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Allotriomorphic Ferrite

An allotriomorph has a shape which does not reflect its internal crystalline symmetry. This is because it tends to nucleate at the austenite grain surfaces, forming layers which follow the grain boundary contours (Fig. 1).

An idiomorph on the other hand, has a shape which reflects the symmetry of the crystal as embedded in the austenite. Idiomorphs nucleate without contact with the austenite grain surfaces; they tend to nucleate heterogeneously on non–metallic inclusions present in the steel.

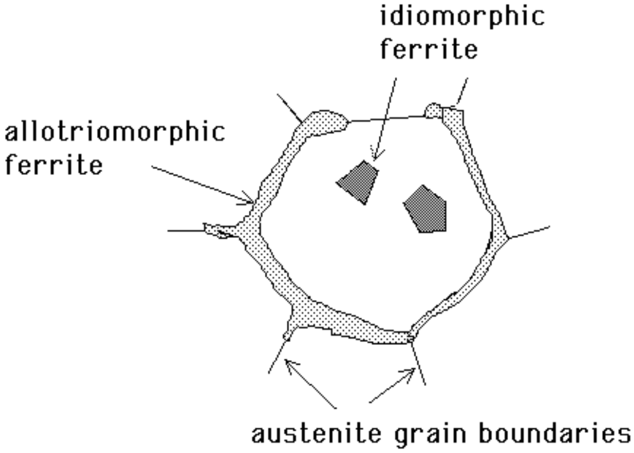

Fig. 1: Allotriomorphic & idiomorphic ferrite.

These are both true diffusional transformations, *i.e.,* there is no atomic correspondence between the parent and product crystals, there is no invariant–plane strain shape change accompanying transformation, the growth rate is either diffusion–controlled, interface–controlled or mixed. Thermal activation is necessary for transformation, which can therefore only occur at high homologous temperatures.

The α/γ interface need not in this case be glissile; the motion of the interface involves diffusion and is not conservative.

Revision of Diffusion–Controlled Growth in Fe–C

The ferrite a different chemical composition from the austenite in which it grows. We shall assume that the growth of ferrite (α) is controlled by the diffusion of carbon in the austenite (γ) ahead of the interface.

As the ferrite grows, so does the extent of its diffusion field. This retards growth because the solute then has to diffuse over ever larger distances. As we will prove, the the thickness of the ferrite increases with the square root of time, *i.e.,* the growth rate slows down as time increases. We will assume in our derivation that the concentration gradient in the matrix is constant, and that the far–field concentration $\overline{c}$ never changes (*i.e.* the matrix is semi–infinite normal to the advancing interface). This is to simplify the mathematics without loosing any of the insight into the problem.

For isothermal transformation in a binary alloy, the concentrations at the interface are given by a tie–lie of the phase diagram as shown in Fig. 2. The diffusion flux of solute from the interface must equal the rate at which solute is incorporated in the precipitate so that:

$$\underbrace{(c^{\gamma\alpha} - c^{\alpha\gamma})\frac{\partial z^*}{\partial t}}_{\text{rate solute partitioned}} = \underbrace{-D\frac{\partial c}{\partial z}}_{\text{diffusion flux from interface}} \simeq D\frac{\overline{c} - c^{\gamma\alpha}}{\Delta z} \tag{1}$$

where z is a coordinate normal to the interface with a value z^* at the position of the interface. Note that the concentration gradient is evaluated at the position of the interface ($z = z^*$).

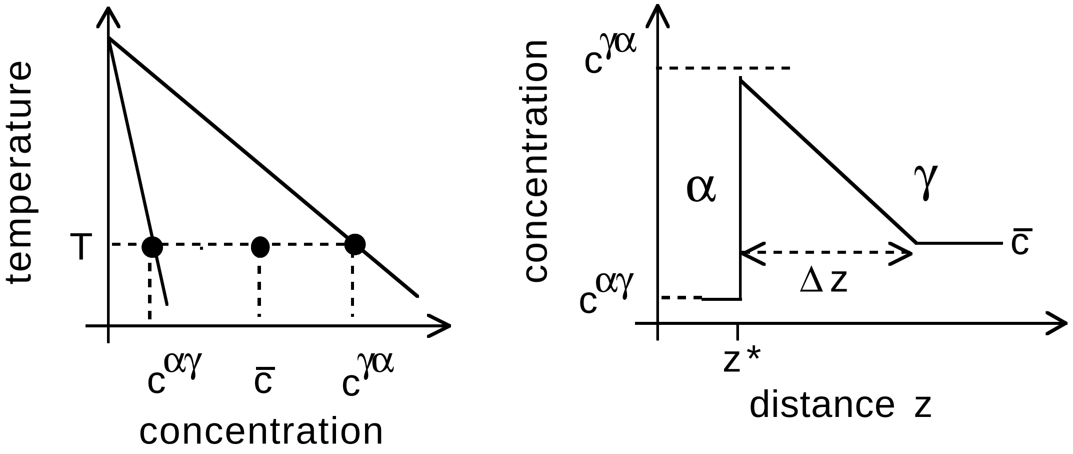

Fig. 2: Phase diagram and its relationship to the concentration profile at the ferrite/austenite interface during diffusion–controlled growth.

A second equation can be derived by considering the overall conservation of mass:

$$(c^{\alpha\gamma} - \overline{c})z^* = \frac{1}{2}(\overline{c} - c^{\gamma\alpha})\Delta z$$

On combining these expressions to eliminate Δz we get:

$$\frac{\partial z^*}{\partial t} = \frac{D(\overline{c} - c^{\gamma\alpha})^2}{2z^*(c^{\alpha\gamma} - c^{\gamma\alpha})(c^{\alpha\gamma} - \overline{c})}$$

It follows that

$$z^* \propto \sqrt{Dt}$$

Ternary Steels

Consider now a ternary steel, say Fe–Mn–C. It would be necessary to satisfy two equations of the form of equation 1, simultaneously, for each of the solutes:

$$\left.\begin{aligned} (c_1^{\gamma\alpha} - c_1^{\alpha\gamma})v &= -D_1 \nabla c_1 \\ (c_2^{\gamma\alpha} - c_2^{\alpha\gamma})v &= -D_2 \nabla c_2 \end{aligned}\right\}$$

where the subscripts refer to the solutes (1 for carbon and 2 for Mn). The interface velocity v is the $\partial z^*/\partial t$ in equation 1.

Because $D_1 \gg D_2$, these equations cannot in general be simultaneously satisfied for the tie–line passing through the alloy composition $\overline{c}_1, \overline{c}_2$. It is, however, possible to choose other tie–lines which satisfy equation 1. If the tie–line is such that $c_1^{\gamma\alpha} = \overline{c}_1$ (*e.g.* line *cd* for alloy A of Fig. 3a), then ∇c_1 will become very small, the driving force for carbon diffusion in effect being reduced, so that the flux of carbon atoms is forced to slow down to a rate consistent with the diffusion of manganese. Ferrite forming by this mechanism is said to grow by a ‘Partitioning, Local Equilibrium’ (or PLE) mechanism, in recognition of the fact that $c_2^{\alpha\gamma}$ can differ significantly from $\overline{c}_2$, giving considerable partitioning and long–range diffusion of manganese into the austenite.

An alternative choice of tie–line could allow $c_2^{\alpha\gamma} \rightarrow \overline{c}_2$ (*e.g.* line *cd* for alloy B of Fig. 3b), so that ∇c_2 is drastically increased since only very small amounts of Mn are partitioned into the austenite. The flux of manganese atoms at the interface correspondingly increases and manganese diffusion can then keep pace with that of carbon, satisfying the mass conservation conditions of equation 1. The growth of ferrite in this manner is said to occur by a ‘Negligible Partitioning, Local Equilibrium’ (or NPLE) mechanism, in recognition of the fact that the

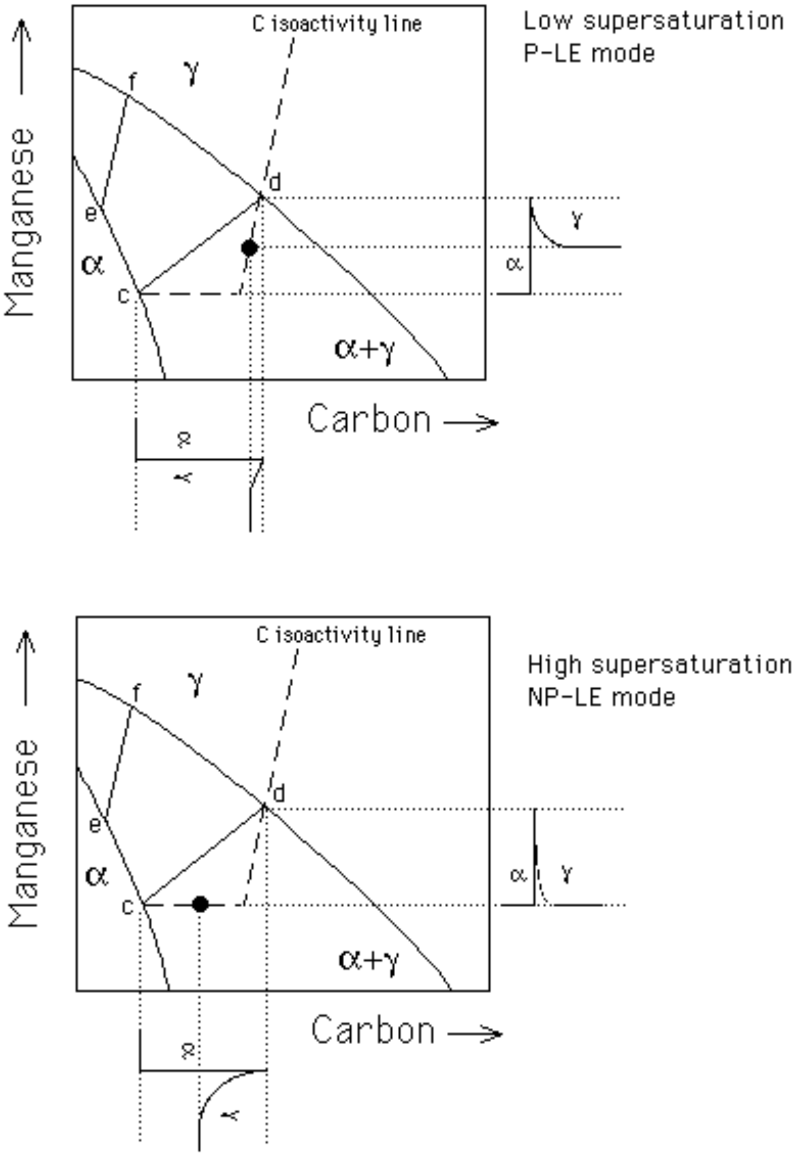

Fig. 3: Schematic isothermal sections of the Fe–Mn–C system, illustrating ferrite growth occurring with local equilibrium at the α/γ interface. (a) Growth at low supersaturations (P–LE) with bulk redistribution of manganese, (b) growth at high supersaturations (NP–LE) with negligible partitioning of manganese during transformation. The bulk alloy compositions are designated by the symbol • in each case.

manganese content of the ferrite approximately equals $\overline{c}_2$, so that little if any manganese partitions into austenite.

What circumstances determine whether growth follows the PLE or NPLE mode? Fig. 4

shows the Fe–Mn–C phase diagram, now divided into domains where either PLE or NPLE is possible but not both. The domains are obtained by drawing right–handed triangles on each tie–line in the $\alpha+\gamma$ phase field and joining up all the vertices. For example, prove to yourself that if you attempt to define NPLE conditions in the PLE domain, then the tie–line determining interface compositions will incorrectly show that both austenite and ferrite contain less carbon than $\overline{c}_1$, a circumstance which is physically impossible.

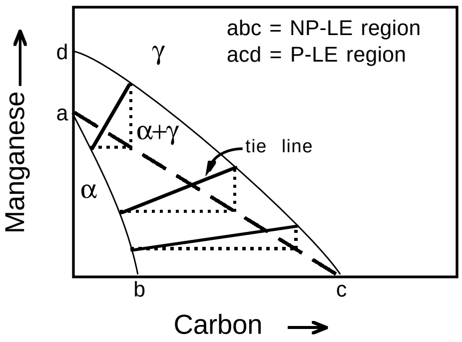

Fig. 4: Regions of the two–phase field where either PLE or NPLE modes of transformation are possible.

Paraequilibrium is a constrained equilibrium. It occurs at temperatures where the diffusion of substitutional solutes is not possible within the time scale of the experiment. Nevertheless, interstitials may remain highly mobile. Thus, in a steel, manganese does not partition between the ferrite and austenite, but subject to that constraint, the carbon redistributes until it has the same chemical potential in both phases.

Therefore, the tie–lines in the phase diagram (Fig. 5) are all virtually parallel to the carbon axis, since Mn does not partition between ferrite and austenite.

Prove to yourself that in an isothermal section of the ternary phase diagram, the paraequilibrium phase boundaries must lie within the equilibrium phase boundaries as illustrated in Fig. 6.

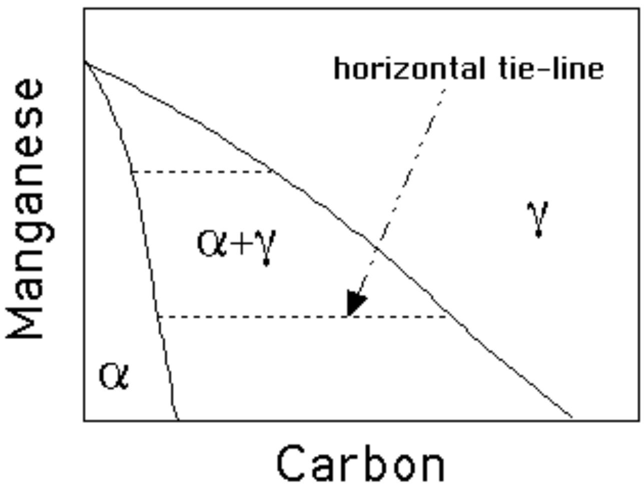

Fig. 5: A paraequilibrium phase diagram.

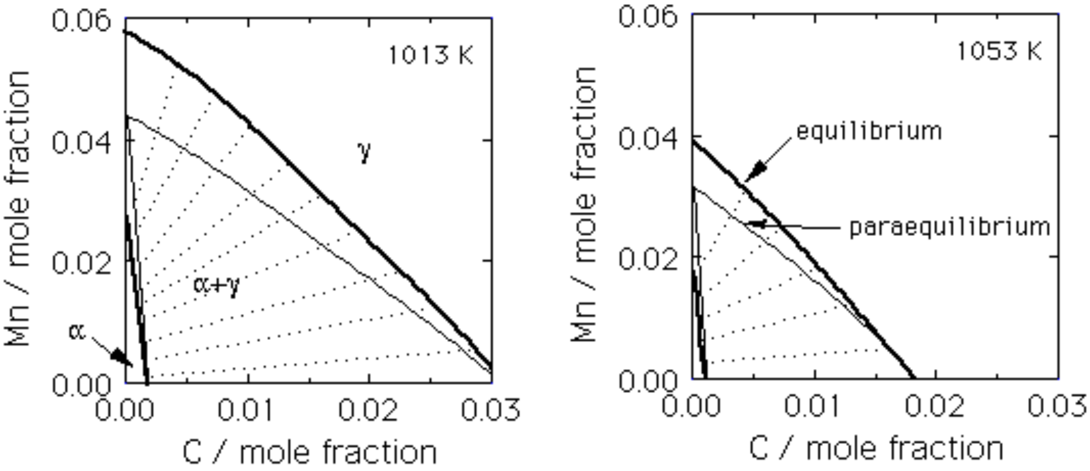

Fig. 6: The paraequilibrium phase field lies within the equilibrium field. The tie–lines illustrated are for equilibrium.