

MATERIAIS CERÂMICOS E VIDROS

GLASS CRYSTALLIZATION AND DEVITRIFICATION

Criteria for Glass Formation

Structural criteria

Goldschmidt criteria

Zachariasen criteria

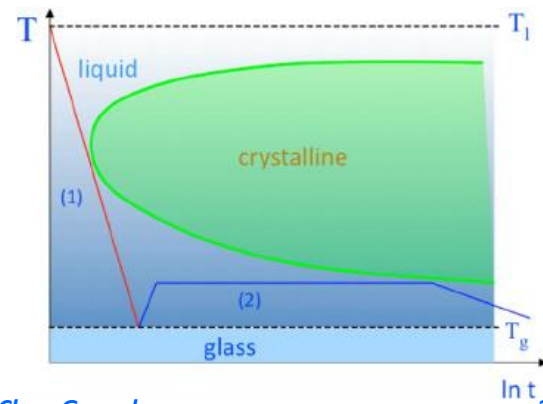
Bonding criteria

Sun

Rawson

Kinetic factors and glass formation

Uhlmann



Glass Formation from a Liquid

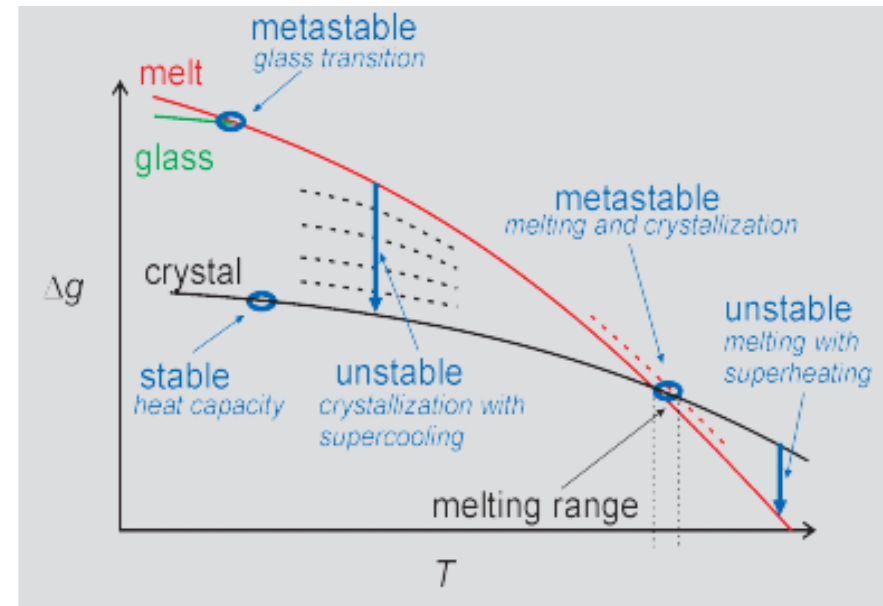
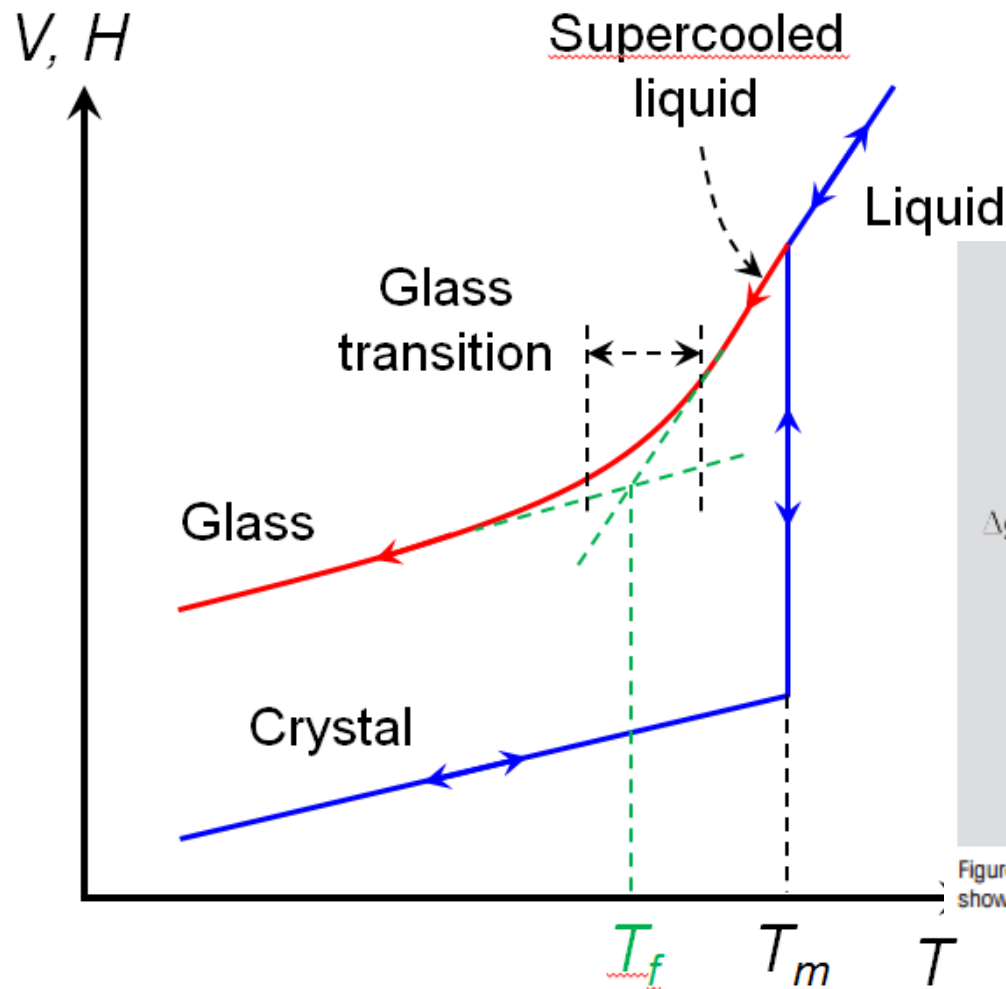
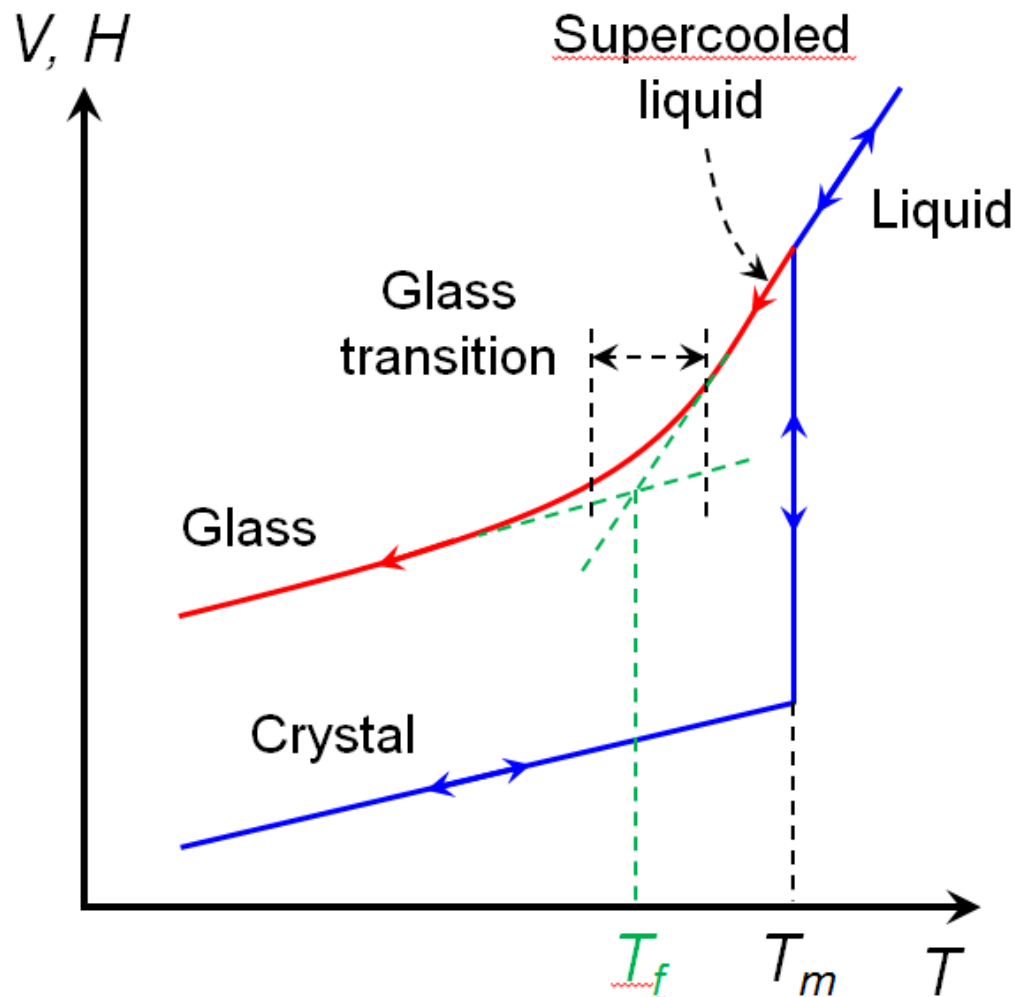


Figure 1. Schematic diagram of free enthalpy as a function of temperature. Processes are shown that occur under local stable, metastable and unstable conditions.

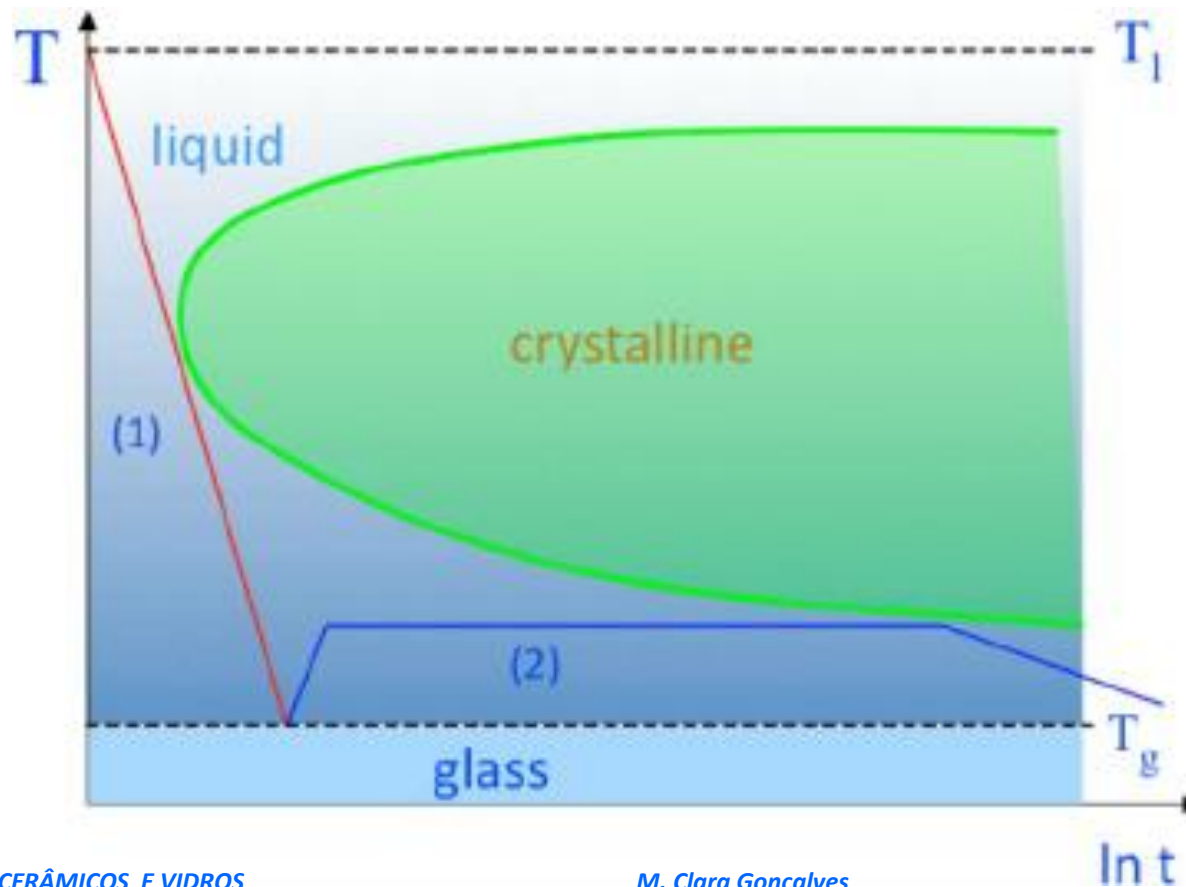
Glass Formation from a Liquid



- ✓ Supercooled liquid transforms to the glassy state when crystallization is kinetically suppressed
- ✓ Extensive variables remain **continuous** during glass transition
- ✓ The glassy state is **different** from supercooled liquid
- ✓ T_f : Fictive temperature

Glass Formation from a Liquid

Uhlmann (1972) made a notable contribution towards the understanding of the influence of kinetic factors in glass formation by using **time-temperature-transformation (TTT) curves** to assess the probability to glass formation for a given substance.

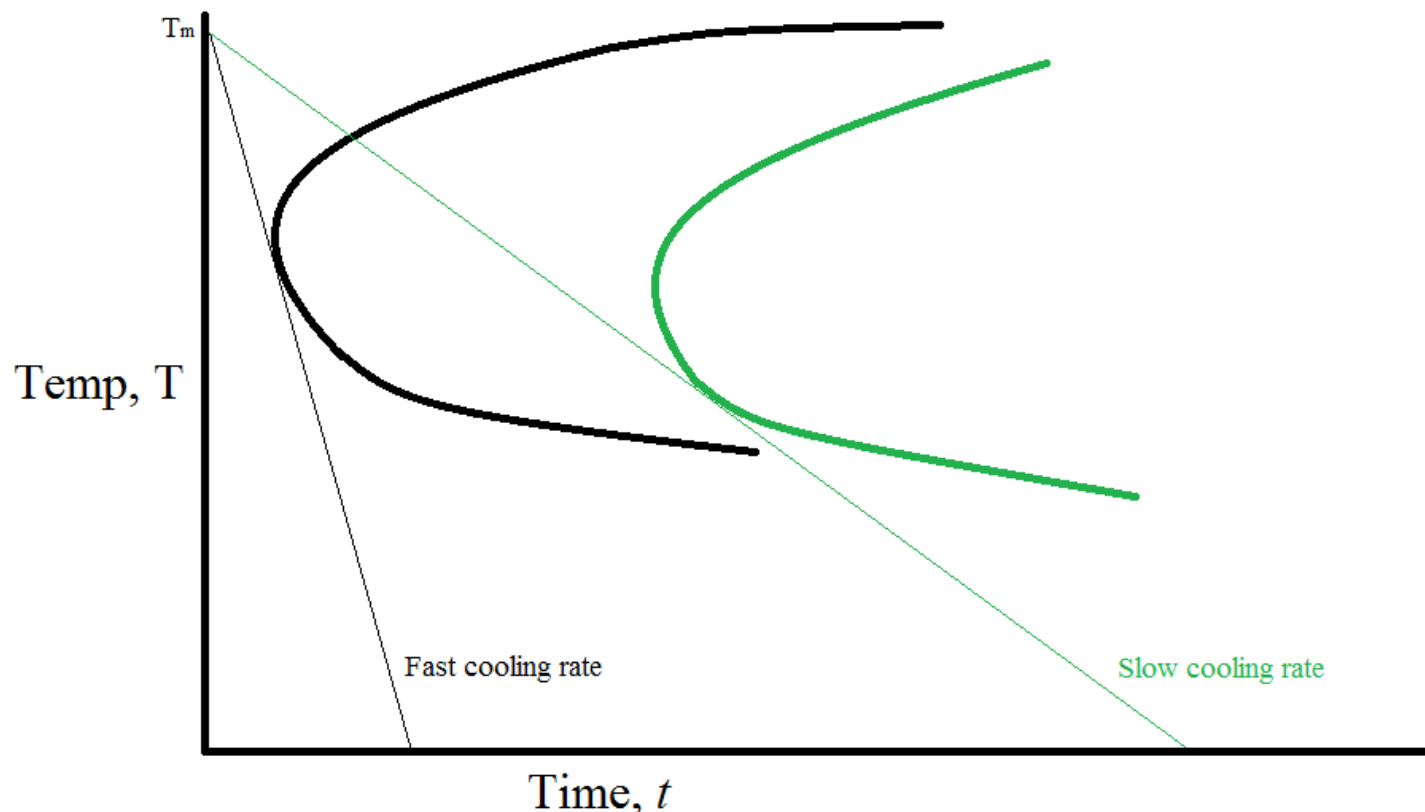


Glass Formation from a Liquid

T_N is the T where the time t_N to crystallize the chosen volume fraction is **minimum**.

T_N represents a **critical value** if crystallization is to be avoided.

$X_t = 10^{-6}$, the chosen volume fraction. Materials with $X_t < 10^{-6}$ are **vitreous**.

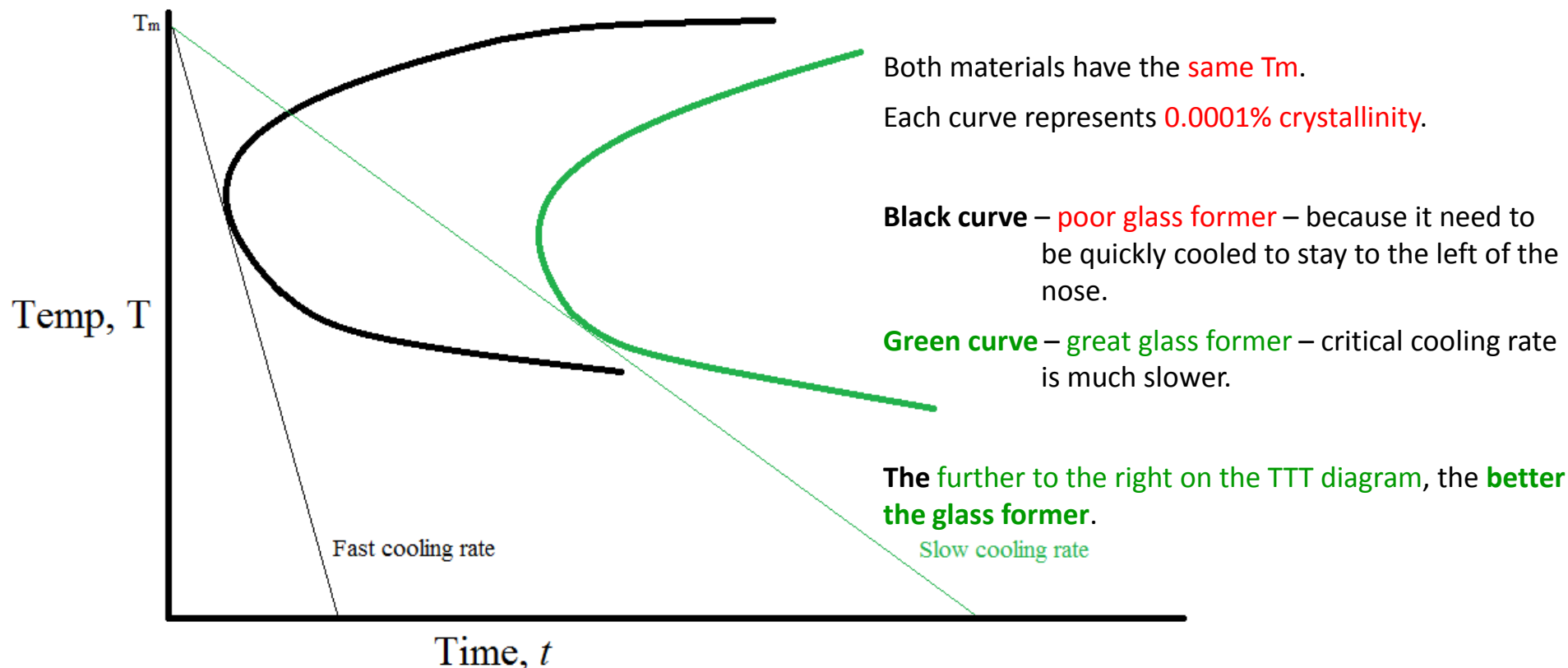


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Glass Formation from a Liquid

Uhlmann defined :

Critical cooling rate

$$R_c \cong \Delta T_N / t_N$$

Critical thickness

$$y_c \cong (D \cdot t_N)^{1/2}$$

Glass Formation from a Liquid

Uhlmann defined :

Critical cooling rate $R_c \cong D T_N / t_N$

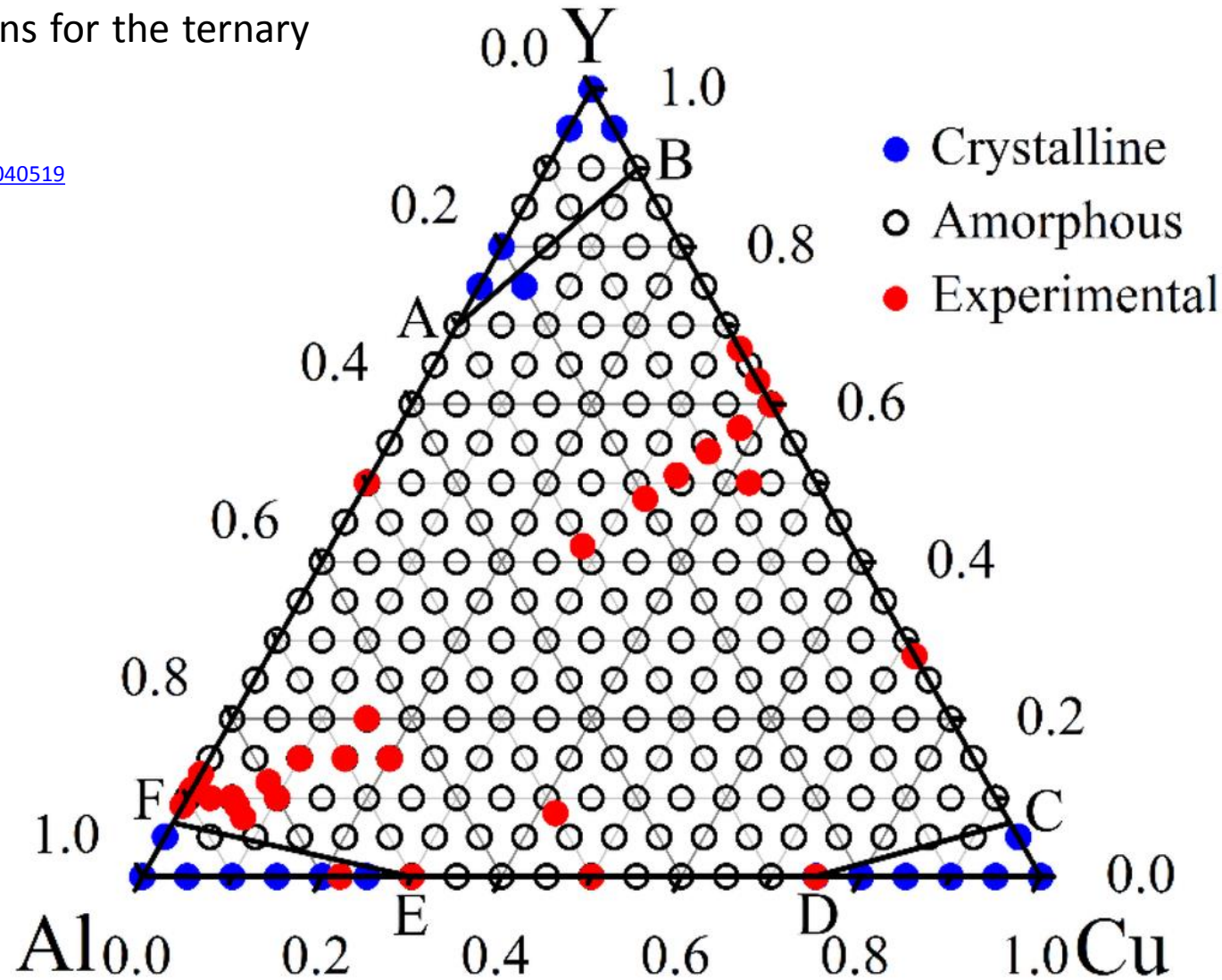
Critical thickness $y_c \cong (D \cdot t_N)^{1/2}$

Values of Critical Cooling Rates, R_c , and Critical Thickness, y_c , for Glass Formation

Substance	R_c (Ks ⁻¹)	y_c (cm)
SiO ₂	2×10^{-4}	400
GeO ₂	7×10^{-2}	7
H ₂ O	10^7	10^{-4}
Ag	10^{10}	10^{-5}

The glass formation region (enclosed by ABCDEF) that are located by the thermodynamic calculations for the ternary Al-Cu-Y system.

Metals **2014**, 4(4), 519-529; doi:[10.3390/met4040519](https://doi.org/10.3390/met4040519)

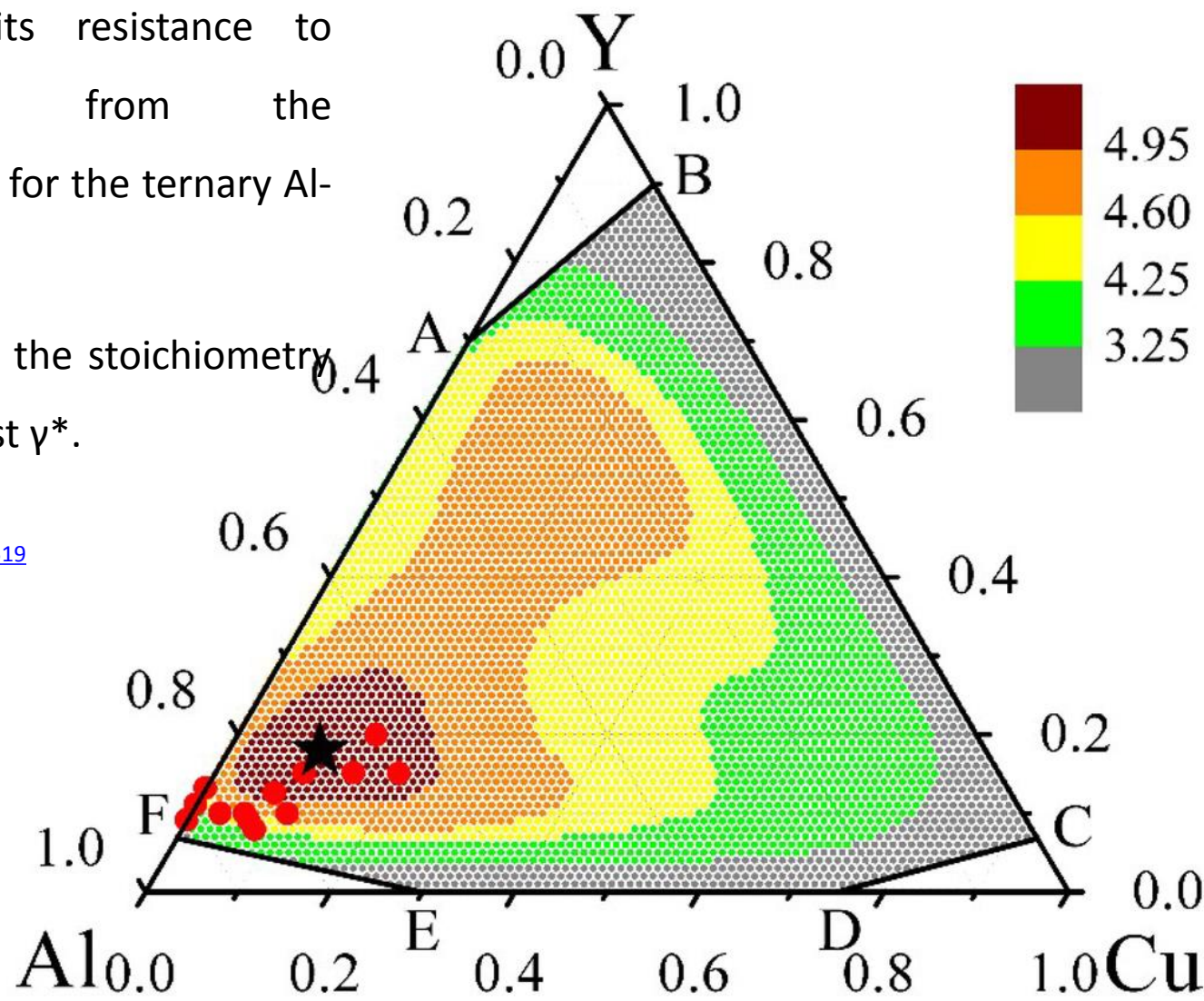


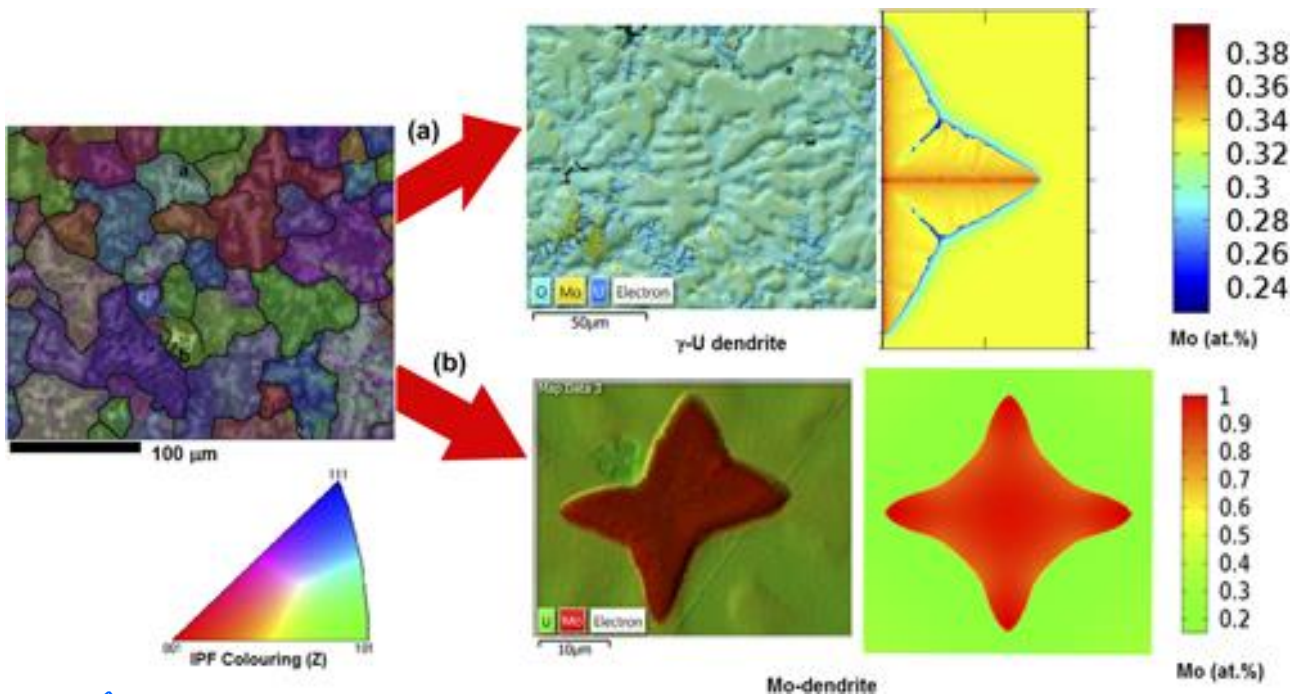
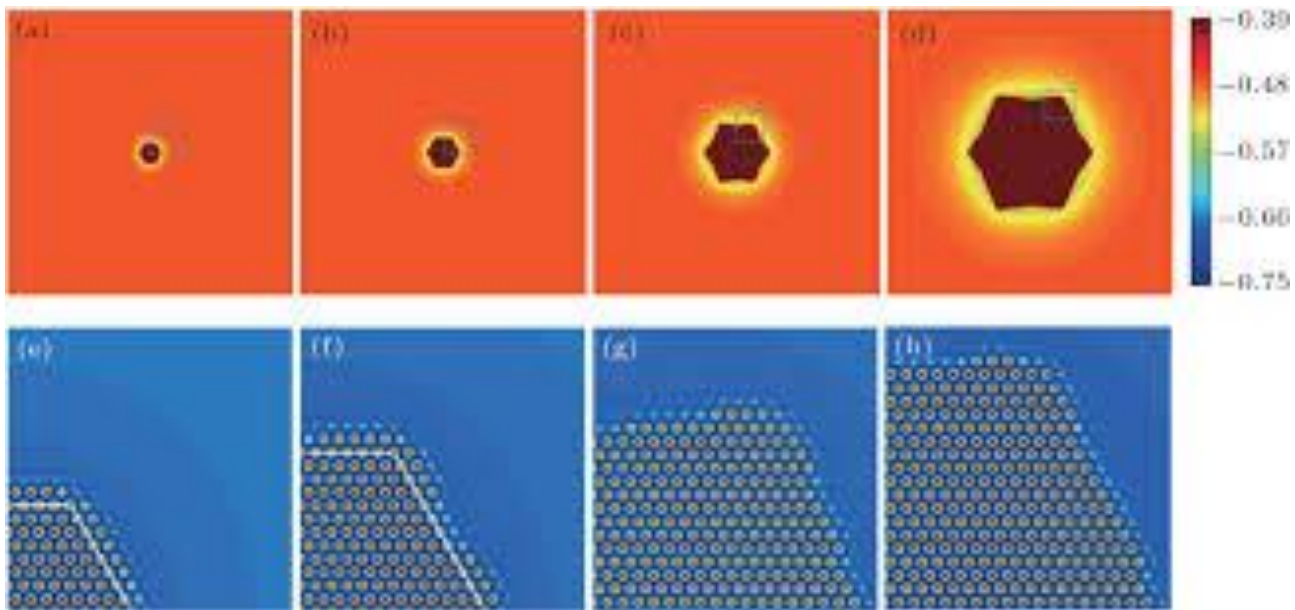
Contour map of the parameter γ^* , that evaluates both the driving force of the amorphous phase and its resistance to crystallization, derived from the thermodynamic calculations for the ternary Al-Cu-Y system.

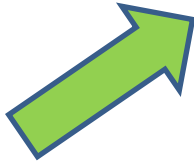
The black asterisk pinpoints the stoichiometry of $\text{Al}_{72}\text{Cu}_{10}\text{Y}_{18}$ with the largest γ^* .

Metals **2014**, 4(4), 519-529; doi:[10.3390/met4040519](https://doi.org/10.3390/met4040519)

● The red dots denote the experimentally observed compositions of glass formation in the Al-rich corner that are reported in the literature.







In **homogeneous nucleation**, the first tiny seeds are of the same constitution as the crystals which growth upon them.

Homogeneous nucleation in which embryos arise due to local fluctuations in the structure of the liquid phase is often difficult to observe experimentally owing to the problem of excluding foreign nuclei such as dust particles.

Homogeneous nucleation occurs at high levels of supersaturation or supercooling of the liquid phase.



In **heterogeneous nucleation** the nuclei can be quite different chemically from the crystals which are deposited.

Nucleation may be
homogeneous or
heterogeneous.

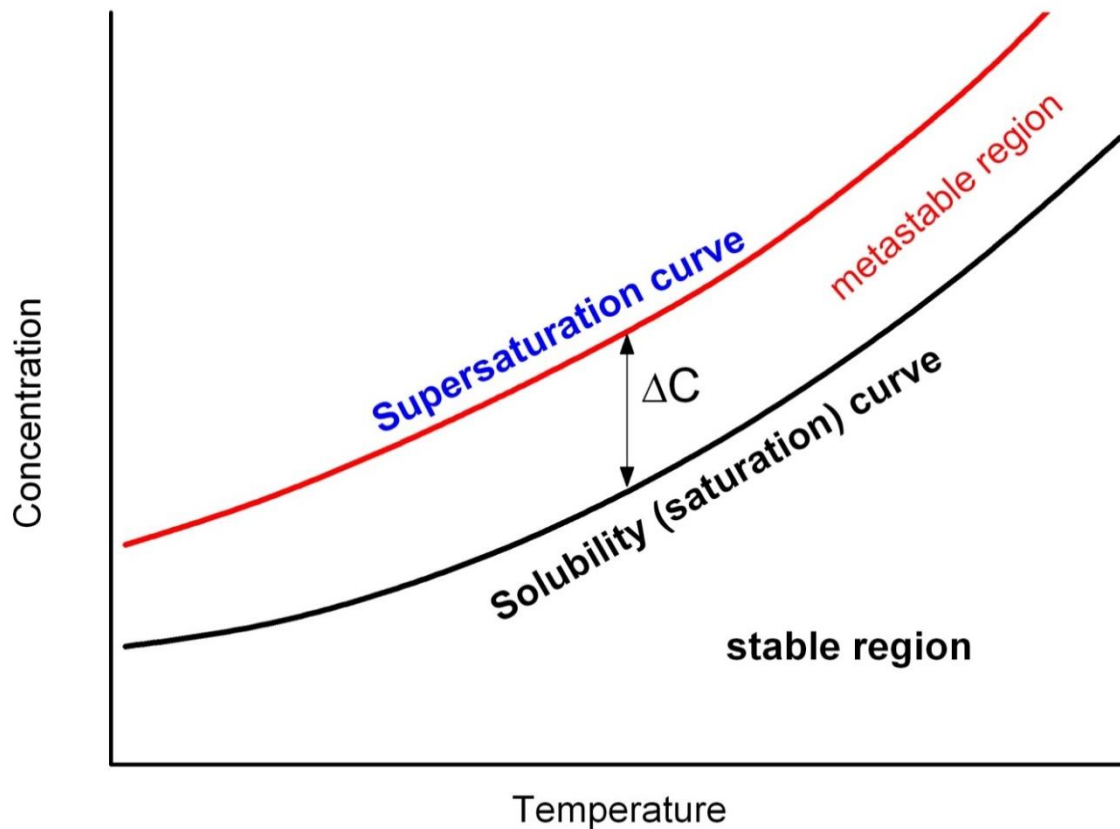
De Coppet (1872) showed that on the average **the life of a supersaturated solution was inversely proportional to the degree of supersaturation**. So, the probability of homogeneous nucleation increases with the degree of supersaturation.

Ostwald (1897) showed that **same supersaturated solutions would last indefinitely** (if foreign nuclei were excluded) without ever spontaneously forming a solid phase – **metastable solutions**. For other supersaturated solutions, the solid phase appears spontaneously after a limited time – **unstable solutions**.

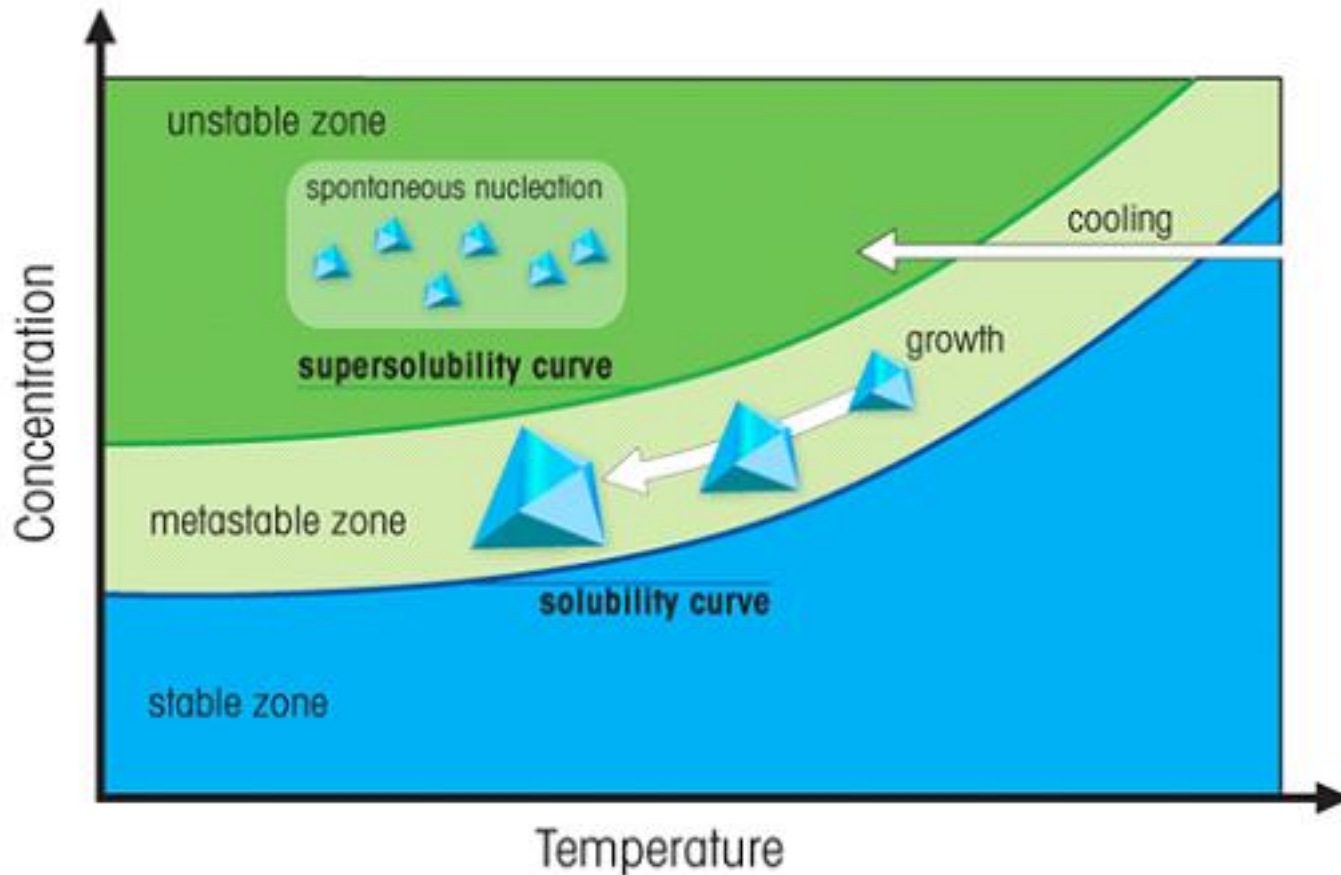
Increase of the concentration will convert a metastable solution to an unstable one and the concentration at the transition point may be called the metastable limit.

For concentrations bellow the metastable limit, spontaneous formation of crystal nuclei does not occur.

For solutions in the neighbourhood of the metastable limit, spontaneous precipitation of crystals can occur when the solutions are exposed to quite small disturbing effects such as variations in P or T or local evaporation.



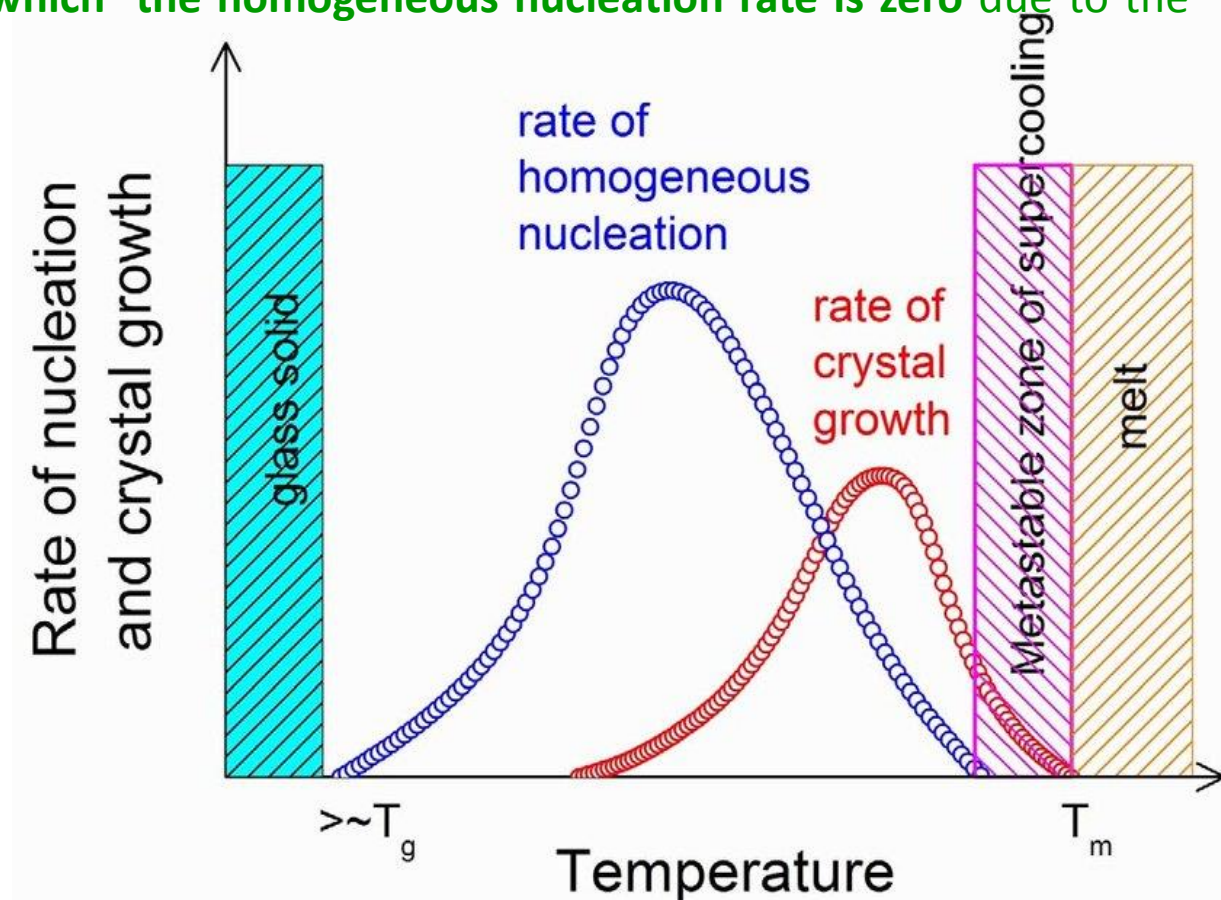
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The **metastable zone of supercooling** below the equilibrium T_m occurs because the very tiny crystal nuclei have melting temperatures appreciably below that of the bulk material.

The **supersaturation in solutions** results from the higher solubility of small crystallites as compared with that of larger crystals (Kevin equation).

It exists a **temperature below which the homogeneous nucleation rate is zero** due to the high viscosity of the melt.



Tamman (1925) showed that **below the equilibrium melting temperature** there exists a temperature interval (**metastable zone**) in which **the nuclei do not form at a detectable rate**.

In this zone crystals can grow if nuclei are provided (i.e. If melted is **seeded** or **inoculated**).

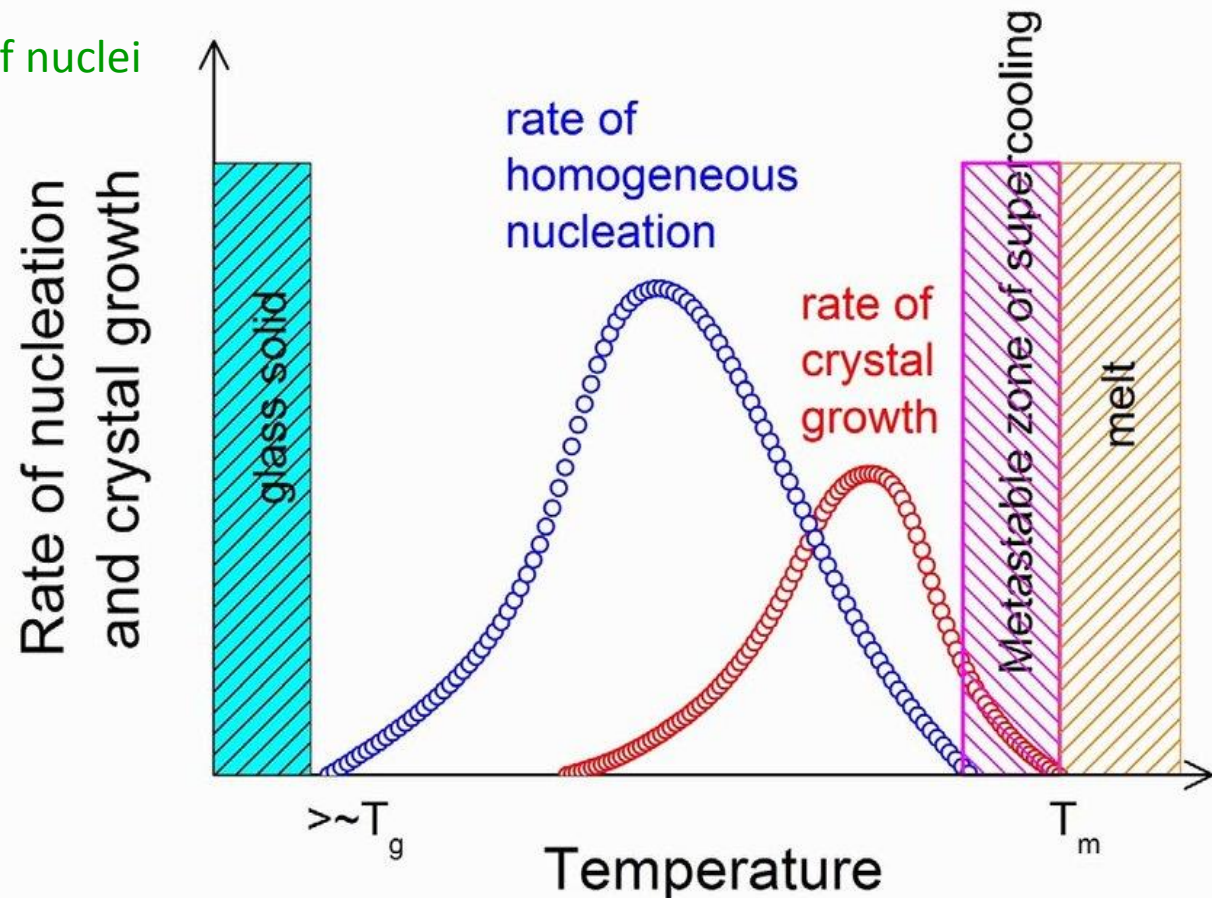
At temperatures below this region the crystallization process is controlled by two factors:

- the rate of formation of nuclei
- the crystal grow rate

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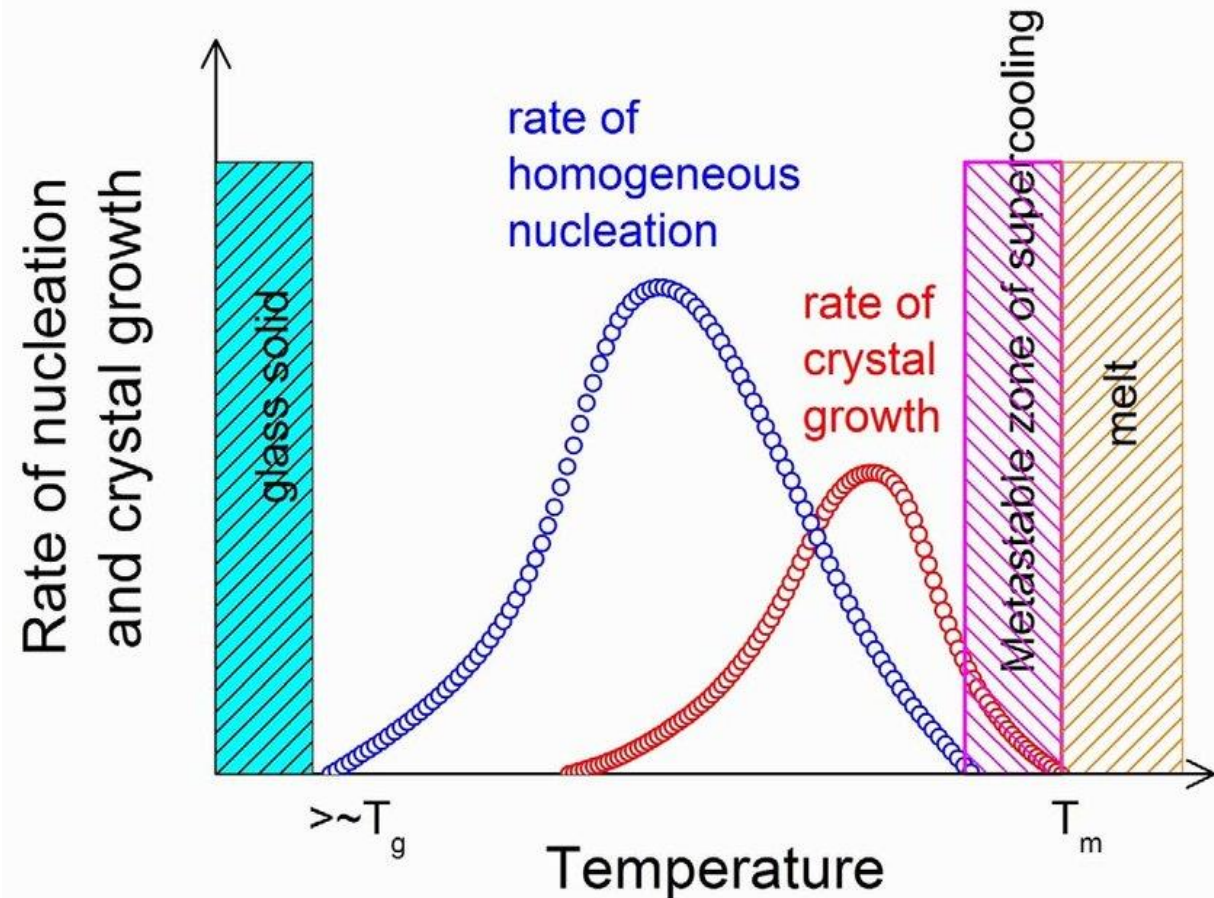
At temperatures below this region the crystallization process is controlled by two factors:

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The crystallization proceeds from **distinct centres** and **crystal growth** takes place by **deposition material upon the first crystals or nuclei**.

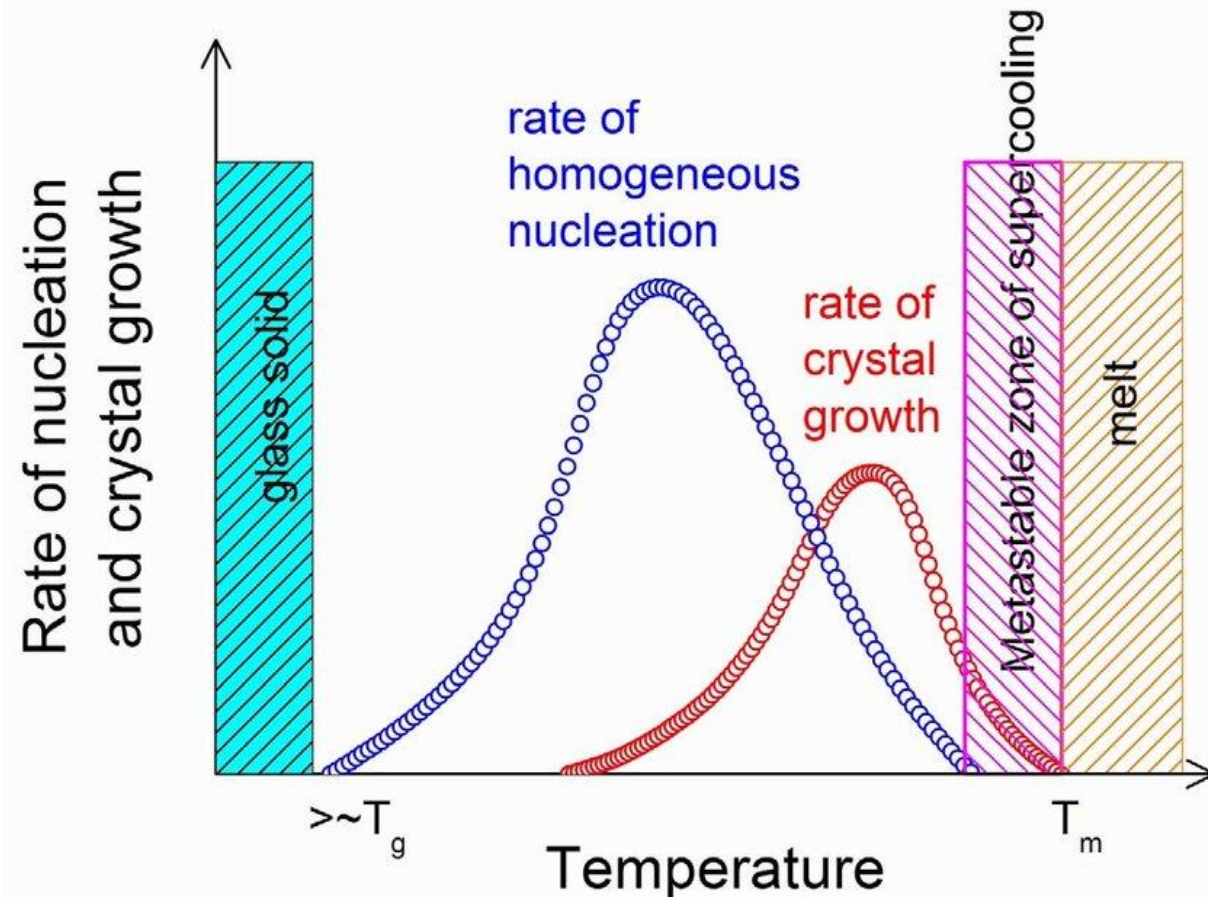
Melts which increase rapidly in viscosity during cooling (such as good glass formers) show maxima in nucleation and crystal growth rates



The crystallization proceeds from **distinct centres** and **crystal growth** takes place by **deposition material upon the first crystals or nuclei**.

Melts which increase rapidly in viscosity during cooling (such as good glass formers) show maxima in nucleation and crystal growth rates

because at the lower T the high η hinders the atomic rearrangements and diffusion processes which are necessary for nucleation and crystal growth.



Glass Formation from a Liquid

The ability of a given oxide to form a glass is related to the crystal structure of that oxide.

Although the properties of the melt, rather than of the solid, must surely be the governing factors. However, in many cases, the short range order in the liquid is the same as in the solid and glass formation in oxide melts probably requires a particular form of short range order.

The difference between the melt and the crystalline solid resides mainly in the different degrees of long-range order. Crystallization therefore requires the transformation of the liquid structure lacking long-range order into a crystalline structure where long-range order prevails.

Glass Formation from a Liquid

The rate at which a liquid can be transformed into a crystal is given by:

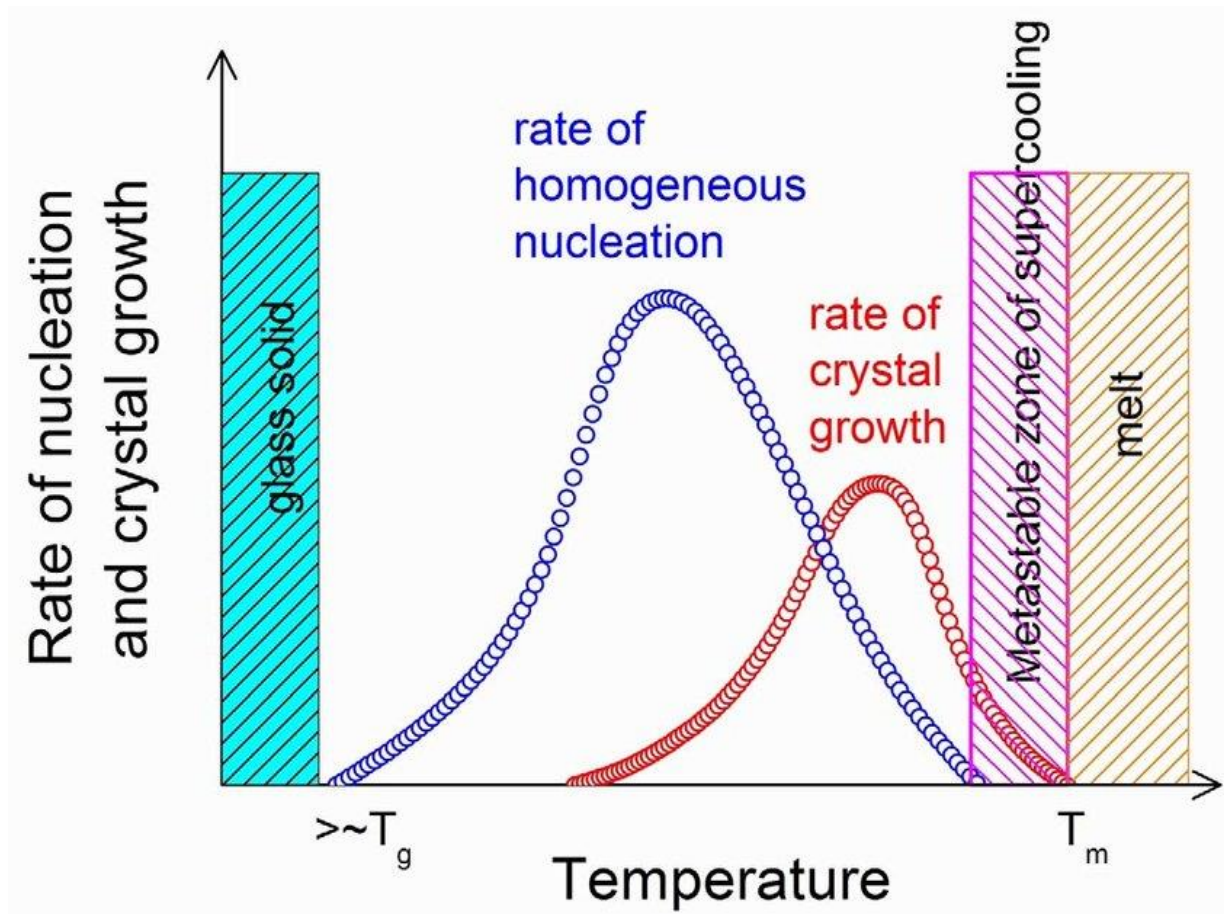
$$X_t = 1 - \exp\left(-\frac{\pi}{3} U^3 I t^4\right)$$

where X_t is the volume fraction crystallized after time t

U is the crystal growth rate

I is the nucleation rate.

Glass formation, which requires X_t remain below the detectable limit, necessitates either U or I or both to be low.



Glass Formation from a Liquid

The problem of glass formation can be considered from the view point of factors that govern **rates of crystal nucleation and growth**.

High rate of nucleation will be favoured by:

- a **low value of interfacial energy** between the crystal nucleus and the liquid (glass melt) phase
- a **high value of the volume free energy change** on transforming from the liquid to the crystalline structure
- a **low value of the activation energy of diffusion**

Glass Formation from a Liquid

The problem of glass formation can be considered from the view point of factors that govern **rates of crystal nucleation** and **growth**.

High rate of crystal growth will be favoured by:

- a **high volume free energy change** resulting from the transformation to the crystalline state
- a **low value of the activation energy** associated with atoms crossing the interface between the liquid and crystal phases

Why Glasses do Form from a Liquid?

Reasons why supercooled melts fail to crystallize:

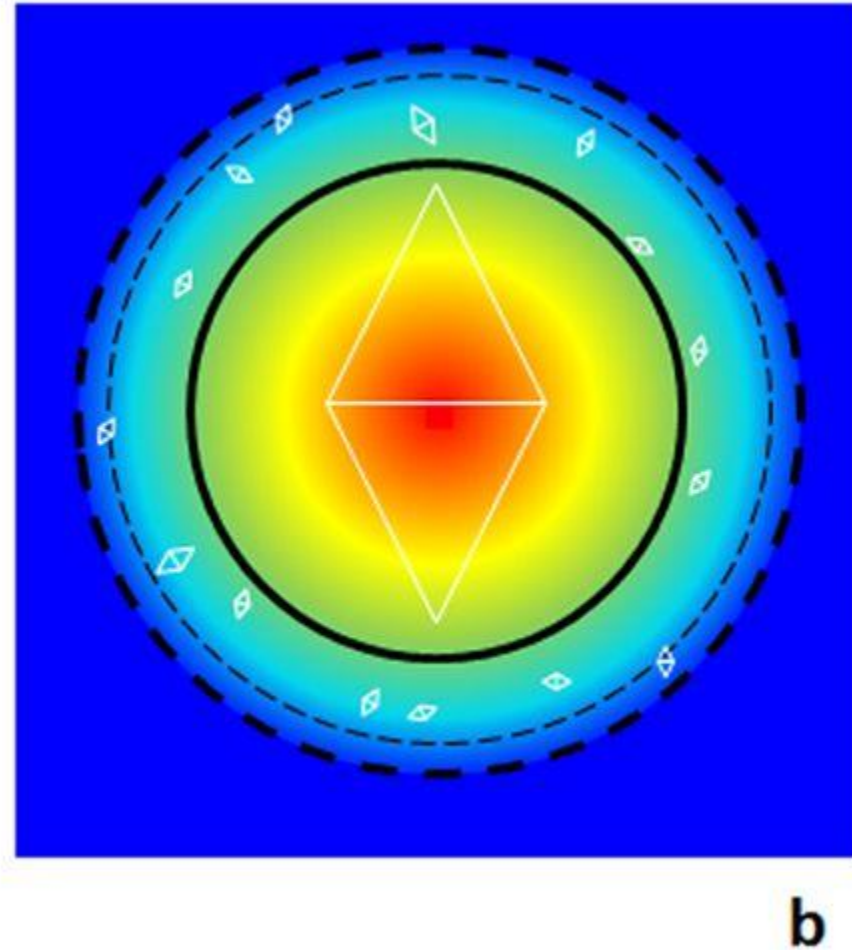
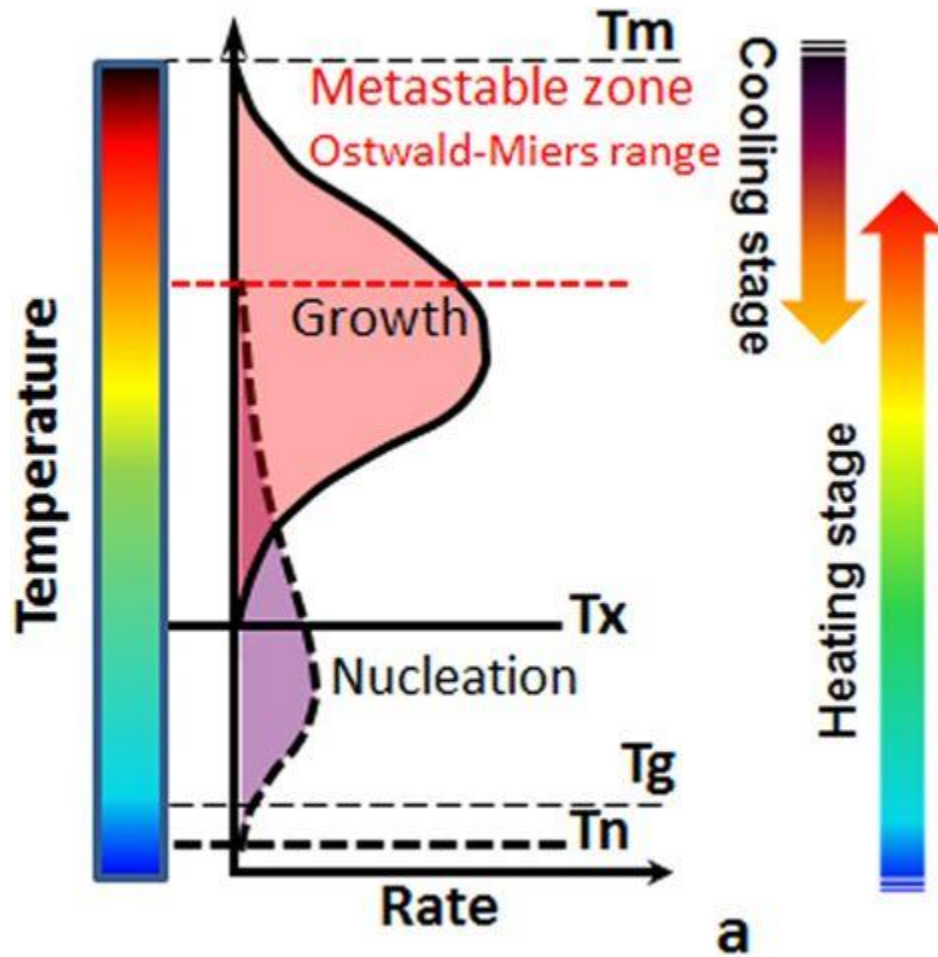
- nucleation rate is very small (**high viscosity**)
- rate of growth of crystals upon the nuclei is negligible at all T (**high viscosity, high activation energy of diffusion**, which decreases as T falls, **consequently low diffusion rate**)

Why heterogeneous nucleation is unlikely to occur :

- **molten glass** is a **good solvent** for most type of accidental 'dirt'

(the most potent nucleation catalysts for the formation of crystalline silicates maybe substances which are close in crystalline structure to the silicates, probably silicates themselves)

Why Glasses do Form from a Liquid?

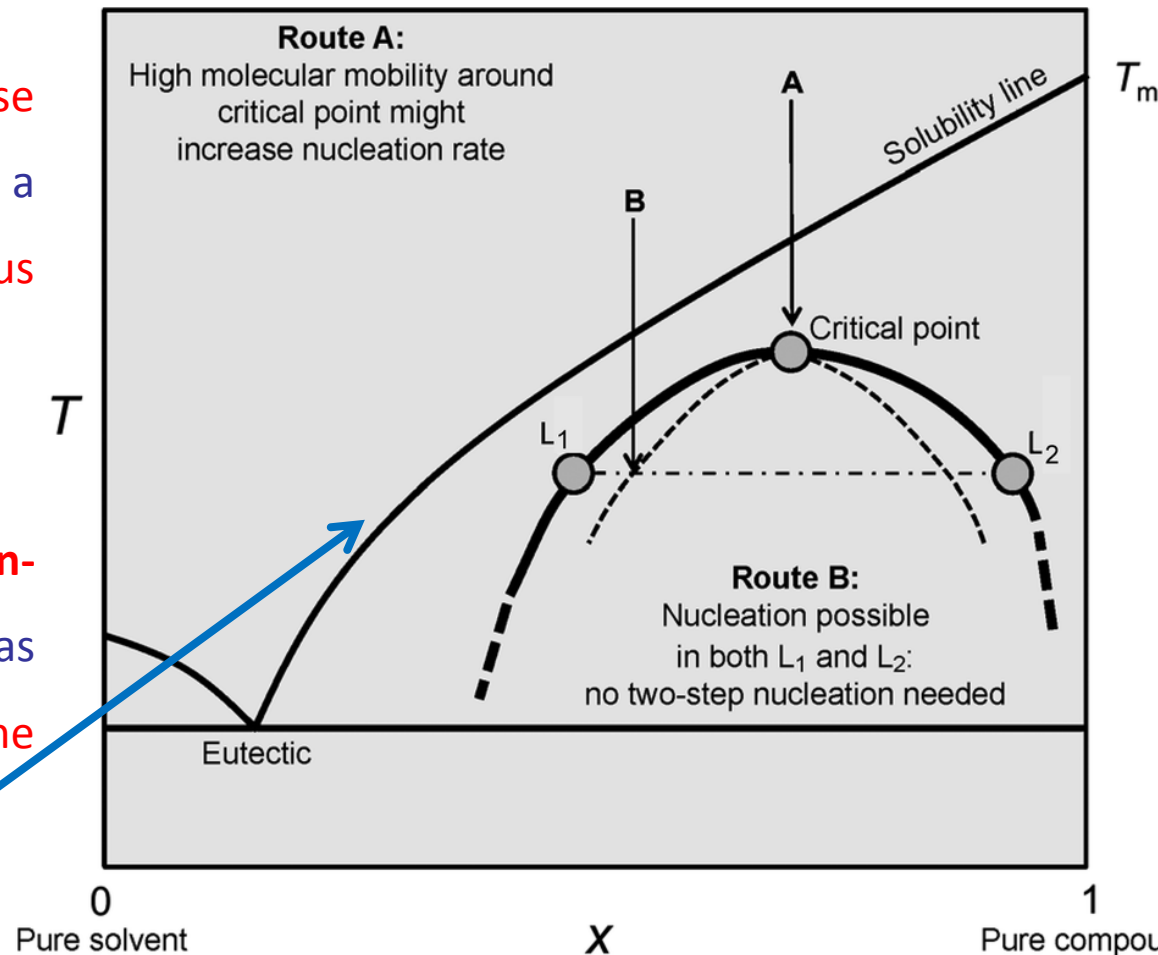


Glass-in-Glass Phase Separation

It has been observed for many glass-forming systems that heat treatment cause separation into **two non-crystalline phases**.

stable immiscibility - if the phase separation takes place in the melt at a temperature above the liquidus temperature

metastable immiscibility (or glass-in-glass phase separation) - whereas phase separation occurs below the liquidus temperature



Glass-in-Glass Phase Separation

If a **phase-separated microstructure** develops in the glass **prior to crystal nucleation and growth**, it is likely that the kinetics of these processes will be significantly affected.

In glass-ceramics, as a general rule, **metastable immiscibility** is probably the more important process.

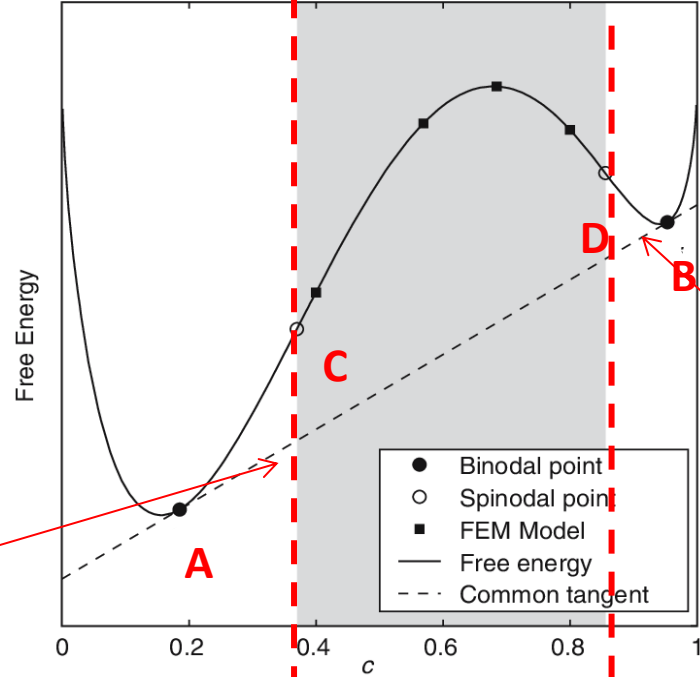
There are **two possible routes** for phase separation in **metastable immiscibility**:



nucleation and growth process (which theory parallels closely that for crystal nucleation and growth)

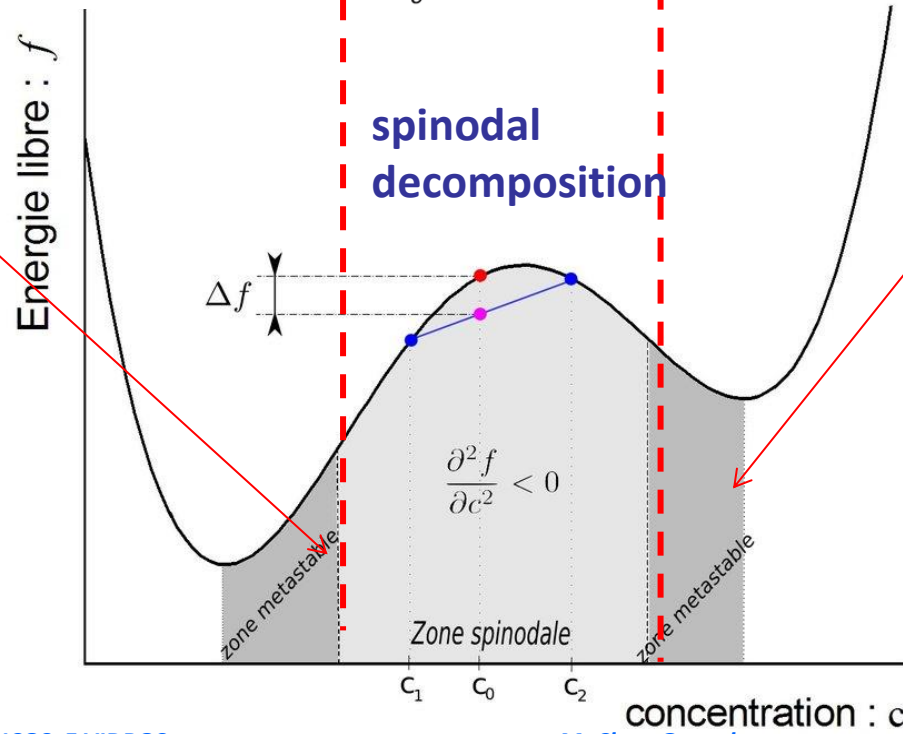


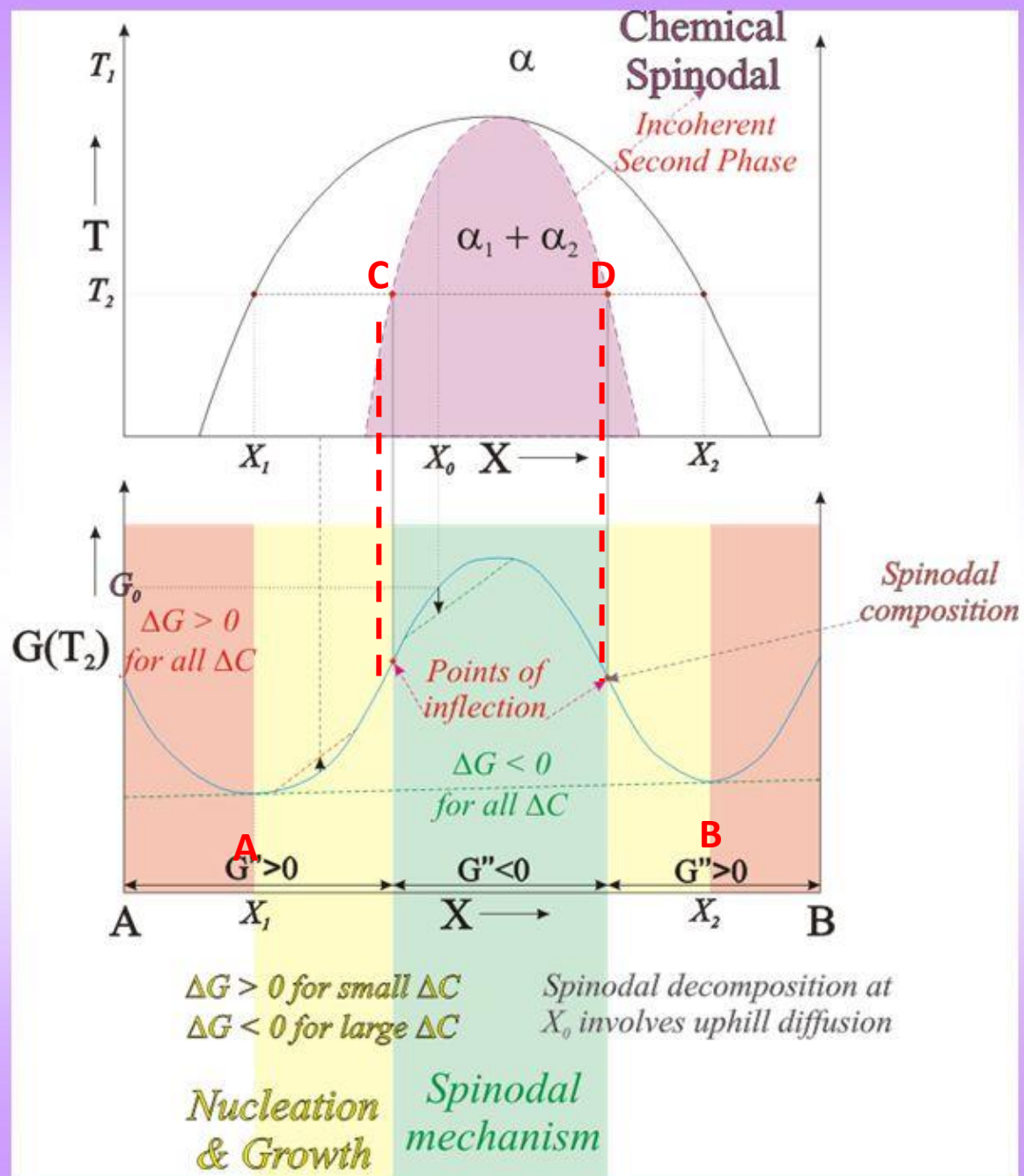
spinodal decomposition (Cahn and co-workers, 1961, 1965)



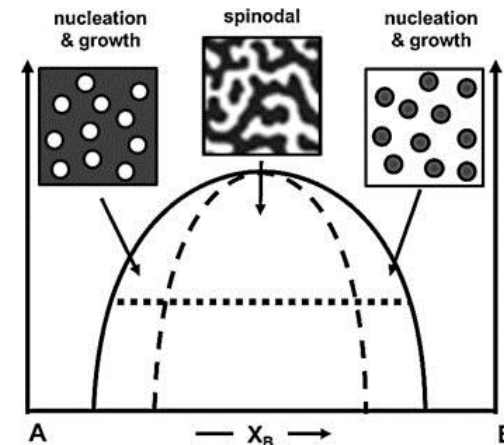
nucleation and growth process

nucleation and growth process





Spinodal decomposition



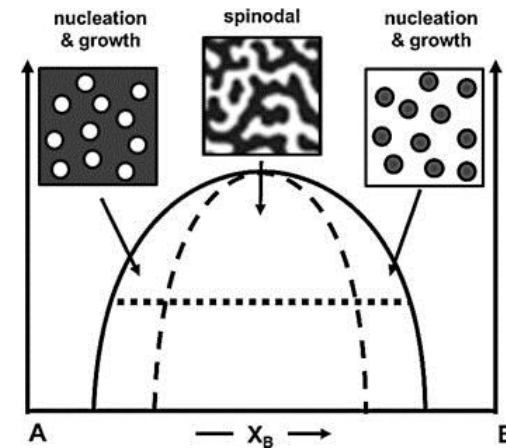
1. The presence of two minimum (A, B) in the free energy *versus* composition curve creates a situation in which the mixture will separate into two phases for compositions lying between A and B.

The free energy of the mixture (given by a point lying on the common tangent to points A and B) will be reduced if the mixture undergoes phase separation.

At low temperatures the two free energy minima are widely separated, but more closer together as the temperature increases.

Thus the loci of the minima trace out an immiscibility dome. Ultimately the two minima coincide at a temperature T_c , known as the upper consolute temperature.

Spinodal decomposition



2. Within the immiscibility dome **two distinct regions arise!**

Points **C** and **D** represent **inflections** in the free-energy curve such that between C and D $\delta^2 F / \delta^2 C$ (the second differential of the free energy versus composition relationship) is **negative**.

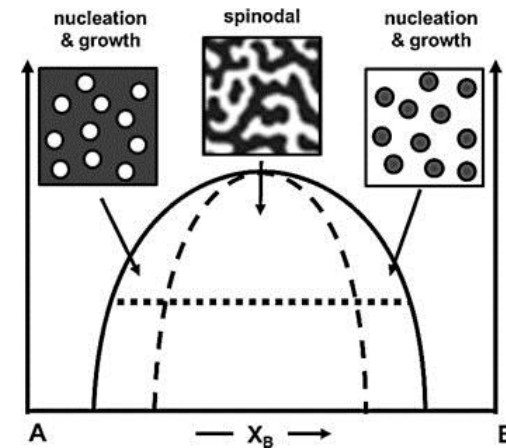
In this region therefore a **small fluctuation in composition** will be associated with **reduction of free energy**, hence such a **fluctuation will be stable** and will tend to **grow**.

Phase separation within this region, which **does not require a nucleation process**, is referred to as **spinodal decomposition**.

As the temperature is raised the points of inflection (C and D) will move closer together and again will coincide at the **consolute temperature**.

Thus the loci of these points will trace out an inner dome.

Spinodal decomposition



3. In the regions between A - C and B - D $\delta^2 F / \delta^2 C$ is positive and here a small composition fluctuation will be associated with an increase of free energy. Such fluctuations will therefore be unstable and tend to redissolve. They will only continue to grow if they attain a critical size.

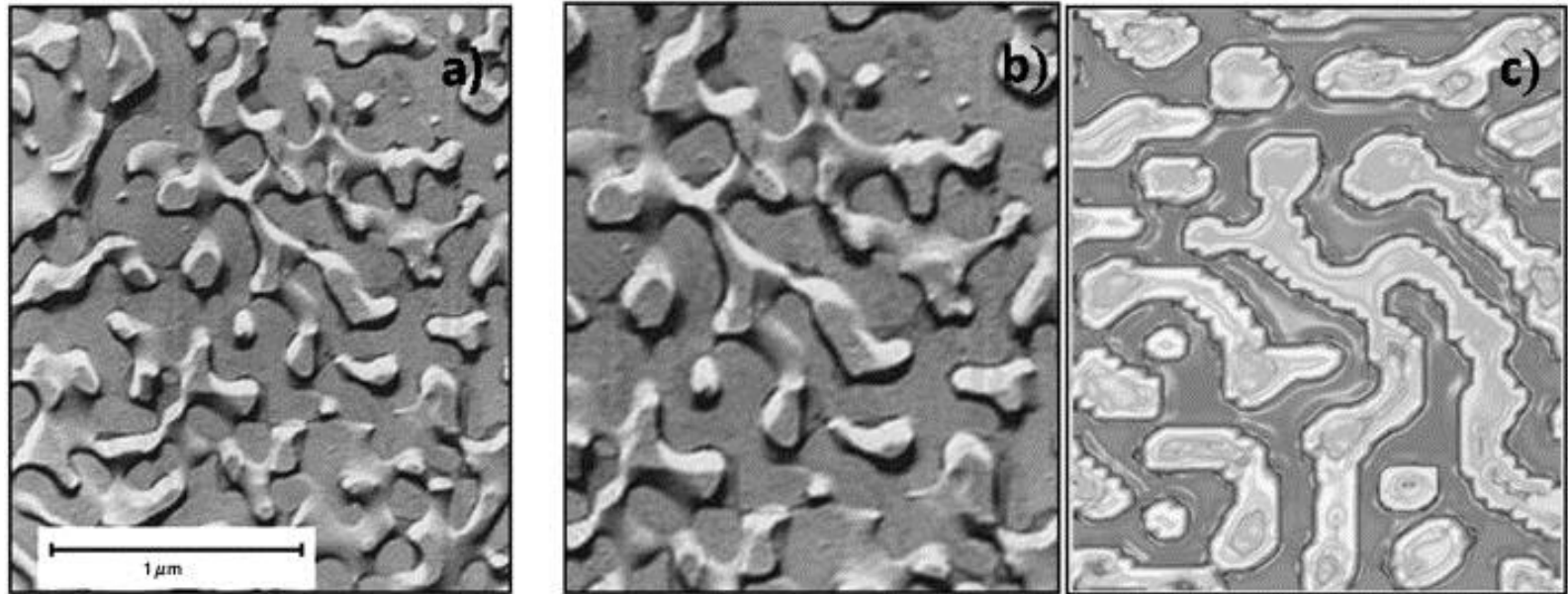
Phase separation within the region outside the spinodal curve will be by a nucleation and growth process.

The precise differences between the effects upon crystal nucleation that might result from prior phase separation of the two forms are not well understood but it seems possible that phase separation by nucleation and growth may play a more important role.

Characteristic features of phase separation by nucleation and growth or by spinodal decomposition

	Nucleation and growth	Spinodal decomposition
A. Phase compositions	At a fixed temperature the nucleated phase composition remains constant	Compositions change until equilibrium is achieved
B. Interface between phases	Clearly defined throughout	Initially diffuse but ultimately becomes sharp
C. Morphology	The nucleated phase generally appears as polyhedral (and non-spherical) particles random in size and spacing; low connectivity Particle size is function of undercooling	The second phase is generally non-spherical, 'threadlike', with irregular spacings and dimensions; high connectivity Wave length is function of undercooling
D. Time	Time dependent on diffusion rate Misfit strains will play a role in particles size	Instantaneous change due to instability – no nucleation barriers Misfit strains will play a role in wavelength dimension

Spinodal decomposition

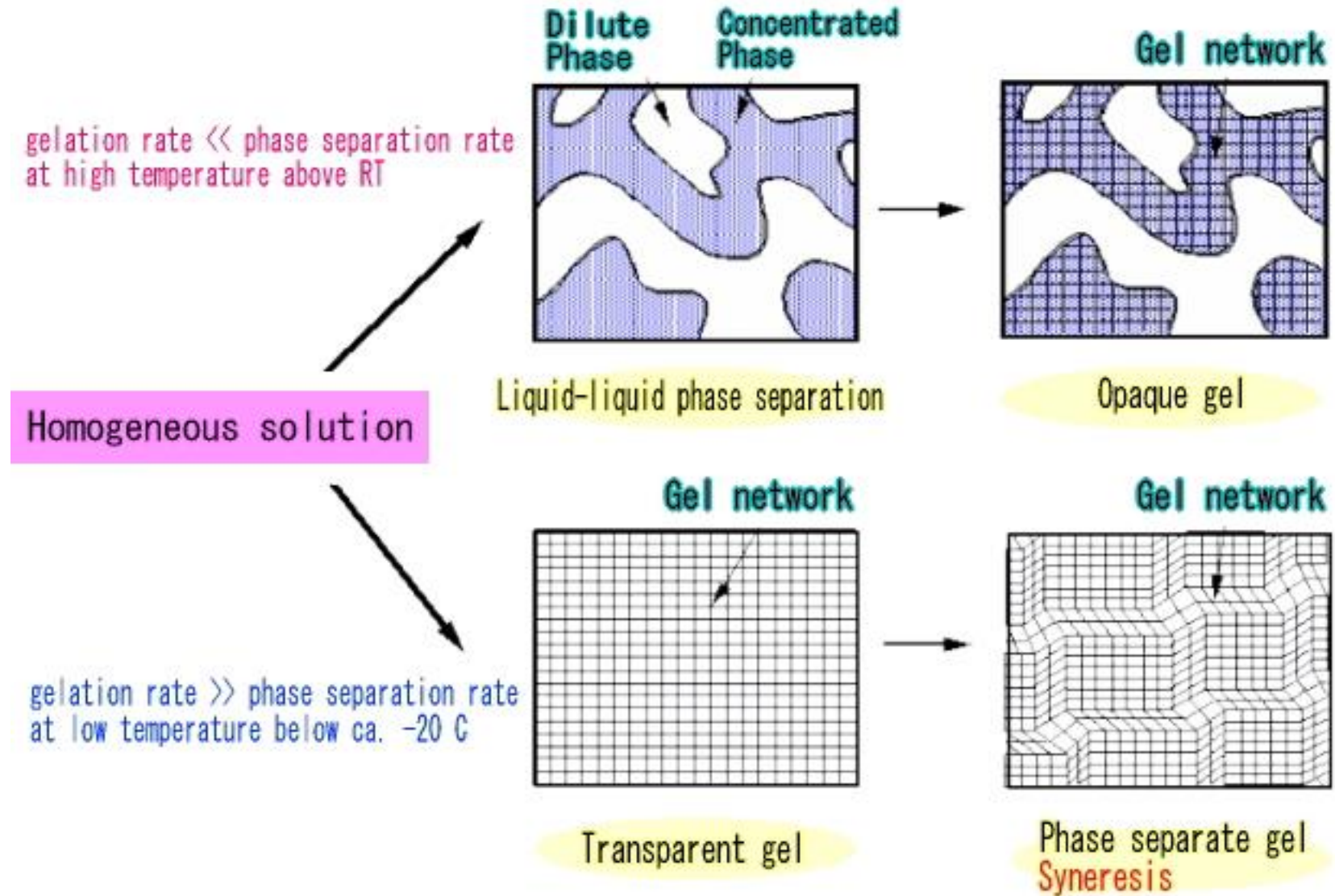


Microstructure of phase separated **Vycor**® glass

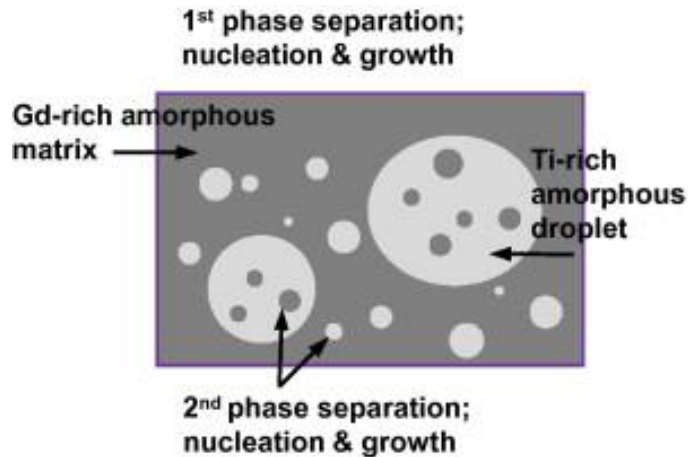
[Calphad Volume 33, Issue 1](#), March 2009, Pages 237-243

<https://doi.org/10.1016/j.calphad.2008.10.004>

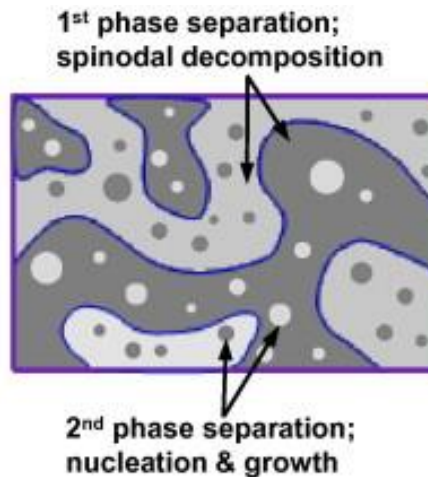
Spinodal decomposition



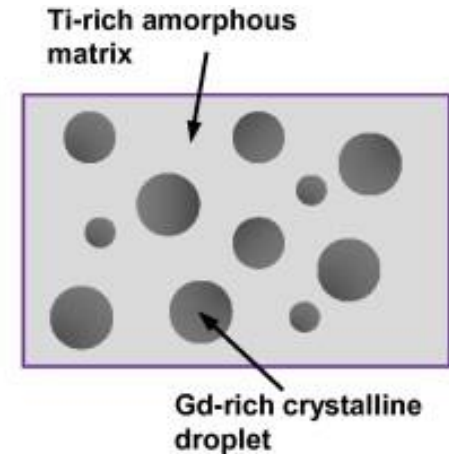
Spinodal decomposition



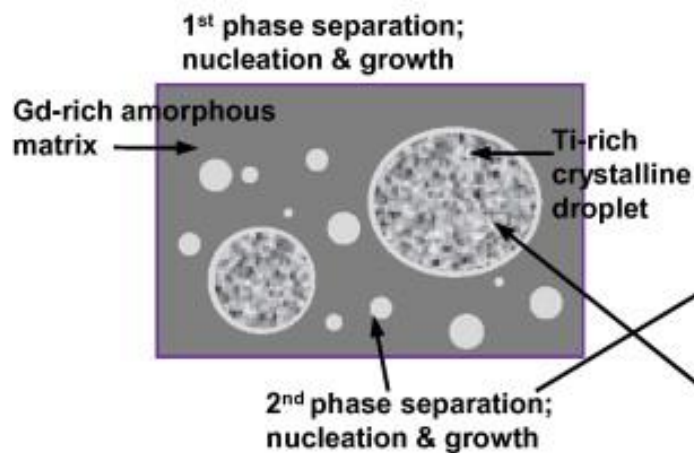
(a) O1 alloy



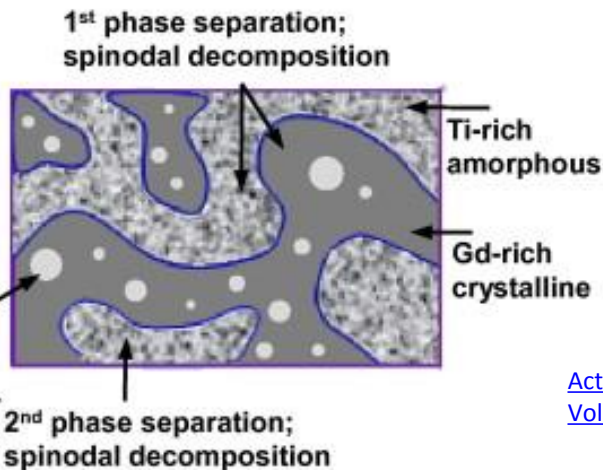
(b) O2 alloy



(c) O3 alloy



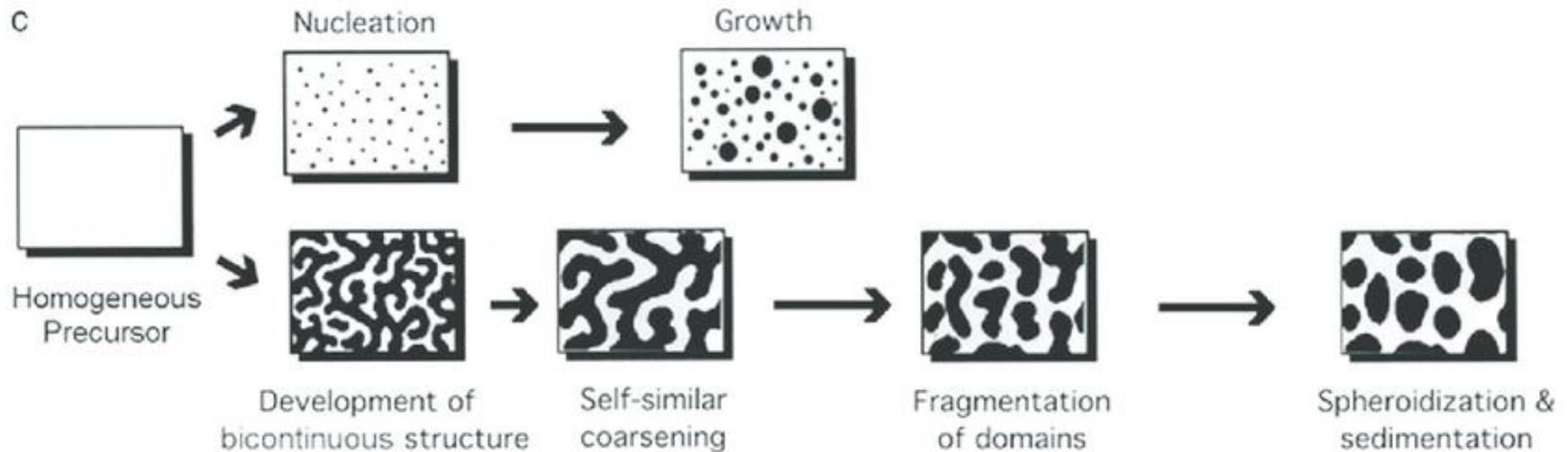
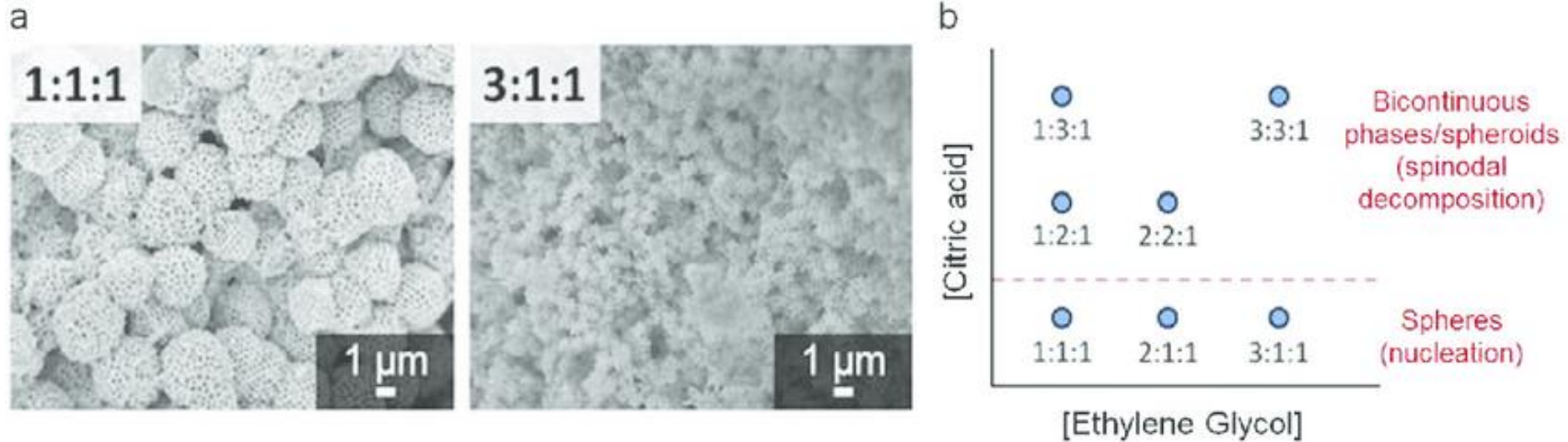
(d) U1 alloy



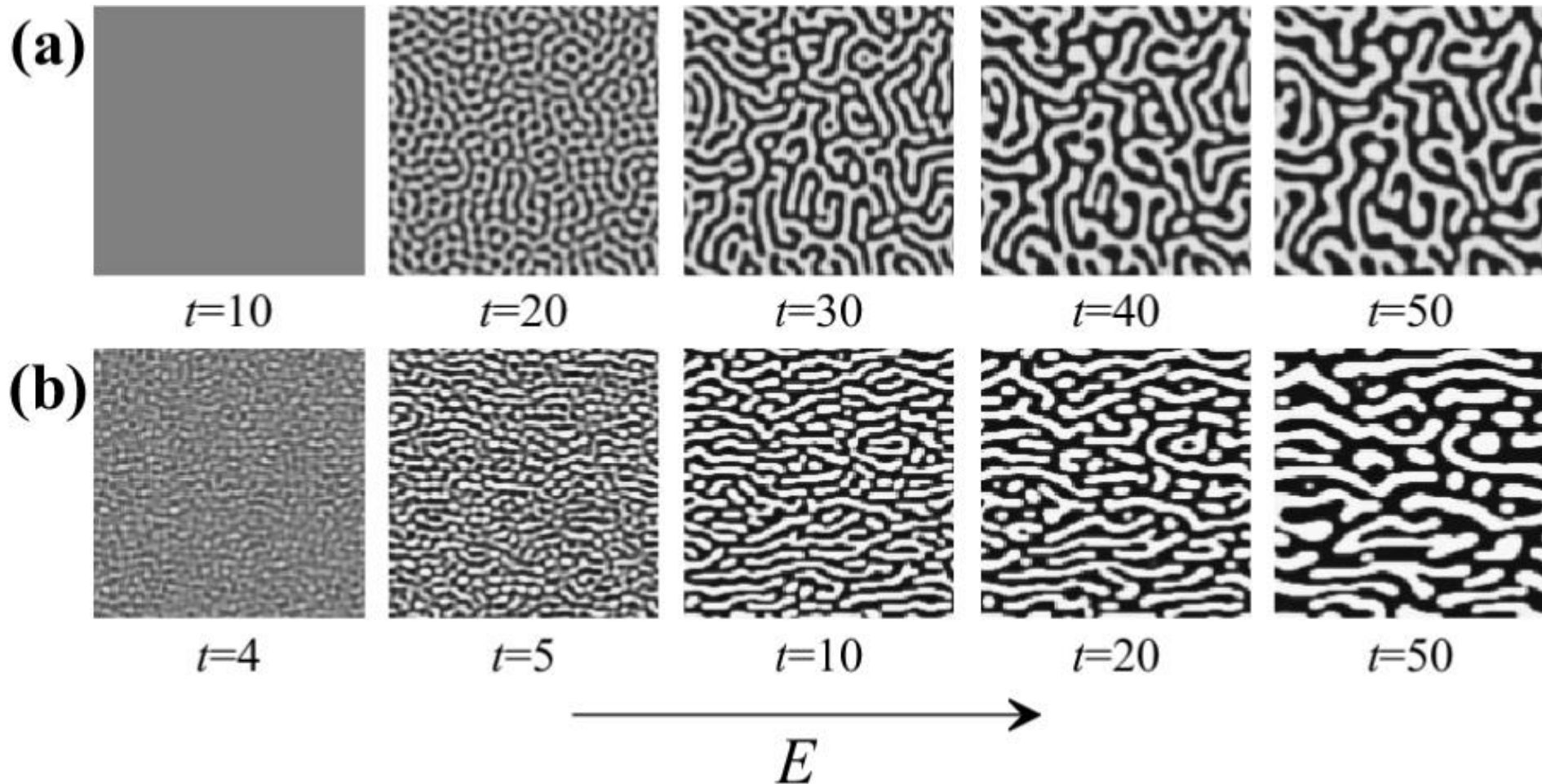
(e) U2 alloy

[Acta Materialia](#)
[Volume 58, Issue 7](#), April 2010, Pages 2483-2491

Spinodal decomposition

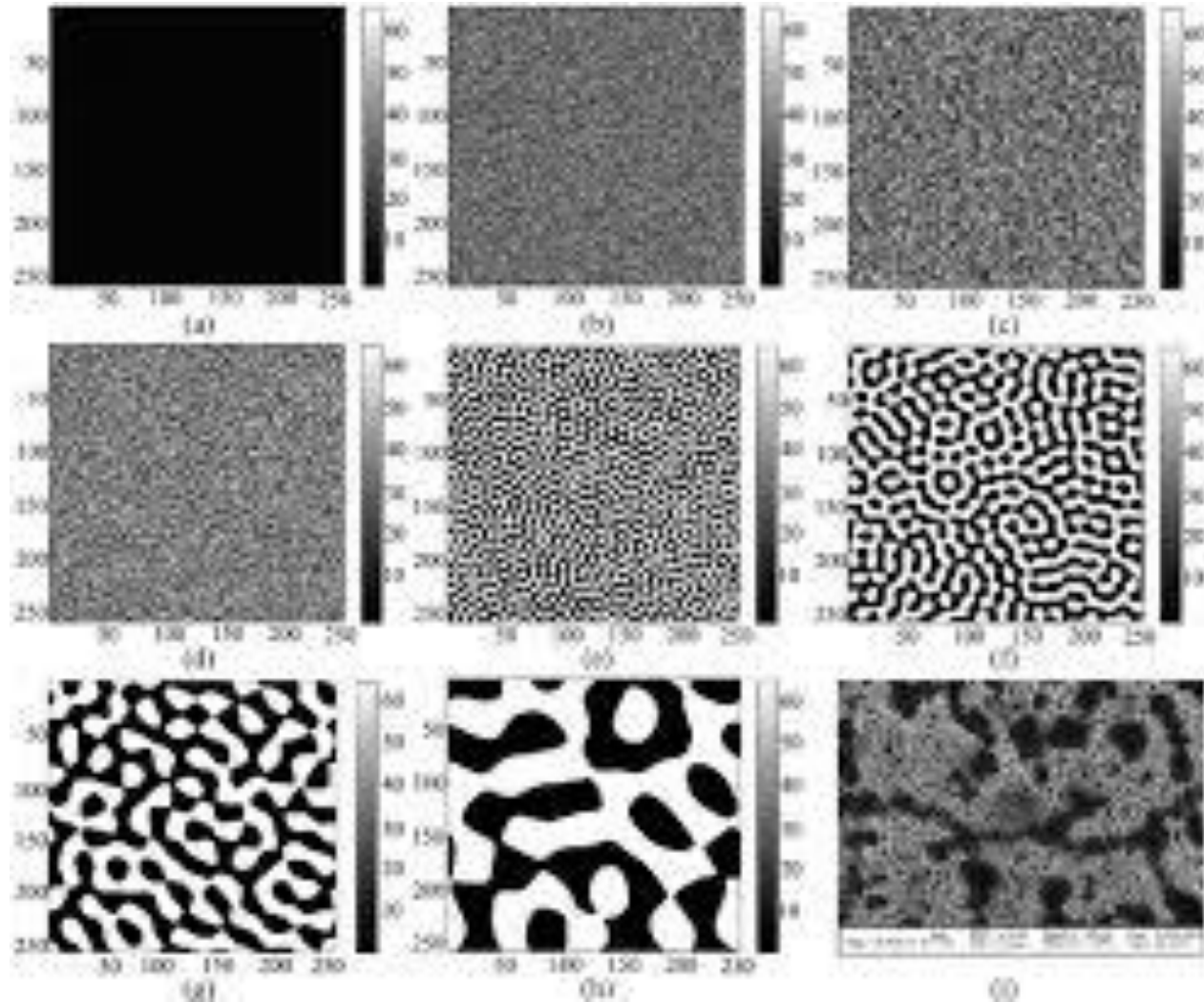


Spinodal decomposition



T. Araki and H. Tanaka, J. Phys. : Condens. Matter 18, L305 (2006)

Spinodal decomposition



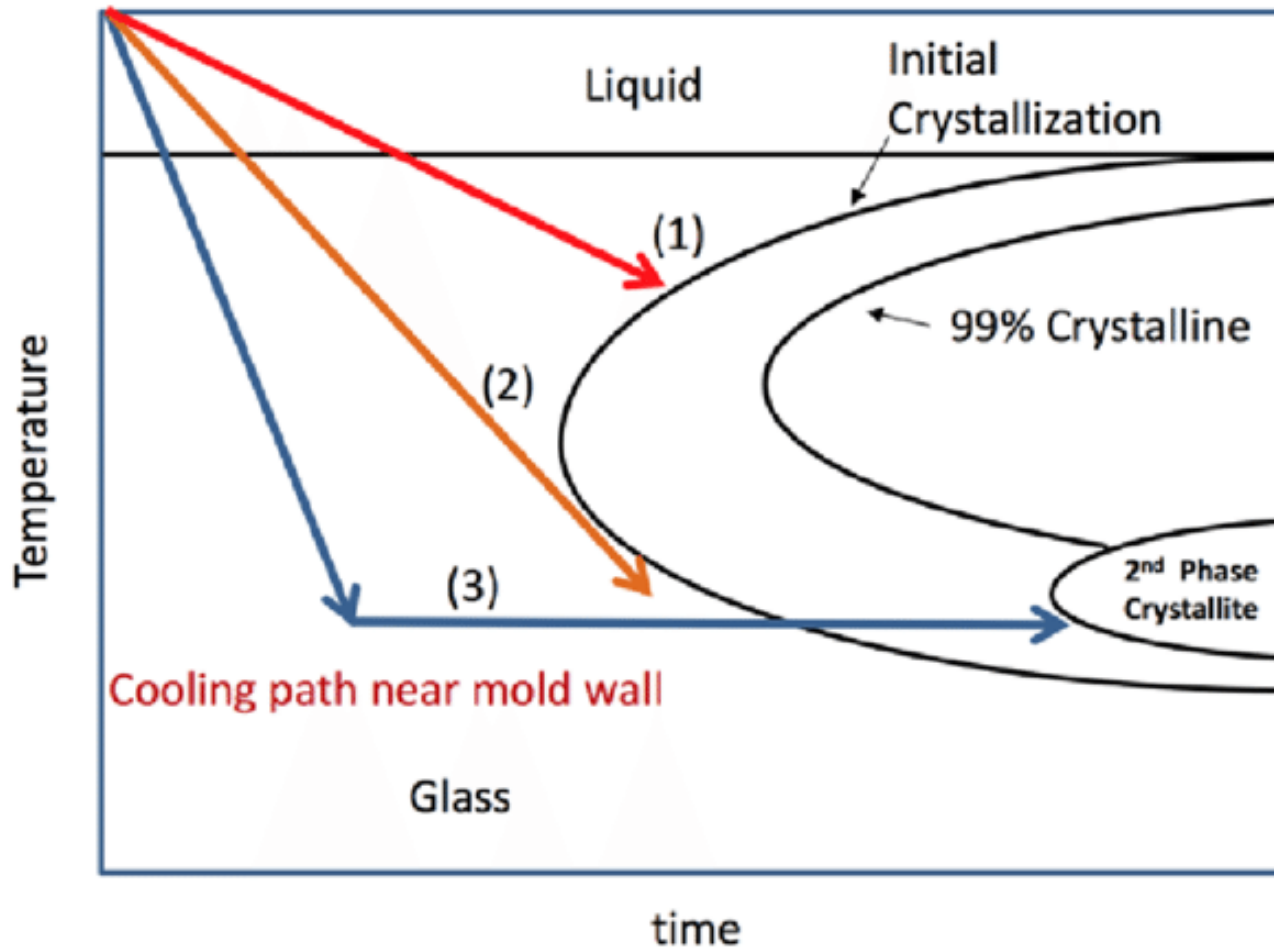
Devitrification

Devitrification implies the growth of crystalline material in the glass and in normal glass-making practice steps are taken to prevent its occurrence.

Devitrification can occur due to one of the following reasons:

- selection of an unsuitable glass composition
- composition locally changed due to prolonged contact and reaction with the furnace refractories
- during glass shaping by holding the glass for long periods within the critical T zone
- presence of impurities or minute scratches or flaws at the glass surface

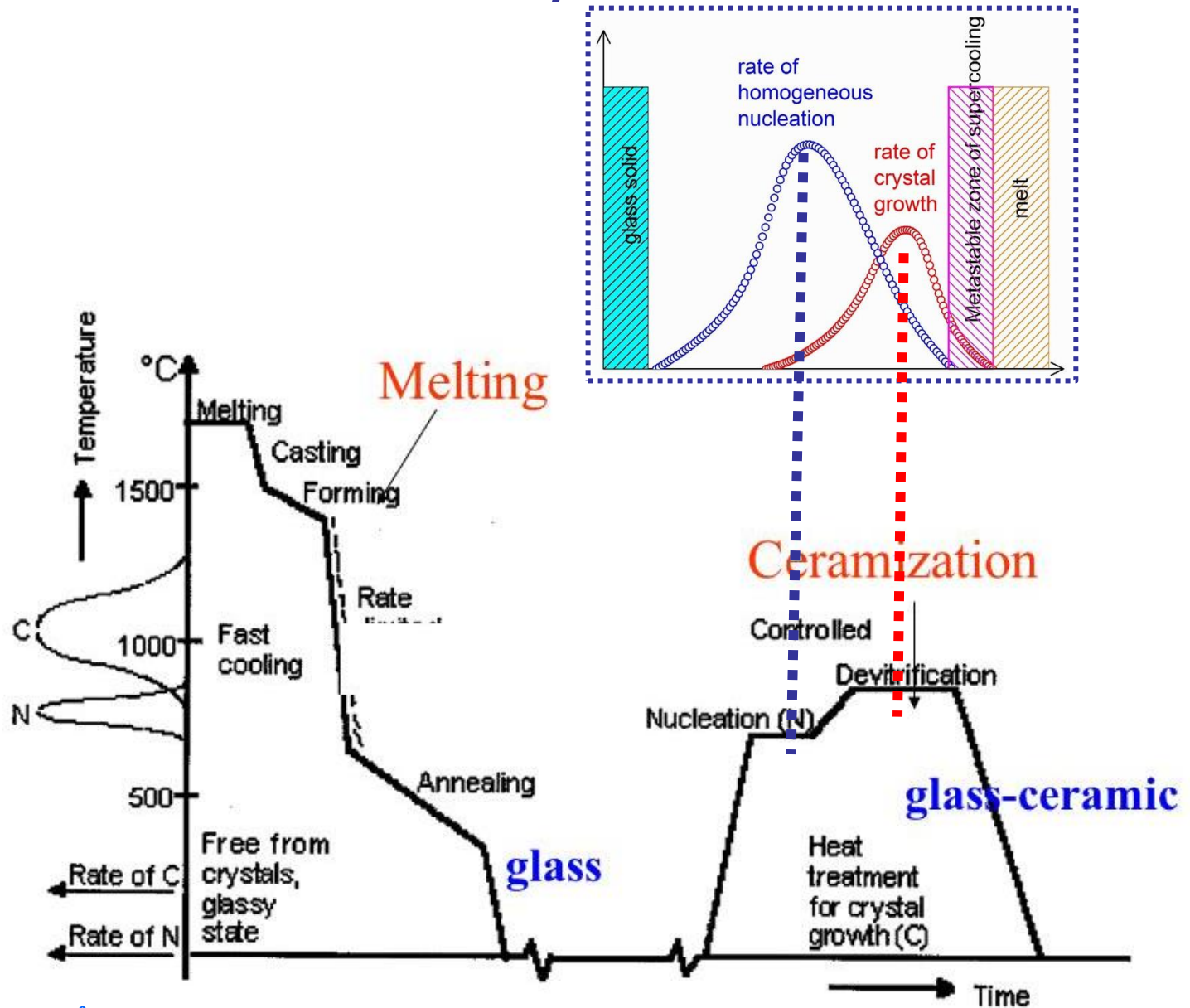
Controlled Crystallization



1. Primary crystallization
2. Critical cooling rate for glass formation
3. Devitrification from super-cooled glass

Controlled Crystallization

Objective
Xtalln.
Glass-
Ceramics
Nucltn.
Rate
Viscosity
CCT vs
TTT



Further reading

- **Introduction to Glass Science and Technology.** J. E. Shelby, 2nd Ed RSC PaperBacks (2005)
- **Les Verres et l'État Vitreux.** J. Zarzycki Masson (1997)
- **Glass Science.** R. H. Doremus Wiley Interscience (1994)
- **Overall aspects of non-traditional glasses. Synthesis, properties and applications.** H C. Vasconcelos, M. C. Gonçalves (eds) **Bentham Science Publishers** (2016)
- **Glass.** M. C. Gonçalves. *In: Materials for Construction and Civil Engineering: Science, Processing, and Design* p. 335-395 M. C. Gonçalves, F. Margarido (eds) Springer, New York (2015)