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SPRING COLLEGE IN MATERIALS SCIENCE ON

"NUCLEATION, GROWTH AND SEGREGATION IN MATERIALS SCIENCE AND ENGINEERING"

(6 May - 7 June 1991)

INTRODUCTORY OVERVIEW OF NUCLEATION, GROWTH AND SEGREGATION PHENOMENA

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These are preliminary lecture notes, intended only for distribution to participants.

Introductory Overview of Nucleation, Growth & Segregation.

Brief Notes & Background Information in relation to the lectures to be given by G. W. Greenwood, University of Sheffield, UK at the International Centre for Theoretical Physics, Trieste, Italy, in May, 1991.

Some useful textbooks are :-

A. H. Cottrell — Introduction to Metallurgy, Edward Arnold, 2nd Edition, 1975.

R. E. Smallman — Modern Physical Metallurgy, Butterworth's 4th Edition, 1985.

R. E. Reed-Hill — Physical Metallurgy Principles, Van Nostrand Reinhold 1964

P. Haasen — Physical Metallurgy, Cambridge, 2nd Edition 1986

D. A. Porter & K. E. Easterling — Phase Transformations in Metals & Alloys, Van Nostrand Reinhold, 1981

J. Burke — The Kinetics of Phase Transformations in Metals, Pergamon Press, Oxford 1965

J. W. Christian — The Theory of Phase Transformations in Metals & Alloys, Pergamon Press, Oxford, 2nd Ed. 1975

W. Kurz & D. J. Fisher — Fundamentals of Solidification, Trans Tech Publications, 1984

Some Basic Information & Data

First consider a pure metal, e.g. Cu.

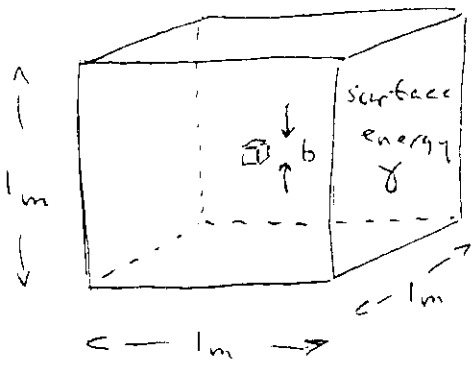
and the approximate values of some of its properties :—

Melting point 1356 K Boiling point 2873 K

Specific latent heat of fusion $\sim 1.8 \times 10^5$ J/kg

" " " vaporisation $\sim 7.3 \times 10^6$ J/kg.

Density $\sim 9 \times 10^3$ kg/m^3.



Thus vaporisation energy per unit volume

$\bar{E}_V \sim 7 \times 10^{10}$ J/m^3

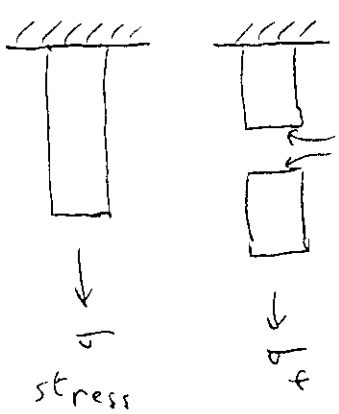
Now separate into n atoms each with surface area A.

Then $nA\gamma \sim \bar{E}_V$ and with atom spacing b

$n \sim 1/b^3$ and $A \sim 6b^2$, so for $b \sim 10^{-10}$ m

$\gamma \sim \bar{E}_V/nA \sim \bar{E}_V b/6 \sim (7\times10^{10}) \times 10^{-10}/6$ J/m^2

Hence the order of magnitude of surface energy $\gamma \sim 1$ J/m^2



1 two surfaces created by fracture.

For a fully brittle solid, Griffith calculated the fracture stress

$$\sigma_f \sim \left(\frac{E\gamma}{b}\right)^{1/2}$$

where E is Young's modulus and the solid is without defects.

Very roughly, such a stress level σ_f would correspond to a strain ε_f or fracture of ~ 0.2, if Hooke's law were to be obeyed up to this point.

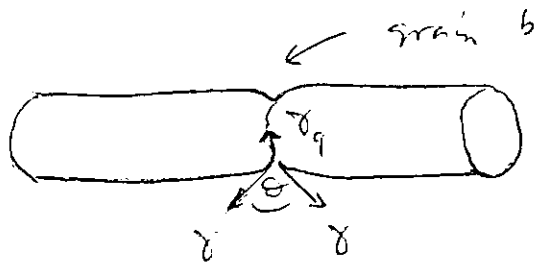
Thus $\varepsilon_f \sim \frac{\sigma_f}{E} \sim \left(\frac{\gamma}{Eb}\right)^{1/2} \sim 0.2$

so that $E \sim \left(\frac{1}{0.04}\right)(\gamma/b) \sim 2 \times 10^{11}$ Pa

The order of magnitude of Young's Modulus $E \sim 2 \times 10^{11}$ Pa

The Shear modulus $G \sim 0.4\, E$

Grain boundaries and interfaces both have energies. We label these γ_g and γ_i respectively.



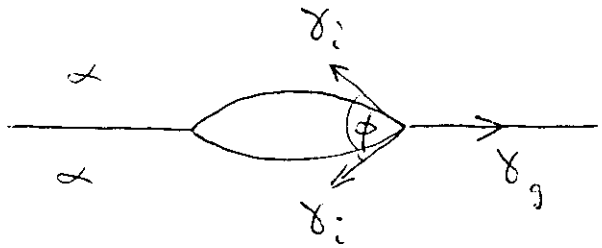
At equilibrium

$$\gamma_g = 2\gamma \cos(\theta/2)$$

Typically $\gamma_g \sim \gamma/3$.

where γ_g is the grain boundary and γ is the surface energy per unit area

For a second phase β on a grain boundary in a matrix α, where both phases are isotropic.



Here

$$\gamma_g = 2\gamma_i \cos(\phi/2)$$

Vacancies

The energy to form a vacancy H_f is of the order

$$H_f \sim E_v / b^3 \sim .10^{-19} \text{ J (per vacancy)}$$

or, since electronic charge $e = 1.6 \times 10^{-19}$ Coulombs

then $H_f \sim 1$ eV (one electron volt).

The number of vacancies is calculated from the Gibbs free energy equation $G = H - TS$

(Do not confuse G here with G used for shear modulus)

Applied to vacancies $\Delta G = H_f - T(\Delta S_c + \Delta S_v)$

where ΔS_c is the configurational entropy introduced by the vacancy, with $\Delta S_c = -k \ln c$.

Here c is the atomic vacancy concentration

k is Boltzmann's constant $= 1.38 \times 10^{-23}$ J/K.

ΔS_v is the entropy due to disturbance of lattice vibrations.

Thus, in equilibrium $0 = H_f + kT \ln c - T\Delta S_v$

so that $\underline{c = [\exp(\Delta S_v / k)][\exp(-H_f / kT)]}$

At the melting temperature $T = T_m = 1356$ K

and with $\exp(\Delta S_v / k)$ typically ~ 10, the vacancy concentration just below T_m, $c \sim 10^{-3}$

Lattice Vibrations

An estimate of the order of magnitude of this frequency f is obtained by assuming simple harmonic motion, where, for a metal of density ρ

$$f \sim (1/2\pi b)(E/\rho)^{1/2}$$

Substituting typical values:-

$$f \sim (1/2\pi \times 10^{-10})(2\times10^{11}/9\times10^{3})^{1/2} \sim 10^{13}\ Hz$$

Vacancy Movement

Lattice vibrations cause vacancy movement at all finite temps. The energy (or more strictly enthalpy) of vacancy movement H_m is often of similar magnitude to the value of H_f. There is again a small entropy term for lattice vibration alteration in the term for the Gibbs free energy.

For atom movement, there are now 2 energy requirements to meet and so the activation energy

$$\text{for diffusion } Q = H_m + H_f$$

It is further noted that often (& especially for fcc metals)

$$\text{for lattice diffusion } Q \sim 18\,R\,T_m$$

& for grain boundary diffusion $Q_g \sim 10\,R\,T_m$

where R is the gas constant $= 8.31\ J/mol\,K$

Diffusion Processes.

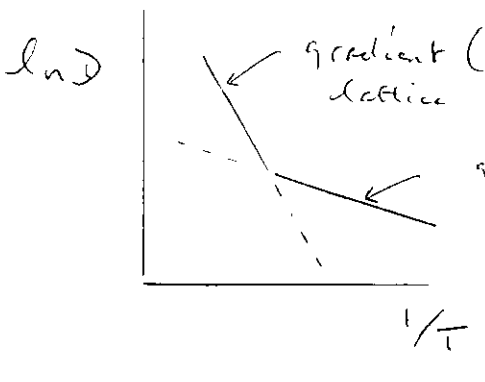
For random diffusion, these are governed by the atomic jump distance b, the lattice vibration frequency f and the value of the energy barrier Q, with a small effect due to entropy change through lattice vibration alteration

Thus $$D = (1/6) f b^2 \left[\exp\left(\frac{\Delta S_v}{k}\right)\right] \exp\left(-\frac{Q}{kT}\right)$$

It is usual to write $(1/6) f b^2 \exp(\Delta S_v/k) = D_0$ and, take Q in units of J/mol, thus replacing k by the gas constant $R = 8.31$ J/mol K (noting that $R = N_A k$ where Avogadro's number $N_A = 6 \times 10^{23}$ mol^{-1})

Hence we arrive at the expression

$$D = D_0 \exp(-Q/RT)$$



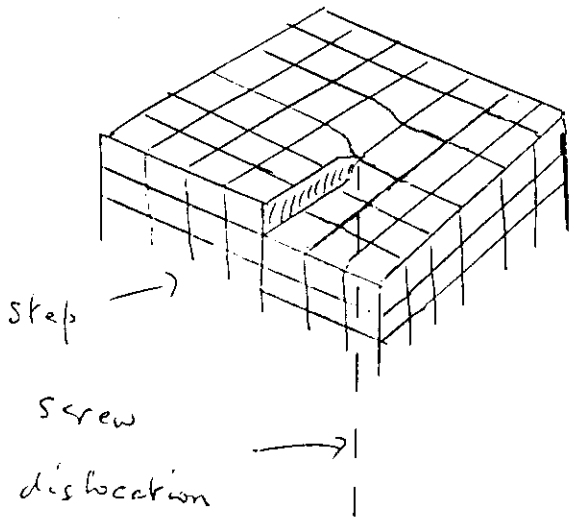
An Arrhenius plot is frequently used

Under steady state concentration gradients we may calculate flux j from Fick's first law $j = -D\, dc/dx$

where dc/dx is the concentration gradient. When c varies with time the second law is used $dc/dt = D\, d^2c/dx^2$

or, in 3 dimensions, $dc/dt = D \nabla^2 c$

Brief Notes on Dislocations.



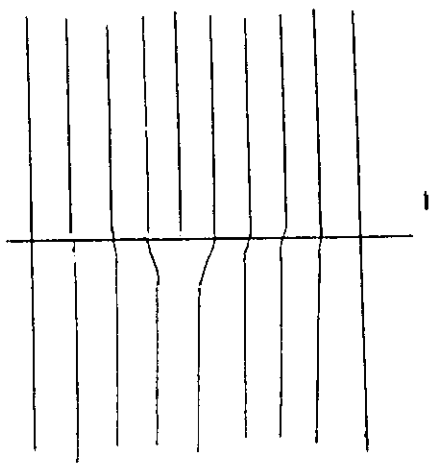
A screw dislocation intersecting a surface creates a step which is a favorable site for nucleation. Note that the step rotates about the screw dislocation and so the step is not eliminated.

The screw dislocation has energy $E_s = (Gb^2/4\pi)\ln(r_1/r_0)$

where r_1 corresponds to the limiting size of the crystal or to the distance of neighbouring dislocations.

r_0 is the dislocation core radius.

This energy per unit line length is typically $E_s \sim 10^{-8}$ J/m



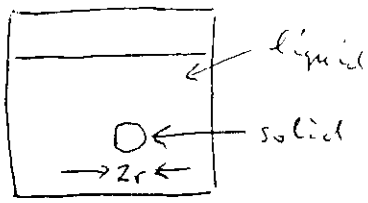
For an edge dislocation the energy

$$E_e = \left[Gb^2/4\pi(1-\nu)\right]\ln(r_1/r_0)$$

where ν is Poissons ratio often $\nu \sim 1/3$

so E_e is slightly less than E_s

The Nucleation of a Solid Sphere in a Cooling Liquid



The free energy change when the solid forms

$$\Delta G = \tfrac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma_i$$

ΔG_v is the difference in free energy/unit vol between the solid & liquid phases and

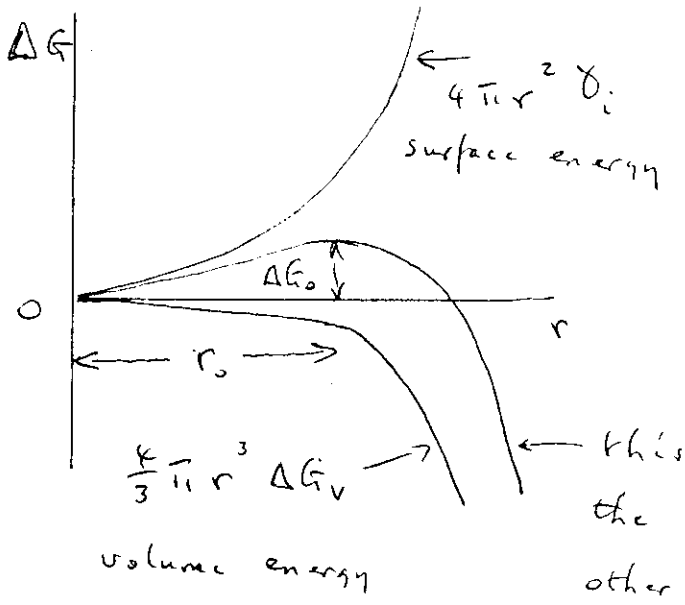
γ_i is interfacial energy.

On nucleation $\frac{d}{dr}(\Delta G) = 4\pi r^2 \Delta G_v + 8\pi r \gamma_i = 0$.

Thus we require $r = r_0 = 2\gamma_i / \Delta G_v$

Particles of solid $> r_0$ can grow. Particles $< r_0$ are unstable and the energy required for nucleation

$$\Delta G = \Delta G_0 = 16\pi \gamma_i^3 / 3(\Delta G_v)^2$$



These features are illustrated by plotting ΔG against r

this curve is the sum of the other two curves.

Free Energy & Temperature

At temperature T the liquid free energy is $G^L = H^L - TS^L$

and similarly for the solid $G^S = H^S - TS^S$

The decrease in free energy on freezing gives the driving force for solidification $\Delta G = \Delta H - T\Delta S$.

where $\Delta H = H^L - H^S$ and $\Delta S = S^L - S^S$.

At equilibrium at the melting temperature $T = T_m$

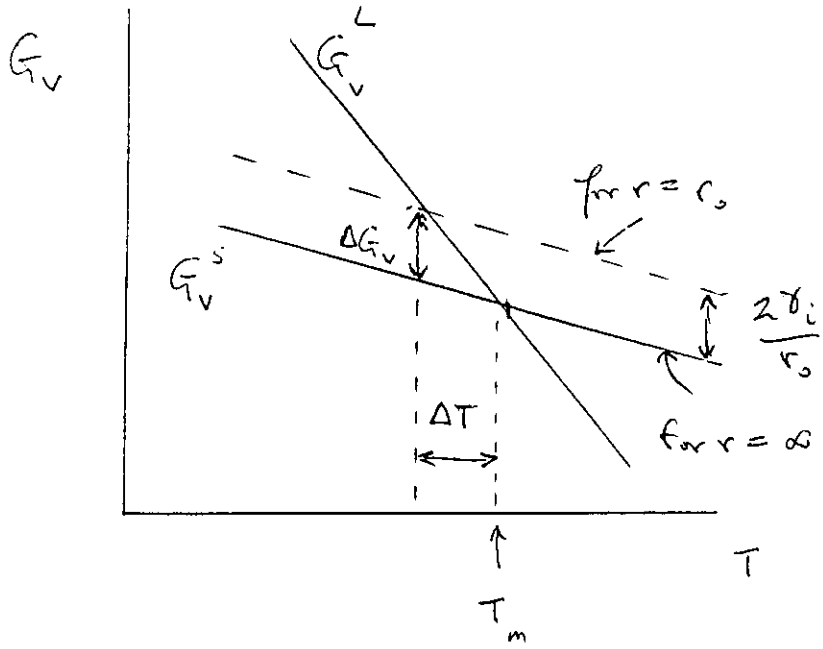
$$\Delta G = \Delta H - T_m \Delta S_m = 0.$$

Hence $\Delta S_m = \Delta H / T_m = L / T_m$

where L is the latent heat of fusion (typically $\Delta S_m \sim R$)

For small undercooling, ignoring specific heats

$$\Delta G = \Delta H - T\Delta S = L - TL/T_m \sim L\Delta T / T_m$$



Relating this to nucleation

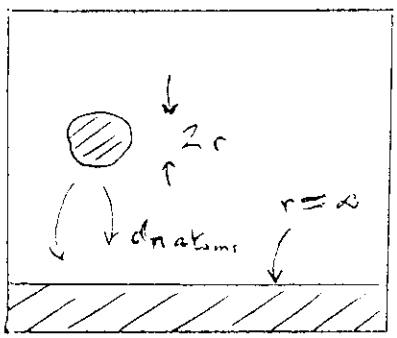
$$r_o = \frac{2\gamma_i}{\Delta G_V} = \frac{2\gamma_i T_m}{L_V \Delta T}$$

and

$$\Delta G_o = \frac{16\pi \gamma_i^3 T_m^2}{3 L_V^2 (\Delta T)^2}$$

where L_V is the latent heat / unit volume

Interface Curvature and Solubility



Transferring dn atoms from the spherical particle decreases its area A by an amount dA.

The area of the plane surface is unchanged.

The free energy change $dG = \gamma_i \, dA/dn$ for each atom transferred

Now $A = 4\pi r^2$ and $n = 4\pi r^3 / 3\Omega$

where Ω is the atomic volume.

Hence $dA/dn = (dA/dr)/(dA/dn) = 2\Omega/r$

The free energy change is thus $2\gamma_i \Omega / r$

It follows that the solubility S_r adjacent to a particle of radius r is enhanced beyond the equilibrium solubility S_0 adjacent to a plane surface by the relation

$$S_r = S_0' \exp\left(2\gamma_i \Omega / kTr\right)$$

This is often written in terms of molar volume V_m $(= N_A \Omega)$ so that

$$S_r = S_0 \exp\left(2\gamma_i V_m / RTr\right)$$

and often this approximates to

$$S_r = S_0 \left[1 + \left(2\gamma_i V_m / RTr\right)\right]$$

The Importance of Surface Curvature

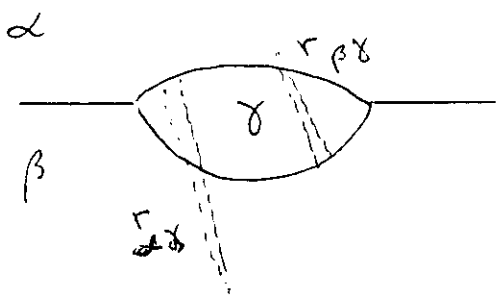
It is important to note that an effective radius of curvature can still be ascribed to anisotropic materials with planar facets. If the facets have energy/unit area $\gamma_1, \gamma_2, \gamma_3 \ldots \gamma_n$ and they are respectively at distances $r_1, r_2, r_3 \ldots r_n$ from the phase centre then

$$\gamma_1/r_1 = \gamma_2/r_2 = \gamma_3/r_3 = \ldots \gamma_n/r_n .$$

This is the Wulff Theorem for equilibrium shape.

The effect of surface curvature is predominant in analysing processes of nucleation and growth. It provides the driving force in particle coarsening and in the sintering of powders and removal of porosity.

With regard to surface curvature, a solute atom bears the same relationship to a precipitate as a vacancy does to a hole.

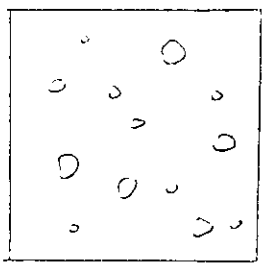


For a phase γ between two phases α and β, the radii of curvature are as shown.

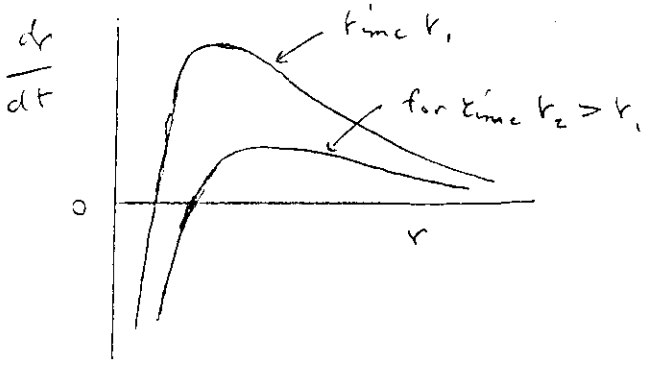
Overview

On the basis of the background information now provided, a very wide range of phenomena related to nucleation, growth and segregation can be presented. Some details will be outlined

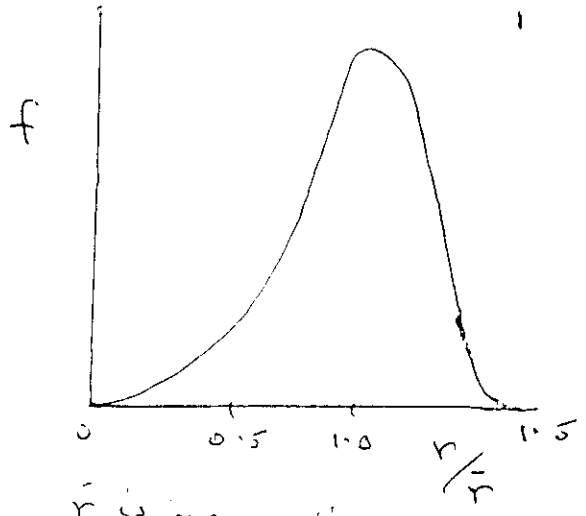
Particle Coarsening.



Here there is a diffusive flux from small to large particles, causing small particles to dissolve and large ones to grow



For the larger particles $dr/dt > 0$.



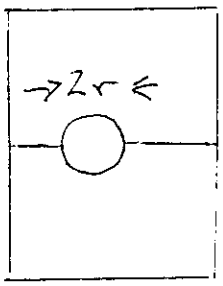
The particle size distribution f shows a constant profile independently of time when plotted against the ratio of particle radius to mean radius.

$\bar{r}$ is mean radius

$$\bar{r}_f^3 - \bar{r}_i^3 = \frac{8 D S \gamma_i \Omega t}{9 k T}$$

$\bar{r}_i$ and $\bar{r}_f$ are initial and final mean radii.

The Nucleation, Growth, Shrinkage and Movement of Holes



A hole will grow on a grain boundary perpendicular to a stress σ if $\sigma > 2\gamma/r$

where γ is the surface energy / unit area.

Grain boundaries have a large influence on holes because grain boundaries can act as sources and sinks for vacancies and operate as fast diffusion paths.

Holes and precipitates have a binding energy to a grain boundary but small holes can more easily move through grain boundary dragging. This can cause their coalescence and growth.

Where holes contain soluble gases, they can coarsen, like precipitates, but the driving force for such bubble growth lies mainly in the decrease of entropy of the gas and not on a decrease in total surface area.

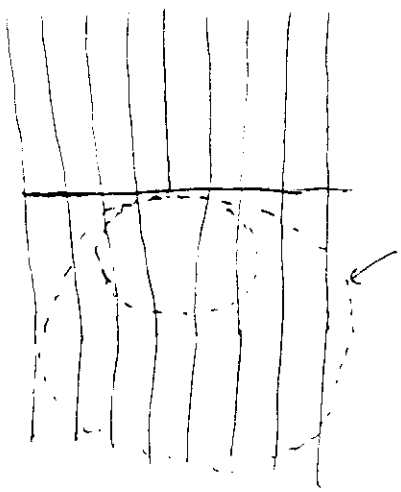
Segregation

In equilibrium, there is often a segregation of elements to reside on, or near, free surfaces, grain boundaries or dislocations.

For surfaces and interfaces, Gibbs showed that the surface concentration of adsorbed atoms per unit area

$$c = -(n/kT)(d\gamma/dn)$$

where there are n atoms per unit volume of segregating atoms $(d\gamma/dn)$ is the change of the surface energy with n.



equipotential lines for equal solute concentration around an edge dislocation

Around an edge dislocation solutes can form 'atmospheres' which become 'condensed' below a critical temperature. The term 'condensed' here implies a complete occupation of the core area by solute

There are also many examples of non-equilibrium segregation which present major problems in castings and the terms micro, macro and inverse segregation will be explained