3.044 Recitation 10

Topics

- Sintering (Stage I and Stage II)
- Evaporation

Sintering Stage Transition

The ratio of the neck/particle radius is the criterion for determining whether sintering is in Stage I or II.

Stage I: Evaporation dominate : $\frac{x}{r} \propto r^{-2/3}t^{1/3}$

We have studied the evaporation/condensation on the surface of sintered particles. In sintering of stage I via evaporation/condensation, the difference in vapor pressure is a function of the change in curvature between inside and outside. When writing the radius of curvature outside (ρ) in terms of radius of particle (r) and neck radius of curvature (x), we can esitmate the difference in vapor pressure as:

$$\triangle p_v \cong \frac{2r\gamma p_{v,0}}{x^2 dRT}$$

Vapor pressure on a flat surface is $p_{v,0}$. Here, γ is the surface tension [J/m^2]. d =molar density [Density/Molar Mass=mol/m^3].

Stage II: Bulk Diffusion from neck to grain boundary dominated: $\frac{x}{r} \propto r^{-3/5}t^{1/5}$

Evaporation Process

:Vapor Pressure:

For evaporation from liquid phase, we use the Clausius-Clapeyron equation to find the vapor pressure (torr) at different liquid temperature (K):

$$\log_{10} \overline{p}_v = -\frac{A}{T} + B + C\log_{10} T + DT$$

If it is a pure element $(X_i = 1)$, $p_{v_i} = X_i \overline{p}_{v_i} = \overline{p}_{v_i}$.

For dilute solution of B in A, Henry's law says

$$p_{v_i} = \gamma_i X_i \overline{p}_{v_i}$$

:Flux: ($\frac{mol}{m^2 s}$)

The criterion for evaporation is the Knudsen Number$= \frac{\lambda}{L} = \frac{k_B T}{\sqrt{2}\pi\sigma^2 p_v L}$. Mean free path, λ, is the average distance that a molecule travels before collision with another molecule. The characteristic length , L, is the representative length of the system. σ is the collision diameter.

Knudsen Number > 1

For large Kn, molecules travel in the space for a long distance without colliding with other molecules. This is assumed to be the case in a vacuum (low pressure). The flux due to evaporation into vacuum is expressed by Langmuir equation :

$$J_{ev,B} = \frac{p_{v,B}}{\sqrt{2\pi MRT}} = \frac{\gamma_B X_B \overline{p}_{v,B}}{\sqrt{2\pi M_B RT}}$$

Mole fraction X_i is the fraction of surface concentration of evaporating element (C_B : $\frac{mol}{m^3}$) and molar density of the host material (d : $\frac{mol}{m^3} = \frac{M}{\rho}$). To make the unit work, choose the same unti system through out. It is more convenient to use $[p_v = Pa]$, $[M = kg/mol]$, $[R = J/mol-K]$, and $[T = K]$.

Evaporation rate or reaction rate is

$$k''_B = J_{ev}/C_B = \frac{\gamma_B \overline{p}_{v,B}}{d_A\sqrt{2\pi M_B RT}} = \frac{\gamma_B \overline{p}_{v,B}}{\sqrt{2\pi M_B RT}} \frac{M_A}{\rho_A}$$

Knudsen Number < 1

For small Kn, molecules collide with others in a short distance. Vapor phase is treated as a continuous phase. Evaporation flux into gas is limited by the mass transfer. Thus

$$J_B = h_D(C_{s,B} - C_{bulk,B})$$

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:Cosine Distribution:

Under high pressure system, flux is a function of $(cos\,\theta)^n$ (See Graphs of Flux vs. cos θ, n vs. (d/λ_0), and n vs. Evaporation rate in the slides 04/27/05 lecture).

Examples

1. To evaporate a dilute solute B from A, we use electron beam melting in a chamber L=0.25m. Assume the average temperature T=2100 K. Data: $M_A = 100\,g/mol$,$\rho_A = 5\,g/cm^3$, $M_B = 50\,g/mol$, $\gamma_B = 1$.

1 $torr$ = 133.322 Pa = 1.33322×10^{-3}atm

k_B :Boltzmann's Constant= $1.3807 \times 10^{-23}\,J/K$

R = 62.363 $litre\,torr/mol-K$ =8.314 $J/mol-K$

$$\log_{10}\overline{p}_{v,A} = -\frac{18950}{T} + 12 - 1.01\log_{10}T$$

$$\log{}_{10}\overline{p}_{v,B} = -\frac{26900}{T} + 10.12 + 0.23\log_{10}T$$

(a) Calculate vapor pressure from pure element for B and A

$$\begin{aligned}
\log_{10}\overline{p}_{v,B} &= -\tfrac{26900}{2100} + 10.12 + 0.23\log_{10}2100 = -1.93 \\
\overline{p}_{v,B} &= 10^{-1.93} = 0.01 \text{ torr} \\
\log_{10}\overline{p}_{v,A} &= -\tfrac{18950}{2100} + 12 - 1.01\log_{10}2100 = -0.38 \\
\overline{p}_{v,A} &= 10^{-0.38} = 0.42 \text{ torr}
\end{aligned}$$

(b) Calculate Kn when the collision diameter is 0.1nm.

$$Kn = \frac{k_B T}{\sqrt{2}\pi\sigma^2 p_v L} = \frac{(1.3807\times 10^{-23}\,J/K)(2100\,K)}{\sqrt{2}\pi(10^{-10}m)^2(0.01\times 133.322\,Pa)(0.25\,m)} = 1.64$$

(c) Calculate evaporation rate

Kn > 1 : Evaporation in vacuum

$$k'' = \frac{\gamma_B\overline{p}_{v,B}}{\sqrt{2\pi M_B RT}}\frac{M_A}{\rho_A} = \frac{(0.01\times 133.322\,Pa)(100\times 10^{-3}kg)/(5000\,kg/m^3)}{\sqrt{2\pi(50\times 10^{-3}kg/mol)(8.314\,J/mol-K)(2100\,K)}} = 3.6\times 10^{-7}\frac{m}{s}$$

2. We want to deposit a coating of A with 5 wt% B.

(a) What is the evaporation ratio?

$$ER_B = \gamma_B \frac{\bar{p}_{v,B}}{\bar{p}_{v,A}} \sqrt{\frac{M_A}{M_B}} = \frac{0.01}{0.42} \sqrt{\frac{100}{50}} = 0.033$$

(b) What should be the composition in the melt?

$$ER_B = \frac{wt\%_{B,v}/wt\%_{A,v}}{wt\%_{B,l}/wt\%_{A,l}} = 0.033$$

$$\frac{wt\%_{B,l}}{100-wt\%_{B,l}} = \frac{5/95}{0.033} = 1.6$$

$$wt\%_{B,l} = 160/2.6 = 61.5\text{wt\% B}$$

** Note : In this example there is one alloying element. Whereas in PS7, there are two alloying elements. **