

Lecture 15: Kinetics of Phase Growth: *single-component or composition-invariant transformation*

Today's topics

- Derivation of the Johnson-Mehl-Avrami equation: the time constant (τ) of phase growth and the “S” shape plot describing the kinetics of phase transformation in term of volume fraction change ($X(t)$).
- Johnson-Mehl-Avrami equation when applied for different geometries of β -phase particles: spherical (3-dimension, $m=3$), disk-shaped (2-dimension, $m=2$) and rod-shaped (1-dimension, $m=1$).

General comments about phase growth

- Once an incipient nucleus has reached its critical size (r^*), the surface energy that restricts the development of the new phase become insignificant and the kinetics for growth are becoming dominated by the limiting kinetic mechanism (i.e., the migration or jumping of atoms from α matrix to β particle) and the thermodynamic driving forces (the difference in chemical potential of α and β phase, $\mu_\alpha - \mu_\beta$).
- If the transformation is of the type that requires no long-range diffusion, then the rate of growth is controlled by the rate of atomic transfer across the growing phase interface.
- However, if long-range diffusion is required, then two different rate-limiting processes can affect growth rate: *Interface Limited Growth* and *Diffusion Limited Growth*. Both of these two processes are temperature dependent --- typically the growth rate is Arrhenius type with growth becoming very slow at low temperatures.
- *Interface Limited Growth*: In this case, growth is limited by how fast atoms can transfer across the α/β interface and not the rate at which atoms can be transported to the growing interface. This is equivalent to growth where no long-range diffusion is required.
- *Diffusion Limited Growth*: In this case, the growth rate is limited by the diffusivity, i.e., how fast the necessary atoms are transfer from the α matrix to the growing β -particles. In general, the rate of diffusion transport falls off very quickly with temperature.

More readings about Johnson-Mehl-Avrami Equation and Phase Transformation

- The Johnson-Mehl-Avrami equation as to be discussed in this lecture describes how solids transform from one phase to another at constant temperature. It can specifically describe the kinetics of crystallization, but can also be applied generally to other phase changes of materials, like chemical reactions.
- The equation is also known as the Johnson-Mehl-Avrami-Kolmogorov equation, or JMAK equation. The equation was popularized by Melvin Avrami in the series of papers published in the Journal of Chemical Physics from 1939 through 1941, so very often it is

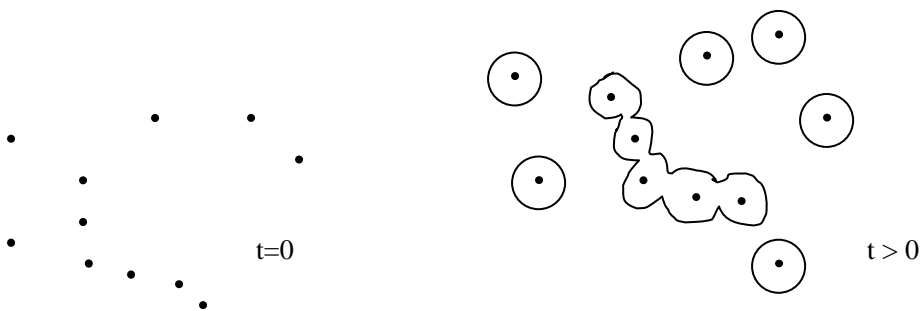
simply called Avrami equation: 1). Avrami, M (1939). "Kinetics of Phase Change. I. General Theory". Journal of Chemical Physics 7 (12): 1103–1112. 2). Avrami, M (1940). "Kinetics of Phase Change. II. Transformation-Time Relations for Random Distribution of Nuclei". Journal of Chemical Physics 8 (2): 212–224. 3). Avrami, M (1941). "Kinetics of Phase Change. III. Granulation, Phase Change, and Microstructure". Journal of Chemical Physics 9 (2): 177–184.

Kinetics of Phase Transformation, Growth:

Consider a sample of α cooled to a temperature $T (< T_{tr})$ and maintained isothermally, where it transforms into *composition-invariant* β .

Thus, once growth begins, $r(t) = r^* + vt \approx vt$

Where “v” is the radial velocity (length/unit time) of the particle growth.



At time t , $r = vt$ for a particle that is isolated. If ‘ n ’ denotes the number of nuclei/per volume (density) originally, the ones that remains isolated at time t will be given by $n(t) = n [1-x(t)]$, where $x(t)$ = volume fraction be transformed. In time dt , the isolated ones grow from r to $r + dr$, and the volume fraction grows by $4\pi r^2 dr \cdot n[1-x(t)]$;

or $dx(t) = 4\pi r^2 dr \cdot n[1-x(t)] = 4\pi n v^3 t^2 dt [1-x(t)]$
 (note: $r(t) = vt$, and $dr = vdt$, and this applies to spherical particles)

then, $\frac{dx(t)}{1-x(t)} = 4\pi n v^3 t^2 dt$

$$-\ln [1-x(t)] = \frac{4\pi n v^3 t^3}{3}$$

$$x(t) = 1 - \exp\left[-\frac{4\pi n v^3 t^3}{3}\right]$$

$$= 1 - \exp\left[-\left(\frac{t}{\tau}\right)^3\right],$$

where, $\tau = \left[\frac{3}{4\pi n v^3}\right]^{1/3} = \left[\frac{3}{4\pi n}\right]^{1/3} \frac{1}{v}$, τ — time constant of the process

In general,

$$x(t) = 1 - \exp\left[-\left(\frac{t}{\tau}\right)^m\right] \quad \text{--- Johnson-Mehl-Avrami equation.}$$

The parameter 'm' depends on shape of β -phase particles (the Dimension!):

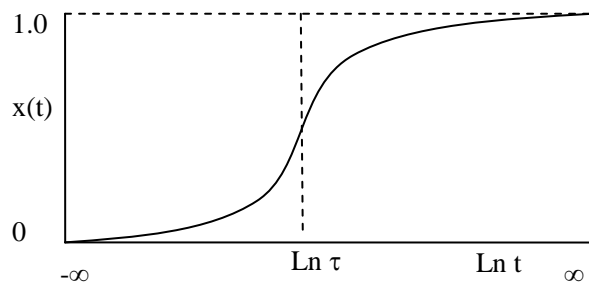
spherical $\rightarrow m=3$; disk-shaped $\rightarrow m=2$; rod-shaped $\rightarrow m=1$

(3D)

(2D)

(1D)

If nucleation occurs concurrently with growth, for 3D spherical particle, m can be 4 or 5 under various conditions. For the irregular shape β -phase particles, m could be non-integer values, as determined in real experiments as shown below.



Plotting $x(t)$ vs. $\ln(t)$ \rightarrow

“S”-shaped plot regardless

of the actual mathematical form.

As $t \rightarrow \infty$ ($\ln t \rightarrow \infty$), then $x(t) \rightarrow 1.0$

As $t \rightarrow 0$ ($\ln t \rightarrow -\infty$), then $x(t) \rightarrow 0$

differentiate: $x(t) = 1 - \exp\left[-\left(\frac{t}{\tau}\right)^m\right]$

$$\frac{dx(t)}{dt} = \frac{mt^{m-1}}{\tau^m} \exp\left[-\left(\frac{t}{\tau}\right)^m\right]$$

multiply both sides by t

$$t \frac{dx}{dt} = \frac{dx}{d \ln t} = m \left(\frac{t}{\tau}\right)^m \exp\left[-\left(\frac{t}{\tau}\right)^m\right]$$

clearly, as $t \rightarrow 0$, $\frac{dx}{d \ln t} \rightarrow 0$

and as $t \rightarrow \infty$, $\frac{dx}{d \ln t} \rightarrow 0$

Both \Rightarrow flat curves

Rewrite the Johnson-Mehl-Avrami equation:

$$\ln \frac{1}{1-x(t)} = \left(\frac{t}{\tau}\right)^m$$

Then, $\ln \ln \frac{1}{1-x(t)} = m \ln t - m \ln \tau$

Plot $\ln \ln \left[\frac{1}{1-x(t)} \right]$ vs. $\ln t$ generates a straight line: the slope is 'm' (which could be a non-integer value), and

the intercept is '- m ln τ ', thus giving the τ . $\tau = \left[\frac{3}{4\pi n} \right]^{1/3} \frac{1}{v}$, time constant as defined above, is a measure of growth rate, $\tau \propto \frac{1}{v}$, and depends on 'n', number of nuclei per volume. It also depends on grain size if nucleation occurs at grain boundaries.

Brief summary of the Kinetics of phase transformation: more general, practical understanding

- *Transformations are often observed to follow a characteristic S-shaped, or sigmoidal profile (as shown above), where the transformation rates are low at the beginning and the end of the transformation but rapid in between.*
- *The initial slow rate can be attributed to the time required for forming a significant number of nuclei of the new phase. During the intermediate period the transformation is rapid as the nuclei grow into particles and consume the old phase while nuclei continue to form in the remaining parent phase.*
- *Once the transformation begins to near completion there is little untransformed material for nuclei to form therein and the production of new particles becomes slow. Further, the particles already existing begin to touch one another, forming a boundary where growth stops.*