

III - High temperature methods

High temperature methods of crystal growth were primitively dedicated to congruently melting compounds. Crystallisation of the solid, eventually on an oriented seed (Czochralski pulling technique), follows the fusion of a part (zone melting, Skull melting, Verneuil flame fusion) or the whole (Bridgman or Stockbarger method) of the starting materials. Zone melting is used mainly for material purification or at very high temperature ; Czochralski, Bridgman and Stockbarger methods can be applied to incongruently melting phases.

1. Zone melting

A sintered rod (length L) of the congruently melting compound is maintained vertically at both ends or horizontally and placed in a controlled atmosphere (figures 12 and 13). A small length (l) is then fused at one end (N) of the rod, either by a high frequency induction coil, by laser heating in a spherical furnace or at the focal point of an elliptical furnace (solar, lamplight or arc furnace). The heat source (or the rod) is then slowly displaced towards the opposite end M of the rod. This operation can be repeated n times from N to M.

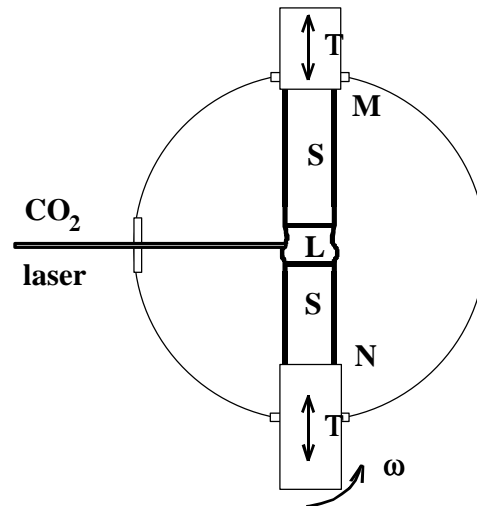


Figure 12. - Principle of zone melting with laser heating.

A crystal seed can be placed at the end N of the rod in order to favour the orientation of the crystal(s) which appear(s). This method is used for the crystal growth of refractory materials : W metal (3410 °C), ZrSiO₄ (zircon), TiO (3000 °C), La₂NiO₄ or La₂CuO₄, Sr₂RuO₄.

Crystal quality is frequently poor and, consequently, this method is mainly used for refining. Impurity concentration levels below 10⁻⁹ or 10⁻¹⁰ molar fraction have been obtained with semiconductors (Si, Ge) or KCl, KBr. Refining implies that impurity solubility C_B^l in the liquid is larger than solubility C_B^s in the solid ($k = x_B^s/x_B^l \approx C_B^s/C_B^l$). The initial impurity concentration is C_0 .

The concentration C_B^s in the solid can be expressed as a function of y , the position of the fused zone along the rod ($0 \leq y \leq L-l$). It is obtained from the input $C_0 \rho S dy$ and output ($k C_1 \rho S dy$) mass transfers of B solute in and out of the liquid ($m_1 = \rho S l$) when the interface moves of dy (figure 13a). Integration gives for a single pass :

$$C_B^s = C_0 \left[1 - (1-k) e^{-k \frac{y}{l}} \right] = C \quad \{11\}$$

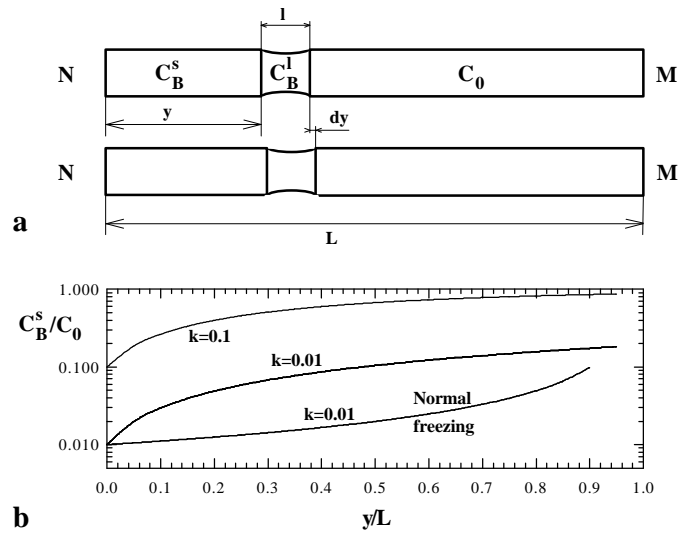


Figure 13. - Geometry (a) and impurity concentration (b) of the rod in zone melting

The variation of the relative concentration C_B^s/C_0 (or C/C_0) is given in figure 13.b for $k=0.1$, $n=1$, $l/L=1/20$ as a function of y/l . This figure shows that for $n=1$, zone melting is less efficient than normal freezing (compare with figure 16 in III-2); however, zone melting is much more efficient when n increases. The efficiency is strongly related to the segregation factor k ($8 \cdot 10^{-3}$, $1 \cdot 10^{-2}$, $1 \cdot 10^{-3}$ for Sn, Ga, As respectively in silicon).