HW 3

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1. Work done on surroundings during infinitesimal growth of precipitate:

$\Delta P dV$

At equilibrium, change in energy $= 0$, so change in interfacial energy $\gamma_e dA = \Delta P dV$

$$\Delta P = \gamma_e \frac{dA}{dV}$$

For spherical precipitates,

$$dA = d(4\pi r^2) = 8\pi r\, dr$$

$$dV = d(4/3\, \pi r^3) = 4\pi r^2 dr$$

$$\Delta P = \gamma_e \frac{8\pi r\, dr}{4\pi r^2 dr} = \frac{2\gamma_e}{r}$$

2.

The LSW theory states that the minimization of surface energy of particles leads to the growth of large particles and the disappearance of small ones. This is because larger particles have a lower area-to-volume ratio. If the process of coarsening is rate-limited by diffusion,

$\langle r \rangle^3 \propto kt$

If adsorption of atoms to the particle surface is rate-limiting:

$\langle r \rangle^2 \propto kt$

The LSW theory was derived for the interface of a small and large particle, where the volume fraction of the ~~growing~~ coarsening phase is close to zero. ~~i.e. no particle-particle interactions~~

The 2 papers could not definetively determine whether square or cube rate law applies. According to S. Tang et al., the rate is controlled by slow diffusion in the γ/γ' interface. ~~The~~ MacKay et al. argued that elastic strain caused by mismatch between γ and γ' lattices explained the deviation from LSW theory. The level of mismatch was varied with Mo-alloying. Tang et al. argued that interfacial dislocations acted as a sink for smaller atoms, leading to chemical gradients, which fueled the diffusion-driven growth.

3. a) The precipitate formed on the grain boundary, since the change in interfacial energy of the system is smaller when the precipitate - grain interface replaces a grain-grain interface than when a precipitate - grain interface ~~replaces an equal area of~~ is formed in a single crystal.

b) The cooling must have been slow enough (in relation to diffusion) to ~~enable~~ prevent a level of undercooling inside the crystal where homogeneous nucleation is possible. In other words, depletion of alloying elements from the matrix to the boundary was faster than the "buildup" of undercooling (driving force for nucleation) inside the matrix.

c). $r = \frac{2\gamma}{\Delta P}$

On boundary C, radius is bigger than on A or B. Since the ΔP can be assumed to be uniform, γ must be different. This may be caused by difference in grain orientation, causing more mismatch.

4. Atoms above the solubility limit of the matrix will diffuse to the boundary. Less "~~new~~" additional interface energy is created when precipitates form at the boundary. The segregated composition may favour the precipitating phase.

5. $\gamma_{\alpha\alpha} = 2\cos\theta\, \gamma_{\alpha\beta}$

$$\cos\theta = \frac{\gamma_{\alpha\alpha}}{2\gamma_{\alpha\beta}} = \frac{600}{2 \cdot 500} = 0.6$$

$$\theta = 53.1^\circ$$

$$\frac{1}{2}(2 + 0.6)(1 - 0.6)^2 = 0.208 = \frac{\Delta G^*_{HET}}{\Delta G^*_{HOM}}$$

$$\Delta G^*_{HET} = 0.208\, \Delta G^*_{HOM}$$

6. a) Regular solution:

$$\Delta G^{mix} = X_A X_B \beta + RT (X_A \ln X_A + X_B \ln X_B)$$

a) $\Delta G^{mix} = X_A (1 - X_A) \beta + RT (X_A \ln X_A + (1 - X_A) \ln (1 - X_A))$

$$= (-X_A^2 + X_A) \beta + RT (X_A \ln X_A + (1 - X_A) \ln (1 - X_A))$$

$$\frac{\partial}{\partial X_A} \Delta G^{mix} = (-2X_A + 1) \beta + RT \left(\ln X_A + X_A \cdot \frac{1}{X_A} + (-1)(\ln (1 - X_A)) + (1 - X_A) \left(\frac{-1}{1 - X_A} \right) \right)$$

$$= (-2X_A + 1) \beta + RT \left(\ln X_A + 1 - \ln (1 - X_A) - 1 \right)$$

$$= (-2X_A + 1) \beta + RT \left(\ln \left(\frac{X_A}{1 - X_A} \right) \right)$$

$$\frac{\partial}{\partial^2 X_A} \Delta G^{mix} = -2\beta + RT \left(\frac{1}{X_A} - \frac{-1}{1 - X_A} \right)$$

$$= -2\beta + RT \left(\frac{1}{X_A} + \frac{1}{1 - X_A} \right)$$

b) $$0 = -2\beta + RT \left(\frac{1}{0.5} + \frac{1}{1 - 0.5} \right) = -2\beta + RT \cdot 4$$

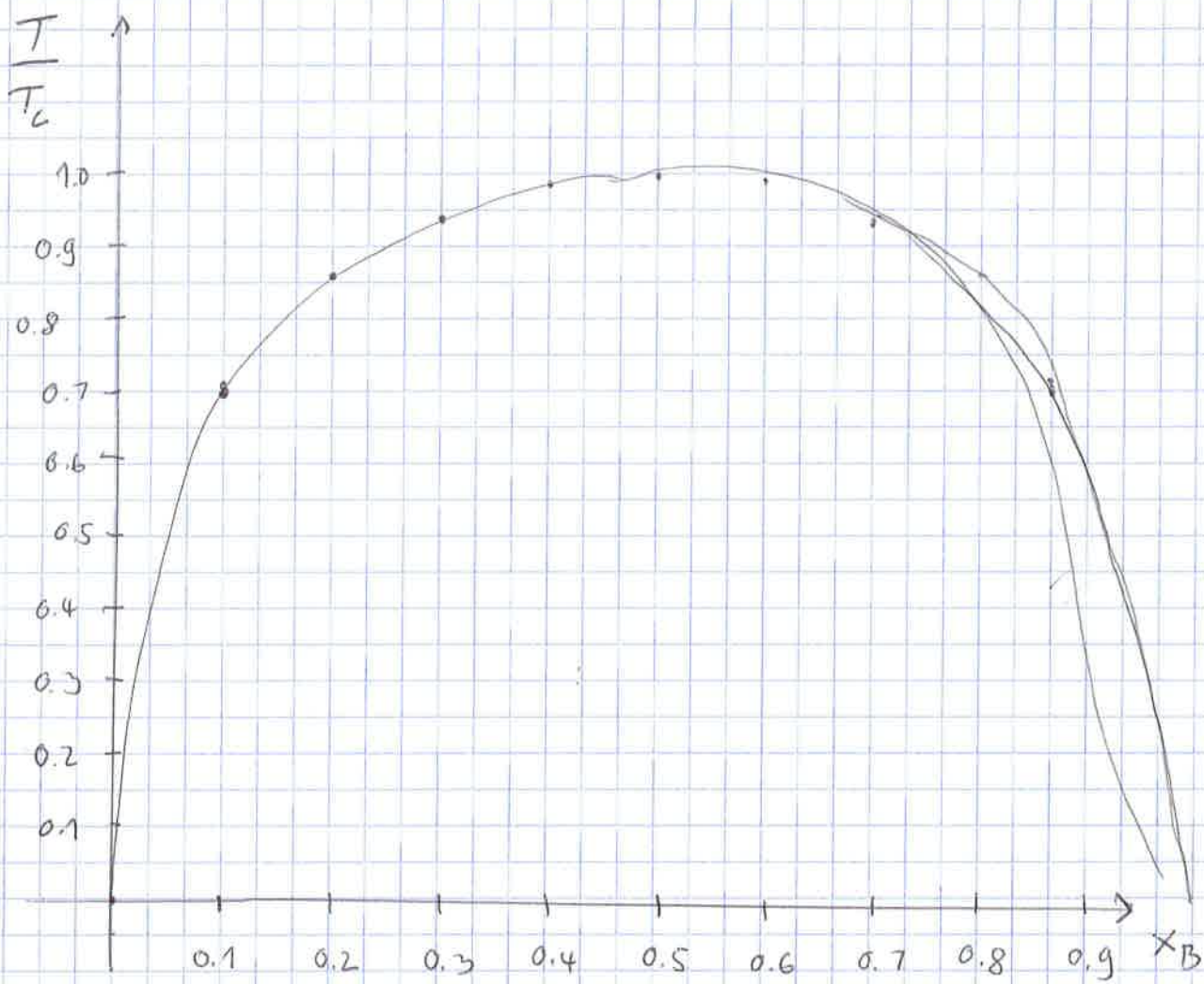
$$T = \frac{+2\beta}{4R} = \frac{\beta}{2R}$$

c) $$(-2X_A + 1) \beta + RT \left(\ln \left(\frac{X_A}{1 - X_A} \right) \right) = 0$$

$$T = \frac{-(-2X_A + 1) \beta}{R \ln \left(\frac{X_A}{X_B} \right)} = \frac{(2X_A - 1) \beta}{R \ln \left(\frac{X_A}{X_B} \right)}$$

$$\frac{T}{T_c} = \frac{(2x_A - 1)\cdot 2}{\ln\left(\frac{x_A}{x_B}\right)} = \frac{(2 - 2x_B - 1)\cdot 2}{\ln\left(\frac{1}{x_B} - 1\right)}$$

$$= \frac{2 - 4x_B}{\ln\left(\frac{1}{x_B} - 1\right)}$$



7. a)

The JMAK theory assumes that the growth rate does not depend on the extent of transformation which is not true at later stages of growth, where nuclei come in contact with each other. The extended volume is the amount of volume growth that would happen if the grains would not impinge on one another.

b) The Avrami exponent may help determine the nucleation site and whether there is site saturation or not. $n=3$ implies that growth is limited to 2 dimensions and nucleation is constant, or that sites are saturated (no nucleation) and growth happens in 3 dimensions. etc.

c) $N = V\dot{N}\,d\tau$ $\qquad V_\beta = \pi r^2 \cdot h$

~~$dV_\beta = \pi r^2 h \dot{g}$~~ $\qquad dV_\beta = \pi h \dot{g}^2 (t-\tau)^2 V\dot{N}\,d\tau$

$$V_\beta = \frac{\pi h}{3} V\dot{N}\dot{g}^2 t^3$$

$$\ln(1-Y) = -\frac{V_\beta}{V} = -\frac{\pi h}{3}\dot{N}\dot{g}^2 t^3$$

$$Y = 1 - \exp(-kt^n), \quad k = \frac{\pi h}{3}\dot{N}\dot{g}^2, \quad n = 3$$