STRENGTHENING MECHANISMS IN PURE METALS AND ALLOYS.

Anything which impedes the free motion and/or generation of dislocations will strengthen the material. A pure metal, either cast or hot-formed is extremely weak, with $\tau_y/G \equiv 10^{-4}$, where τ_y = yield strength in shear and G is shear modulus. These yield strengths are the order of 1000 psi, or the equivalent, a few MPa. There are enough dislocations to give lots of easy slip, but not enough to get in one another's way.

From the discovery of metals as useful tool materials humans have been trying to strengthen them. The techniques fall into the following general classes, which will be considered in turn.
1. Solid solution strengthening
2. Second phase strengthening
3. Work or strain hardening
4. Grain size hardening

Note that the terms hardening and strengthening are used interchangeably, and similarly yield stress and yield strength. Most strengthening increments will be in terms of $\Delta \tau_y/G$, the ratio of the increase in yield stress in shear to the shear modulus. The strengthening increments are additive, and an alloy may combine 2, 3, or even all 4 of the mechanisms.

1.   SOLID SOLUTION STRENGTHENING.

Most metals will dissolve significant amounts (tenths of an atomic per cent or more) of at least a few other elements. A few, like titanium, dissolve almost everything in the periodic table. The alloying element may replace a solvent atom in the lattice, becoming a substitutional solute, or fit into a position between the lattice atoms, becoming an interstitial solute. The sketch below shows τ_y for substitutional and interstitial solutes.
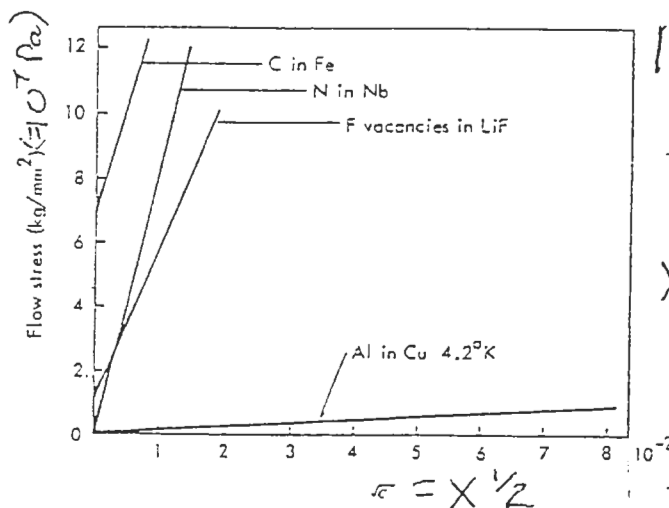
$1 \, kg/(mm)^2 = 10^7 \, Pa$

$X = \dfrac{Moles}{Mole}$

$\tau = X^{1/2}$

Substitutional atoms are almost never exactly the same size as the atoms they replace, and therefore strain the crystal lattice, either expanding or contracting it. Interstitial atoms invariably have to push their nearest neighbors out of the way to fit, and thereby also strain the lattice. These strains provide bumps in the road as dislocations try to pass, serving as pinning points, as shown below.

The mean distance between pinning points <u>on the slip plane</u>, $\overline{\ell}$, is shown from analysis to vary as $X^{-1/2}$, where of course X= atomic fraction solute. The added stress needed to bow between these points and ultimately break away from them is proportional to ℓ^{-1}, which gives the $X^{1/2}$ dependence shown in the first figure. Many people have tried to calculate the strength of the pinning in terms of atomic size, etc., but none has been very successful. The best people can do is take

$$\Delta\tau_y \,/G = K_{ss}X^{1/2}$$

Where K_{ss} = experimentally determined constant peculiar to each matrix and solute.

The reason the interstitial solutes in BCC metals strengthen so strongly is that they displace their nearest neighbors a lot, while the matrix actually contacts in the other two directions. That way the strain energy is not so great as to preclude solubility. The big, anisotropic deformation creates large shear stresses which strongly pin the dislocations, as with carbon in martensite, which is extraordinarily hard.

2. PRECIPITATION AND SPINODAL HARDENING

Heat treatment of a solid alloy at a temperature where the solid solution is subject to precipitation results in (surprise) precipitation. Heat treatment of Al-4 wt.% Cu gives very large number of Cu-rich particles. Heat treating martensite gives huge numbers of fine iron carbide particles, which may or may not be exactly the composition of cementite. It is also possible to introduce small second phase particles by powder metallurgy and other techniques. Alloys may also be subject to spinodal decomposition, which tends to produce two phases of the same crystal structure but in roughly equal proportions.

Let us first consider precipitation hardening with only a small volume fraction of the precipitating phase. Dislocations may pass freely through particles only if the particles have the same crystal structure and orientation as the matrix. Almost always the particles have a different crystal structure than the matrix, so the particles serve as obstacles. The dislocations may

bypass the particles either by cutting them, leaving behind a high energy interface, or by looping around the particles, leaving behind a dislocation loop. Whichever process can occur at the lower stress will occur. Particle volume fractions of up to 0.1 are possible, and particle sizes may be less than 1 nm.

a,   Cutting: Imagine displacing the two halves of a cementite particle by $a/2<111>$, the Burgers vector of the BCC Fe lattice. A high energy interface of $\gamma \cong 1 J/m^2$ would be introduced. Cutting usually occurs when there are a very high number of small particles, as you will soon see. To calculate the degree of strengthening, imagine passing a dislocation 1 m long over 1 m^2 of slip plane. Every particle which cuts the slip plane will be cut, leaving behind a high energy interface.

From quantitative metallography, the area of particle/unit area of slip plane equals the volume of particle per unit volume of material. The relationship is kind of obvious if you think about it. Imagine taking a tiny slice of the material which includes the slip plane. The volume fraction of particle in that slice has to be the same as in the bulk, and since the slice is so thin, one may count up area fraction to get the volume fraction. It is the same as taking a very thin slice out of an olive loaf. Area fraction equals volume fraction.

Side View

Plan View
Slip plan
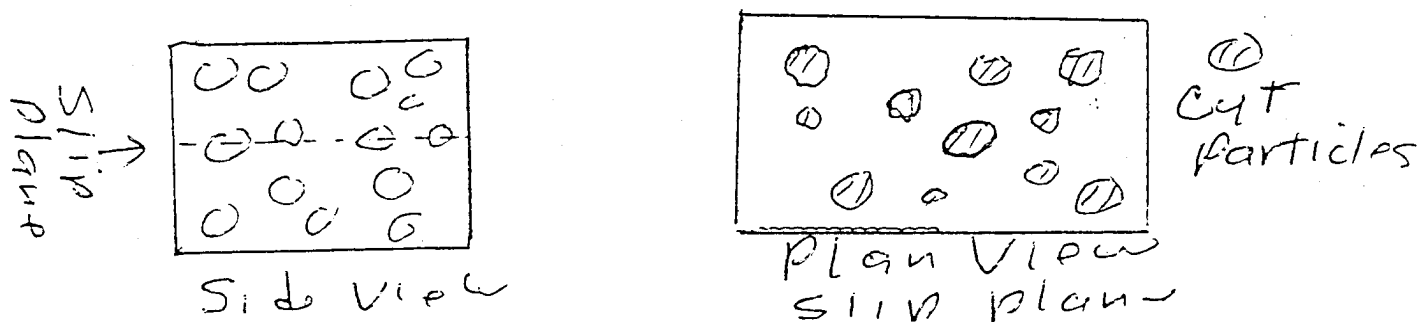
Cut particles

The work done in moving the dislocation over the unit area of plane equals the work done in cutting the particles. Thus: $\Delta\sigma_y b \cdot 1 \cdot 1 = f\gamma$, or, normalizing to G:

$$\Delta\tau_y/G = f\gamma /bG$$

b.   Looping: The dislocation may also loop around the particles as shown below. Looping is somewhat similar to operation of the Frank-Read source, in that the dislocations re-connect on the far sides of the particles, re-creating the original dislocation and leave loops around all the bypassed particles. From quantitative metallography, the distance between particles of radius, r, , measured in the slip plane is $r/f^{1/2}$. From dislocation theory, the

added stress needed to bow a dislocation out between pinning points ℓ apart is approximately $\Delta\tau_y = Gb/\ell$, so that

$$\Delta\tau_y/G = b\, f^{1/2}/r.$$

The sequence of events is shown below.
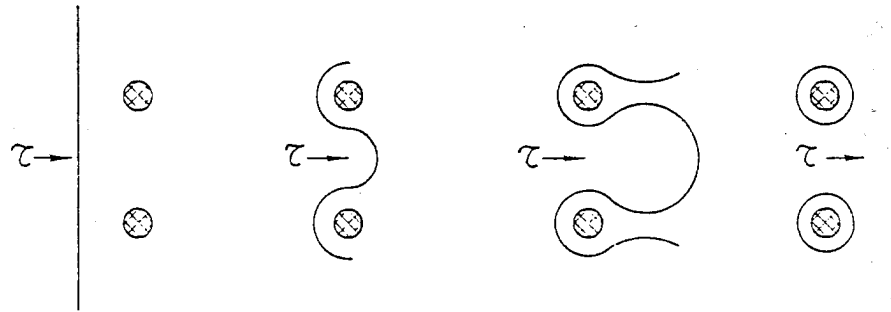
Cutting vs. looping: You should notice that the stress to loop increases greatly as r decreases, whereas the cutting stress is independent of r. Obviously, at small enough r, cutting is favored, which is observed experimentally. Nanometer diameter carbide particles in tempered martensite are cut, whereas micron-sized particles in alloys are looped around. Every time a dislocation goes by, another loop is left, which in time decreases the space the loop has to squeeze through. Cutting does not make the particles more resistant to passage of future dislocations. This situation is illustrated by the experimental results below.
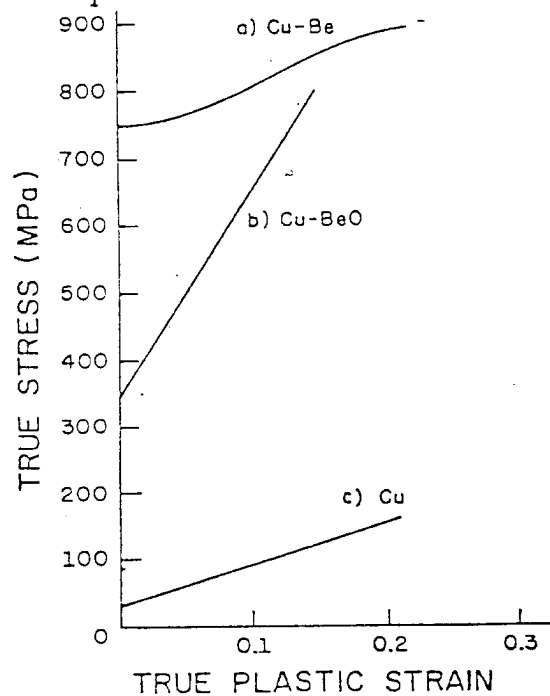

Figure 11.10 Stress–strain curves at 77 K. (a) For a precipitation hardened Cu-Be single crystal (precipitate volume fraction = 20%). These precipitates are cut by dislocations. (Adapted with permission from [6], p. 69.) (b) For a Cu crystal containing 2.8% of BeO which does not deform plastically. (c) For a pure Cu single crystal. (Adapted with permission from [6], p. 69.)

Stress strain plots are shown for:
- Cu hardened with very fine Be-rich precipitates, which are cut.
- Cu strengthened with a similar volume fraction of large, BeO particles which are looped around. This alloy work hardens rapidly.
- Pure, single crystal Cu.

Of course the Cu-Be and pure Cu undergo strengthening, due to the increase in the dislocation density during plastic deformation.

c.   Spinodal decomposition often produces approximately equal volumes of two phases, which may differ in lattice parameter or in shear modulus. It is inherent in spinodal composition that the two phases are fully coherent. Kato Acta Met._29, 79-87 (1981) did the analysis of spinodal strengthening which will be outlined here.

Phases of differing lattice parameter may maintain coherency only by assuming elastic strain, which of course generates internal stresses. The analysis considered a BCC alloy which had undergone decomposition by producing compositional waves in the <100> directions. Slip in BCC crystals is on {110} planes in <111> directions. Kato plotted the resolved shear stress on the (110) slip plane as shown on the next page.

The shear stress in the plane showed maxima and minima which formed ridges, as in a plowed field. A [1̄11] dislocation lying in the slip plain would thus be neither pure screw or pure edge, but would instead lie in a mixed orientation along one of the stress minima. Slip would only occur when the applied stress was great enough to force the dislocation out of the minimum over the next maximum.
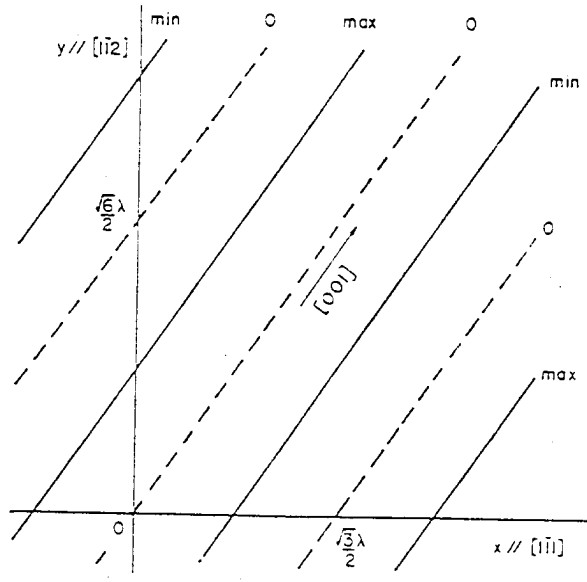
Kato calculated that:
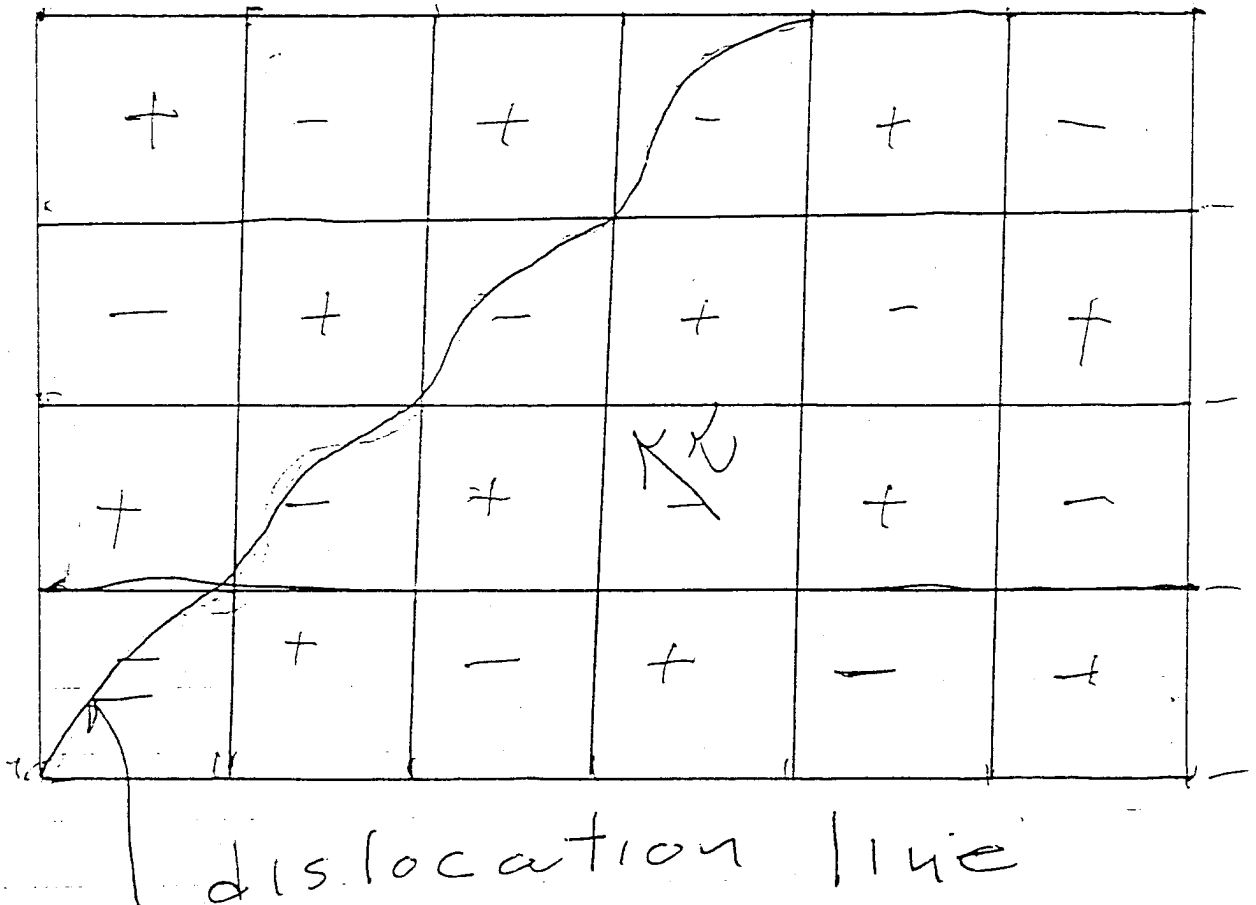
$$\Delta\tau_y = A\eta Y/2$$

where A = amplitude of composition wave, $\eta = (1/a)(da/dX)$ is the compositional variation of the lattice parameter, a, and Y is a function of the elastic constants, C_{11} and C_{12}. If the material is elastically isotropic, $Y = 2G(1+v)/(1-v)$ so that:

$$\Delta\tau_y/G = A\eta\ (1+v)/(1-v)$$

is the strengthening increment due to lattice parameter difference.

The distribution of internal shear stress on (110) slip plane

Dislocation line curving to lie mostly in low-modulus regions.

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Modulus strengthening may be understood by realizing that the strain energy of a dislocation line is proportional to G. Therefore, the dislocation line would lie mostly in low-G regions, as shown on the previous page, with + denoting high-G and - denoting low G regions. Kato showed that

$$\Delta\tau_y = 0.33b\Delta G/\lambda,$$

where b = Burgers vector, ΔG = modulus difference between high and low modulus regions, and λ = wavelength of composition waves.

Experimental tests were done in Fe-47.8 at. % Cr alloys where G_{Cr} = 12×10^{10}Pa, G_{Fe} = 8.6×10^{10} Pa, η = 0.004, and λ = 20 nm. The change in tensile yield was 400 MPa, which corresponds to a 200 MPa increase in $\Delta\tau_y$. The two differ because the resolved shear stress is approximately half the tensile stress. The calculated increment in $\Delta\tau_y$ was 84 MPa due to misfit and 98 MPa due to modulus, for a total of 182 MPa, in good agreement with the experimental 200 MPa. Spinodal decomposition thus may be a very effective strengthening mechanism.

3.   WORK/STRAIN HARDENING

The more dislocations there are in a metal, the more they get in one another's way and the harder it is to push them by one another in plastic deformation. If two parallel dislocations lie in the same slip plane each exerts a stress on the other of~$Gb/2\pi r$, where r = dislocation spacing. If the dislocations do not lie in the same slip plane, or are not parallel, a similar relation applies, though with some sort of geometrical fudge factor.

Averaging over edge vs. screw, all sorts of orientations and all else, one still estimates that it will take a added resolved stress of $\Delta\tau_y$ = $Gb/2\pi r$ to push the dislocations past one another, where r is now the spacing on a polished section. We write ρ_d as the dislocation density in #/m^2 or m/m^3, as you wish. Approximately, $r^{-2} = \rho_d$ Then, we may write:
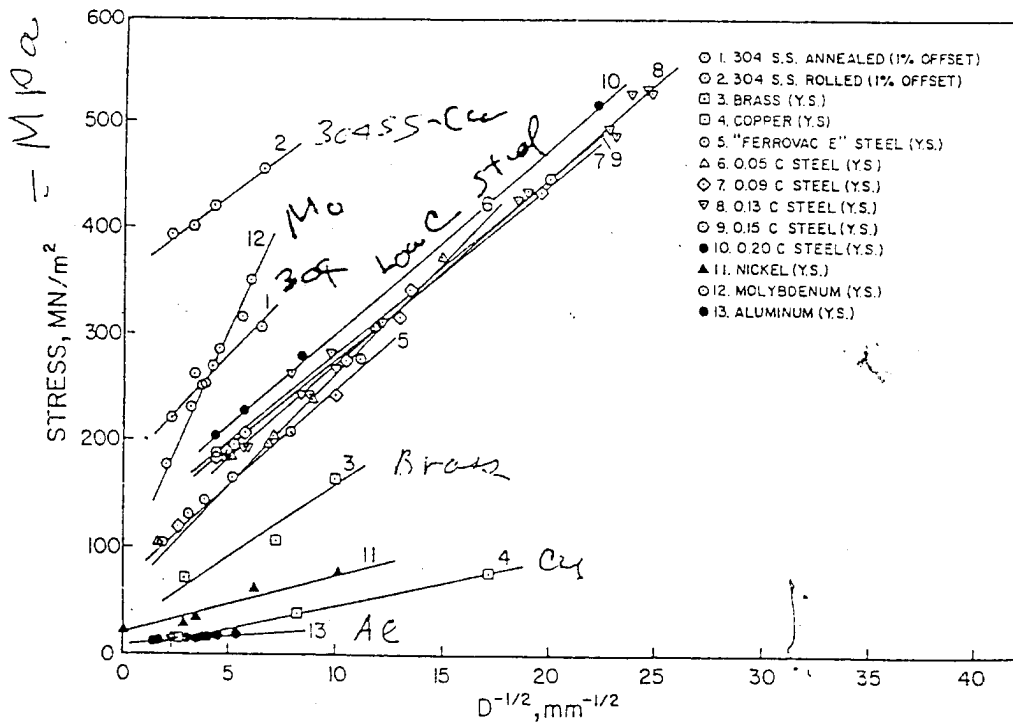
$$\Delta\tau_y/G = b\,\rho_d^{1/2}/2\pi$$

A severely cold worked material may have ρ_d~10^{15}/m^2. There is no very good relationship between ρ_d and the amount of plastic strain.

4.   GRAIN SIZE STRENGTHENING

Heavy cold work of a metal, followed by annealing, gives rcrystallization, the replacement of the deformed grains with new, strain-free, low dislocation density grains. Annealing at a relatively low temperature, say, somewhat below half the absolute melting point, will give very fine grains, whereas annealing at a high temperature gives large grains.

Obviously the proper annealing temperature for a given alloy has to be determined experimentally. The yield strength has been found to vary with grain size (d = average grain diameter) as shown below for a number of pure metals and alloys. The relationship between τ_y and $d^{-1/2}$ is fairly accurately linear, up to a grain size which approaches the diameter of the test specimen. At that point surface effects are to be expected. However, a different straight line is obtained for different alloys. Theoreticians have had little luck in calculating $\Delta\tau_y$ as a function of $d^{-1/2}$. The linear relationship between τ_y and $d^{-1/2}$ is known as the Hall-Petch relationship, after two British metallurgists of the 50's and 60's. The Hall-Petch relationship is rationalized in terms of the greater difficulty in operating a Frank-Read source in small grains. The lengths of dislocation which bow out are likely to be shorter and require a larger stress to bow out and operate. Also, back stresses from emitted dislocation which have piled up at the grain boundaries will become important earlier is small grains.

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