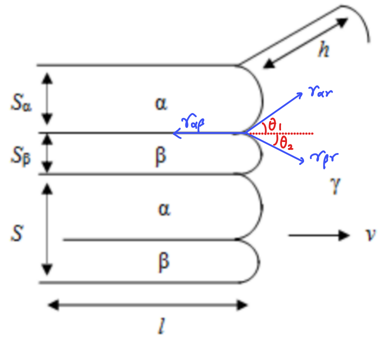
AMSE502 Phase Transformations 상변태론 HW#6

신소재공학과 20222244 조 우 택

1 a) Why the tip of each layer has a curvature?

sol) α, β, liquid 사이의 interfacial energy 가 각각 다르고, 그 balance를 맞추기 위해 tip에 curvature가 존재한다.



$\gamma_{\alpha\beta} = \gamma_{\alpha r}\cos\theta_1 + \gamma_{\beta r}\cos\theta_2$ ... ①

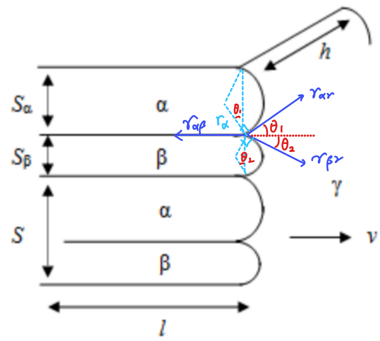
$\gamma_{\alpha r}\sin\theta_1 = \gamma_{\beta r}\sin\theta_2$

$\theta_1 = \theta_2 = 90°$ 일 때 lamella는 curvature를 가지지 않는다.

$\gamma_{\alpha\beta} = 0$, $\gamma_{\alpha r} = \gamma_{\alpha\beta}$ 가 되고, 이 값은 현실과 거리가 멀다.

∴ 각각의 layer는 curvature를 가진다.

b) Estimate the radius of curvature for each layer as a function of layer thickness.



$S_\alpha = 2r_\alpha\cos\theta_1$

$S_\beta = 2r_\beta\cos\theta_2$

$\gamma_{\alpha r}\sin\theta_1 = \gamma_{\beta r}\sin\theta_2$

$\gamma_{\alpha r}^2\sin^2\theta_1 = \gamma_{\beta r}^2\sin^2\theta_2$

$\gamma_{\alpha r}^2(1-\cos^2\theta_1) = \gamma_{\beta r}^2(1-\cos^2\theta_2)$

$\gamma_{\alpha r}^2 - \gamma_{\alpha r}^2\cos^2\theta_1 = \gamma_{\beta r}^2 - \gamma_{\beta r}^2\cos^2\theta_2$

$\cos^2\theta_2 = \frac{1}{\gamma_{\beta r}^2}\left(\gamma_{\beta r}^2 - \gamma_{\alpha r}^2 + \gamma_{\alpha r}^2\cos^2\theta_1\right)$

$= 1 - \frac{\gamma_{\alpha r}^2}{\gamma_{\beta r}^2}(1-\cos^2\theta_1)$

$\cos\theta_2 = \sqrt{1 - \frac{\gamma_{\alpha r}^2}{\gamma_{\beta r}^2}(1-\cos^2\theta_1)}$ ... ②

식 ②를 식 ①에 대입

$\gamma_{\alpha\beta} = \gamma_{\alpha r}\cos\theta_1 + \gamma_{\beta r}\cos\theta_2$

$= \gamma_{\alpha r}\cos\theta_1 + \gamma_{\beta r}\sqrt{1 - \frac{\gamma_{\alpha r}^2}{\gamma_{\beta r}^2}(1-\cos^2\theta_1)}$

$\gamma_{\alpha\beta} - \gamma_{\alpha r}\cos\theta_1 = \gamma_{\beta r}\sqrt{1 - \frac{\gamma_{\alpha r}^2}{\gamma_{\beta r}^2}(1-\cos^2\theta_1)}$

$\gamma_{\alpha\beta}^2 - 2\gamma_{\alpha\beta}\gamma_{\alpha r}\cos\theta_1 + \gamma_{\alpha r}^2\cos^2\theta_1 = \gamma_{\beta r}^2 - \gamma_{\alpha r}^2(1-\cos^2\theta_1)$

$\cos\theta_1 = \frac{\gamma_{\alpha\beta}^2 - \gamma_{\beta r}^2 + \gamma_{\alpha r}^2}{2\gamma_{\alpha\beta}\gamma_{\alpha r}}$

$\therefore r_\alpha = \frac{S_\alpha}{2\cos\theta_1} = \frac{S_\alpha\gamma_{\alpha\beta}\gamma_{\alpha r}}{\gamma_{\alpha\beta}^2 - \gamma_{\beta r}^2 + \gamma_{\alpha r}^2}$ ... ③

같은 방법으로,

$r_\beta = \frac{S_\beta}{2\cos\theta_2} = \frac{S_\beta\gamma_{\alpha\beta}\gamma_{\beta r}}{\gamma_{\alpha\beta}^2 - \gamma_{\alpha r}^2 + \gamma_{\beta r}^2}$ ... ④

c) Show that the free energy increase due to the capillary effects is exactly the same as that obtained by considering the α/β interfacial energy.

sol) ΔG of capillary effect

$$\Delta G = \frac{2\gamma_{\alpha r}}{r_\alpha} V_\alpha + \frac{2\gamma_{\beta r}}{r_\beta} V_\beta$$

$$V_\alpha = \frac{S_\alpha}{S} V_m^L \quad , \quad V_\beta = \frac{S_\beta}{S} V_m^L$$

$$\therefore \Delta G = \left(\frac{2\gamma_{\alpha r}}{r_\alpha} S_\alpha + \frac{2\gamma_{\beta r}}{r_\beta} S_\beta \right) \frac{V_m^r}{S}$$

$$= \left(2\frac{\gamma_{\alpha\beta}^2 - \gamma_{\beta r}^2 + \gamma_{\alpha r}^2}{\gamma_{\alpha\beta}} + 2\frac{\gamma_{\alpha\beta}^2 - \gamma_{\alpha r}^2 + \gamma_{\beta r}^2}{\gamma_{\alpha\beta}} \right) \frac{V_m^L}{S} \qquad (\text{from } ③, ④)$$

$$= \frac{2\gamma_{\alpha\beta}}{S} \cdot V_m^L$$

Therefore, the free energy increase due to the capillary effects is exactly the same as that optained by considering the α/β interface energy.

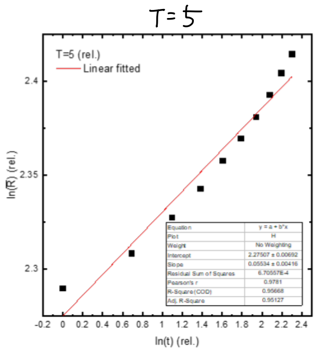
[2] a) $\bar{R} = kt^n$

$\ln \bar{R} = \ln k + n \ln t$

$\ln \bar{R}$ 과 $n \ln t$ 가 비례한다.

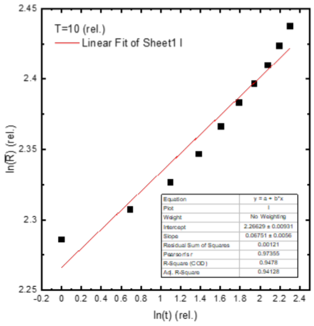
[Fig 1]

T=5



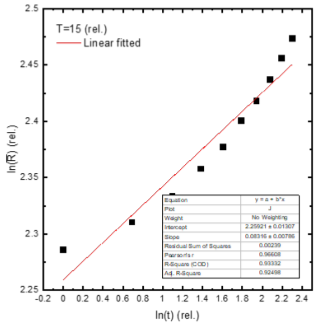
$n = 0.05534$

T=10



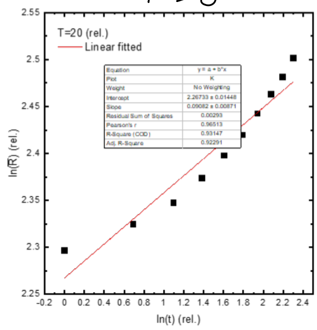
$n = 0.06751$

T=15



$n = 0.08316$

T=20



$n = 0.09082$

b) [Fig 1] 로부터,

T가 증가할수록 grain size가 커진다.

$$\frac{d\bar{R}}{dt} = \lambda v = \lambda v_0 \exp\left(-\frac{\Delta G^*}{RT}\right)\frac{\Delta G_{df}}{RT} = nkt^{n-1}$$

$$\frac{d\bar{R}}{dt} = \lambda v = \lambda v_0 \exp\left(-\frac{\Delta G^*}{RT}\right)\left(1 - \exp\left(-\frac{\Delta G_{df}}{RT}\right)\right)$$

if $\Delta G_{df} \ll RT$

$$\frac{d\bar{R}}{dt} = \lambda v_0 \exp\left(-\frac{\Delta G^*}{RT}\right)\frac{\Delta G_{df}}{RT}$$

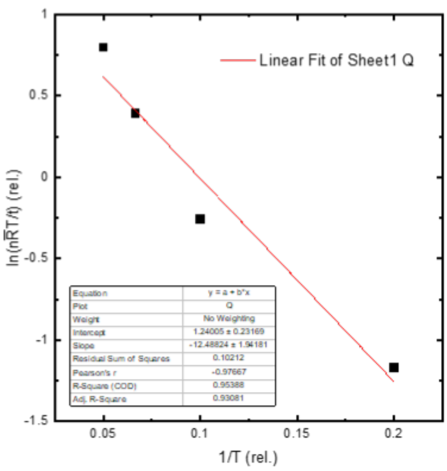
$$= nkt^{n-1}$$

$$\ln(Tnkt^{n-1}) = \ln\left(\lambda v_0 \frac{\Delta G_{df}}{R}\right) - \frac{\Delta G^*}{RT}$$

if ΔG_{df} = constant,

$$\ln(Tnkt^{n-1}) = -\frac{\Delta G^*}{RT} + C \qquad (C는\ 상수)$$

$$\ln\left(\frac{n\bar{R}T}{t}\right) = -\frac{\Delta G^*}{RT} + C$$



$\therefore \Delta G^* = -12.5R$