

第二章 液态金属及其加工

2.1 液态金属的结构与性质

2.2 液态金属凝固结晶的热力学与动力学

2.3 液态金属的冶金处理

2.2 液态金属凝固结晶的热力学与动力学

- 金属凝固结晶的热力学条件
- 均质形核
- 异质形核
- 晶体生长

凝固的热力学条件

$$\begin{aligned}\Delta G &= G_L - G_S \\ &= (H_L - TS_L) - (H_S - TS_S) \\ &= (H_L - H_S) - T(S_L - S_S) \\ &= \Delta H - T\Delta S\end{aligned}$$

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

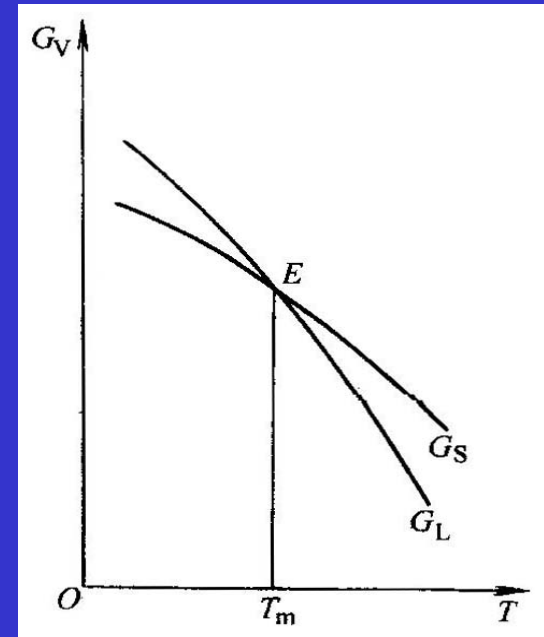
$$\Delta G_v = \Delta H_v - T\Delta S_v = \frac{\Delta G_m}{V_m}$$

凝固的热力学条件

$$\Delta G_V = \Delta H_V - T_m \Delta S_V = 0$$

$$\Delta S_V = \frac{\Delta H_V}{T_m}$$

$$\Delta G_V = \frac{\Delta H_V \Delta T}{T_m} = \frac{\Delta H_m \Delta T}{V_m T_m}$$



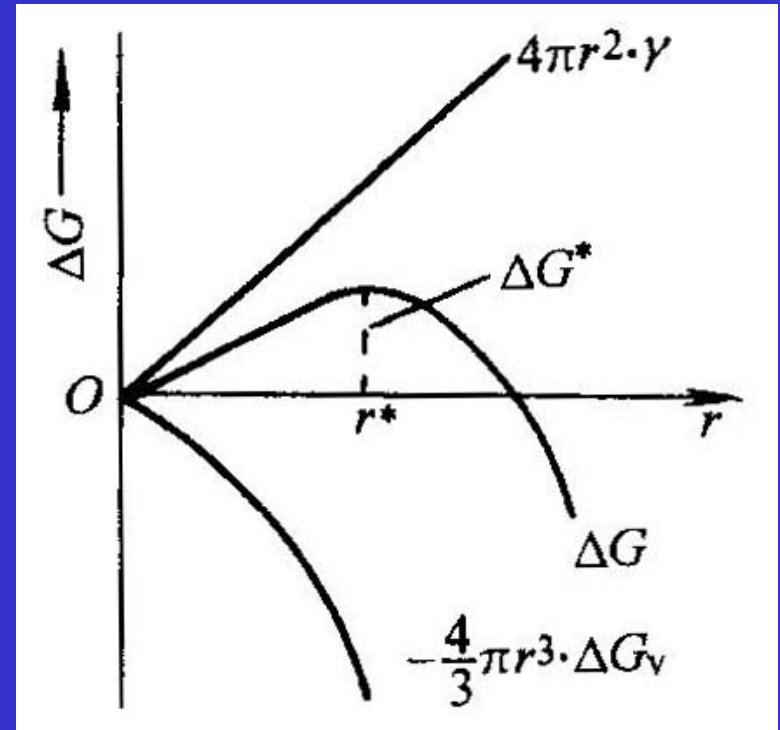
液 - 固两相自由能与温度的关系

均质形核

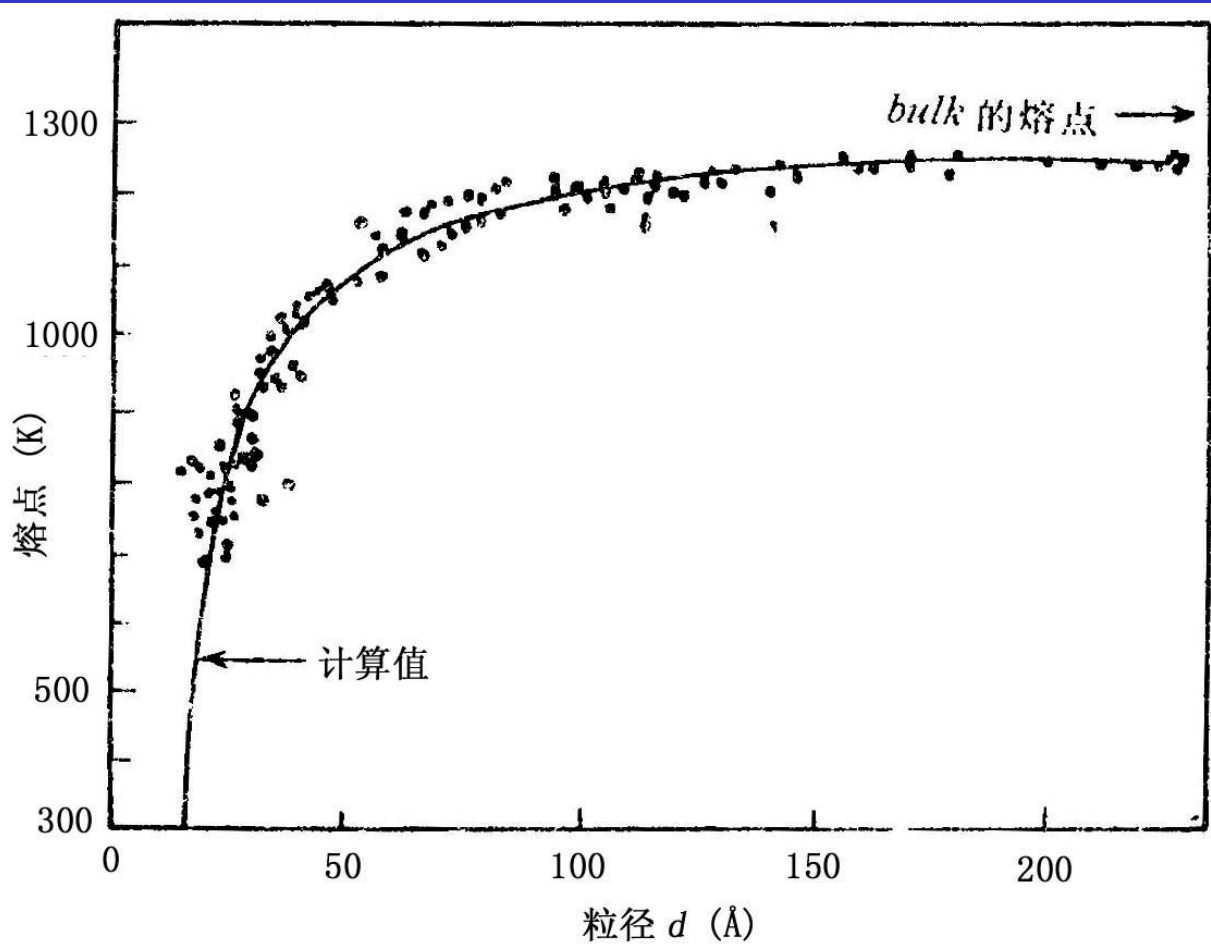
$$\Delta G_{\text{均}} = -\frac{4}{3}r^3 \Delta G_V + 4\pi r^2 \sigma_{CL}$$

$$r_{\text{均}}^* = \frac{2\sigma_{CL}}{\Delta H_V} \cdot \frac{T_m}{\Delta T}$$

$$\Delta G_{\text{均}}^* = \frac{16}{3} \pi \frac{\sigma_{CL}^3 T_m^2}{\Delta H_V^2 \Delta T^2} = \frac{1}{3} A^* \sigma_{CL}$$



小尺寸金属的熔点



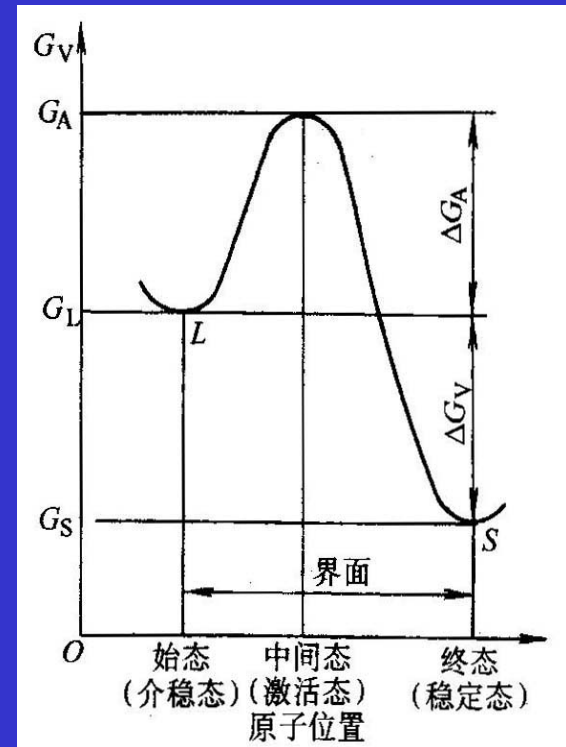
Au 微粒的熔点与粒径的关系

均质形核

$$I_{\text{均}} = f_0 N^*$$

$$N^* = N_L \exp\left(-\frac{\Delta G_{\text{均}}^*}{k_B T}\right)$$

$$f_0 = N_s v_p \exp\left(-\frac{\Delta G_A}{k_B T}\right)$$

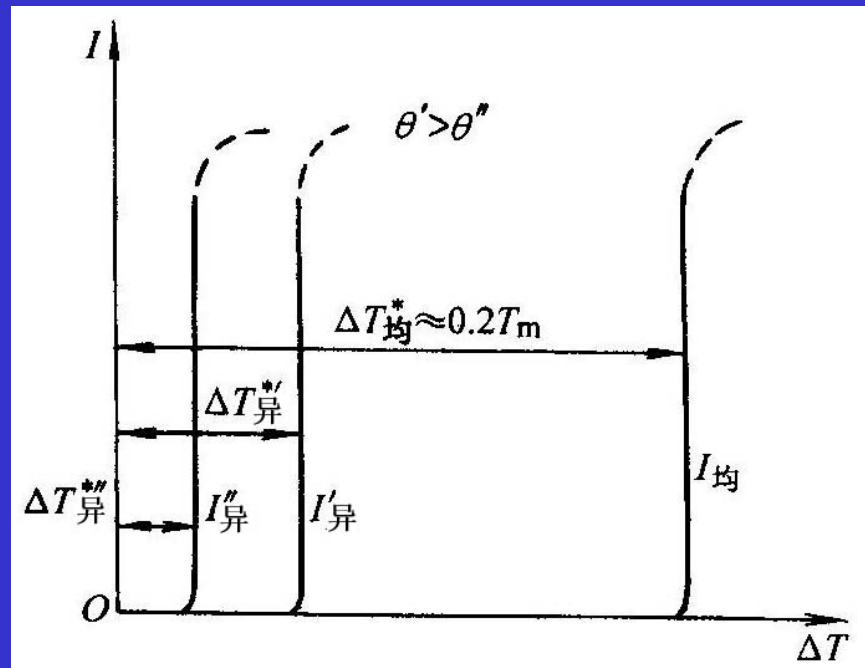


金属原子在结晶过程中的自由能变化

均质形核率

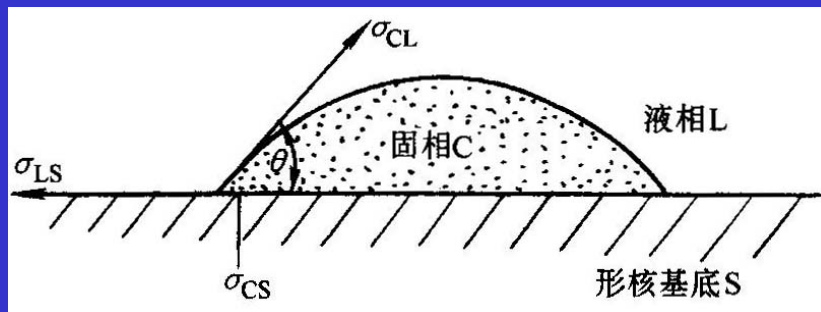
$$I_{\text{均}} = \nu N_S p N_L \exp\left[-\left(\frac{\Delta G_A + \Delta G_{\text{均}}^*}{k_B T}\right)\right] = k_1 \exp\left[-\left(\frac{\Delta G_A + \Delta G_{\text{均}}^*}{k_B T}\right)\right]$$

$$I_{\text{均}} \propto e^{-\frac{1}{\Delta T^2}}$$



异质形核

$$\sigma_{LS} = \sigma_{CS} + \sigma_{CL} \cos \theta$$



$$\Delta G_{\text{异}} = -V_C \Delta G_V + A_{CS} (\sigma_{CS} - \sigma_{LS}) + A_{CL} \sigma_{CL}$$

$$V_C = \int_0^\theta \pi (r \sin \theta)^2 d(r - r \cos \theta) = \frac{\pi r^3}{3} (2 - 3 \cos \theta + \cos^3 \theta)$$

$$A_{CL} = \int_0^\theta 2\pi r \sin \theta (r d\theta) = 2\pi r^2 (1 - \cos \theta)$$

$$A_{CS} = \pi (r \sin \theta)^2 = \pi r^2 \sin^2 \theta = \pi r^2 (1 - \cos^2 \theta)$$

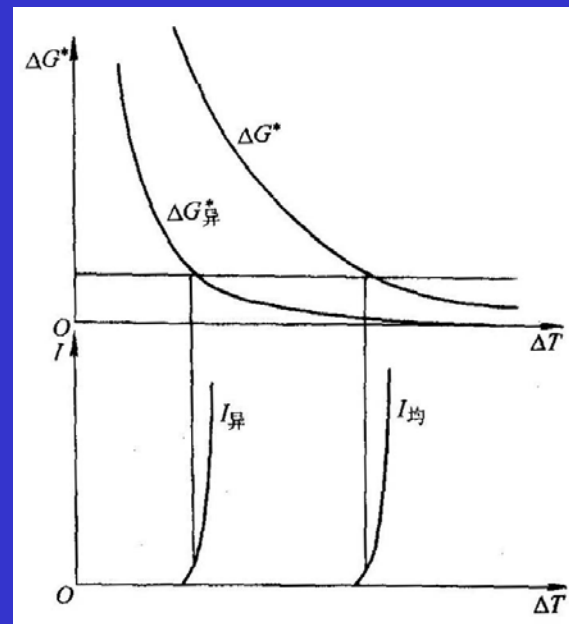
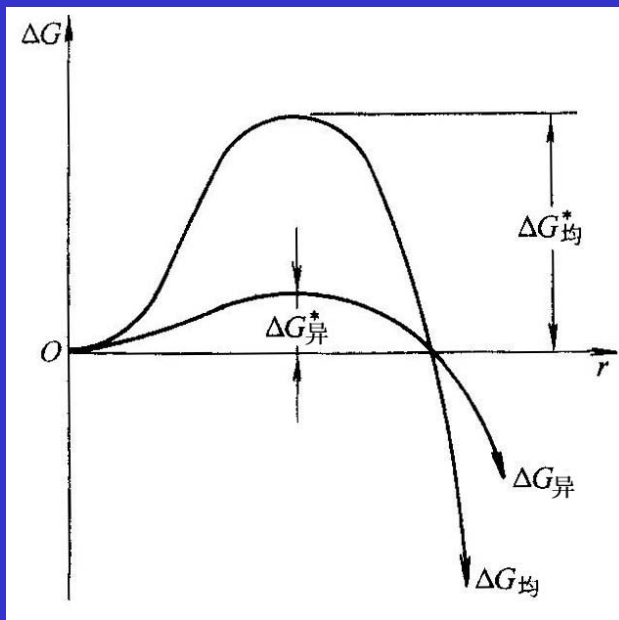
$$\Delta G_{\text{异}} = \left[-\frac{4}{3} \pi r^3 \Delta G_V + 4\pi r^2 \sigma_{CL} \right] \cdot \left[\frac{2 - 3 \cos \theta + \cos^3 \theta}{4} \right]$$

$$f(\theta) = \frac{2 - 3 \cos \theta + \cos^3 \theta}{4} = \frac{(2 + \cos \theta)(1 - \cos \theta)^2}{4}$$

$$\Delta G_{\text{异}} = \Delta G_{\text{均}}^* f(\theta)$$

$$r_{\text{异}}^* = \frac{2\sigma_{CL}}{\Delta G_V} = \frac{2\sigma_{CL}}{\Delta H_V \Delta T} T_m$$

$$\Delta G_{\text{异}}^* = \frac{16\pi\sigma_{CL}^3}{3\Delta G_V^2} \cdot f(\theta) = \Delta G_{\text{均}}^* \cdot f(\theta) = \frac{1}{3} A^* \sigma_{CL} \cdot f(\theta)$$



异质形核率

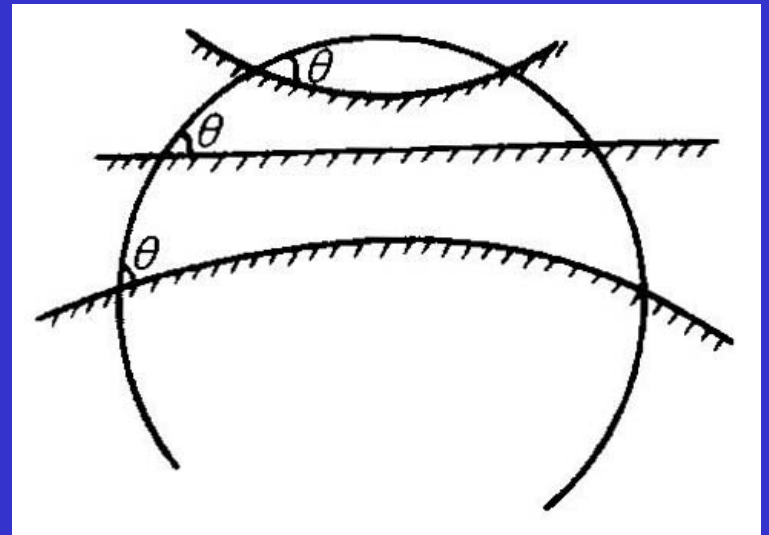
$$I_{\text{异}} = f_1 N_1^* = f_1 N_L^* \exp\left(-\frac{\Delta G_{\text{异}}^*}{k_B T}\right)$$

$$= f_1 N_L^* \exp\left[-\frac{\Delta G_{\text{均}}^* f(\theta)}{k_B T}\right]$$

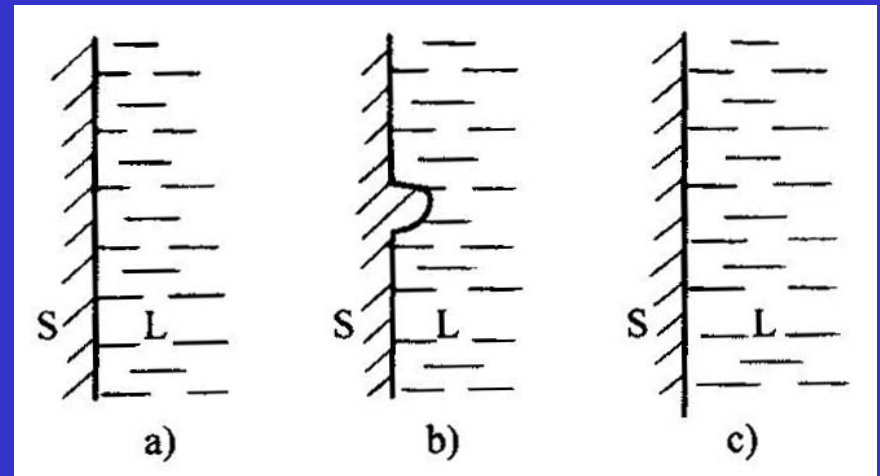
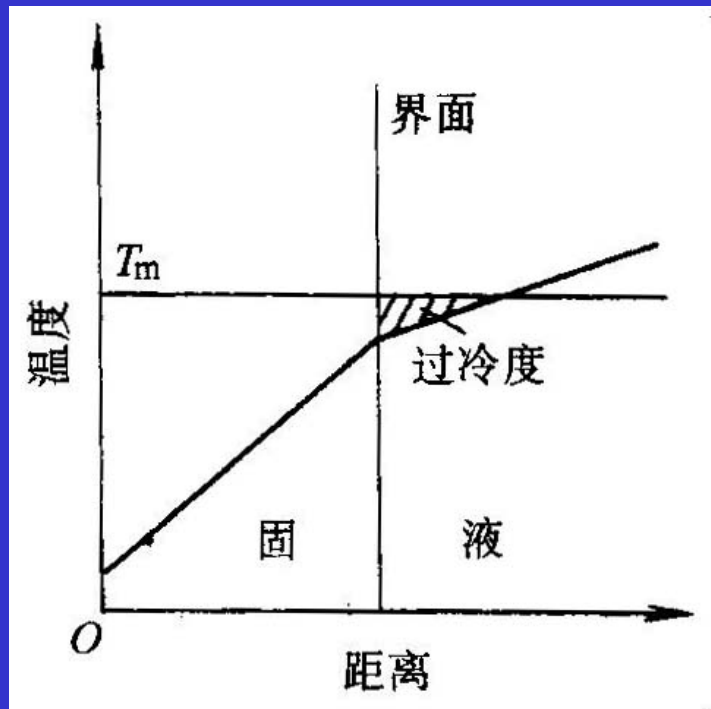
$$= f_1 N_L^* \exp\left[-\frac{B \cdot f(\theta)}{\Delta T^2}\right]$$

影响异质形核率的因素

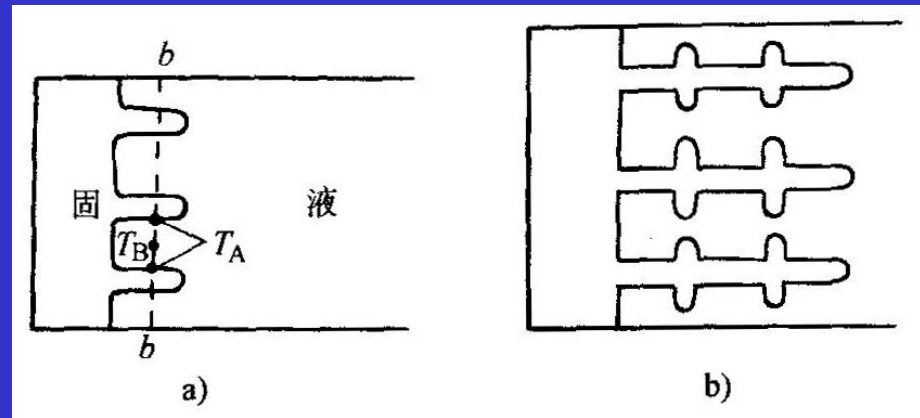
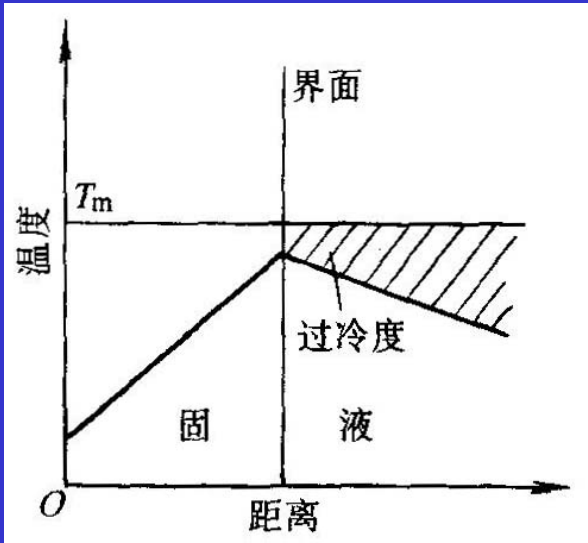
$$\delta = \frac{|a_s - a_c|}{a_c} \times 100\%$$



正温度梯度下的凝固界面形态



负温度梯度下的凝固界面形态



Jackson因子与界面形态

$$\Delta G_s = \Delta H - T\Delta S = (\Delta u + P\Delta V) - T\Delta S \approx \Delta u - T\Delta S$$

$$\frac{\Delta H_0}{\nu}(\eta + B)$$

$$\frac{\Delta H_0}{\nu}(\eta x + B)$$

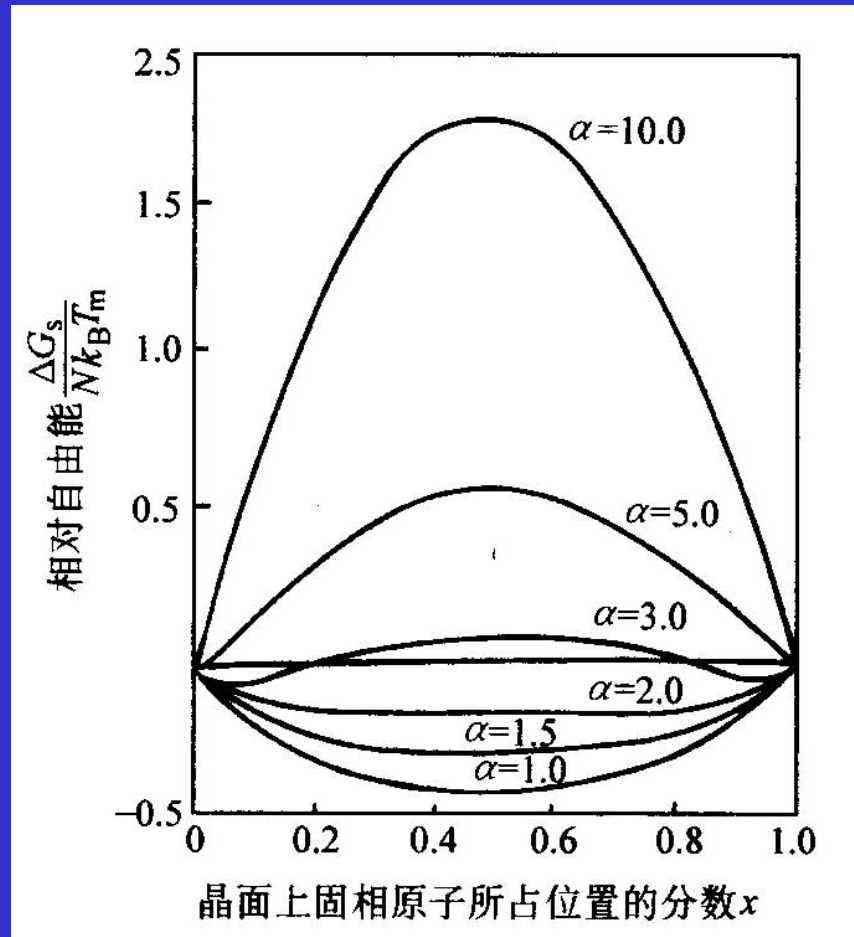
$$N_A \left[\frac{\Delta H_0}{\nu}(\eta + B) - \frac{\Delta H_0}{\nu}(\eta x + B) \right] = \frac{\Delta H_0 N_A}{\nu} \eta (1 - x) = \Delta u$$

$$\Delta S = -N_A k_B [x \ln x + (1 - x) \ln(1 - x)]$$

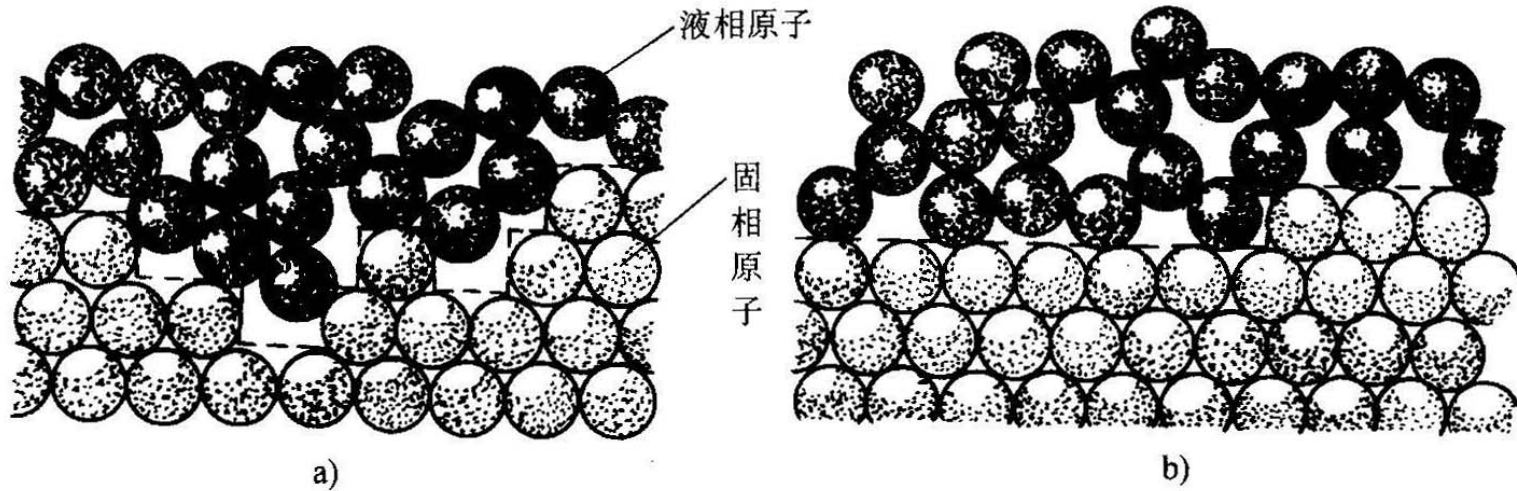
$$\frac{\Delta G_s}{N_A k_B T_m} = \alpha x(1 - x) + x \ln x + (1 - x) \ln(1 - x)$$

Jackson因子与界面形态

$$\alpha = \frac{\Delta H_0}{k_B T_m} \cdot \frac{\eta}{\nu}$$

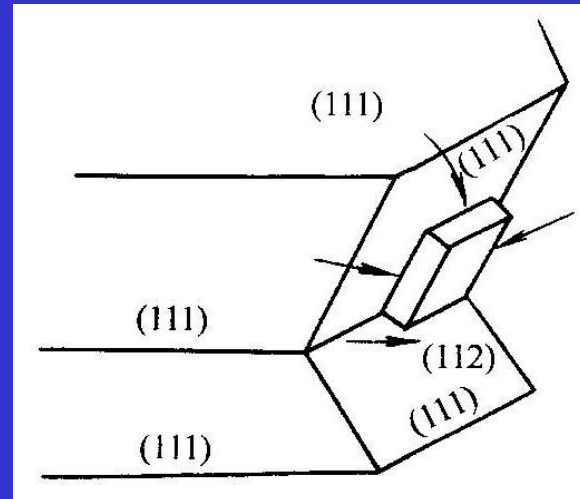
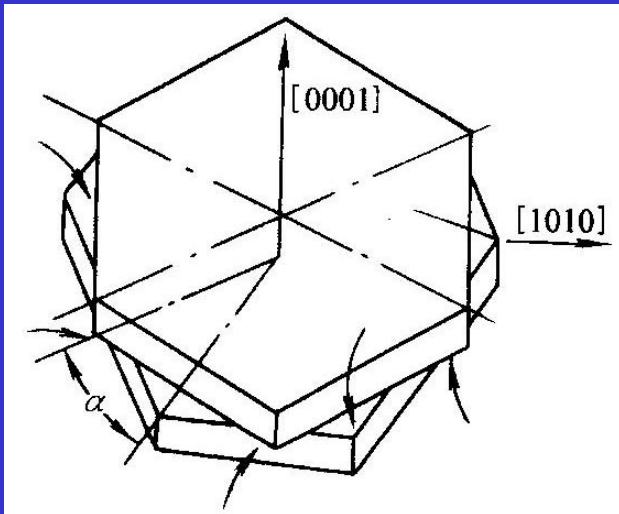
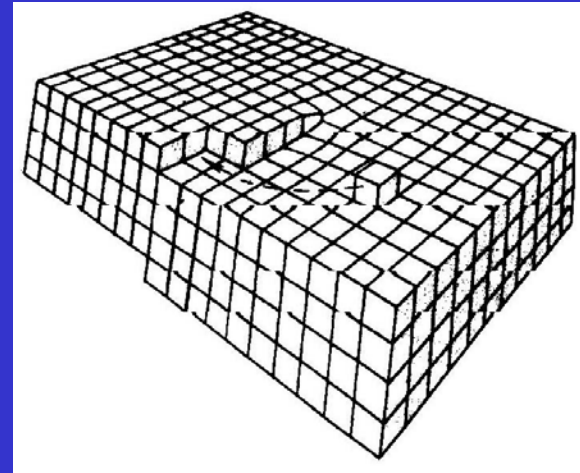
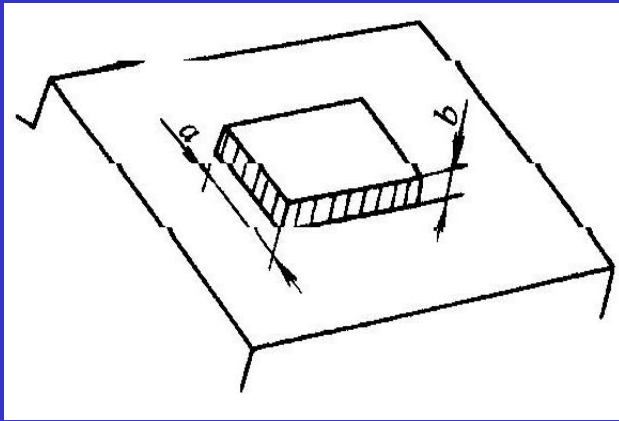


粗糙与光滑界面



a) 粗糙界面模型 b) 平整界面模型

二维和缺陷生长机制



不同生长机制的生长速度与过冷度的关系

连续生长

$$v_1 = K_1 \cdot \Delta T_K$$

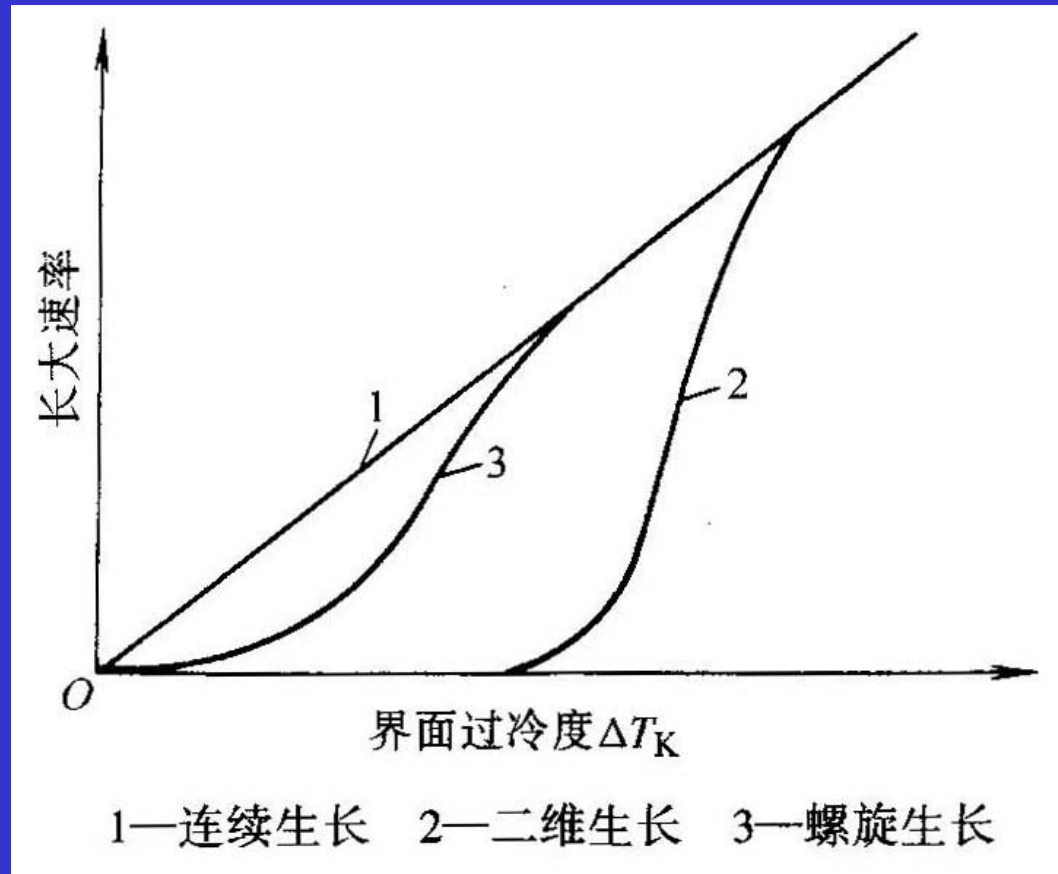
二维台阶生长

$$v_2 = K_2 \cdot e^{-B/\Delta T_K}$$

螺旋位错生长

$$v_3 = K_3 \cdot \Delta T_K^2$$

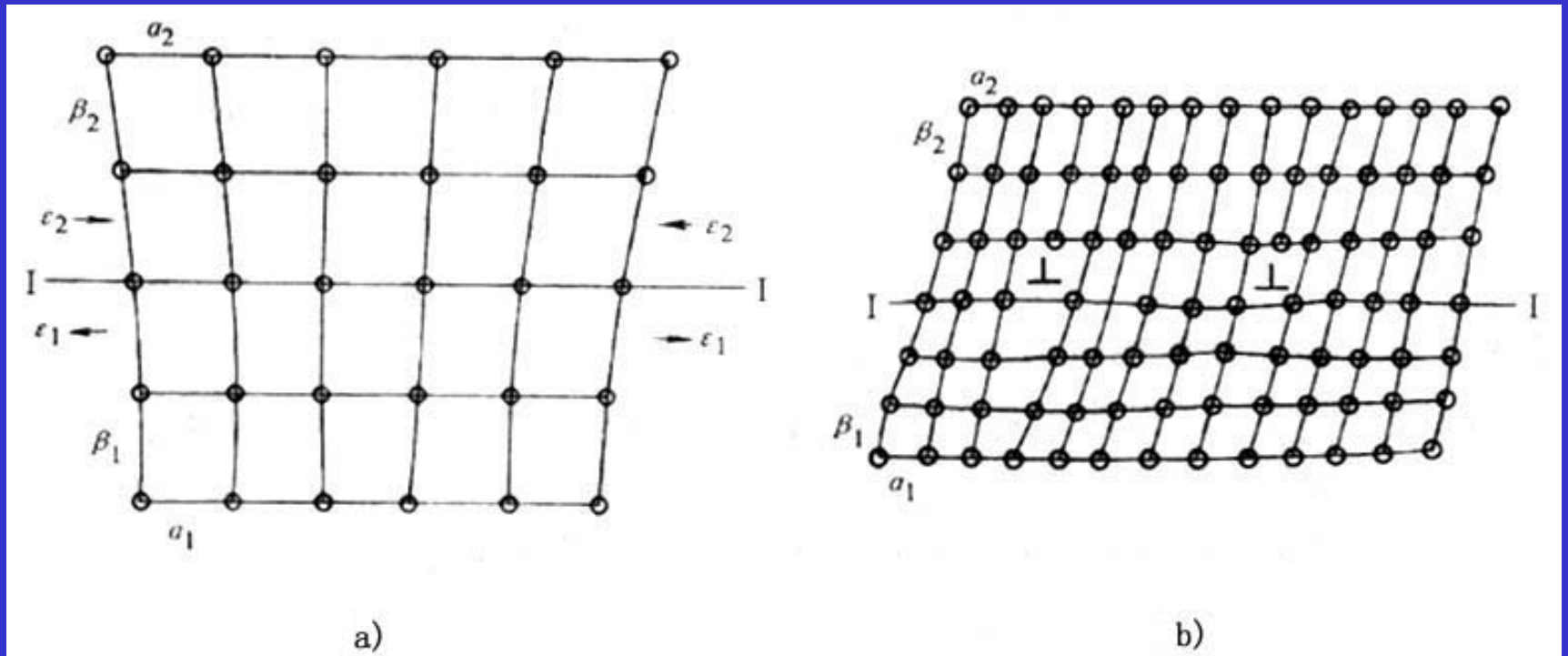
不同生长机制的生长速度与过冷度的关系



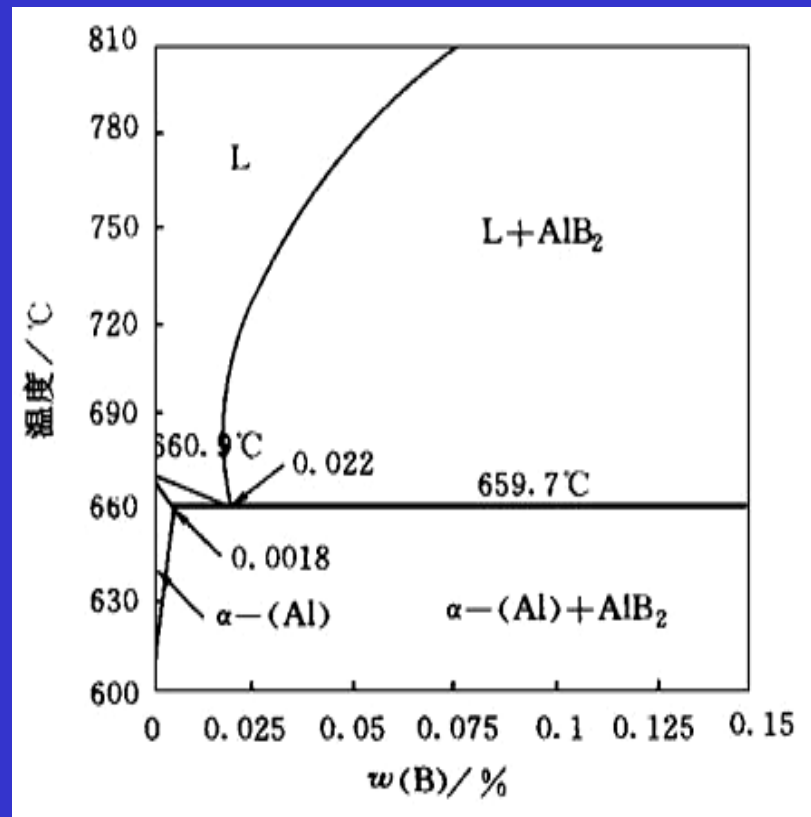
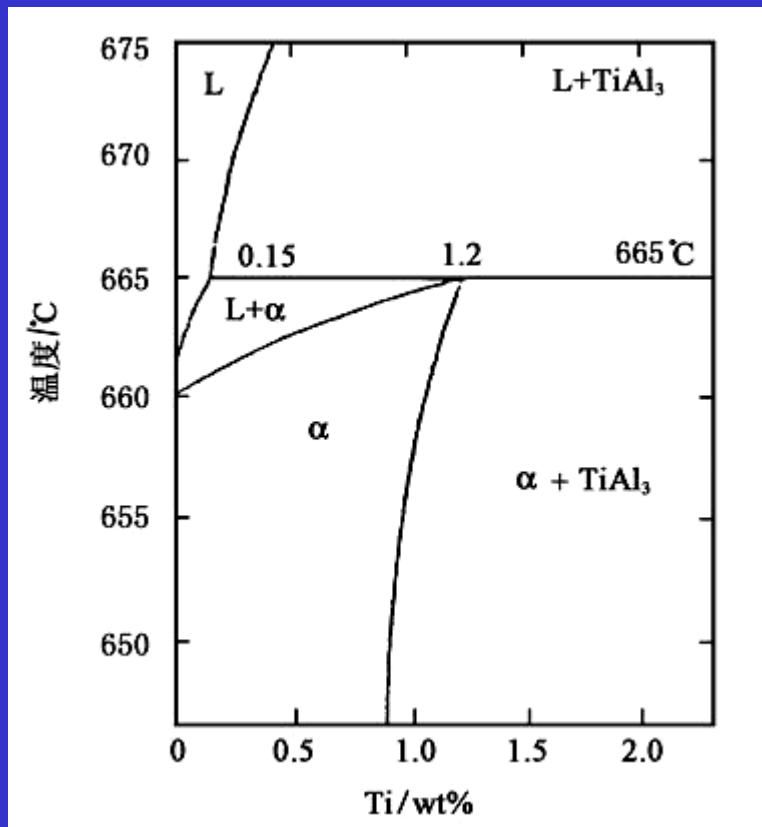
2.3 液态金属的冶金处理

- 影响形核的冶金处理
- 影响生长的冶金处理

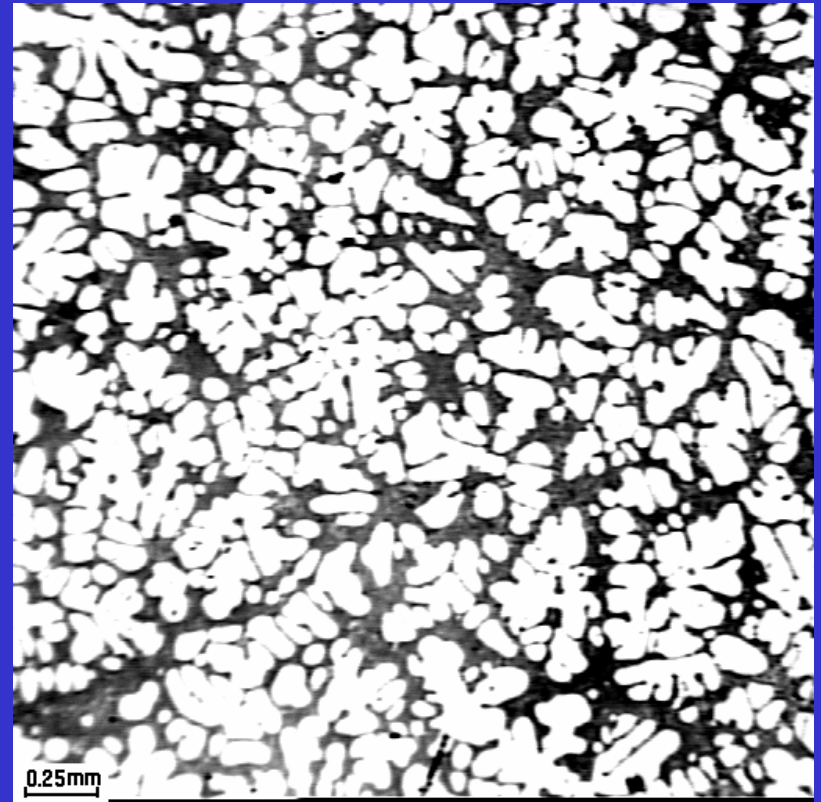
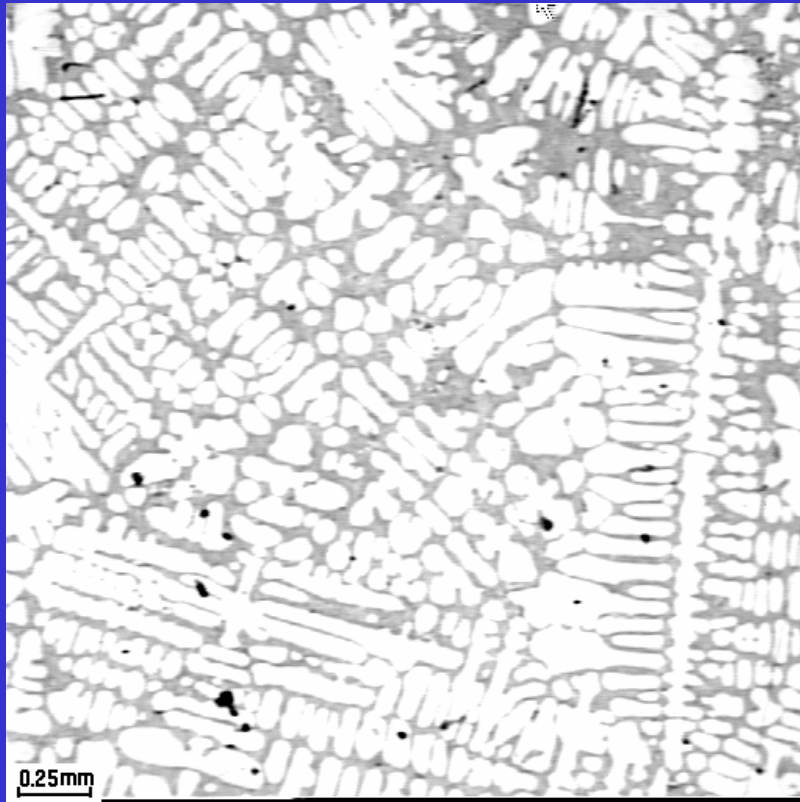
共格和半共格关系



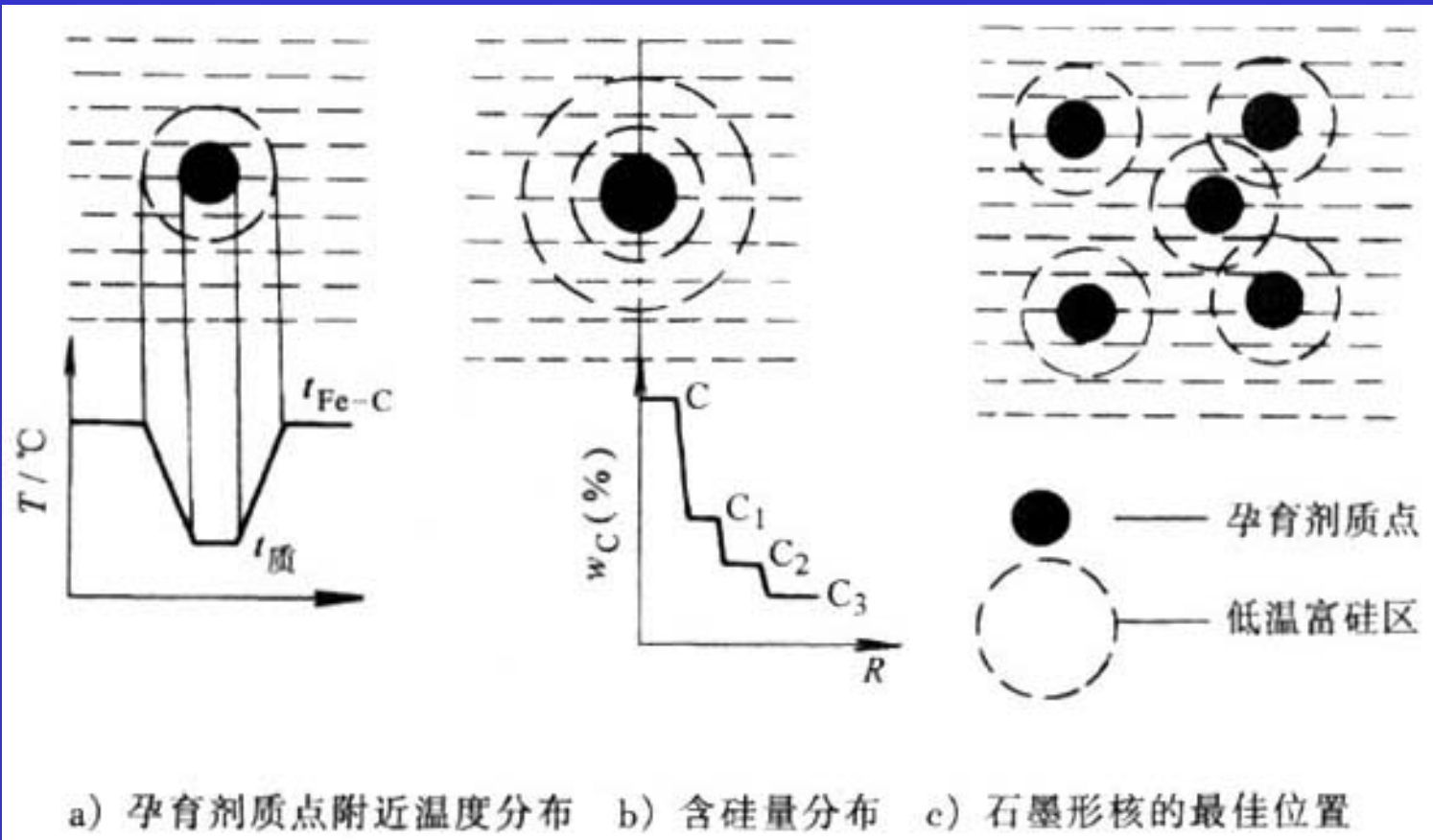
Al-Ti 和 Al-B 相图



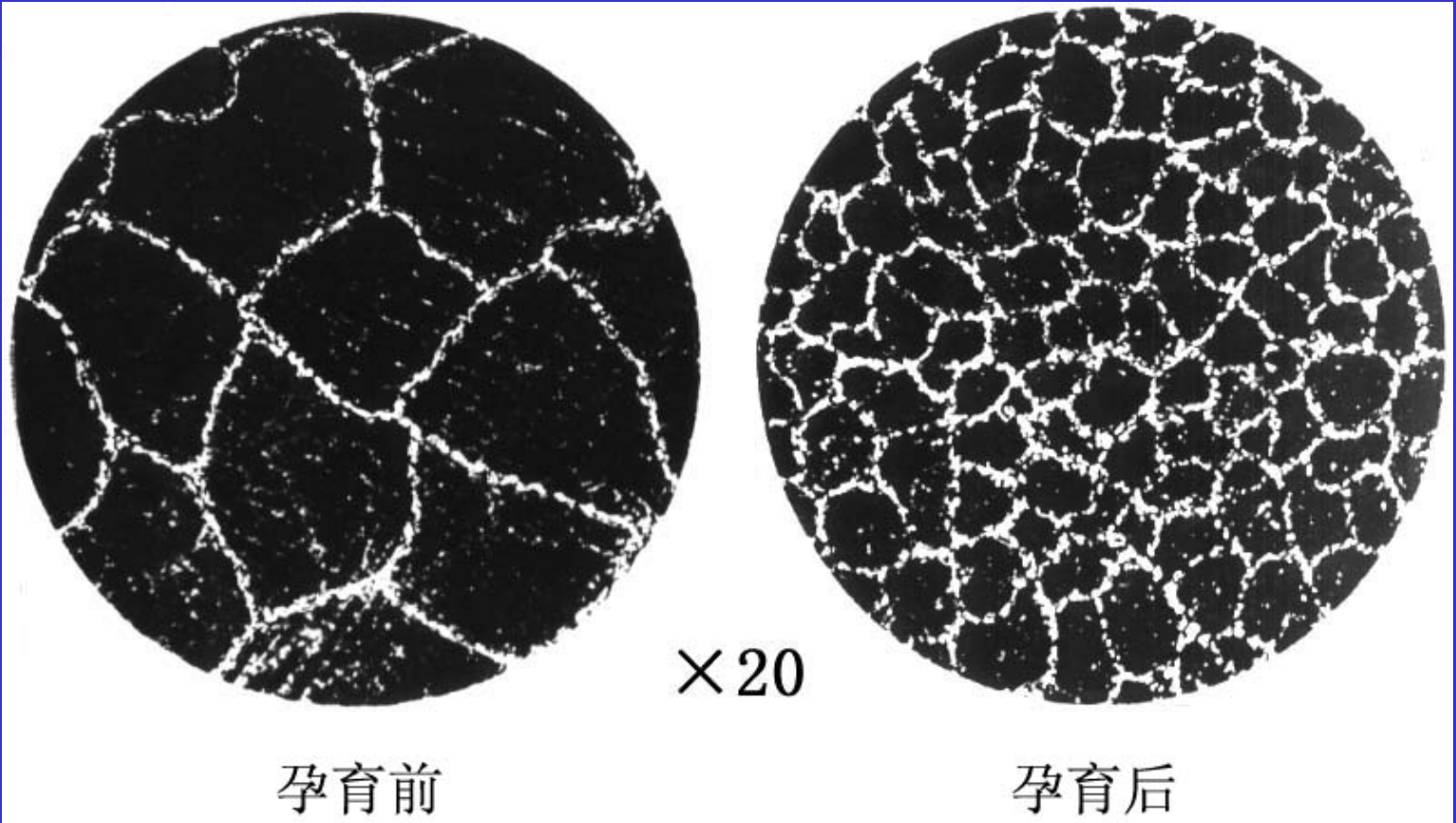
细化处理前后Al-7Si合金的组织



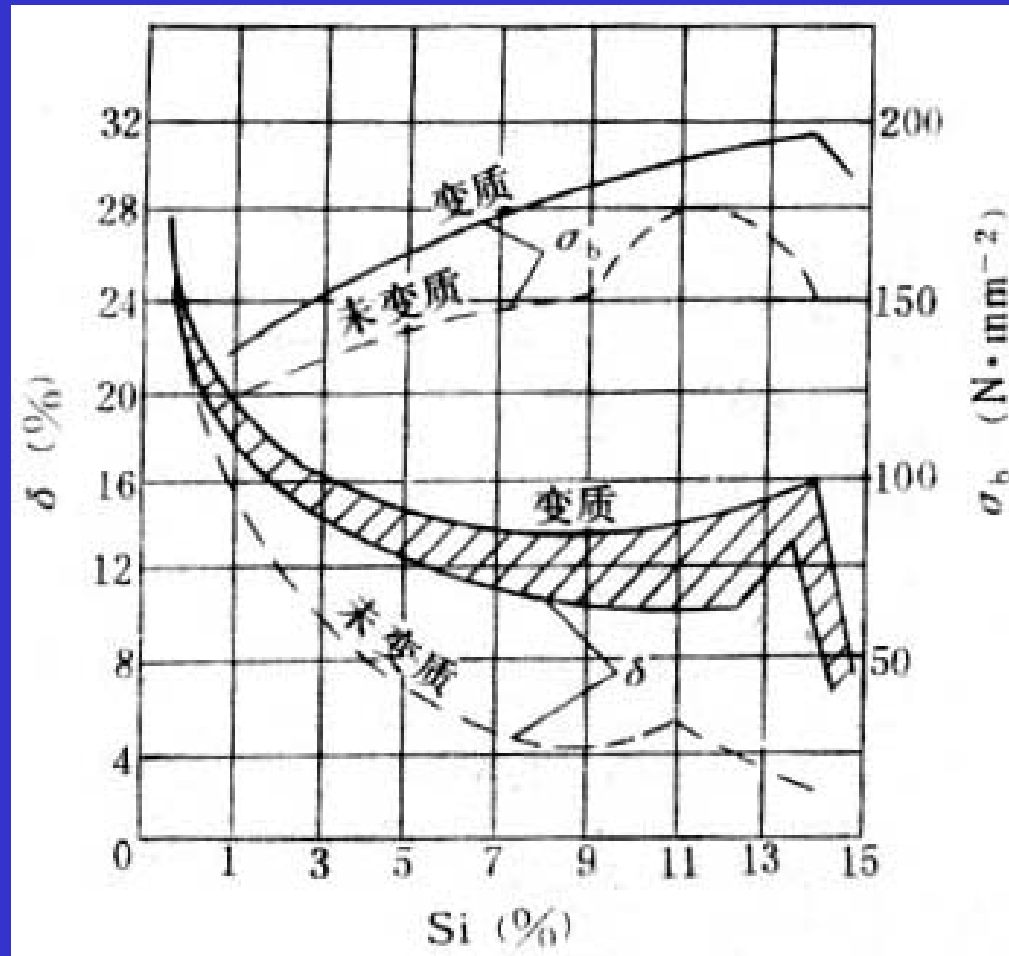
Si对铸铁的孕育作用机理



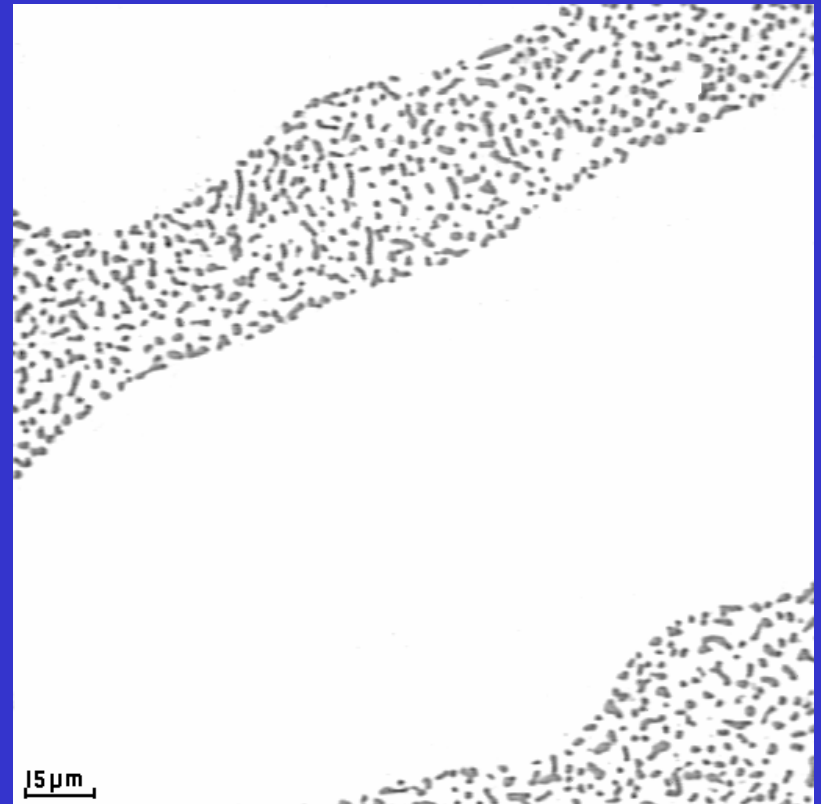
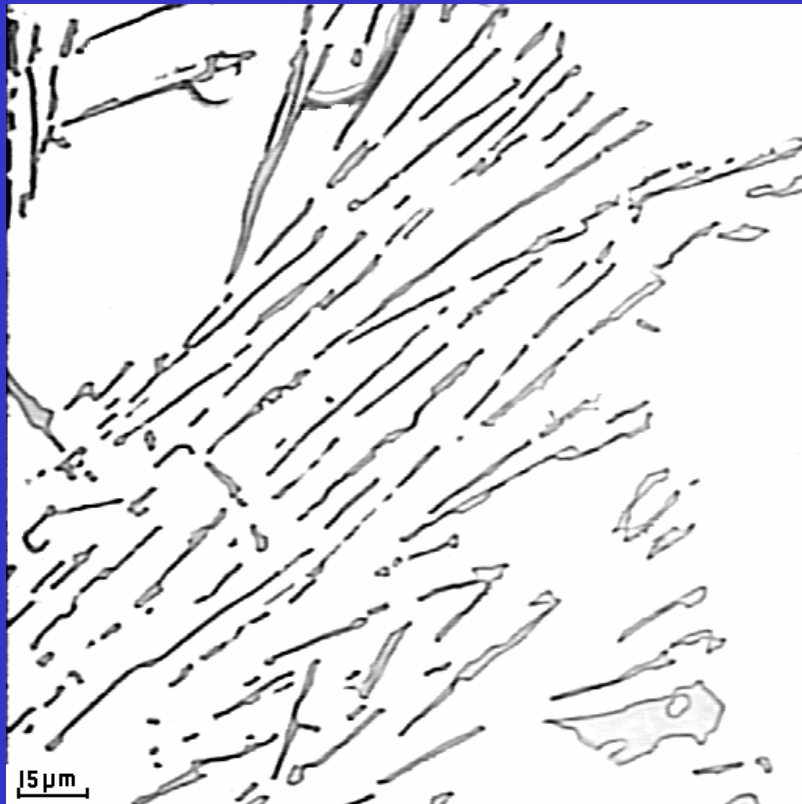
孕育前后的灰铁晶粒度



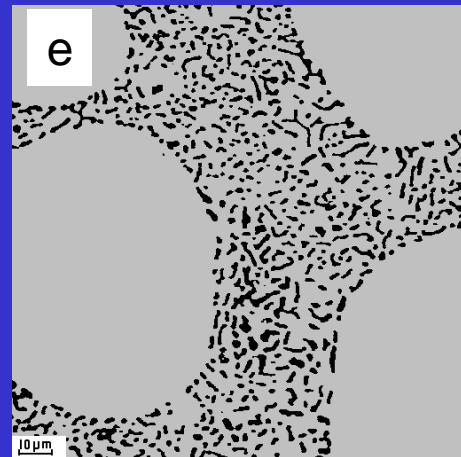
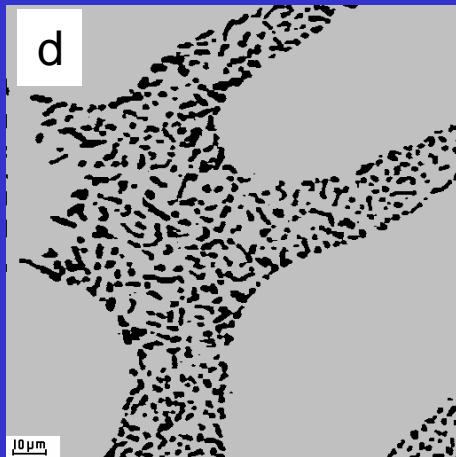
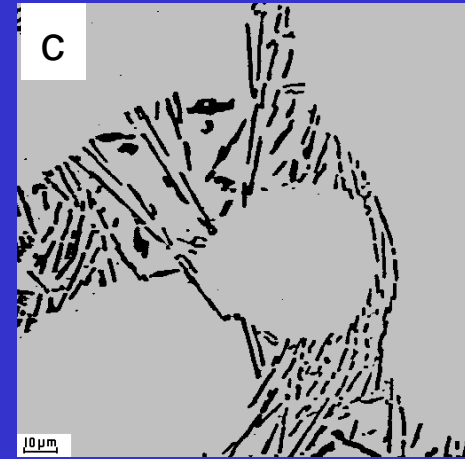
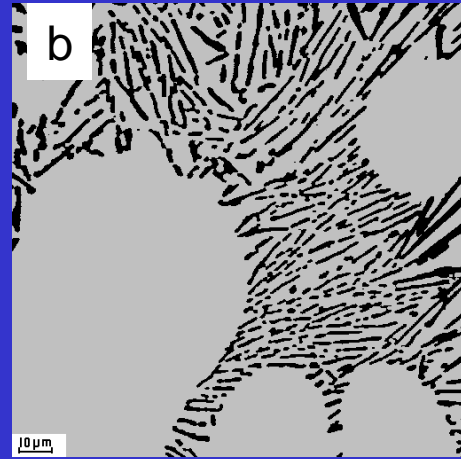
变质处理对Al-Si合金性能的影响



Al-7Si合金变质前后的硅相形态

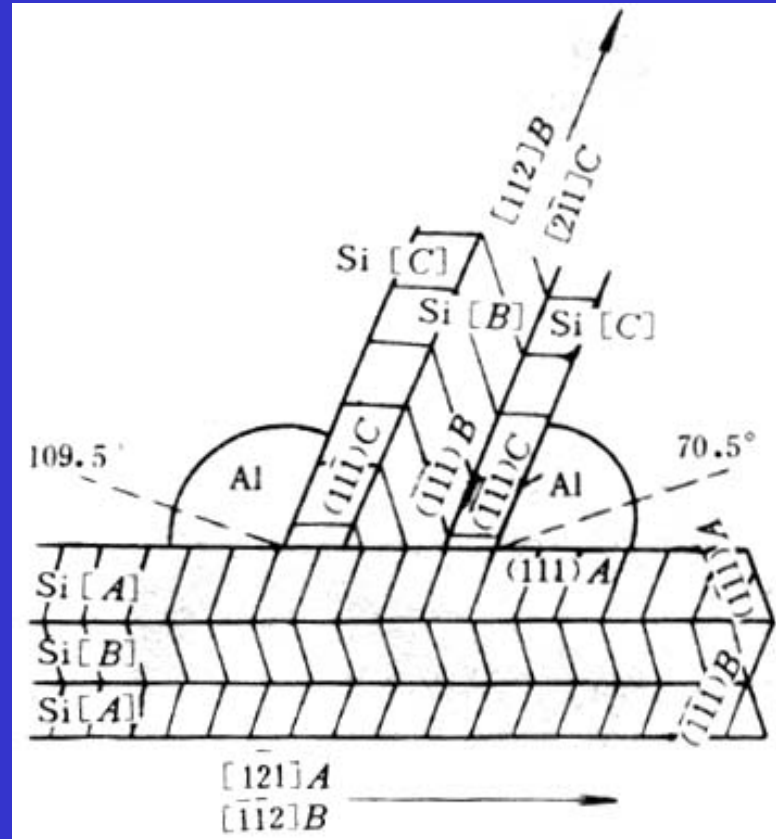


Sr对亚共晶铝硅合金的变质作用

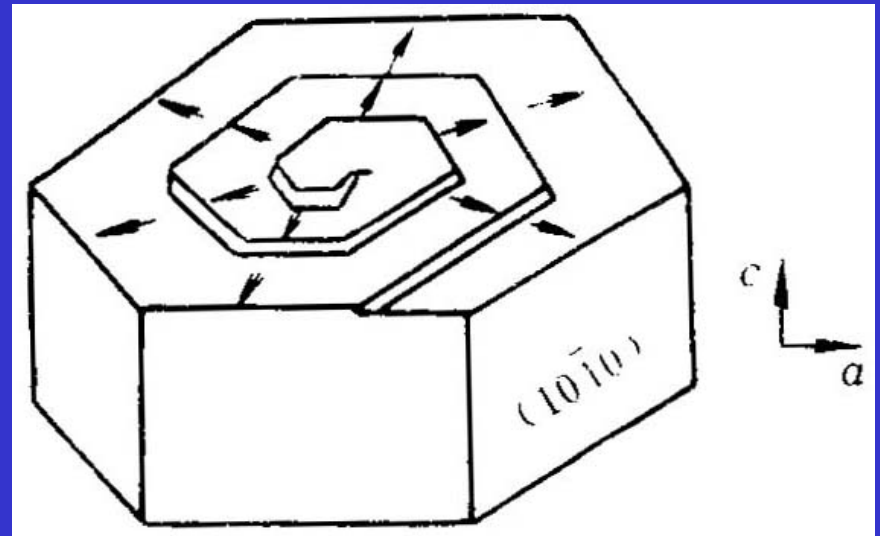
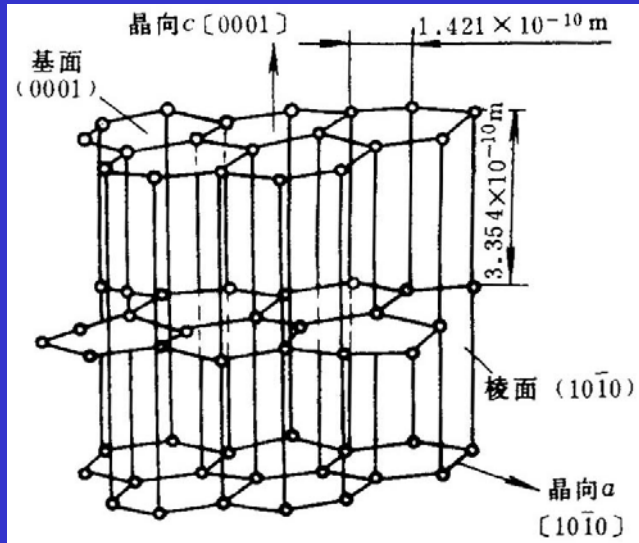


- a unmodified
- b 0.005wt%Sr
- c 0.010wt%Sr
- d 0.015wt%Sr
- e 0.020wt%Sr

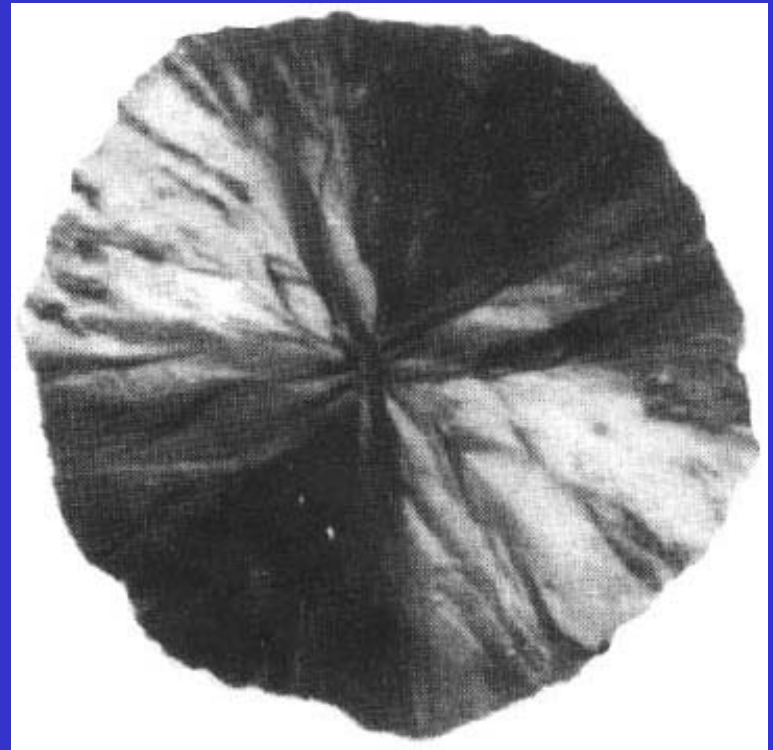
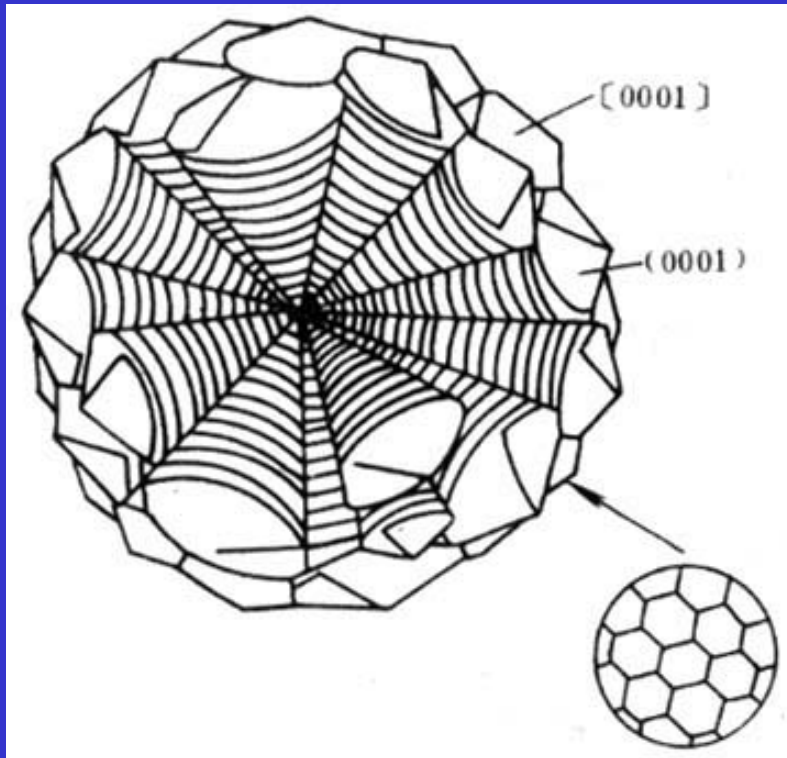
Si相的孪晶与大角度分枝



石墨结构与生长方式



球状石墨的生长模型



球化前后的石墨组织

