↑
Per atom

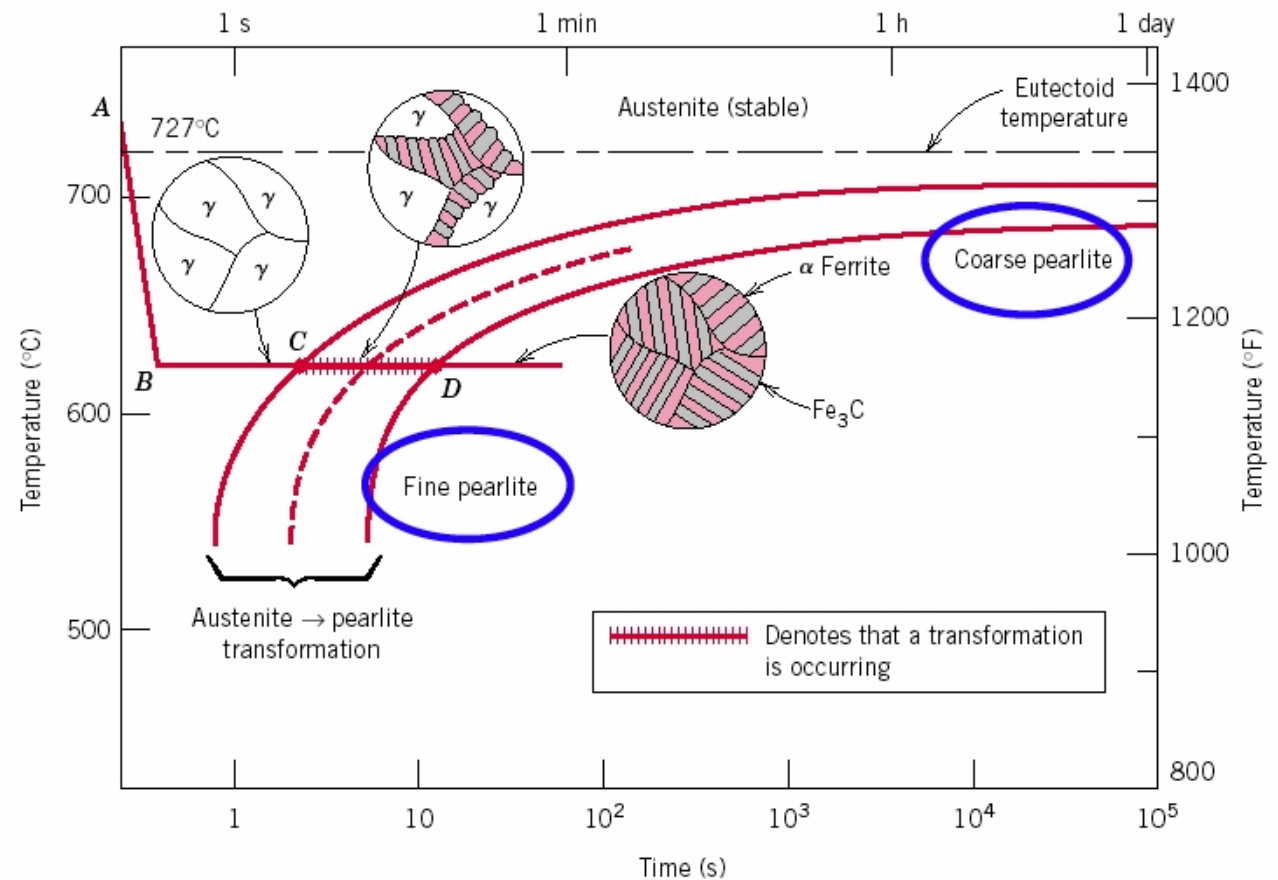
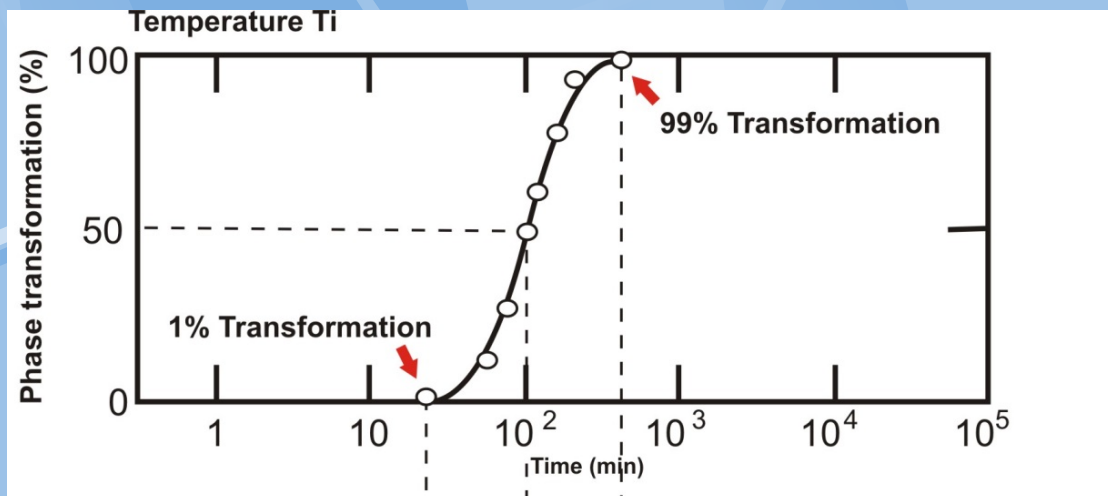
↑
Per mole



Percent recrystallization of pure copper at different T

TTT křivky

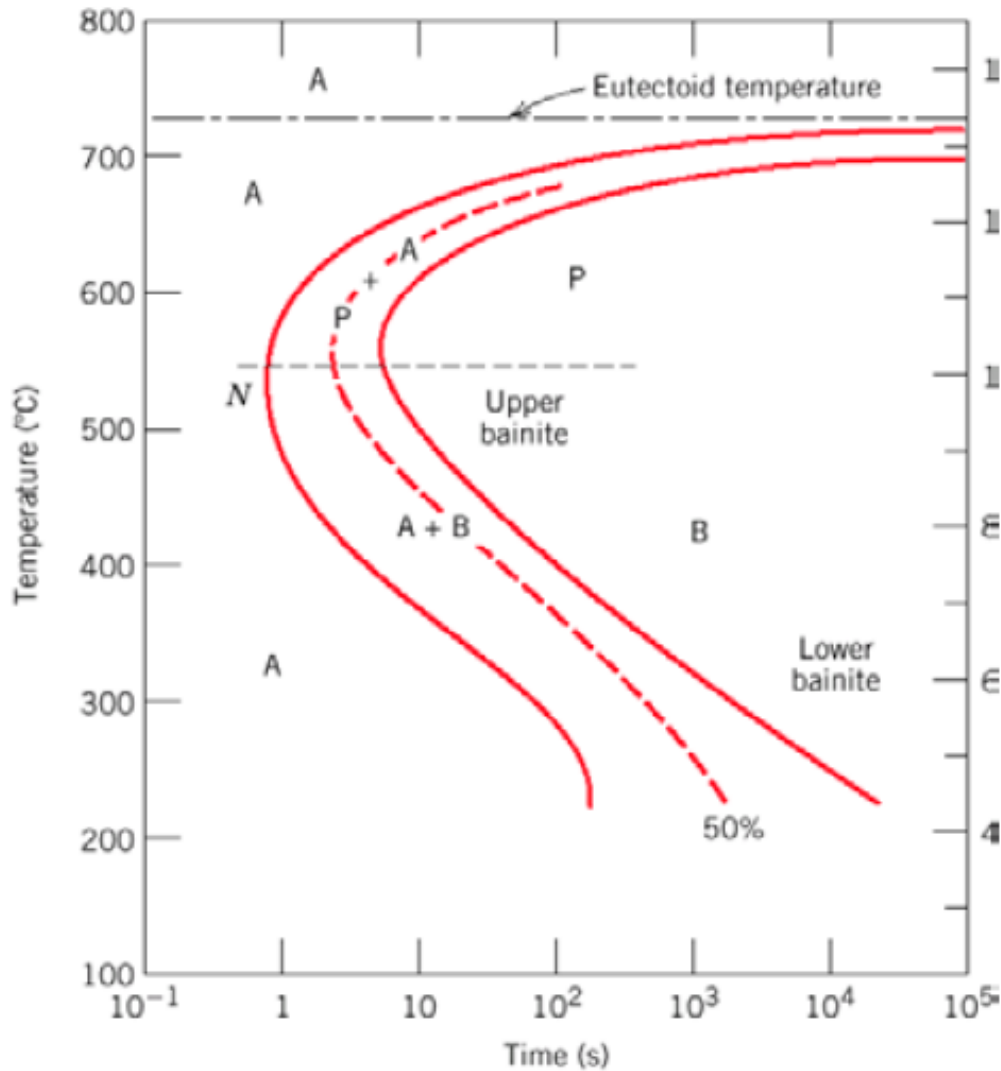
Rozsah
fázové
transformace



TTT Diagrams

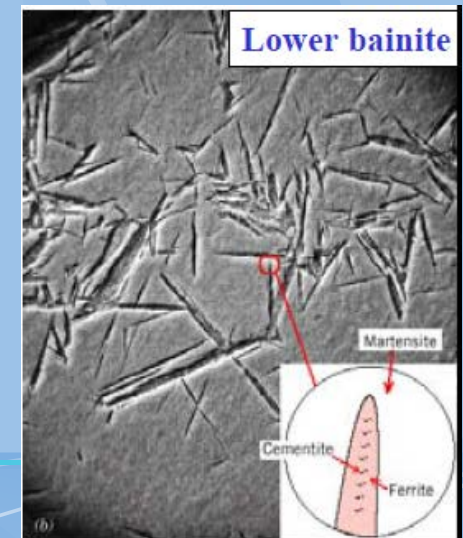
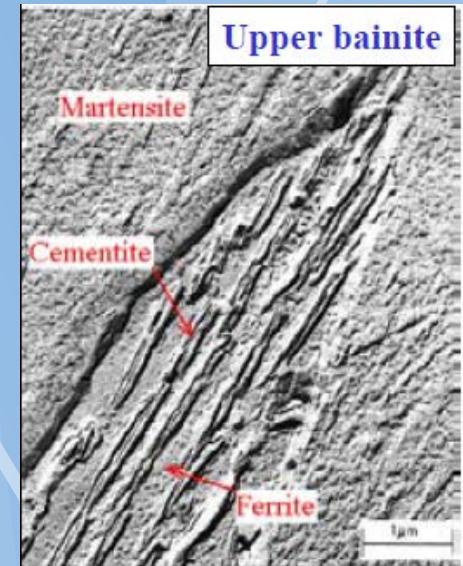
- The family of S-shaped curves at different T are used to construct the TTT diagrams.
- The TTT diagrams are for the **isothermal** (constant T) transformations (material is cooled quickly to a given temperature before the transformation occurs, and then keep it at that temperature).
- At low temperatures, the transformation occurs sooner (it is controlled by the rate of nucleation) and grain growth (that is controlled by diffusion) is reduced.
- Slow diffusion at low temperatures leads to fine-grained microstructure with thin-layered structure of pearlite (**fine pearlite**).
- At higher temperatures, high diffusion rates allow for larger grain growth and formation of thick layered structure of pearlite (**coarse pearlite**).
- At compositions other than eutectoid, a proeutectoid phase (ferrite or cementite) coexist with pearlite. Additional curves for proeutectoid transformation must be included on TTT diagrams.

Formation of Bainite Microstructure (I)



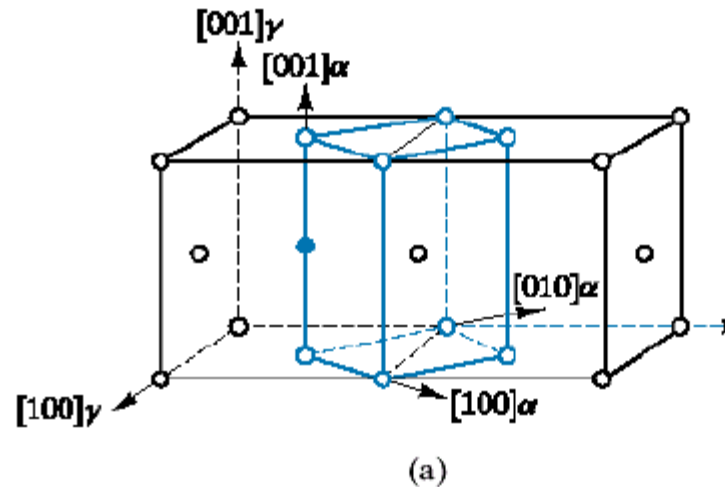
If transformation temperature is low enough ($\leq 540^\circ\text{C}$) bainite rather than fine pearlite forms.

Bainite: cementite and dislocation-rich ferrite

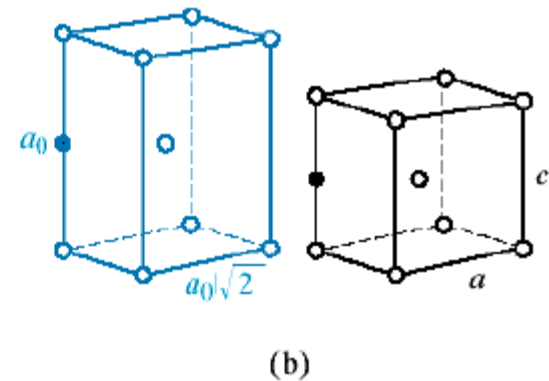


Martenzitická transformace (při kalení)

Introduction to Materials Science, Chapter 10, Phase Transformations in Metals

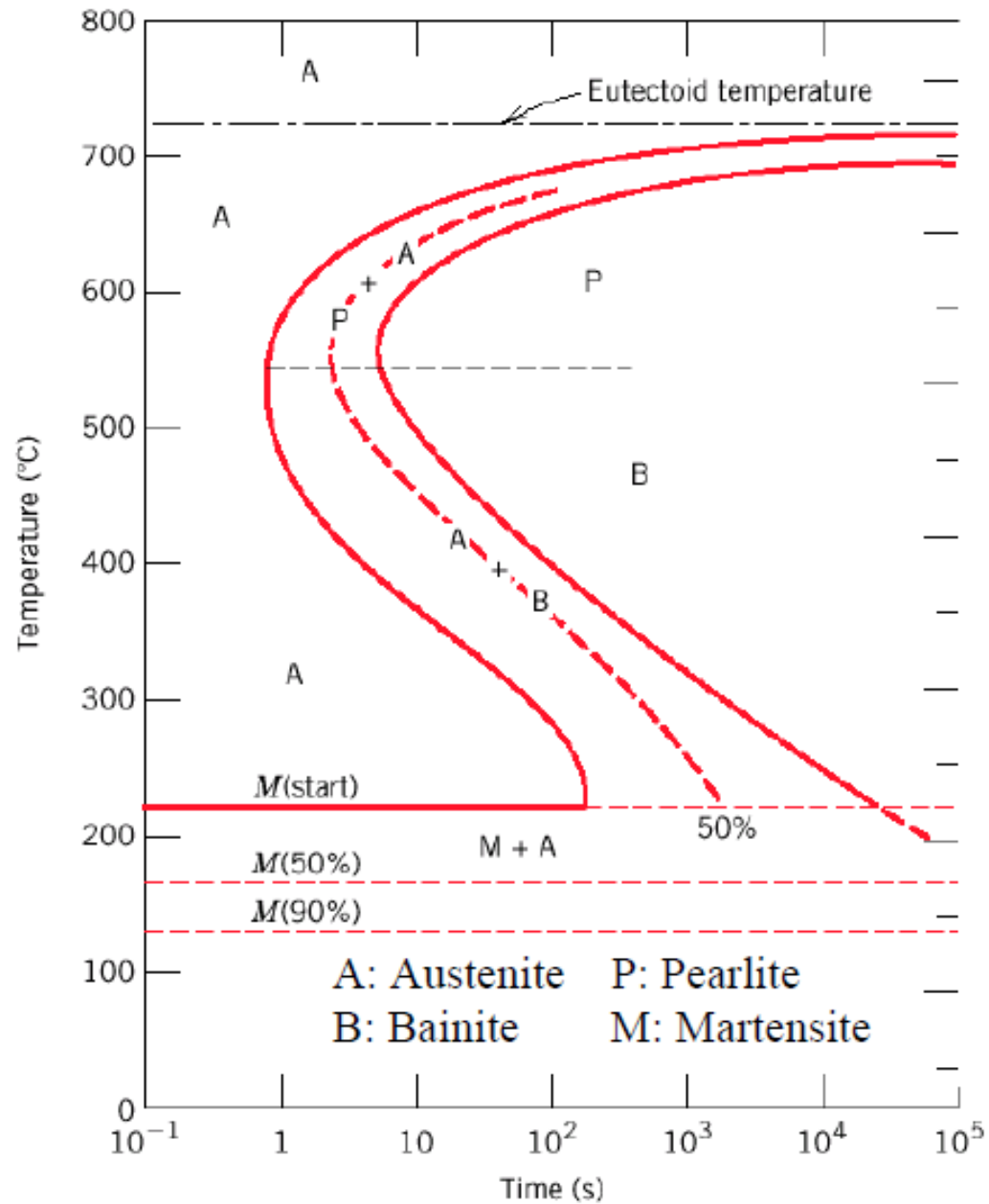


- Each atom displaces a small (sub-atomic) distance to transform FCC γ -Fe (austenite) to martensite which has a Body Centered Tetragonal (BCT) unit cell (like BCC, but one unit cell axis is longer than the other two).

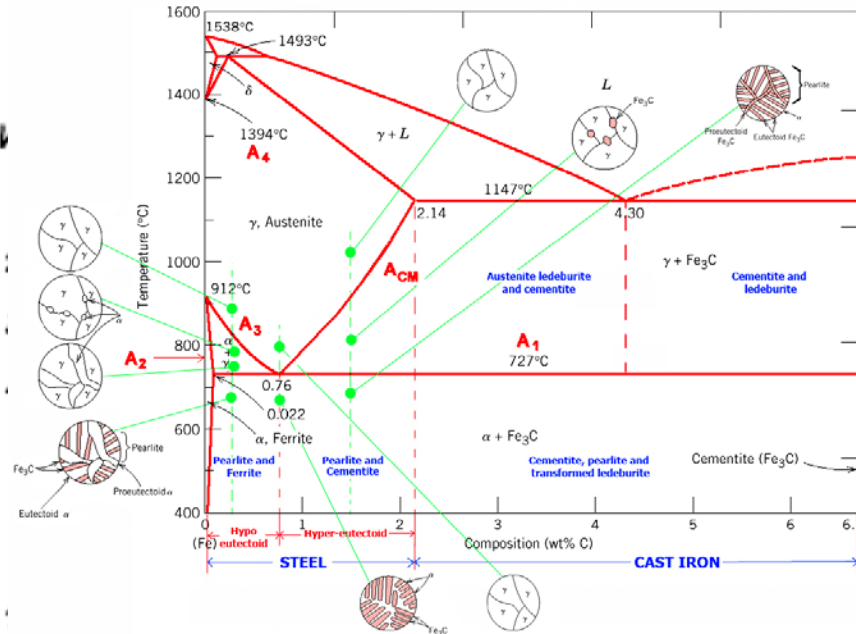
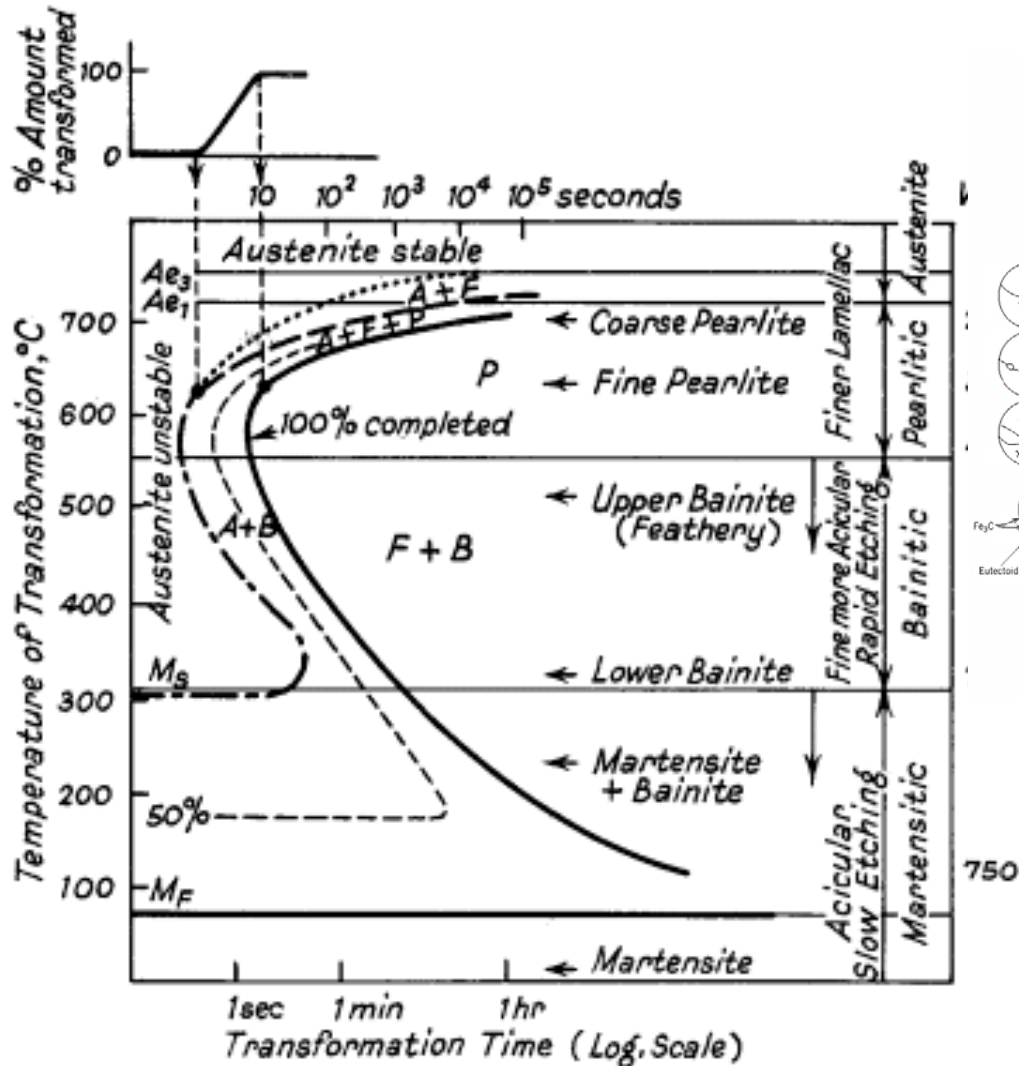


The martensitic transformation involves the sudden reorientation of C and Fe atoms from the FCC solid solution of γ -Fe (austenite) to a body-centered tetragonal (BCT) solid solution (martensite).

TTT Diagram including Martensite

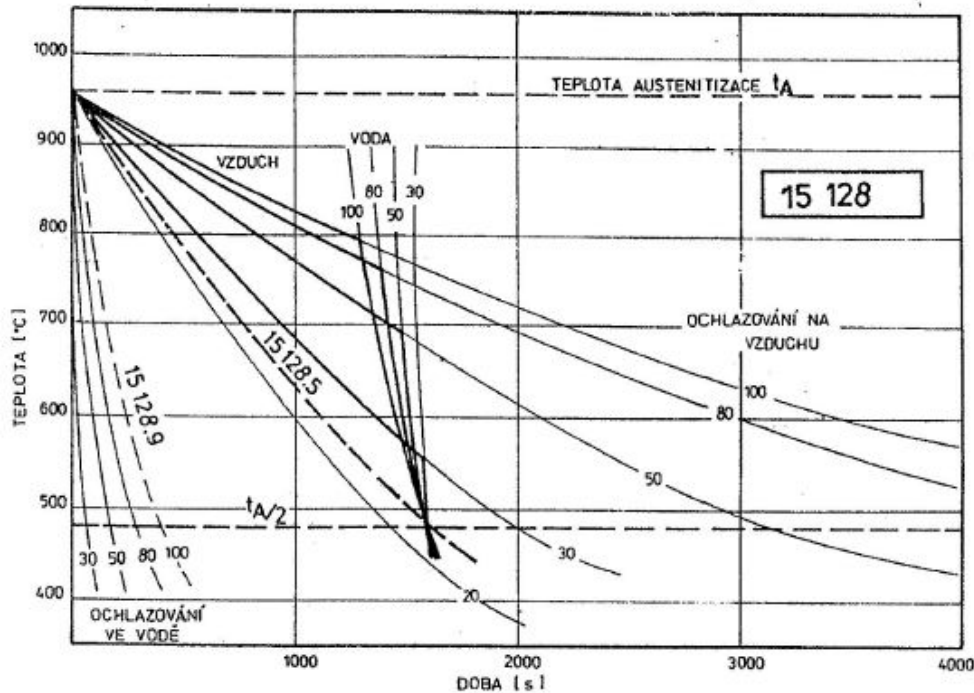


Ideal TTT-curve for 0,65% carbon steel depicting time interval required for beginning, 50% and 100% transformation of austenite at a constant temperature
 A= Austenite F= Ferrite P = Pearlite B = Bainite

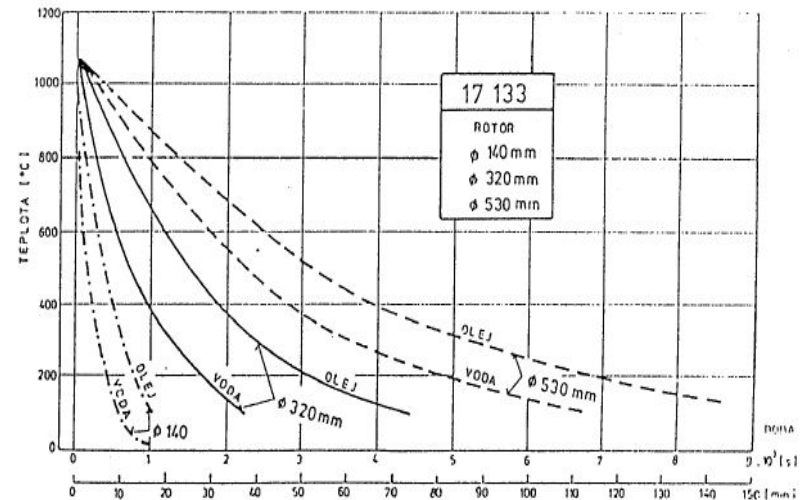
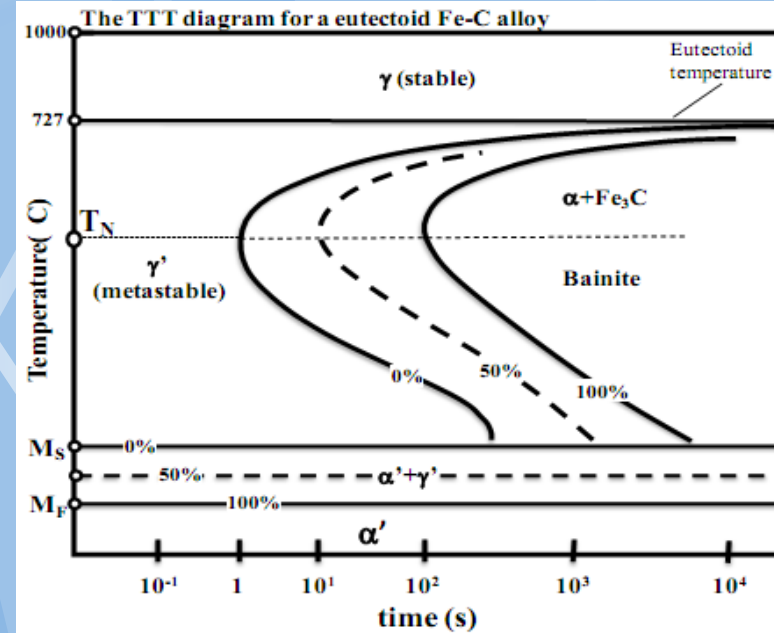


Martenzit: teragonální BCT (prodloužená BCC) mřížka přesycena uhlíkem

Role reálné rychlosti ochlazení

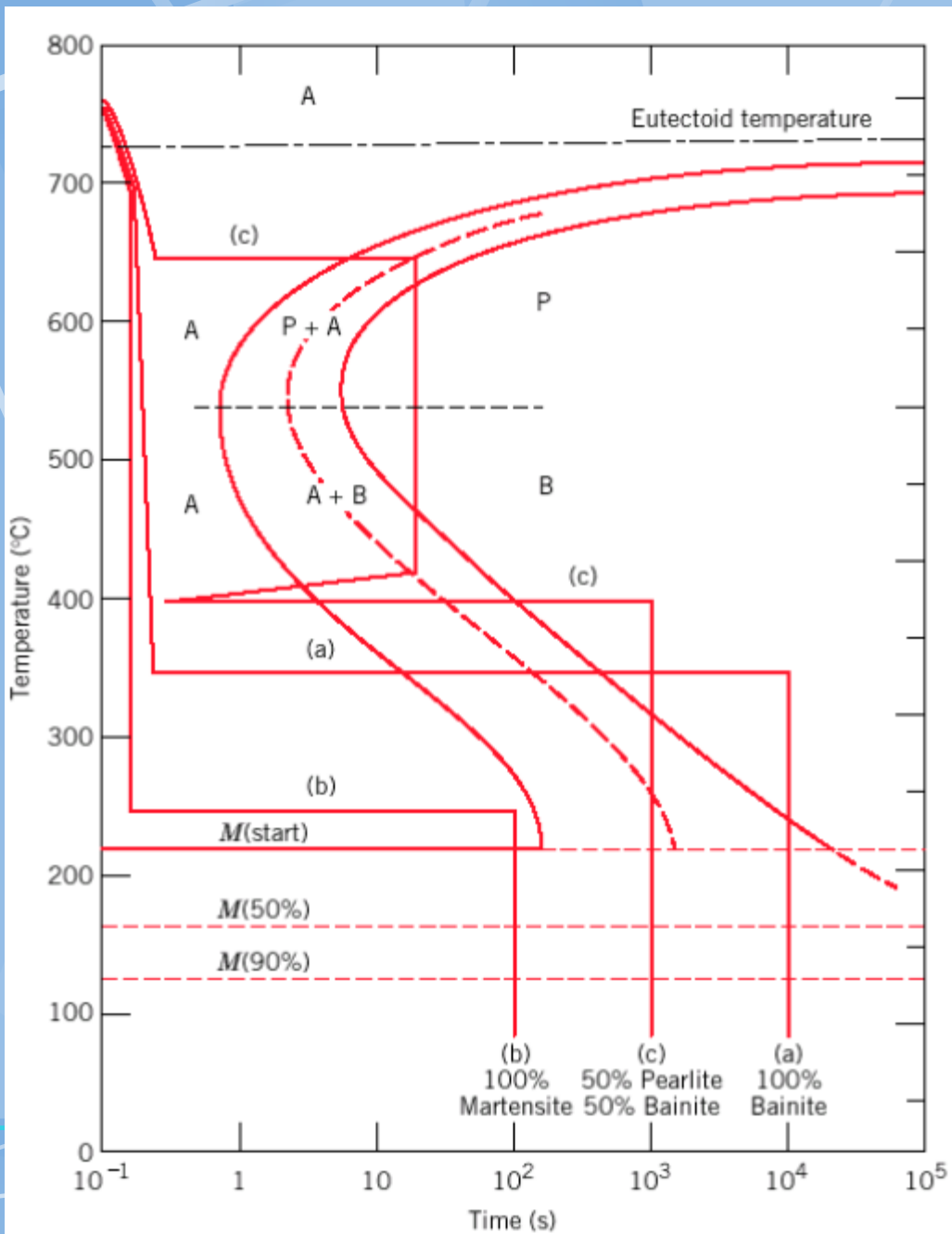


Obr. 4 Průběh ochlazování tlustých plechů z oceli 0,5 Cr-0,5 Mo-0,3 V na vzduchu a ve vodě



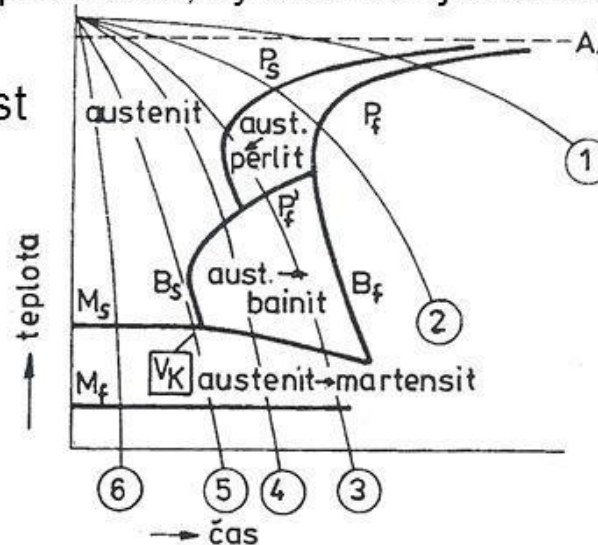
Obr. 5 Ochlazování rozdílných průměrů rotoru z oceli 17 133 v oleji a ve vodě

Tepelné zpracování ocelí

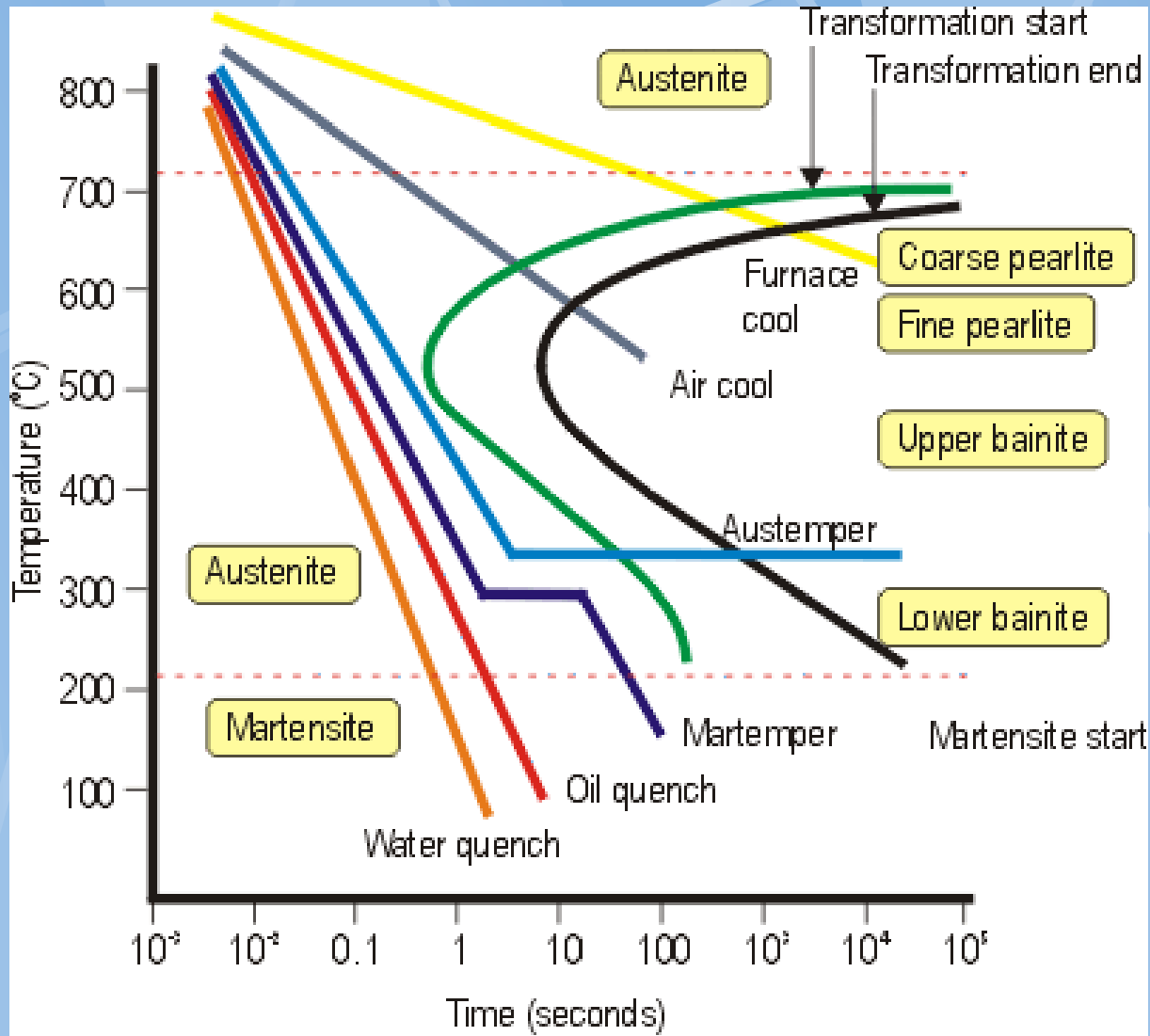


RYCHLOST OCHLAZOVÁNÍ

- » 1, 2 malá rychlost ochlazení, vznik perlitu
- » 3 vyšší rychlost ochlazení, vznik bainitu následně martenzitu
- » 4 přichází přímo k bainitické přeměně, výsledkem je bainit + martenzit
- » 5 kritická ochlazovací rychlost

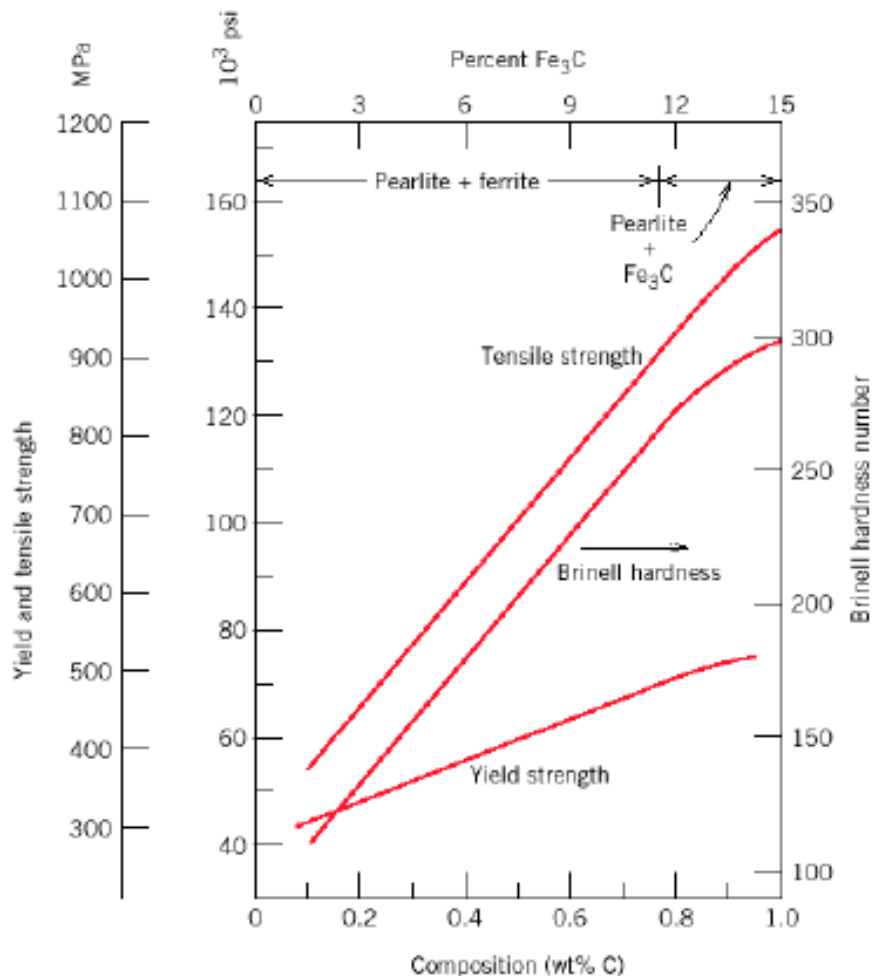


Vliv rychlosti ochlazování na rozpad austenitu



Mechanical properties of Fe-C alloys

Cementite is harder and more brittle than ferrite - increasing cementite fraction therefore makes harder, less ductile material.



Mechanical Behavior of Fe-C Alloys (II)

The strength and hardness of the different microstructures is inversely related to the size of the microstructures (fine structures have more phase boundaries inhibiting dislocation motion).

Mechanical properties of bainite, pearlite, spheroidite

Considering microstructure we can predict that

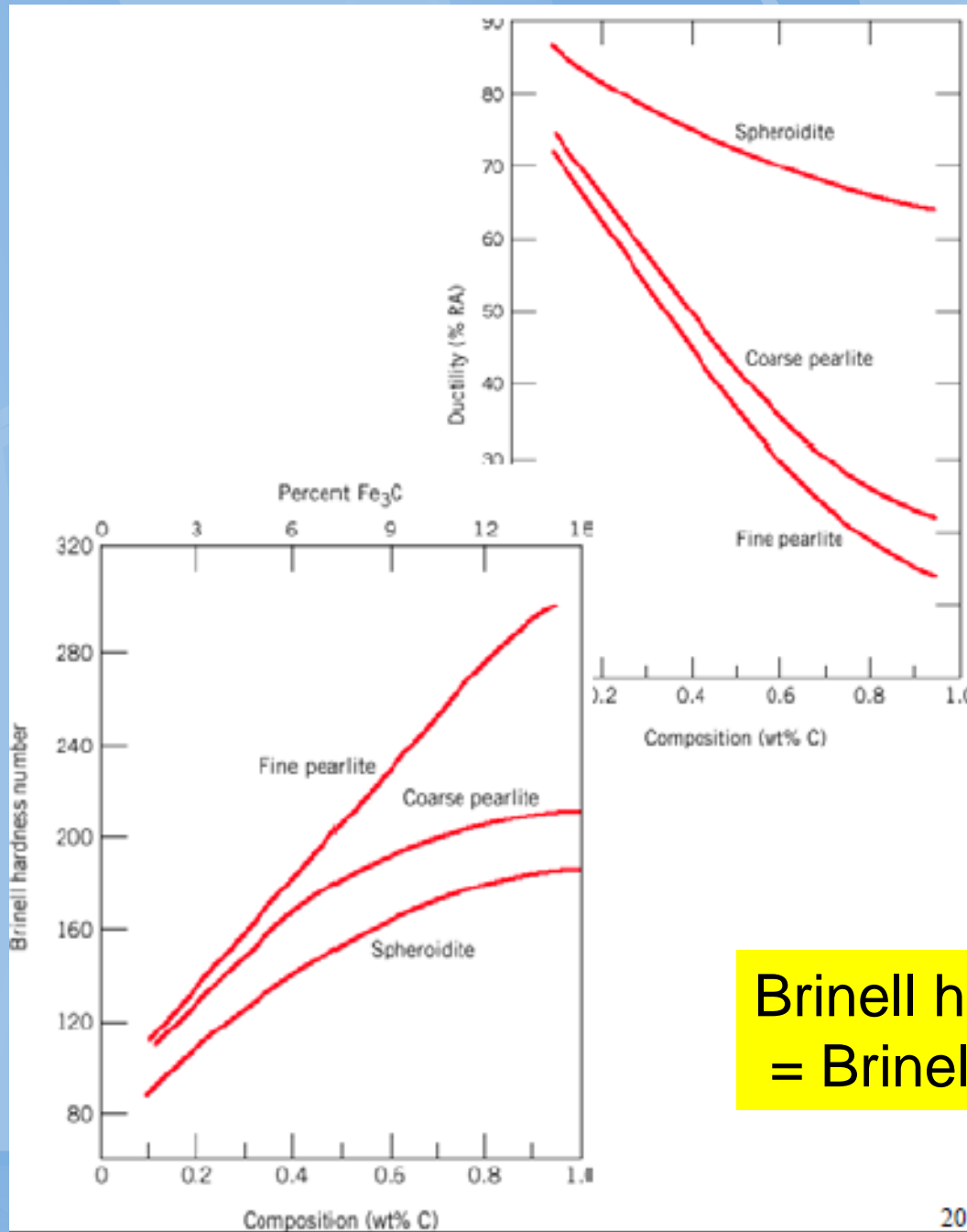
- Spheroidite is the softest
- Fine pearlite is harder and stronger than coarse pearlite
- Bainite is harder and stronger than pearlite

Mechanical properties of martensite

Of the various microstructures in steel alloys

- Martensite is the hardest, strongest and the most brittle

The strength of martensite is not related to microstructure. Rather, it is related to the interstitial C atoms hindering dislocation motion (solid solution hardening, Chapter 7) and to the small number of slip systems.



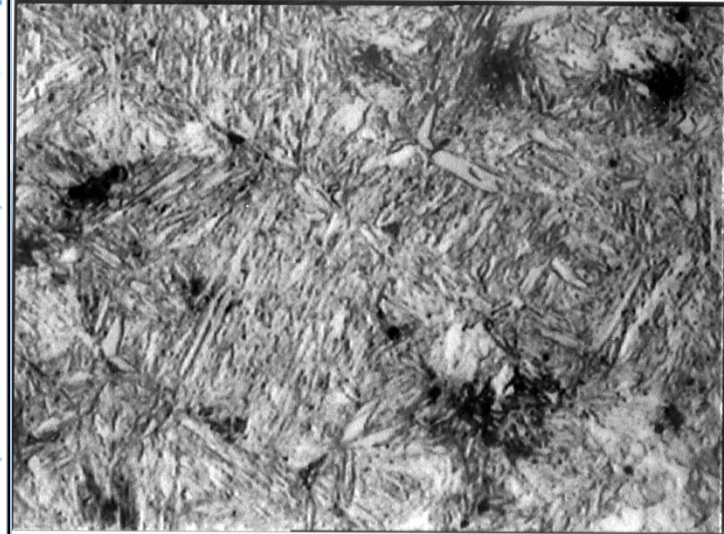
ductility
= kovatelnost

Brinell hardness number
= Brinellovo číslo tvrdosti

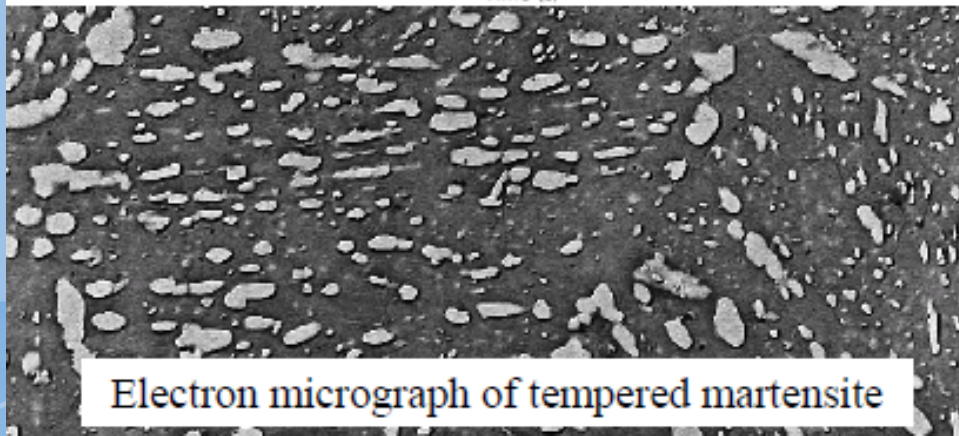
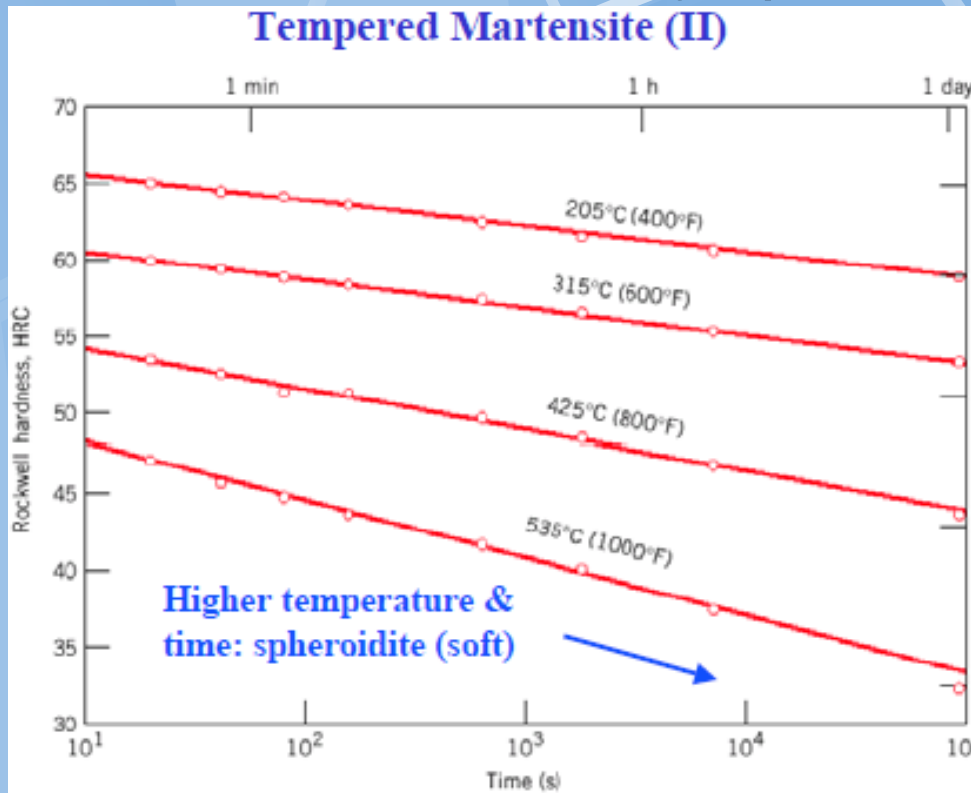
Martenzit

Martensite is so brittle that it needs to be modified for practical applications. This is done by heating it to 250-650 °C for some time (tempering) which produces **tempered martensite**, an extremely fine-grained and well dispersed cementite grains in a ferrite matrix.

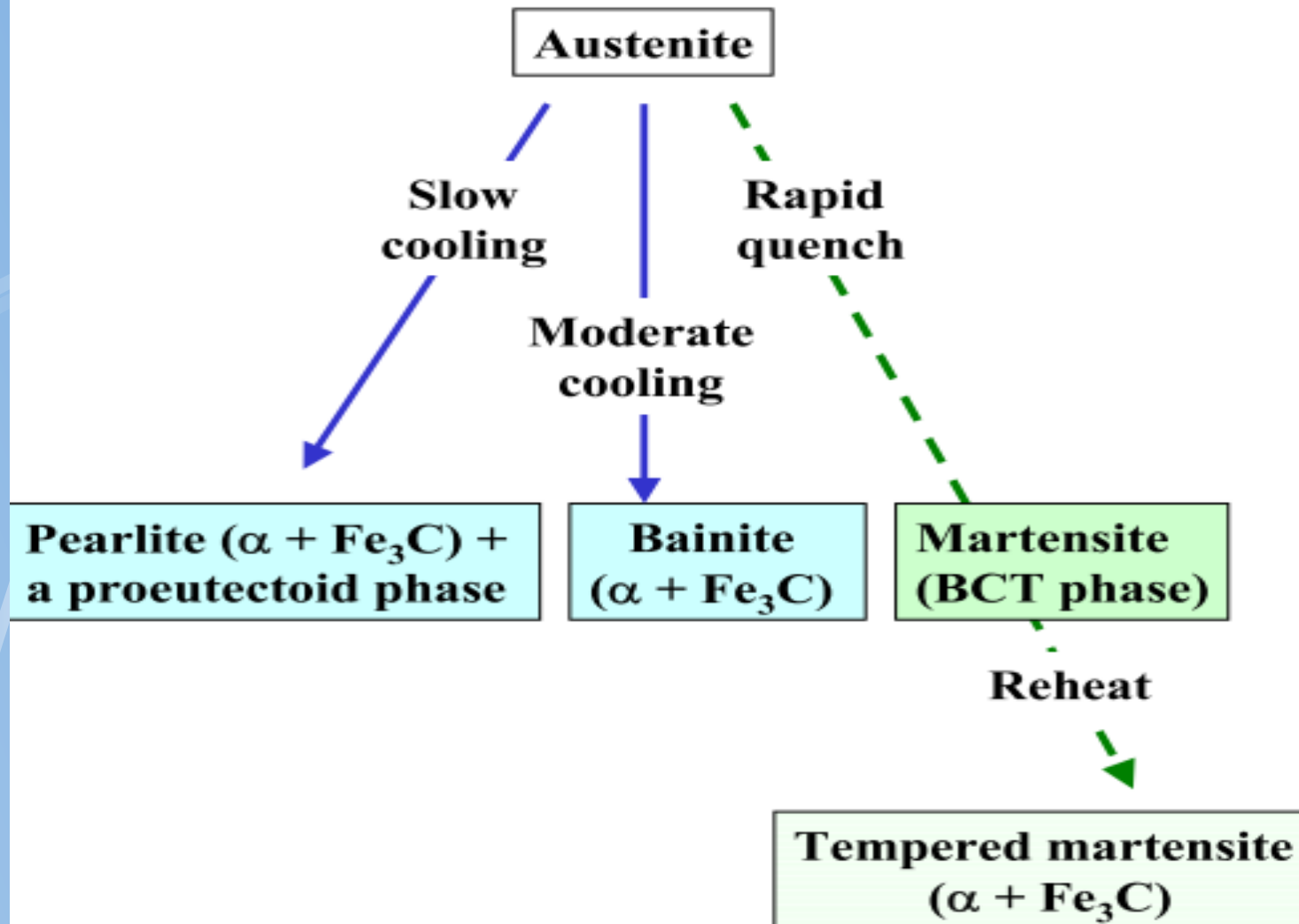
- Tempered martensite is less hard/strong as compared to regular martensite but has enhanced ductility (ferrite phase is ductile).
- Mechanical properties depend upon cementite particle size: fewer, larger particles means less boundary area and softer, more ductile material - eventual limit is spheroidite.
- Particle size increases with higher tempering temperature and/or longer time (more C diffusion) - therefore softer, more ductile material.



Temperovaný (popuštěný) martenzit



Summary of austenite transformations

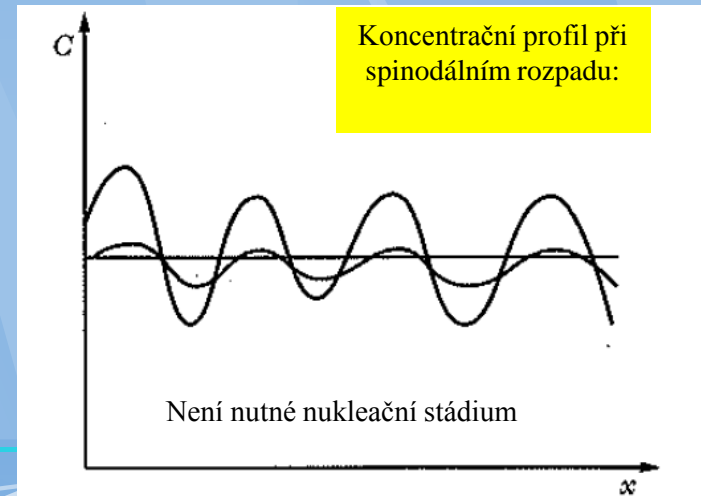
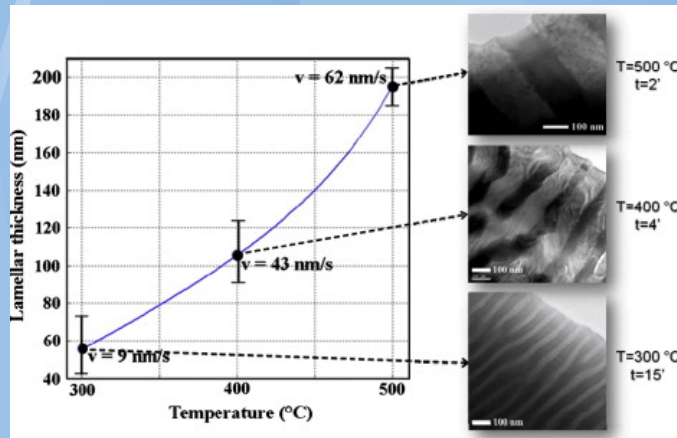
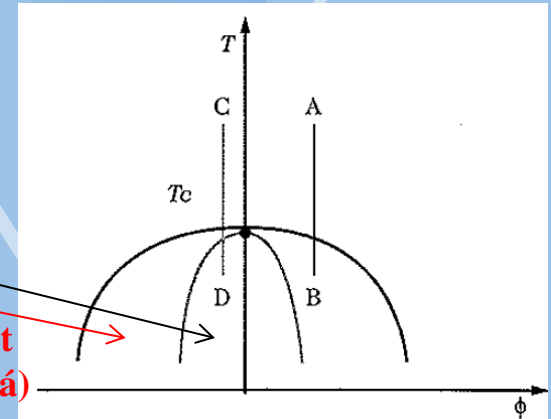
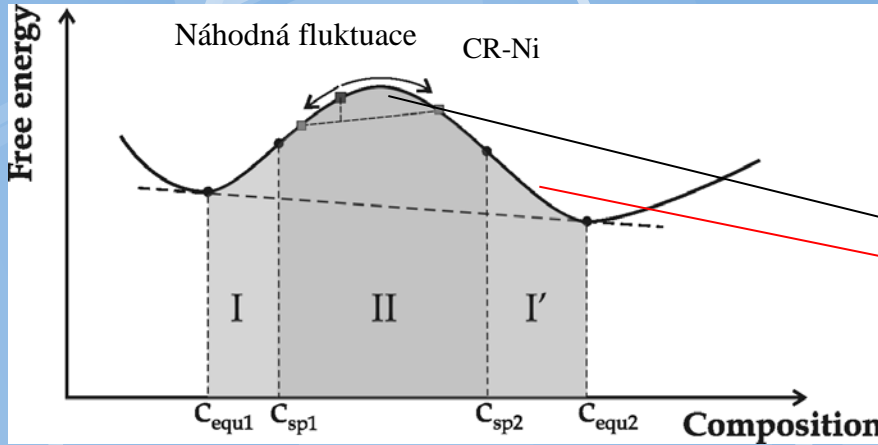


Solid lines are diffusional transformations, dashed is diffusionless martensitic transformation

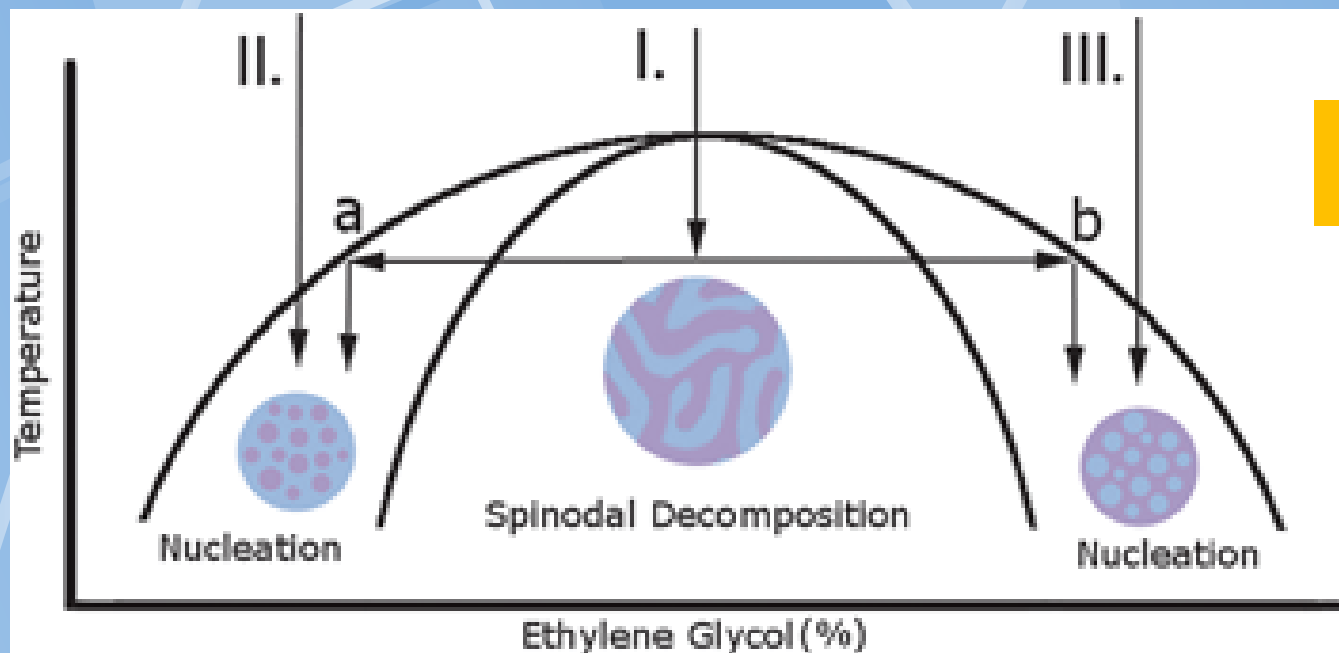
1. Spinodální rozpad – fázová přeměna bez nukleace

Spinodální rozpad (fázová přeměna)

Motiv ve FD:



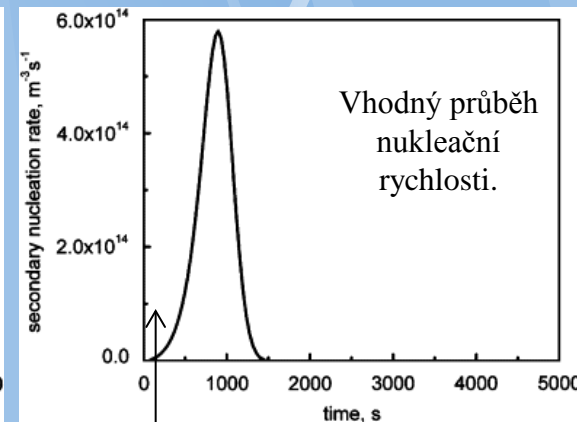
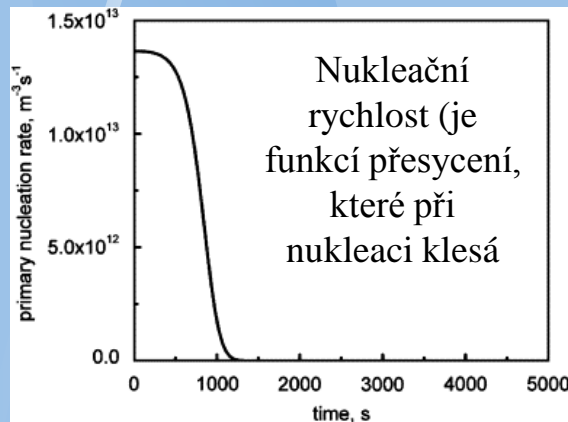
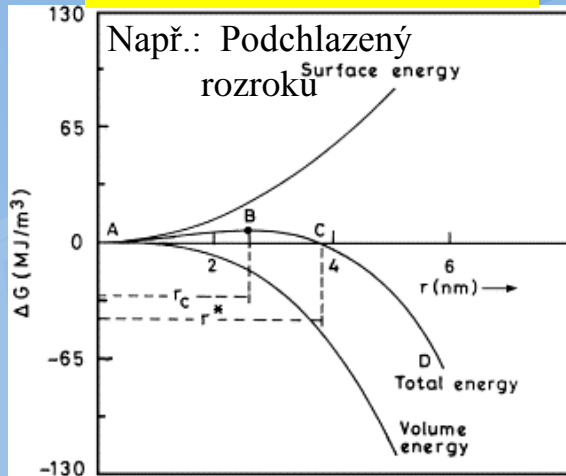
Oblast nukleace a spinodálního rozpadu



Schematic phase diagram for the NM–EG mixture, showing the different quench pathways employed in this study. (I) Proposed pathway for the formation of bridged bijels through combined spinodal decomposition and nucleation and growth. (II) Off-critical quench in a NM-rich mixture. (III) Off-critical quench in an EG-rich sample.

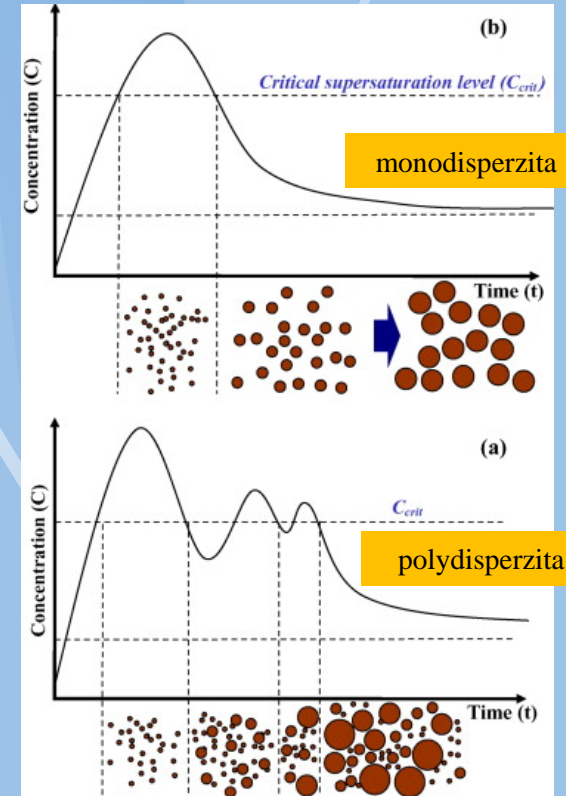
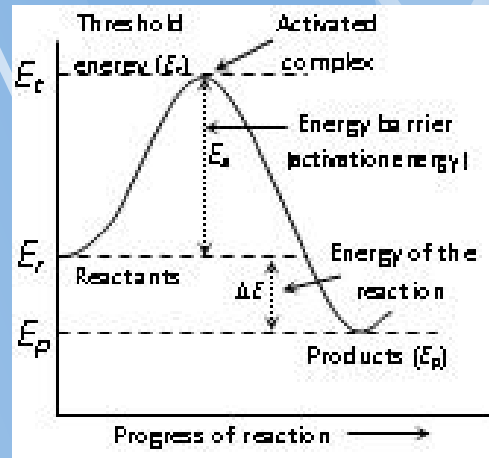
Nukleace, růst, polydispersita

Fázové přeměny



Trigering

Chemické reakce



Schematic illustration of nucleation and growth mechanisms Cu based on LaMer's model: (a) mechanism for polydisperse particles and (b) mechanism for monodisperse particles.
<http://www.sciencedirect.com/science/article/pii/S0021979707003207>

Homogenní a heterogenní nukleace z liquidu

driving force for solidification, ΔG_v exists below the equilibrium melting temperature, T_m and that this is approximately proportional to the degree of undercooling ΔT :

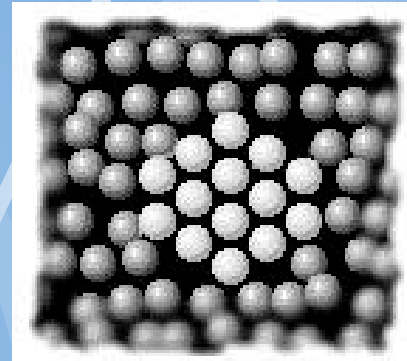
$$\Delta G_v = \frac{\Delta H_v \Delta T}{T_m}$$

Homogenní nukleace:

$$\Delta G_{(r)} = \frac{4}{3} \pi r^3 \Delta G_v + 4 \pi r^2 \gamma_{SL}$$

$$r^* = \frac{-2\gamma_{SL}}{\Delta G_v} = \frac{-2\gamma_{SL} T_m}{\Delta H_v \Delta T}$$

$$\Delta G^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_v^2} = \frac{16\pi\gamma_{SL}^3 T_m^2}{\Delta H_v^2 \Delta T^2}$$



Heterogenní nukleace:

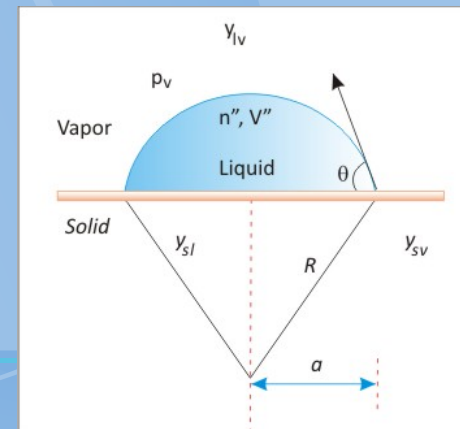
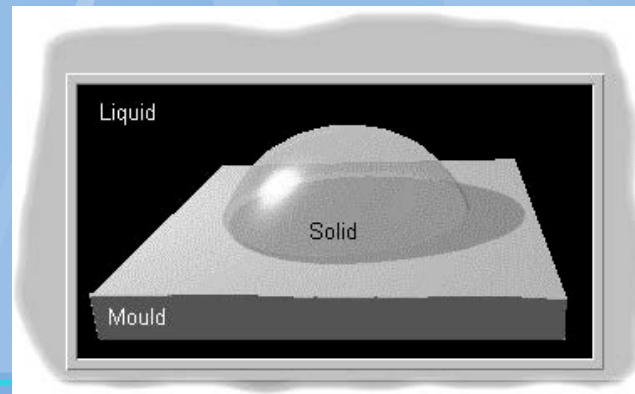
$$\Delta G_{(r)} = V\Delta G_v + A_{SL}\gamma_{SL} + A_{SM}\gamma_{SM} - A_{SM}\gamma_{ML}$$

$$r_{het}^* = \frac{-2\gamma_{SL}}{\Delta G_v} = r_{hom}^*$$

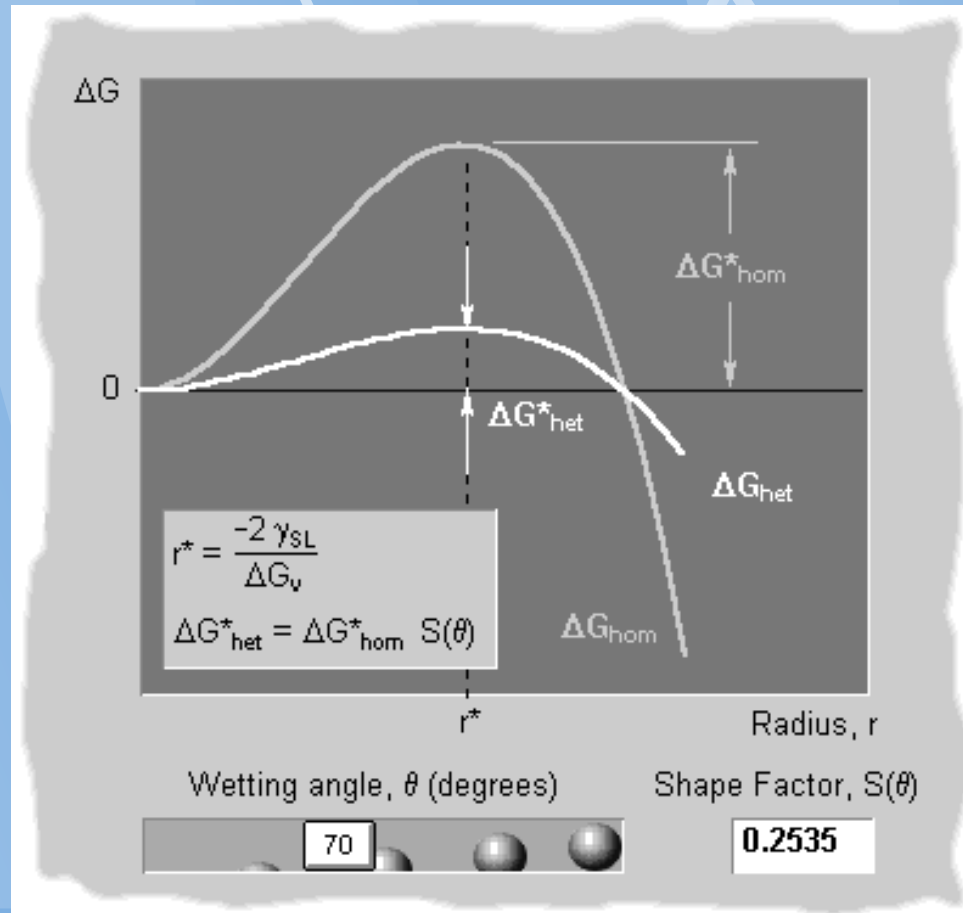
θ ..úhel smáčení

$$S(\theta) = \frac{(2 + \cos\theta)(1 - \cos\theta)^2}{4}$$

$$\Delta G_{het}^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_v^2} S(\theta) = \Delta G_{hom}^* S(\theta)$$



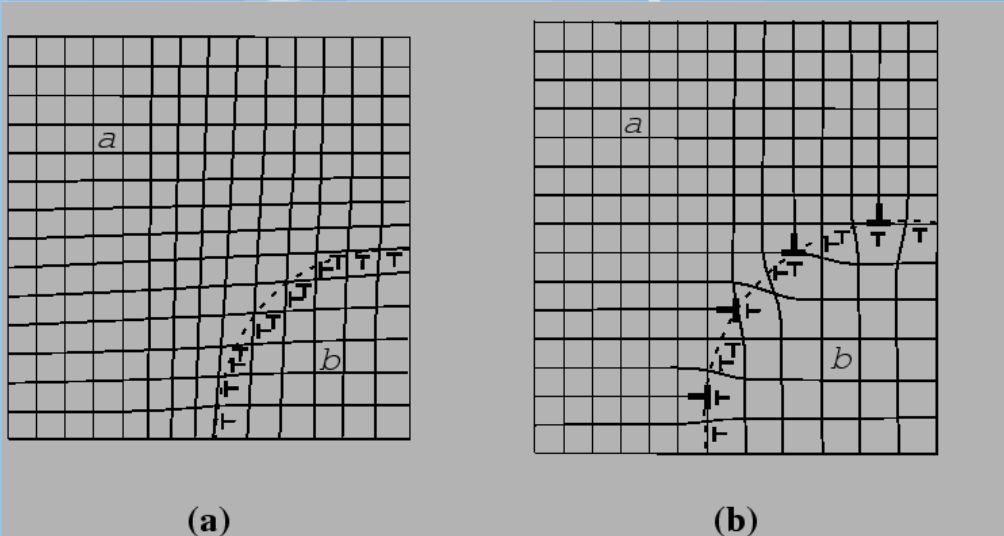
Snížené energetické bariéry



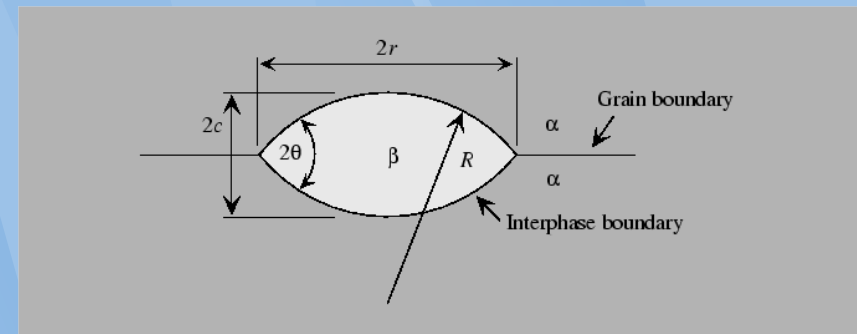
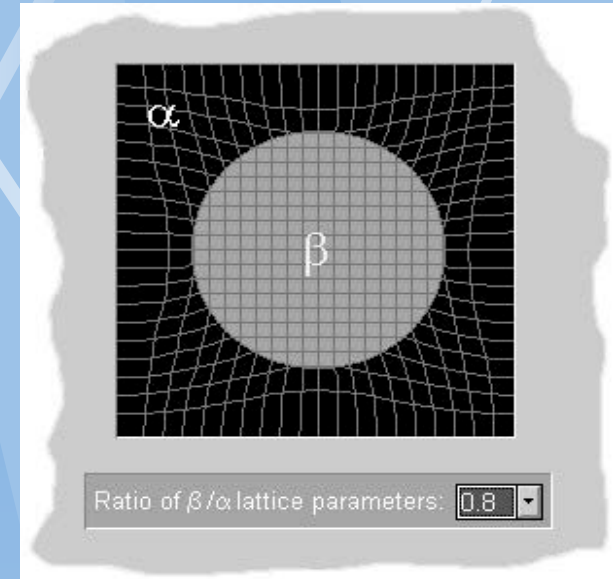
Homogenní a heterogenní nukleace v tuhém stavu

$$r^* = \frac{-2\gamma_{\alpha\beta}}{(\Delta G_v + \Delta G_s)}$$

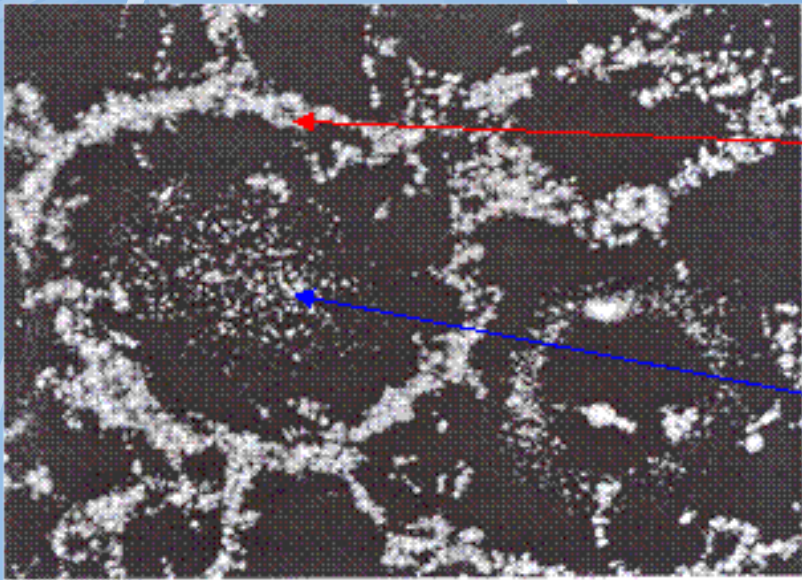
$$\Delta G^* = \frac{16\pi\gamma_{\alpha\beta}^3}{3(\Delta G_v + \Delta G_s)^2}$$



Interfacial structure for (a) coherent and (b) semicoherent interfaces between matrix phase and particle phase. Smaller dislocation symbols represent *coherency dislocations* and larger ones in (b) represent *anticoherency dislocations*.



Reálné podmínky



domain of heterogeneous nucleation

domain of homogeneous nucleation

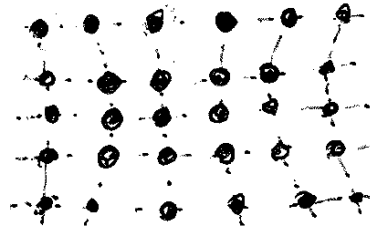
Arsenic precipitates in single crystal GaAs

Způsoby překonání nukleační bariéry

- je-li σ ^{krit. relativně plynný} malé (kapalný stav) náhodnými flukvacemi (viz. přiblížené Boltzmann. rozdělení kin. en. částic)

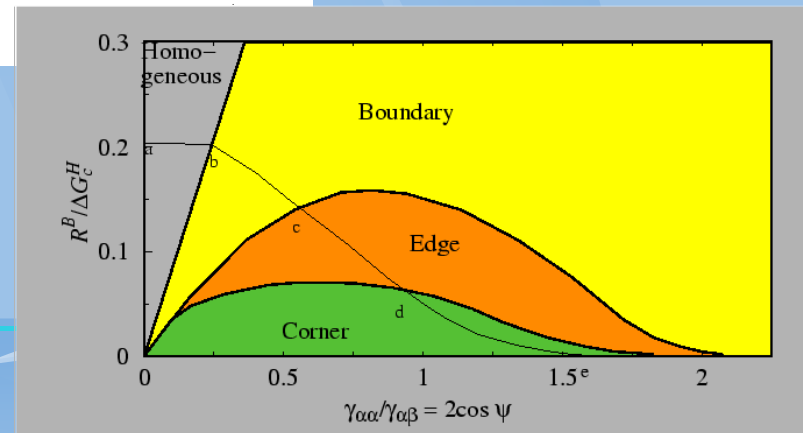
- přechodem přes metastabilní stav (tuhá fáze)

- zátokem met. fáze s nekoherentním rozhraním
- zátokem s koherentním rozhraním (snížení σA)
(koincidence mřížek)



- nukleací na nečistotách - vlnětky

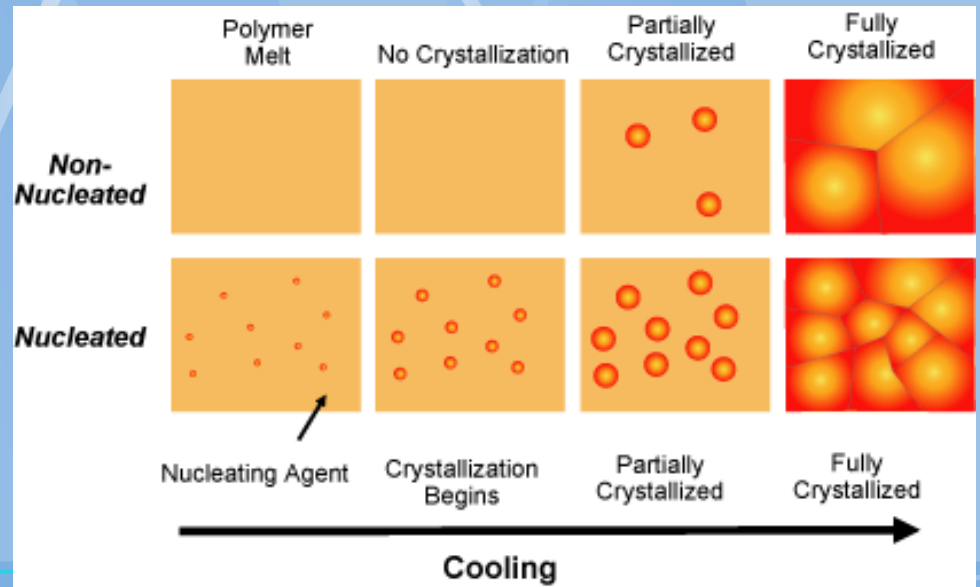
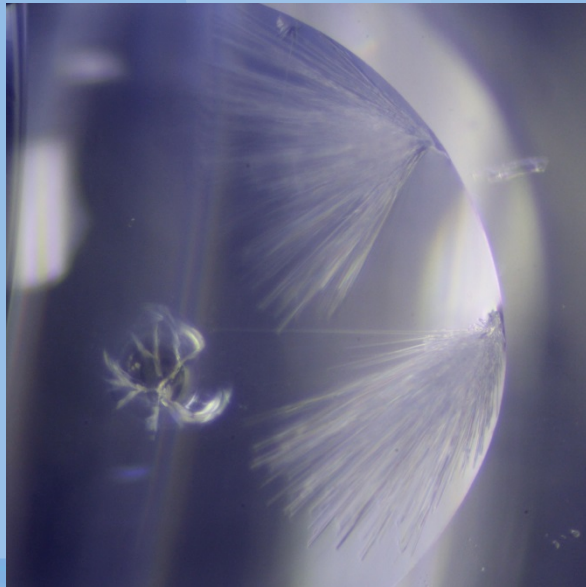
- nukleací v místech porušení kryst. mřížky (dislokace, hranice zrn, ...)



Metody usnadňující dosažení rovnovážného stavu

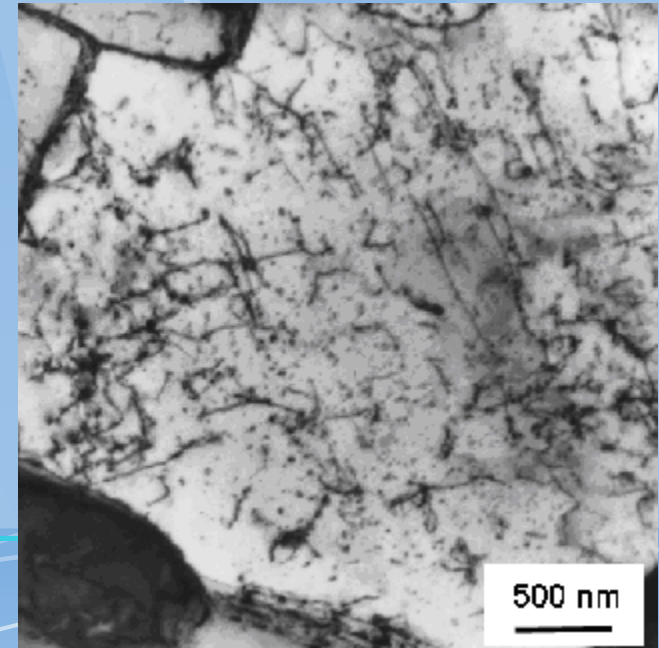
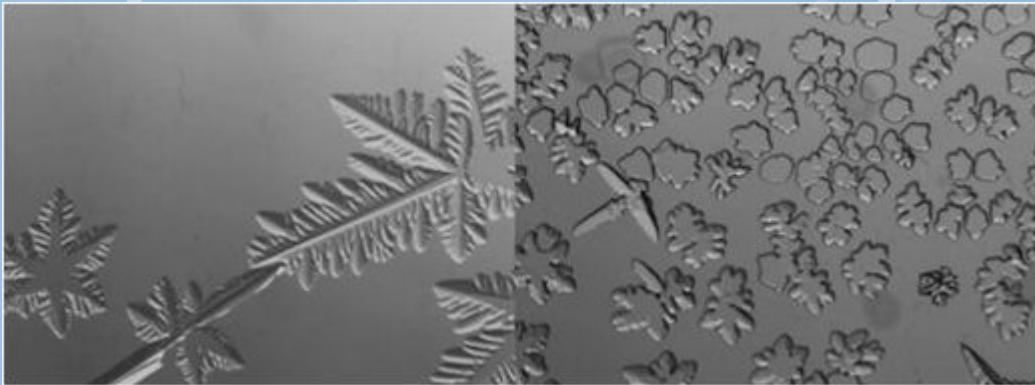
- krajně metastab. výchozí stav (vzniká větší spektrum nových fází, zůstanou však ier stabilní) ! vliv na hustotu nukl. center
- vnesení nukleačních center
- vnesení zárodků slab. fáze

Očkování



Faktory ovlivňující růst nové fáze

1. přesycečnost původní struktury (nsp. „stupeň nestability“)
2. Teplota – mění difúzní koeficienty \Rightarrow ovlivňuje rychlost transportu složek
3. Účhozí stav (v pevné fáze) – dislokační hustota a ztko materiálu.

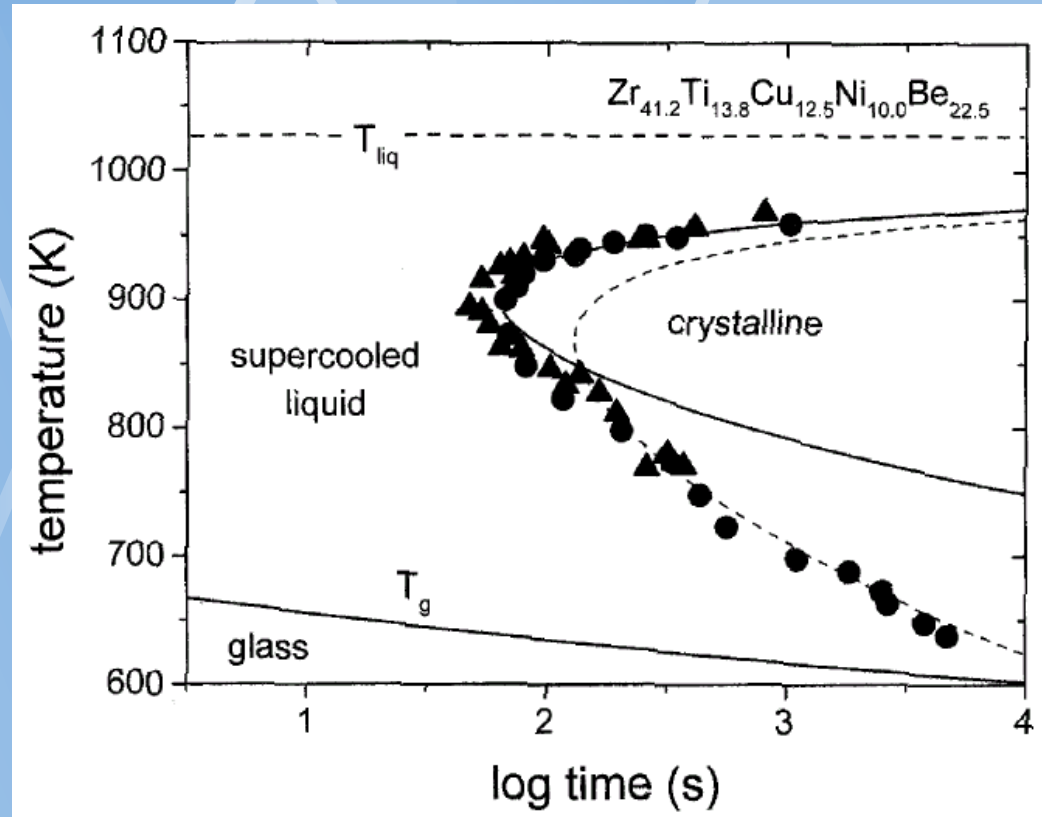


Diskuse

Magnetická levitace

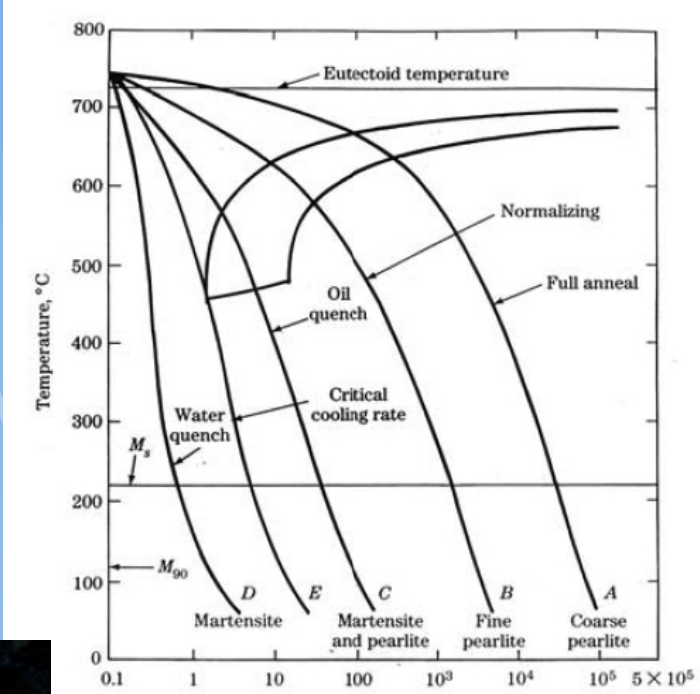
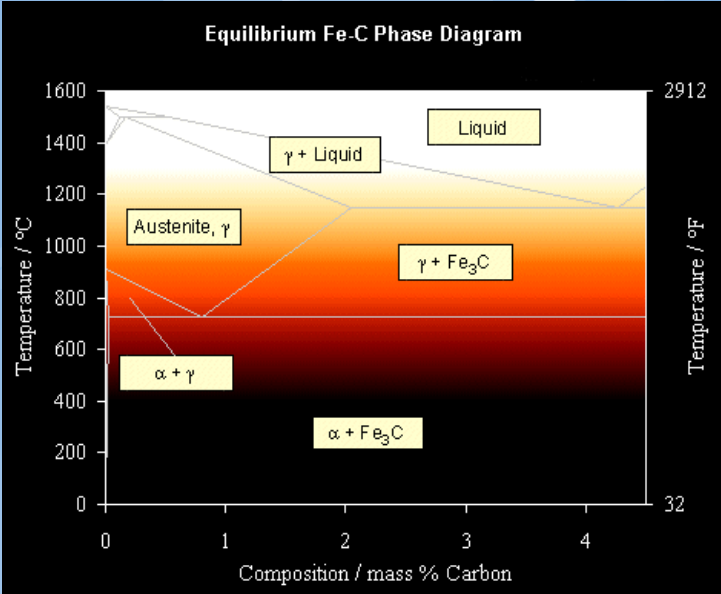


Kovová skla

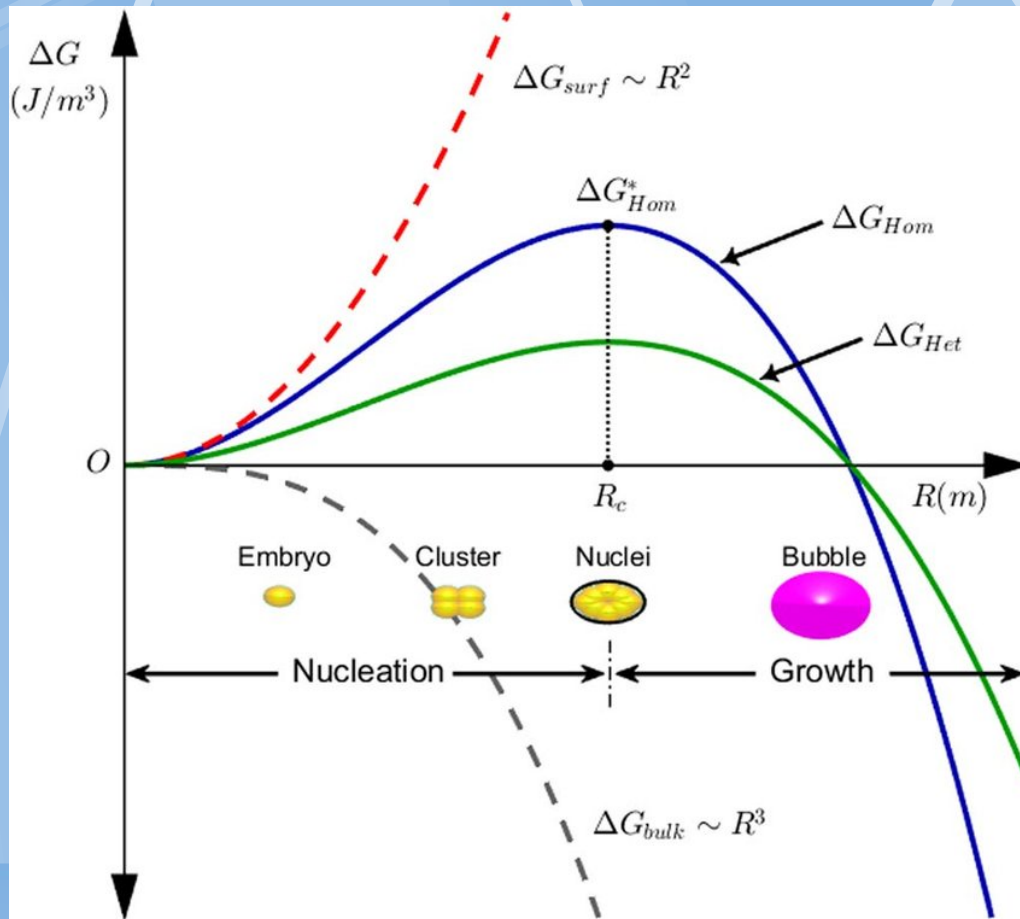


Metalurgická magie

The Legend of Damascus Steel

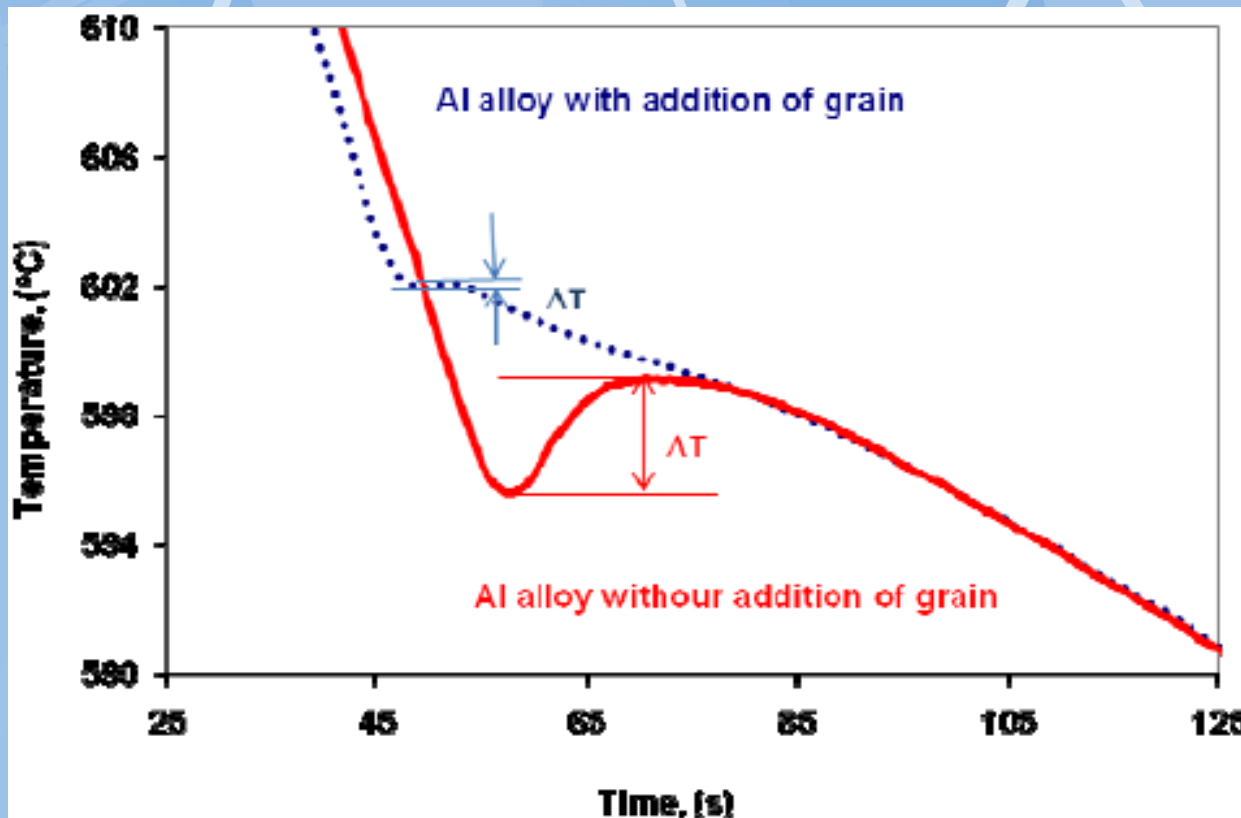


Gibbs energy of nucleation

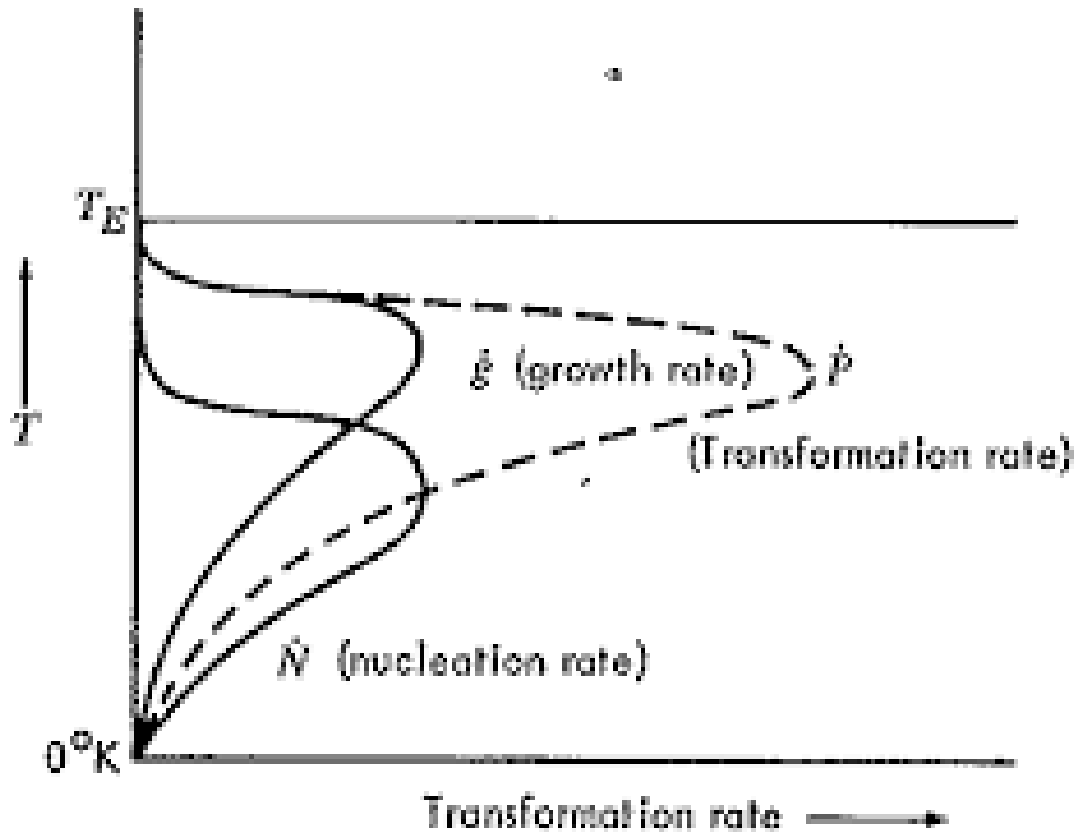


Nucleation effects (undercooling)

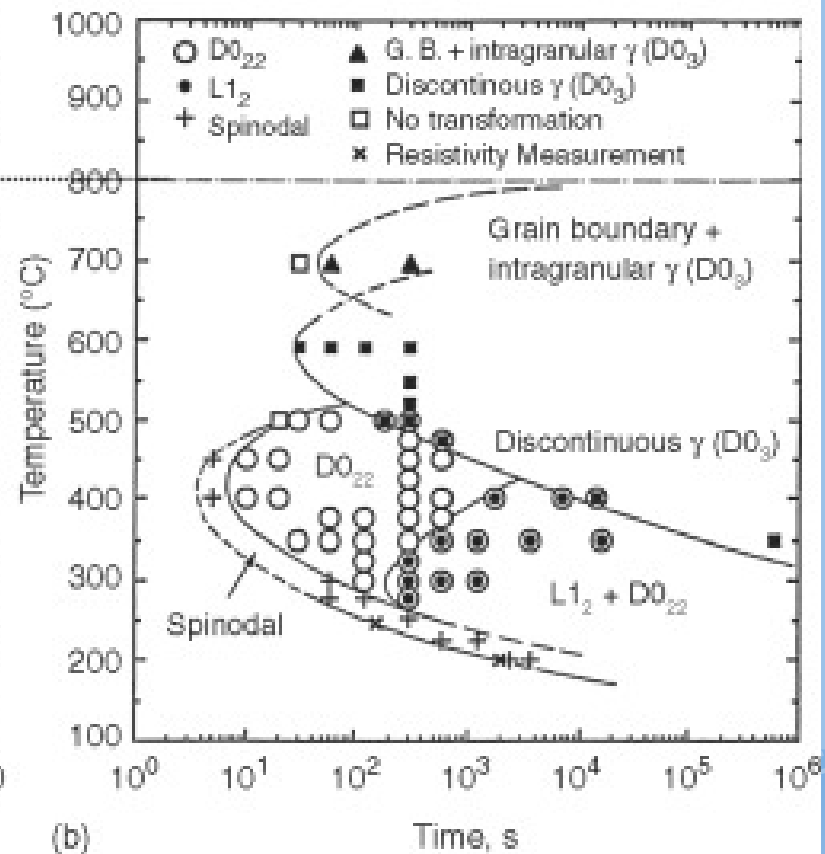
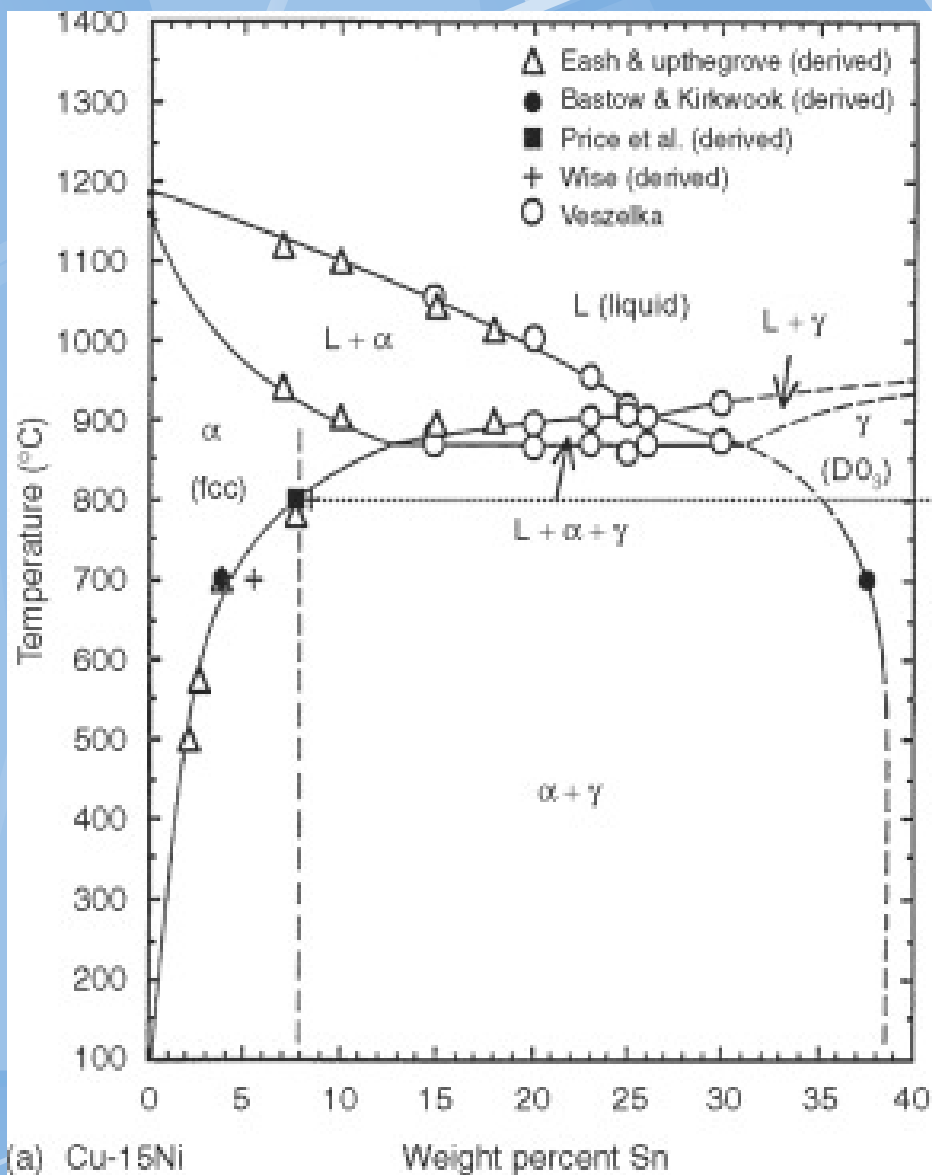
Undercooling can be removed by addition of grain seeds or decreased by heterogeneous nucleation.



Rate of nucleation and growth



See details in:
<http://people.virginia.edu/~lz2n/mse209/Chapter10c.pdf>



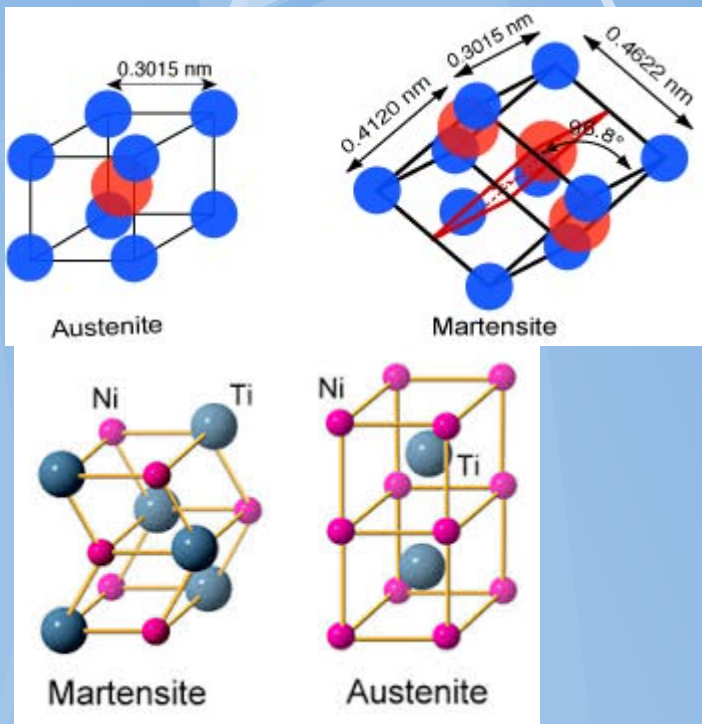
Phase transformations. Kinetics.

Phase transformations (change of the microstructure) can be divided into three categories:

- **Diffusion-dependent with no change in phase composition or number of phases present** (e.g. melting, solidification of pure metal, allotropic transformations, recrystallization, etc.)
- **Diffusion-dependent with changes in phase compositions and/or number of phases** (e.g. eutectoid transformations)
- **Diffusionless phase transformation** - produces a metastable phase by cooperative small displacements of all atoms in structure (e.g. martensitic transformation discussed in later in this chapter)

Materiály s tvarovou pamětí

SMA: Shape memory alloy. .

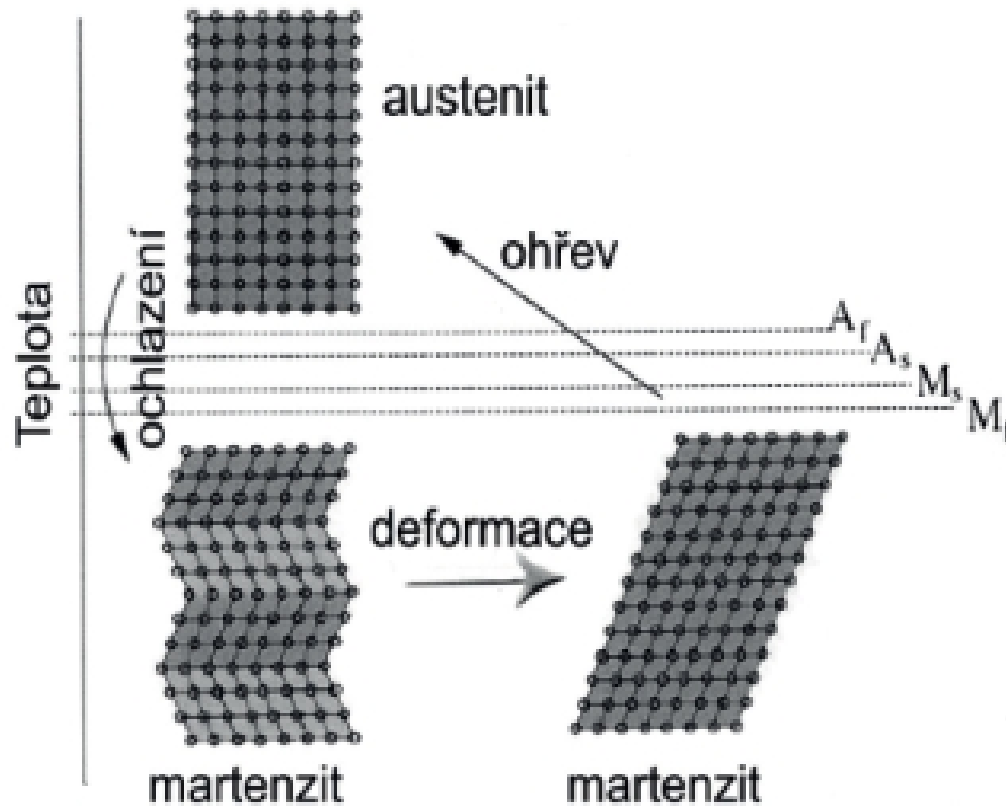


Tvarová paměť byla poprvé sledována u mosazi v roce 1939, od 60. let zájem o tuto oblast stoupá. V roce 1962 byla zkoumána ekviatomární slitina **Ni** a **Ti**, u níž byla objevená mimořádně výrazná tvarová paměť. K tomuto objevu dospěl [William J. Buehler](#) z **Naval Ordnance Laboratory** ve White Oak v Marylandu, USA. Podle složení a místa vzniku se tato slitina nazývá **NITINOL**. Mezi další materiály s tvarovou pamětí patří keramické materiály jako je oxid zirkoničitý (ZrO_2), oxid hořečnatý (MgO), oxid ceričitý (CeO_2), dále také [polyuretany](#) a některé kovové slitiny jako například měď-hliník-nikl, měď-zinek-hliník, železo-mangan-křemík.

Deformace materiálu s tvarovou pamětí

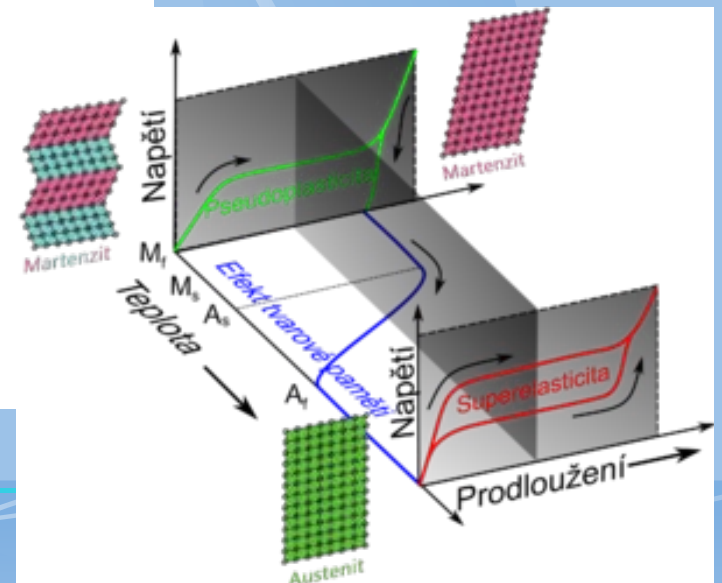
VIDEO:

https://smartwires.eu/index.php?id_product=9&controller=product&id_lang=7



Obr. 1 Pletený stent

<https://www.engineering.sk/strojarnstvo-extra/2742-kovove-materialy-s-tvarovou-pameti>



Obr. 4 Schéma martenzitické transformace SMA materiálů

3 Cu . Al, 3 Cu . Zn (běžná mosaz, tvarová paměť se objevuje až v nízkých teplotách), Cu-Al-Ni, Cu-Al-Mn, Ni-Ti-Cu, Ni-Ti-Hf a mnoho dalších. Existuje celá řada dalších kovů, u kterých se tento jev vyskytuje, ale ty nejsou moc využívány, protože mají jen slabý efekt nebo jsou nestabilní. Všechny tyto slitiny patří do skupiny **intermetalik**,

Navštiv stránky

<http://people.virginia.edu/~lz2n/mse209/Chapter10c.pdf>