Chapter 9.
SOLID SOLUTIONS

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Solid Solutions

Solid Solution $\Big\{$ Substitution S.S $\longrightarrow$ Cu−Ni

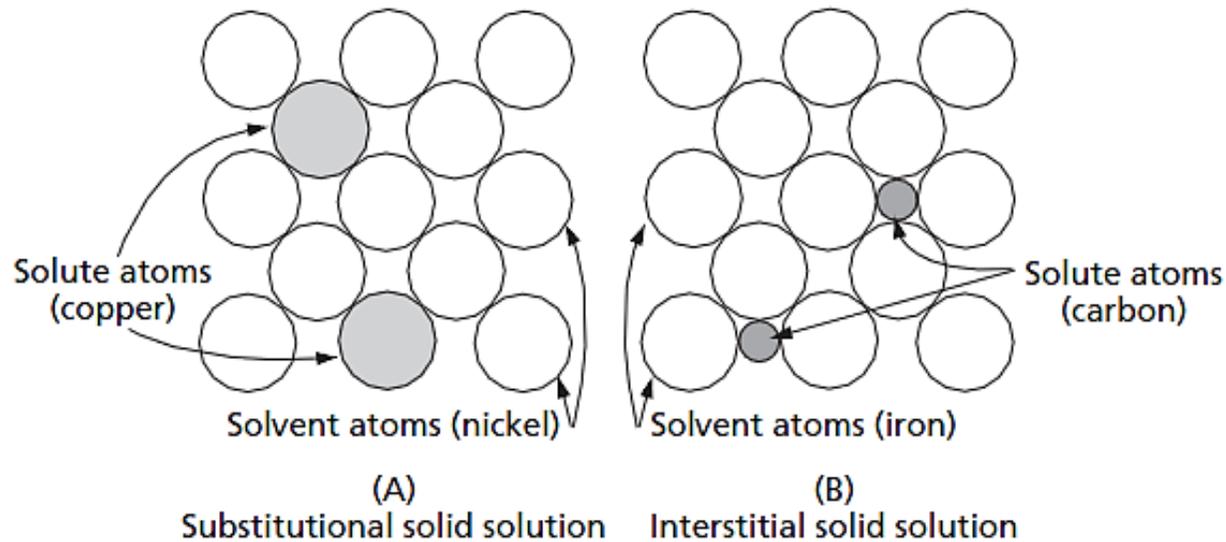Interstitial S.S $\longrightarrow$ Fe−C

Fig.9.1 The two basic form of solid solutions. Note: In the interstitial example on the right, carbon is shown in solid solution in the face−centered cubic form of iron. Fig.9.2 considers carbon dissolved interstiially in the body−centered cubic form of iron.

Intermediate Phases

The crystal structure of Cu-Zn phase (β brass) is bcc.

Cu $\longrightarrow$ fcc

Zn $\longrightarrow$ hcp $\bigg\}$ $\longrightarrow$ Cu-Zn (β brass) $\longrightarrow$ bcc   (Solid Solution)
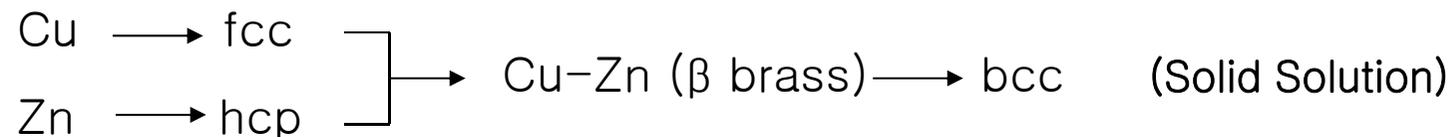
Because this **body-centered cubic structure** can exist over a range of composition (it is the only stable phase at room temperature between 47 and 50 weight percent of zinc)

When carbon is added to iron, $Fe_3C(6.67wt\%C)$ phases occur as a fixed compound. It is named as **intermetallic compound.**

Interstitial Solid Solution

Hume-Rothery

Extensive interstitial solid solutions occur only if the solute atom has **an apparent diameter smaller than 0.59 that of the solvent.**

Atomic size is not the only factor that determines whether or not an interstitial solid solution will form.

The ability of **transition elements** (*Ex. Fe, V, W, Ti, Cr, Th, Zr, Mn, U, Ni, Mo*) to dissolve interstitial atoms is believed to be due to their <u>unusual electronic structure</u>. All transition elements possess an incomplete electronic shell inside of the outer, or valence, electron shell. The non-transitional metals, on the other hand, have filled shells below the valency shell.

Solubility of carbon in body-centered cubic iron

The number of carbon atoms in an iron crystal is roughly equivalent to the number of vacancies found in crystals.
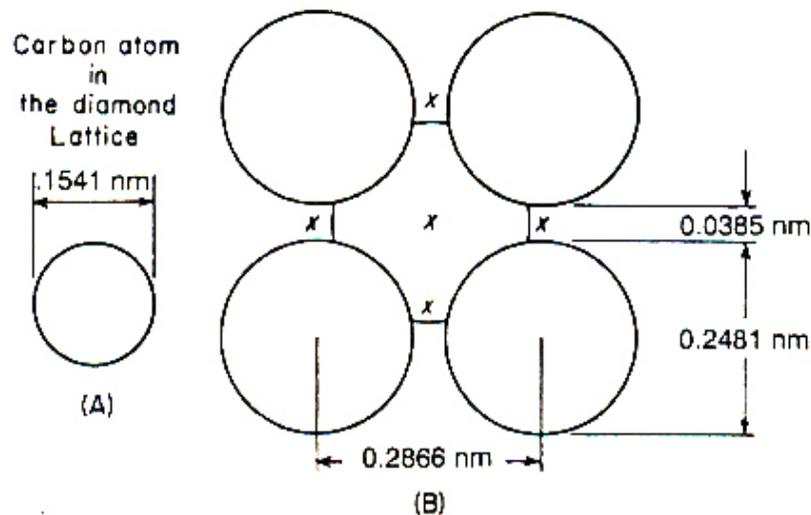

Fig.9.2 The interstitial positions in the body-centered cubic iron unit cell that may be occupied by carbon atoms.

w_c ⟶ The work of introducing the interstitial atom into crystal.

n_c ⟶ The number of carbon atoms in an iron crystal.

The internal energy if the crystal (in the presence of carbon atoms) will be increased by the amount $n_c w_c$

$$\frac{n_v}{n_o} = e^{-w_v / kT}$$

The ratio of vacancies to atoms in the crystal. (7.39)

The preceding, more exact, equation, including the intrinsic entropy, can also be expressed as follows:

$$\frac{n_v}{n_o} = B e^{-w_v / kT} = B e^{-Q_f / RT}$$

The calculation of mixing entropy differs from that used for the mixing entropy associated with vacancies in a crystal lattice because vacancies and atoms interchange positions, while carbon atoms do not interchange with iron atoms. *Thus the entropy of mixing associated with the carbon atoms involves only the distribution of the carbon atoms in the interstitial sites.*

There are three interstitial sites per Fe atom, whereas two atoms exist in b.c.c. iron lattice. The entropy of mixing is thus

$$S_m = k \cdot \ln \frac{(3n_{Fe})!}{n_c!(3n_{Fe} - n_c)!}$$

With the aid of Stirling's approximation $(\ln(x)! \cong x \cdot \ln(x) + x)$

$$S_m = k[3n_{Fe} \ln 3n_{Fe} - n_c \ln n_c - (3n_{Fe} - n_c) \ln(3n_{Fe} - n_c)]$$

Let the ΔG_c represent the increase in the Gibbs free energy of the system due to the presence of carbon atoms in solid solution in the iron; then

$$\Delta G_c = n_c g_c - TS_m$$

Where g_c is the free energy associated with a single carbon atom.

A minimum G_c $\longrightarrow$ $\Delta G_c / dn_c = 0$

$$\Delta G_c / dn_c = g_c + kT[\ln n_c - \ln(3n_{Fe} - n_c)] = 0$$

Which leads to

$$\frac{n_c}{(3n_{Fe} - n_c)} = e^{-g_c / kT}$$

For a dilute solution, where , $n_c \ll n_{Fe}$, this reduces to

$$C = Be^{-Q_c / RT}$$

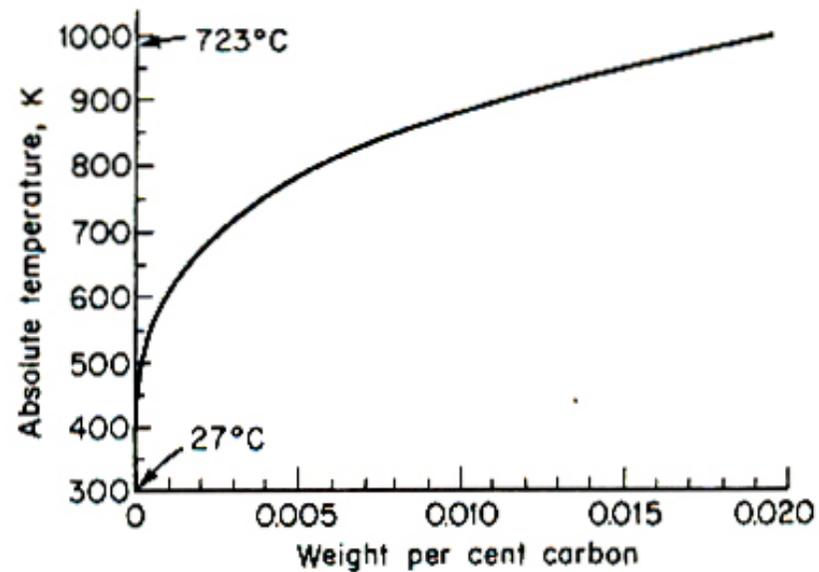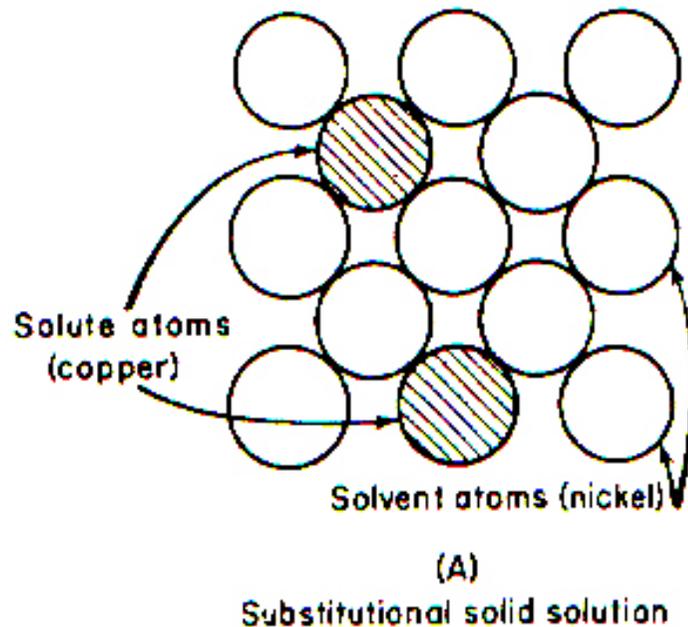Fig.9.3 Solubility of carbon in alpha-iron (body-centered cubic iron)

Substitutional solid solutions and the Hume-Rothery rules

Solute atoms (copper)

Solvent atoms (nickel)

(A)

Substitutional solid solution

Copper = 0.2551nm

Nickel = 0.2487nm ;

only 2% different size between Cu and Ni

But in case of the copper-sliver system, its solubility equal to only a fraction of 1% at room temperature, whereas the diameter of sliver is about 13% larger than that of copper.

Hume-Rothery Rules

The size factor is only a necessary condition for a high degree of solubility. It is not a sufficient condition, since other requirements must be satisfied.

① Size effect (less than 15%)

② Lattice type

③ Relative valence

## Interaction of dislocations and solute atoms

Displacement of the atoms around the center of a dislocation results on a complex two-dimensional strain pattern with the dislocation line at its center.

Dislocation atmospheres

① Substitutional solutes & dislocation($\perp$)

A large solute atom expands the surrounding lattice, while a small one contracts it. There distortions may be largely relieved if the solute atom finds itself in the proper place close to the center of a dislocation.

(A)
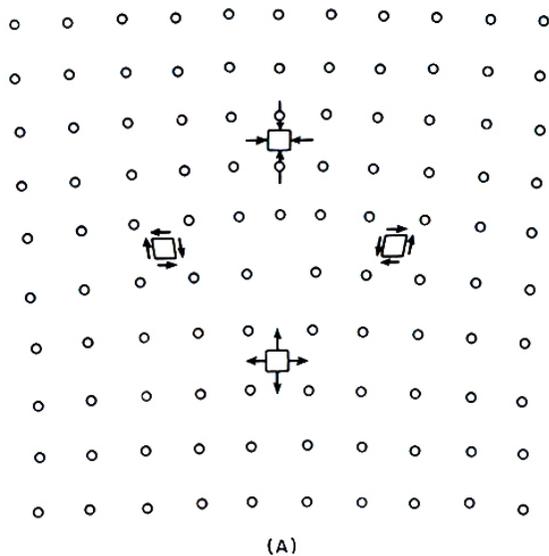
The free energy of the crystal will be lowered when a small solute atom is substituted for al larger solvent atom *in the compressed region of a dislocation in, or close to, the extra plane of the dislocation*.

Similarly, large solute atoms are drawn to lattice positions below the edge.

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② Interstitial solutes & dislocations

Interstitial atoms are drawn toward the expanded regions of edge dislocations.

In the body-centered cubic lattice, the distortions (expansions) are in <100> directions. A nonspherical lattice distortion such as this will react with the shear strain field of a screw dislocation.

At high temp., diffusion rates are rapid, and solute atoms concentrate quickly around dislocation.

If the solute atoms have a mutual attraction,

————————————————→   Forming new phase at dislocation.

If not,   —————————————→   Dislocation atmospheres.

Dislocation atmospheres   **→**   T↗ → solute atoms move in lattice
depend on T   → E of the entropy of crystal ↗

The formation of a dislocation atmosphere

Cottrell and Bilby (1949)

Assumption : A difference in size between the substitutional solute atoms and the solvent atoms should result in strains in the lattice centered at the solute atoms.

The effective radial strain of a solute atom is then taken as

$$\varepsilon = \frac{r' - r}{r}$$

$r' \longrightarrow$ The radius of the solute atom

$r \longrightarrow$ The radius of the solvent atom

A volume strain $\longrightarrow$ $\Delta V = 4\pi r^2 \Delta r = 4\pi \varepsilon r^3$

This hydrostatic stress equals $\sigma_m = -\frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$

Elastic interactive energy

$$U_i = \sigma_m \cdot \Delta V$$

The interaction energy

$$\therefore U = -\frac{4}{3}\pi\varepsilon r^3(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$$

Expressed in polar coordinates

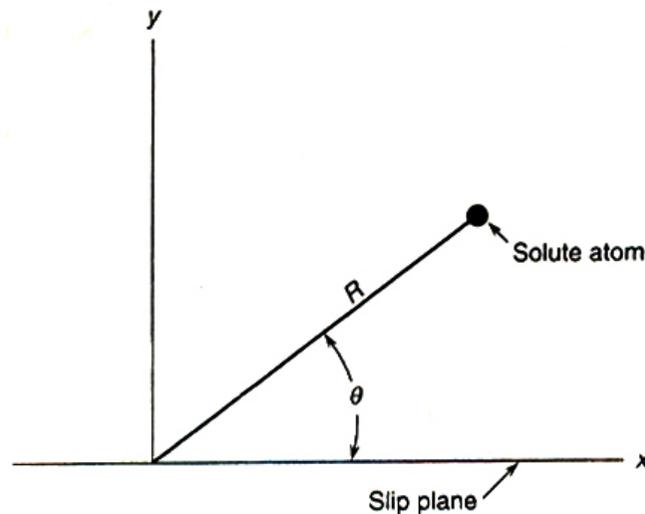$$U = \frac{4(1+\upsilon)\mu b \varepsilon r^3 \sin\theta}{3(1-\upsilon)R} \qquad U = \frac{A\sin\theta}{R}$$

Where θ and R are defined in Fig.9.5 and

$$A = \frac{4(1+\upsilon)}{3(1-\upsilon)}\mu b \varepsilon r^3 \qquad \text{(A : Interaction constant)}$$

The evaluation of A

The evaluation of the interaction constant A will now be considered for the metal iron where

$$b = 2.48 \times 10^{-10} m$$

$$r = 1.24 \times 10^{-10} m$$

$$\mu = 7 \times 10^{-11} Pa$$

$$\upsilon = 0.33$$

$$A = 8.8 \times 10^{-29} \varepsilon Nm^2$$

If the solute atom radius is 10% larger than the iron atom, A would equal,
$$A = 8.8 \times 10^{-30} Nm^2$$

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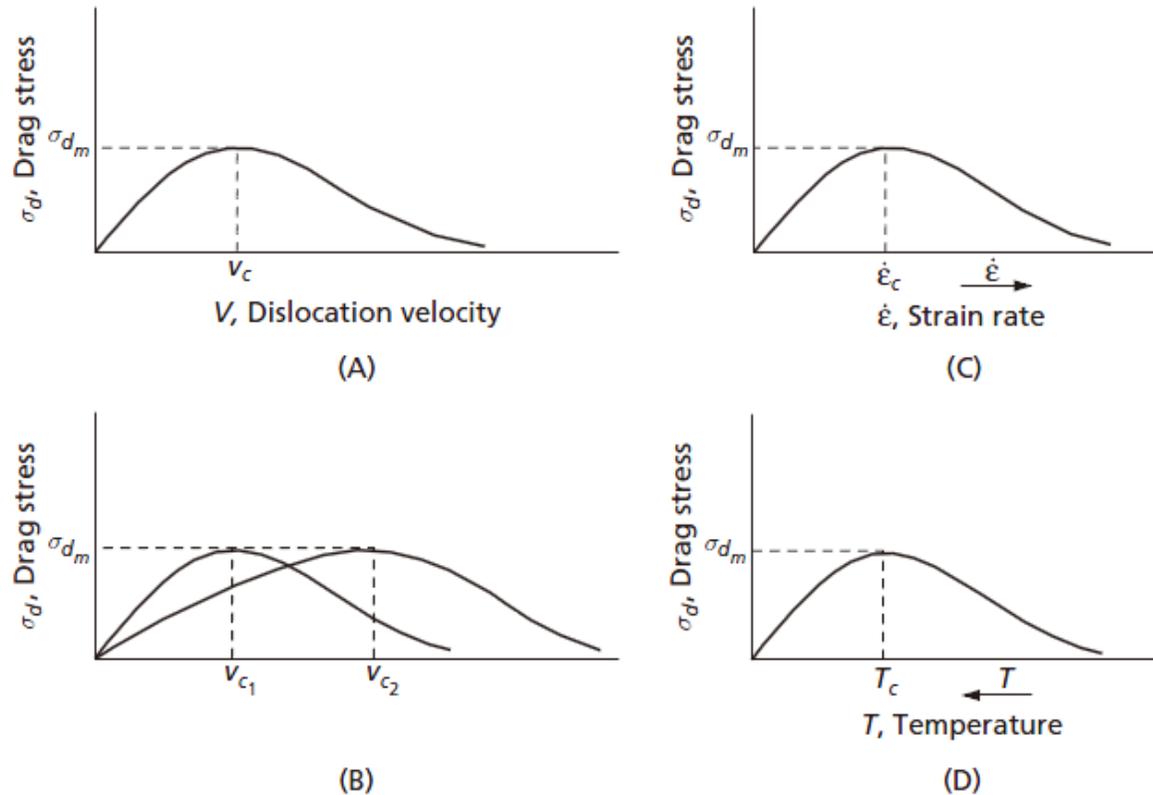The drag of atmosphere on moving dislocations

FIG. 9.6 Variation of the drag–stress with, (A) the dislocation velocity, (B) the dislocation velocity at two different temperatures, (C) the strain rate, and (D) the temperature at constant strain rate

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The sharp yield point and Luders bands

When the stress-strain curves of metals deformed in tension are plotted, two basic types of curves are observed, as shown in Fig.9.7.
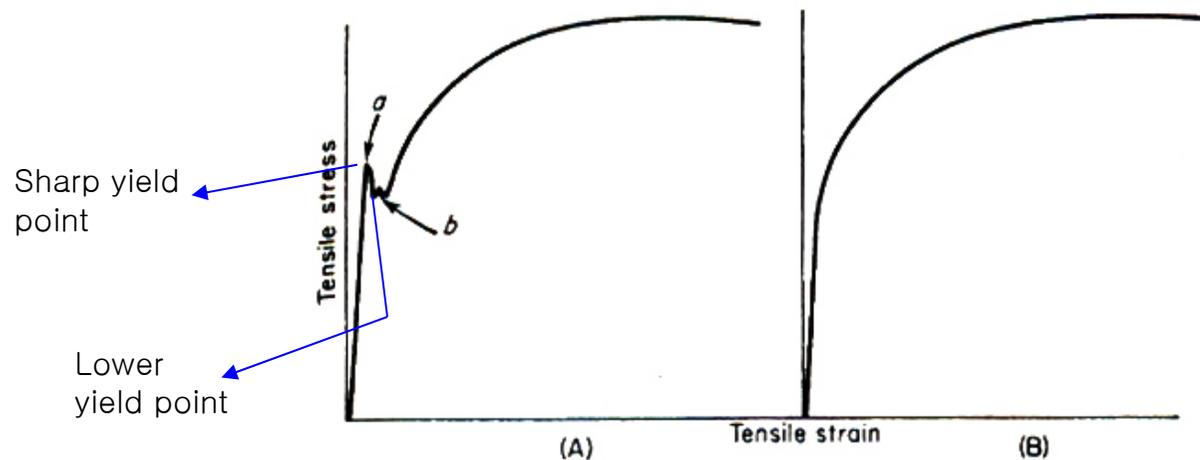

Fig.9.7 (A) Tensile stress-strain curve for a metal exhibiting a sharp yield point. (B) stress-strain curve for a metal that dose not exhibit a sharp yield point.

Its existence is of considerable concern to manufacturers who stamp or draw thin sheets.

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In general, deformation start at positions of stress concentration as discrete bands of deformed material, called Luders bands.
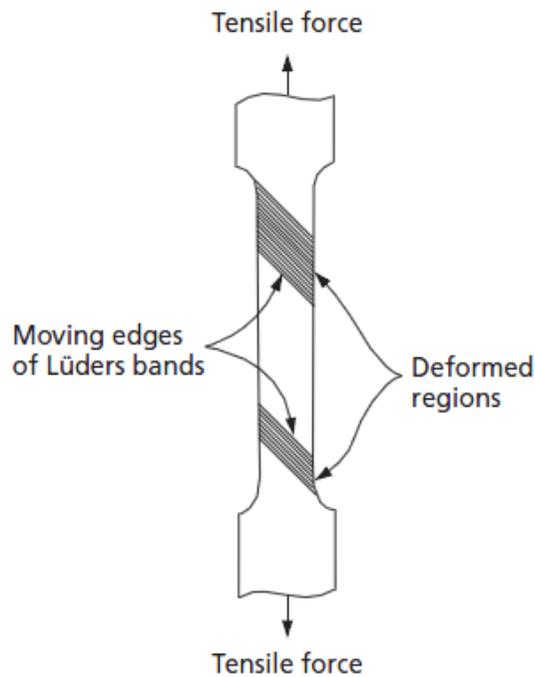

Fig.9.8 Luders bands in a tensile-test specimen.

This occurs at an almost constant stress and explains the horizontal part of the stress-stain curve at the lower yield point.

Annealed steel sheet id often given a slight reduction in thickness by rolling, which amounts to about a 1% strain. This is called a *temper roll*, and it produces a very large number of Luders band nuclei in the sheet.

The theory of sharp yield point

Cottrell

The interaction between dislocations and solute atoms

The atmosphere of solute atoms that collect around dislocations serves to pin down, or anchor, the dislocations. Additional stress, over that normally required for movement, is needed in order to free a dislocation form its atmosphere.

Johnston & Gilman

For LiF

In effect, this theory postulates that in a metal with a very low initial dislocation density, the first increments of plastic strain cause an extremely large relative increase in the dislocation density.

This rapid dislocation multiplication at the beginning of a tensile test can produce a yield drop.
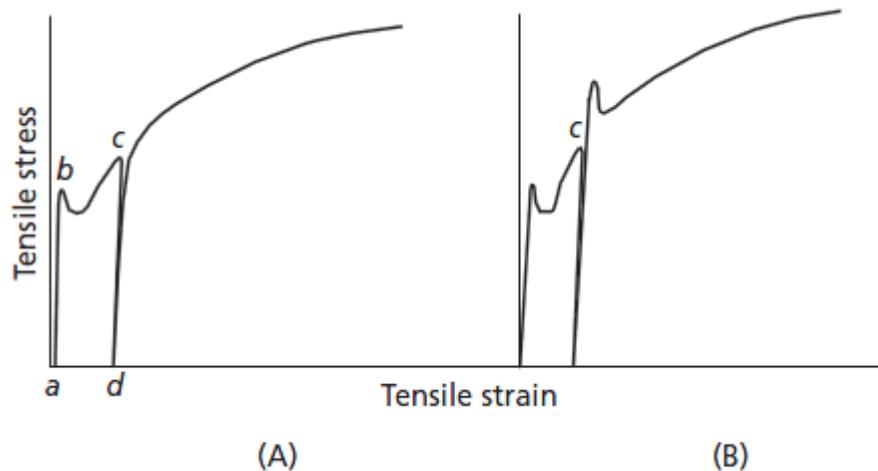
Solid Solutions

Strain aging

Fig.9.9 strain aging. (A) Load removed from specimen at point c and specimen reloaded within a short period of time (hours). (B) Load removed at point c and specimen reloaded after a long period of time (months)

Metal behaves as a result of aging after plastic deformation, that is called *Strain aging*.

Solute atoms must diffuse through the lattice in order to accumulate around dislocations, the reappearance of the yield point is a function of time.
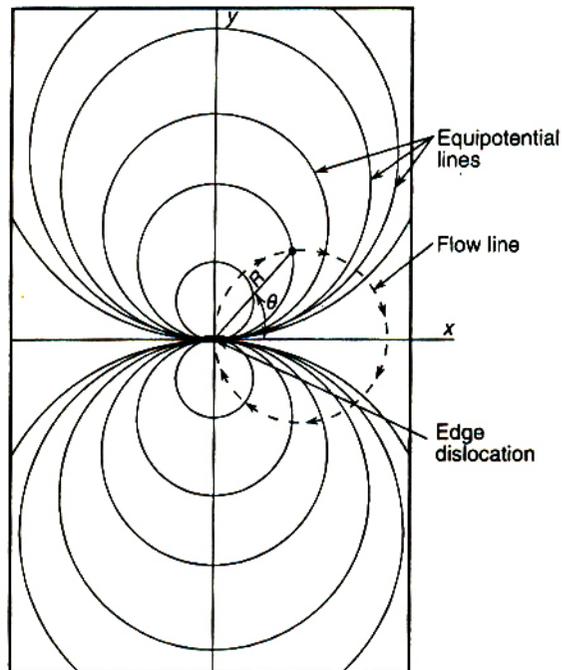
The Cottre-Bilby theory of stain aging

It deals with the time and temperature dependent growth of solute atmospheres near dislocations.

The interaction energy

$$U = \frac{A \sin \theta}{R}$$

The carbon atoms experience, F, due to this energy gradient. A result of this force of this force is that the carbon atoms may attain a drift velocity that can be computed with the aid of Einstein equation.

Equipotential lines

Flow line

Edge dislocation

$$v = (D/kT) \cdot F$$

Dynamic strain aging

For strain aging, the higher the temperature the faster the yield point reappears.

At sufficiently high temperature, the interaction between the impurity atoms and the dislocations should occur during deformation.

When aging occurs during deformation, the phenomenon has been called *dynamic strain aging*.

Actual sharp load drops are often observed as shown in Fig. 9.16. It is common to call the phenomenon associated with these serrations the Portevin-LeChatelier effect.

One of the most significant aspects of dynamic strain aging, observed primarily in metals containing interstitial solutes, is that the work hardening rate can become abnormally high during dynamic strain aging and, at the same time, it can become strain-rate and temperature dependent.
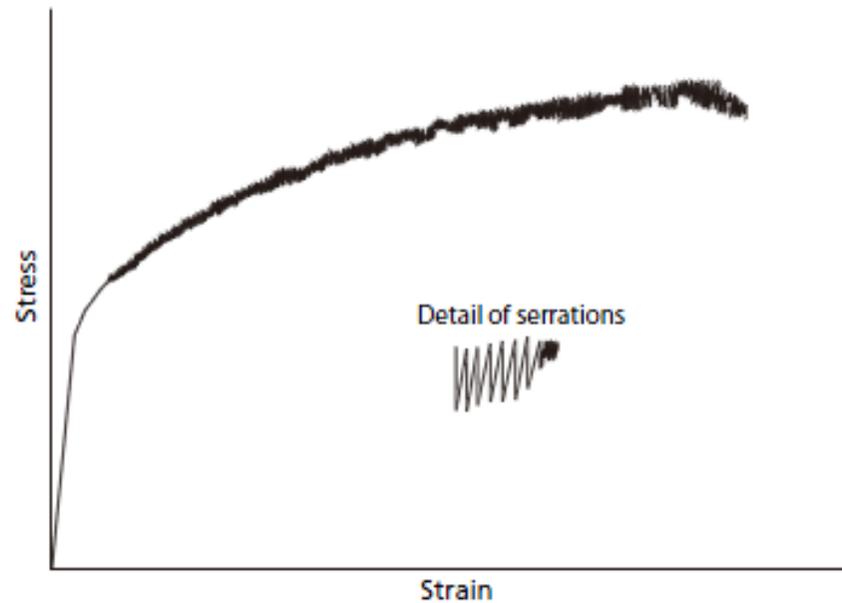
FIG. 9.16 Discontinuous plastic flow is a common aspect of dynamic strain aging. This diagram indicates one form of serrations that may be observed
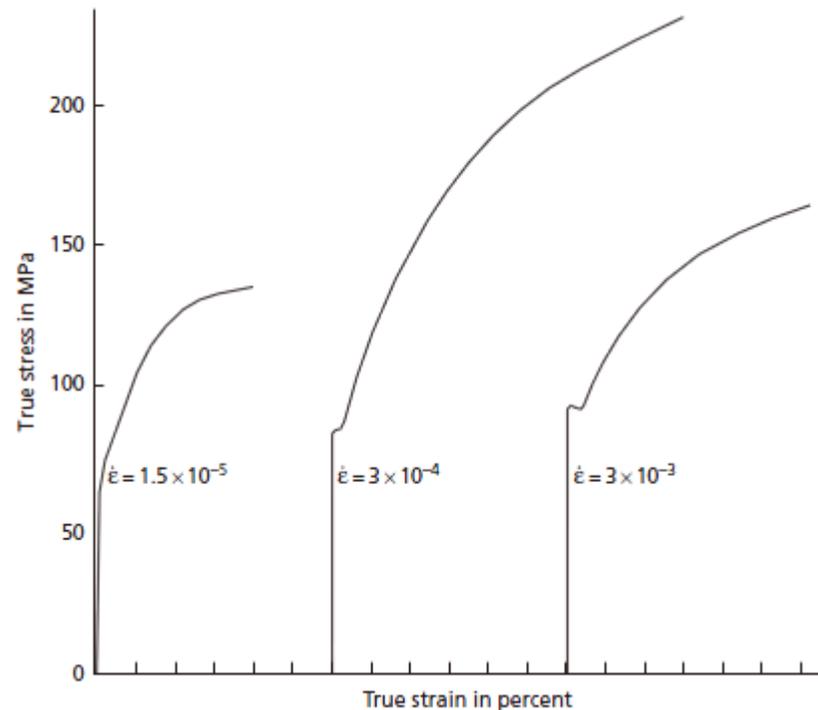
FIG. 9.17 In the temperature range of dynamic strain aging, the work hardening rate may become strain-rate dependent. This figure shows the stress-strain curves for three titanium specimens deformed at 760 K at different rates