Lecture 14: Rate of Nucleation
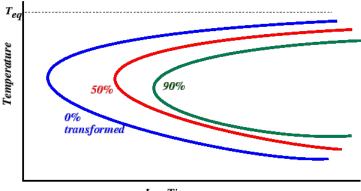
Today's topics

- Two energetic factors that affect nucleation rate: the activation energy barrier (ΔG^*) that needs to be overcome to produce a critical-size nucleus, and the activation energy for an atom to migrate across the interface separating the nucleus and matrix, and thus get attached to the growing incipient nucleus.
- Temperature dependence of nucleation rate: an approximate treatment by Turnbull.
- Overall kinetics of a phase transformation depends on both nucleation and grain growth.
- Effect of nucleation rate on the kinetics of solid→solid phase transformation: time-temperature-transformation (TTT) diagrams.

About Nucleation Rate (Kinetics)

- Nucleation is a competition between the capillary forces (surface energies) that resist the creation of new interfaces and a driving force to grow a more stable phase.
- The overall rate of nucleation is a product of the equilibrium number of critical size nuclei and the frequency that atoms successfully transfer from the parent phase into the nucleus.
- Practical application of nucleation and growth kinetics is often made from Time-Temperature-Transformation (TTT) diagrams. TTT diagrams contain several curves, each representing a particular constant value fraction of total transformed volume after a particular time for a fixed annealing temperature. The diagrams are usually determined by experiment, but their common "C"-shape follows from nucleation and growth kinetics.

- Exact mathematical description of nucleation rate is difficult to derive. An approximate treatment, which describes the temperature dependence, was first given by Turnbull.

In a phase transformation, say α→β, β-phase must nucleate and grow. The kinetics of such phase transformation is cooperatively determined by two kinetic factors: Nucleation and Growth, as depicted in Figure 5.24 cited from the Book, "Phase Transformations in Metals and Alloys", by D. A. Porter, K. E.

(a) Beginning   End

(b) Nucleation sites
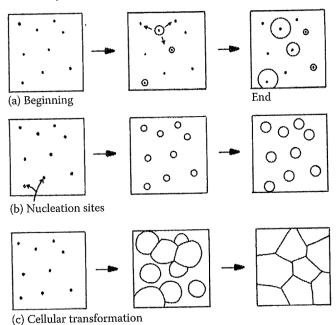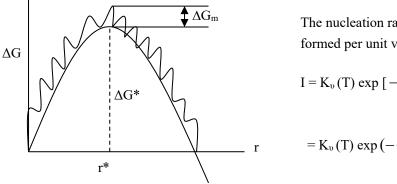
(c) Cellular transformation

FIGURE 5.24
(a) Nucleation at a constant rate during the whole transformation. (b) Site saturation—all nucleation occurs at the beginning of transformation. (c) Cellular transformation.

Here in this Lecture, we only focus on the kinetics of nucleation.

For nucleation to occur, the cluster size must be greater than the critical nucleus size, r^*, at which the activation barrier is ΔG^*. Additionally, there is also a barrier (ΔG_m) for an atom to cross the interface separating the nucleus and the matrix. So, the rate of nucleation (I) consists of these two factors.

The nucleation rate, defined as number of nucleus formed per unit volume in unit time, is given by

$$I = K_\upsilon(T) \exp\left[-\frac{(\Delta G^* + \Delta G_m)}{K_B T}\right]$$

$$= K_\upsilon(T) \exp\left(-\frac{\Delta G^*}{K_B T}\right) \exp\left(-\frac{\Delta G_m}{K_B T}\right)$$

Where K_B is the Boltzmann constant, and T is the temperature.

The pre-exponent factor $K_\upsilon(T)$ is given by

$$K_\upsilon(T) = n^* N_0 \upsilon \left(\frac{r^{*2} \gamma_{\alpha\beta}}{\Delta G_m K_B T}\right)^{1/2} \qquad \text{(no derivation)}$$

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Where, N_0 = number of atoms/unit volume, n^* = number of surface atoms across a nucleus, and υ is the atomic vibration frequency.

According to Turnbull, theoretical value of K_υ for mercury just below the melting point is $\sim 10^{35}$. Experimentally, Turnbull estimated to be $\sim 10^{42\pm2}$.
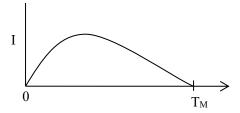
From previous Lectures, we have,

$$\Delta G^* = \frac{16\pi}{3} \frac{\gamma_{\alpha\beta}{}^3}{(\Delta G_V)^2} = \frac{16\pi}{3} \frac{\gamma_{\alpha\beta}{}^3}{(\Delta S_V)^2 (\Delta T)^2}$$

- As T decreases, $\Delta T = T_M - T$ increases, then ΔG^* decreases and $\exp\left[-\dfrac{\Delta G^*}{K_B T}\right]$ increases.

  Thus, as T is lowed below T_M, the nucleation rate increases --- $T\downarrow$, $\Delta T\uparrow$, $\Delta G^*\downarrow$, $I\uparrow$

- Meanwhile, as T decreases, $\exp\left[-\dfrac{\Delta G_m}{K_B T}\right]$ decreases,

➔ The net effect combining the two terms above is that **the nucleation rate, I, must go through a maximum, as depicted in the diagram below.**

Now consider two extreme conditions:

1. when $T \rightarrow T_M$, $\Delta G^* \rightarrow \infty$, then, $\exp\left[-\dfrac{\Delta G^*}{K_B T}\right] \rightarrow 0$, and meanwhile, the term $\exp\left[-\dfrac{\Delta G_m}{K_B T}\right] \rightarrow$ a finite

    value. So, **I = 0 × finite ➔ 0**

2. when $T \rightarrow 0$, ΔG^* is finite, but $\Delta G^*/K_B T \rightarrow \infty$, then, $\exp\left[-\dfrac{\Delta G^*}{K_B T}\right] \rightarrow 0$, and meanwhile the term $\exp$
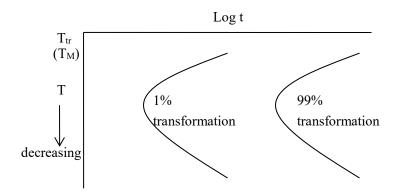
    $\left[-\dfrac{\Delta G_m}{K_B T}\right]$ also $\rightarrow$ 0. So, **I = 0 × 0 ➔ 0**

Thus, the nucleation rate, *I*, **must exhibit a maximum between 0 and T_M**, as shown above in the diagram.

Effect of Nucleation Rate on the Kinetics of Solid—>Solid Phase Transformation as described by

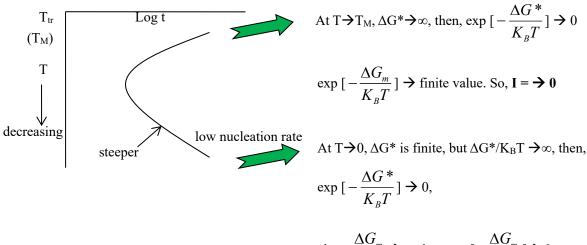**Time-Temperature-Transformation (TTT) Diagrams:**

It is a tradition in the metallurgical literature to plot phase transformation kinetics in a Time-Temperature-Transformation (TTT) Diagram, log(time) on x-axis vs. temperature (T) on y-axis. The following TTT diagram is for α—>β (solid-solid) transformation.

Log t

T_{tr}
(T_M)

T

↓

decreasing

1%
transformation

99%
transformation

The above figure shows the time required at any temperature for the formation of ∼1% of the β-phase, and also for the formation of ∼99% of the β-phase.

The former is essentially the beginning of transformation (nucleation stage), while the latter is the end of transformation (the end of growth stage).
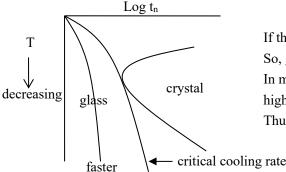
For the nucleation part:

T_{tr}
(T_M) Log t

T

↓

decreasing

steeper

low nucleation rate

At T→T_M, ΔG*→∞, then, $\exp\left[-\dfrac{\Delta G^*}{K_B T}\right] \to 0$

$\exp\left[-\dfrac{\Delta G_m}{K_B T}\right] \to$ finite value. So, **I = → 0**

At T→0, ΔG* is finite, but ΔG*/K_BT →∞, then,

$\exp\left[-\dfrac{\Delta G^*}{K_B T}\right] \to 0,$

also, $\dfrac{\Delta G_m}{K_B T} \to \infty$, then, $\exp\left[-\dfrac{\Delta G_m}{K_B T}\right] \to 0$

So, $\exp\left[-\dfrac{\Delta G^*}{K_B T}\right]\exp\left[-\dfrac{\Delta G_m}{K_B T}\right] \to 0$, **I = → 0**

<u>Implications of TTT diagram in glass forming system, ceramics and metals:</u>
To form a glass, a molten mass contains SiO_2 and other constituents, usually alkali oxides, alkaline earth oxides,

aluminum oxides, etc, has to be cooled at a rate faster than needed for forming crystals (the quartz). If the cooling rate is fast enough, the nose of the TTT curve can be avoided → leading to formation of a glass.

Note: lime (calcium oxide (CaO), generally obtained from limestone), and magnesium oxide (MgO) and aluminium oxide (Al2O3) are usually added to the silica to provide better chemical durability. The resulting glass contains about 70 to 74% silica by weight and is called a soda-lime glass.

Log t_n

T

↓

decreasing   glass   crystal

faster   ← critical cooling rate

If the cooling rate is greater than the critical rate, glass forms.
So, glass formation can be controlled by cooling rate.
In most silicate system, nucleation is slow, due to
high viscosity (network formation) – low diffusivity.
Thus, glass formation can be achieved at modest cooling rate

In metals, nucleation occurs rapidly. To form metallic glass (amorphous), one has to cool the liquid metals very fast (10^6 degree/sec). The process is called <u>Splat cooling</u>.

The first reported metallic glass was an alloy (Au75Si25) produced at Caltech by W. Klement (Jr.), Willens and Duwez in 1960. This and other early glass-forming alloys had to be cooled extremely rapidly (on the order of one megakelvin per second, 10^6 K/s) to avoid crystallization.
--- https://en.wikipedia.org/wiki/Amorphous_metal

For a eutectoid carbon steel (0.78% C) of thin section, if the quench starting at 750 °C and ending at 450 °C takes place in 0.7 seconds (a rate of 430 °C/s) no pearlite will form and the steel will be martensitic with small amounts of retained austenite. For steel 0-0.6% carbon the martensite has the appearance of lath, and is called lath martensite. For steel greater than 1% carbon it will form a plate like structure called plate martensite. Between those two percentages, the physical appearance of the grains is a mix of the two. The strength of the martensite is reduced as the amount of retained austenite grows. If the cooling rate is slower than the critical cooling rate, some amount of pearlite will form, starting at the grain boundaries, where it will grow into the grains until the martensite start temperature (Ms) is reached, then the remaining austenite transforms into martensite at about half the speed of sound in steel. --- https://en.wikipedia.org/wiki/Martensite