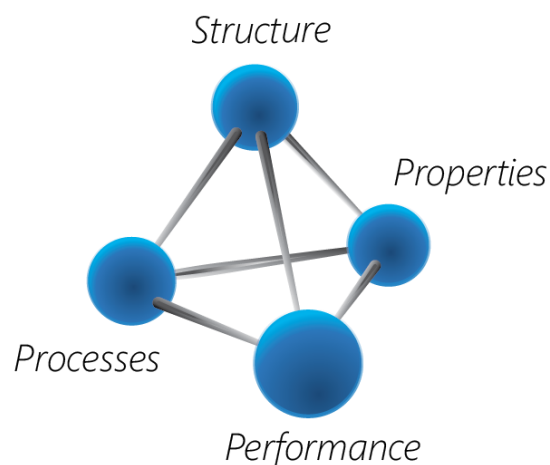


CES EduPack Structure and Mechanism Notes



Mike F Ashby

Engineering Department, Cambridge University, UK
and Granta Design Ltd, Cambridge, UK

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This Booklet is part of a set based on Mike Ashby's work to help introduce students to materials, processes and rational selection. The Teaching Resources website aims to support teaching of materials-related courses in Design, Engineering and Science. Resources come in various formats and are aimed primarily at undergraduate education.

www.teachingresources.grantadesign.com

Abstract

This is a set of 2-page summaries of the mechanisms that underlie a range of material properties with schematics illustrating the associated structures at an atomic level.

Contents

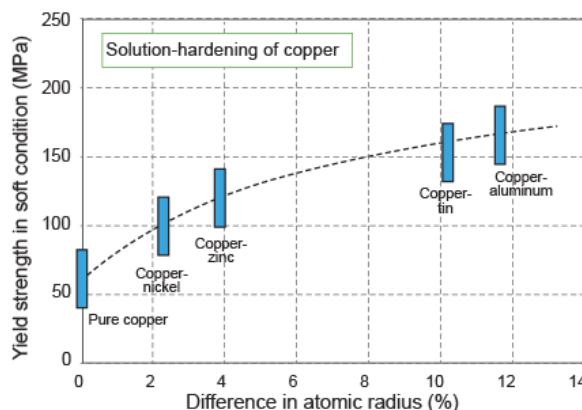
1. Solid solution strengthening
2. Strain hardening
3. Precipitation and dispersion strengthening
4. Grain size strengthening
5. Toughening
6. Electron scattering
7. Phonon scattering
8. Domain wall pinning

1. Solid solution strengthening

Solid solutions

Substitutional solid solutions form when atoms of one element substitute for those of another. The atomic sizes and electronic structures of elements differ; the greater the difference the more limited is the solid solubility. This is expressed more fully in the Hume-Rothery solubility rules requiring

- Similar atomic size (to within 15%)
- Similar crystal structure
- Similar electronegativity (energy of ionization) so that compounds don't form
- Similar valence



Thus, copper and nickel with the same valence and crystal structure, similar electronegativity and atomic sizes that differ by $\epsilon = 2.4\%$ show complete (100%) solid solubility; copper and lead with the same crystal structure but differing electronegativity and atomic sizes that differ by $\epsilon = 36\%$ have a maximum mutual solubility of 0.1%.

The mechanism of solution strengthening

Solid solution strengthening is strengthening by deliberate additions of impurities or, more properly said, by *alloying*. The addition of zinc to copper makes the alloy brass – copper dissolves up to 30% zinc. The zinc atoms replace copper atoms to form a *random substitutional solid solution*. The zinc atoms are bigger than those of copper ($\epsilon = 3.8\%$), and, in squeezing into the copper lattice they distort it. This roughens the slip plane, so to speak, making it harder for dislocations to move, thereby adding an additional resistance to dislocation motion. The figure illustrates that the concentration of solute, when low, is on average

$$c = \frac{b^2}{L^2}$$

where L is the spacing of obstacles in the slip plane and b is the atom size. Thus

$$L = \frac{b}{c^{1/2}}$$

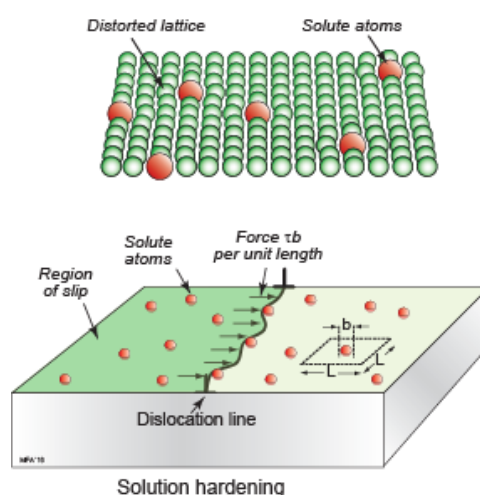
The shear stress τ needed to force the dislocation through a field of obstacles has the form

$$\tau = \alpha \epsilon^{3/2} \frac{Gb}{L}$$

where G is the shear modulus, α is a dimensionless constant and ϵ , as before, is the size mismatch. Combining the last two equations gives the contribution of solid solution, τ_{ss} , to the shear stress required to move the dislocation:

$$\tau_{ss} = \alpha \epsilon^{3/2} E c^{1/2}$$

τ_{ss} Increases as the square root of the solute concentration. Alloying elements differ in their mismatch of size and thus in the extent to which they distort the host crystal, changing ϵ . When the mismatch in size is small (as in copper-zinc alloys) the strengthening is modest; when it is larger (copper-tin alloys, $\epsilon = 10.4\%$) the



strengthening is greater. Size mismatch also limit the maximum solubility (see Hume-Rothery's rules, above) setting an upper limit for the concentration c that can be dissolved, so the most effective mismatch is an intermediate one.

Examples: Alloys that derive their strength from a solid solution

Solid solutions are single-phase alloys, although they may show segregation like that of the dendritic alpha brass shown in the figure. Multi-phase alloys can suffer from corrosion because of electrolytic cells set up between the phases; single phase alloys avoid this particular problem. The table gives examples of alloys that derive their strength from solid-solution. High-entropy alloys are among them: although they contain five or more components, they all form a single solid solution (the name "high entropy" derives from the high entropy of mixing that results from the multiple components).

Solution hardened alloys
α -Brass (Copper – Zinc)
Bronze (Copper – Tin)
Monel (Copper – Nickel)
Gunmetal (Copper – Tin – Zinc)
Nichrome (Nickel – Chromium)
Austenitic stainless steels (Iron – Nickel – Chromium)
Rose gold (Gold – Copper)
White gold (Gold – Nickel)
High entropy alloys (Fe-Cr-Mn-Ni-Co solid solution)



Microstructure. Alpha-brass.
(<http://www.georgesbasement.com/Microstructures/NonFerrousAlloys/Lesson-1/Specimen05.htm>)

Applications of solid solution strengthened alloys

Solid solution hardening provides strength without compromising corrosion resistance. Brasses, bronzes, monels and gunmetals are used for pumps, taps, valves, heat exchangers; condensers, ships propellers, marine fittings and architectural cladding. Nichromes and austenitic stainless steels are strong, ductile and oxidation resistant to high temperatures. High entropy alloys, particularly, have good creep resistance.

Links at Level 2 to:

- Materials – brass, bronze, nichrome, stainless steel
- Processes – all sand, die and investment casting
- Phase diagrams – copper nickel, copper-zinc; copper-tin; nickel-chromium; iron-chromium-nickel (ternary)
- Property-process profiles - 1. Copper alloys; 3. Stainless steels

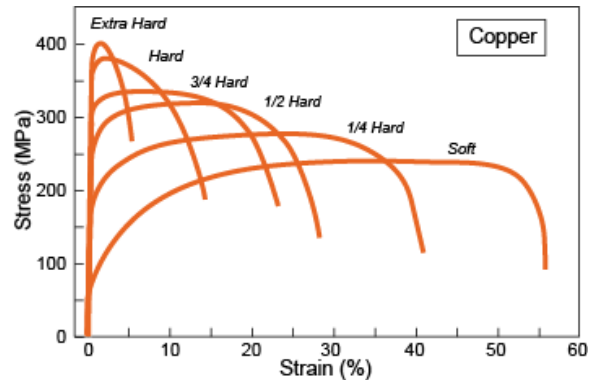
Further Reading

Askeland, D.R., Phulé, P.P. and Wright W.J. (2010) *The Science and Engineering of Materials*, 6th edition, Ch. 10.
Callister, W.D. and Rethwisch, D.G. (2014) "Materials Science and Engineering", 9th Edition Ch. 7.9.
Shackelford, J.F. (2014) "Introduction to materials science for engineers", 8th edition, Ch. 2.

2. Strain hardening

Strain hardening

The rising part of the stress-strain curve of a ductile metal is called *strain-hardening*: it is caused by the accumulation of dislocations generated by plastic deformation. Metals can be shaped compacting by deformation: rolling, forging, drawing, swaging or wire drawing. If the deformation is at room temperature, the metal strain-hardens. The figure shows the way the stress-strain curve of a metal – here, copper – changes with increasing strain hardening. The yield and tensile strength rise and the elongation and fracture toughness decrease (See also record for Toughening).



The mechanism of strain hardening.

The *dislocation density*, ρ_d , is defined as the length of dislocation line per unit volume (m/m^3). Even in an annealed soft metal, the dislocation density is around $10^{10} \text{ m}/\text{m}^3$, meaning that a 1cm cube (the size of a cube of sugar) contains about 10 km of dislocation line. When metals are deformed, dislocations multiply, causing their density to grow to as much as $10^{17} \text{ m}/\text{m}^3$ or more – 100 million km per cubic centimeter. A moving dislocation now finds that its slip plane is penetrated by a forest of intersecting dislocations with an average spacing $L = \rho_d^{-1/2}$.

A shear stress τ exerts a force τb per unit length on a dislocation, causing it to move in the direction of the force, where b is the Burger's vector. As a dislocation advances, it shears the material above the slip plane relative to that below, and that creates a little step called a *jog* in each forest dislocation. The jogs have potential energy – they are tiny segments of dislocation of length b – with the result that each exerts a pinning force $p = Gb^2/2$ on the moving dislocation. Assembling these results into equation gives the contribution of strain hardening (expressed here as a shear stress τ_{wh}) of

$$\tau_{wh} \approx \frac{Eb}{2} \sqrt{\rho_d}$$

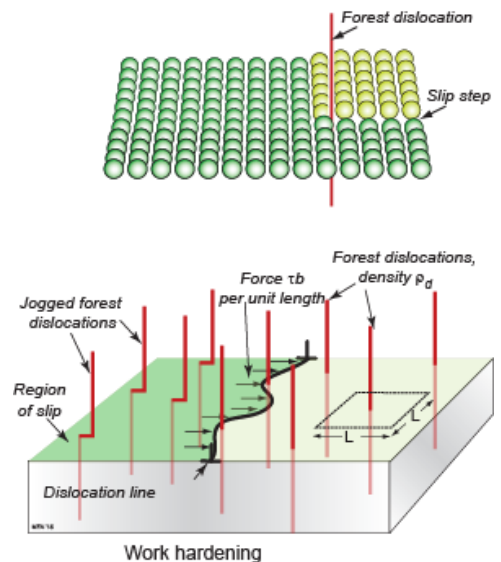
The greater the density of dislocations, the smaller the spacing between them and the greater their contribution to τ_{wh} . The contribution of the forest dislocation density to the yield strength can be estimated using Taylor's equation:

$$\Delta\tau_{wh} = \alpha M G b \sqrt{\rho_d}$$

where α is a constant, M is the Taylor factor, and G is the shear modulus. The upper estimate of the dislocation density can be estimated from the strain $\Delta\epsilon$ as:

$$\sqrt{\rho_d} \cdot b = \Delta\epsilon$$

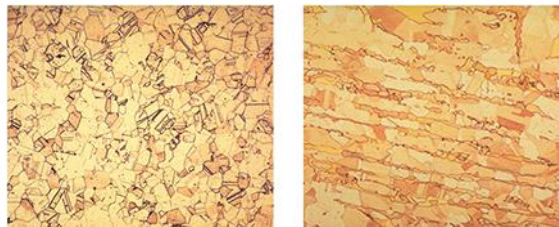
All metals strain-harden. It can be a nuisance: if you want to roll thin sheet, strain-hardening quickly raises the yield strength so much that you have to stop and *anneal* the metal (heat it up to remove the accumulated dislocations) before you can go on – a trick known to blacksmiths for centuries. But it is also useful: it is a potent strengthening method, particularly for alloys that cannot be heat-treated to give precipitation hardening.



Alloys that derive their strength from strain hardening.

The table gives examples of alloys that derive their strength from strain hardening.

Strain hardened alloys
Cold rolled / deep drawn steel
"Piano" (Patented) steel wire
1000 / 3000 / 5000 series Al-alloys in the "H" condition
Wrought Z-series magnesium alloys
Copper in the "Hard" conditions
Cu-Al Bronzes in the "Hard" condition
Cu-Zn Brasses in the "Hard" condition
Cu-Sn Bronzes in the "Hard" condition



Microstructure. A metal (here, a copper alloy) before and after deformation. The grain size is about 0.1 mm.

Applications of strain hardened alloys

Strain hardening provides strength without compromising corrosion resistance, electrical or thermal conductivities. Rolled steels, copper alloys and aluminum alloys in the "half hard" or "hard" conditions derive much of their room-temperature strength from strain hardening. Strain hardening is less effective at higher temperatures at which recovery or recrystallization start to remove the stored dislocations responsible for the increase in strength.

Links at Level 2 to:

- Materials – Non age-hardened wrought aluminum alloys; Wrought magnesium alloys; Wrought copper alloys, Carbon, low alloy and stainless steels.
- Processes – all Deformation processing records.
- Property-process profiles - 1. Alloying and working: Copper alloys.

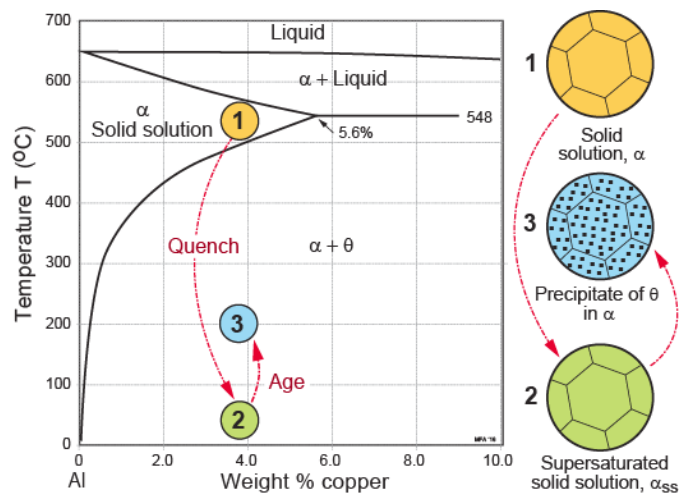
Further Reading

Askeland, D.R., Phulé, P.P. and Wright W.J. (2010) *The Science and Engineering of Materials*, 6th edition, Ch. 8.
 Callister, W.D. and Rethwisch, D.G. (2014) "Materials Science and Engineering", 9th Edition Ch. 7.10.
 Shackelford, J.F. (2014) "Introduction to materials science for engineers", 8th edition, Ch. 6.

3. Dispersion and precipitation strengthening

Precipitation strengthening

An effective way to impede dislocations is to disperse small, strong particles in their path. One way to make such a microstructure is to disperse small solid particles of a high melting point compound into a liquid metal, and to cast it to shape, trapping the particles in place – it is the way that metal matrix composites such as Al-SiC are made. An alternative is to form the particles *in-situ* by a *precipitation* process, exemplified by the aluminum-copper system. If an alloy with the composition Al-4% Cu is solution-heat treated at 550 °C, the copper dissolves in the aluminum matrix and remains trapped if the alloy is quenched to room temperature. Subsequent ageing at 200 °C allows the copper to precipitate, first as nano-scale copper-rich zones (“GP zones”) subsequently growing to precipitates of the θ phase (CuAl_2). Copper alloyed with a little beryllium, similarly treated, gives precipitates of the compound CuBe . Age hardening magnesium alloys, precipitation hardened stainless steels, nickel-based superalloys and high strength titanium alloys all rely on a heat treatment like this.

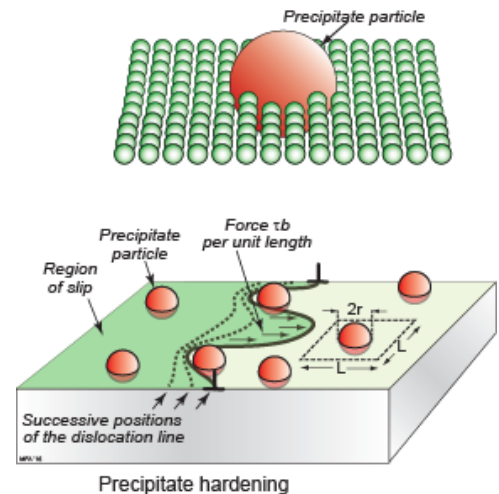


The mechanism of precipitation strengthening

A shear stress τ exerts a force τb per unit length on a dislocation, causing it to move in the direction of the force, where b is the Burger's vector. The figure shows how particles obstruct dislocation motion. If the particles are too strong for the dislocation to slice through them, the force τb pushes the dislocation between them, bending it to a tighter and tighter radius against its line tension. The radius is at a minimum when it reaches half the particle spacing, L ; after that it can expand under lower stress. The *critical configuration* is the semicircular one: here the total force τbL on one segment of length L is just balanced by the force $2T$ due to the line tension $T \approx Eb^2/2$ acting on either side of the bulge, as in the schematic. The dislocation escapes when

$$\tau_{ppt} = \frac{2T}{bL} \approx \frac{Eb}{L}$$

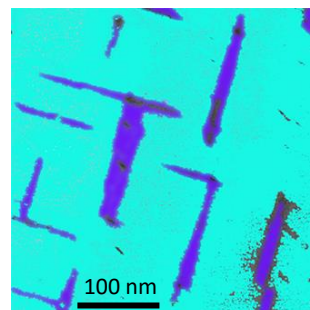
where τ_{ppt} is the contribution of precipitation strengthening to the shear strength of the material. Precipitation strengthening is an effective way to increasing strength: precipitate-hardened aluminum alloys can be 15 times stronger than pure aluminum.



Examples of materials that rely on precipitation or dispersion strengthening

Light-weight aluminum and magnesium alloys derive their strength from precipitation strengthening. Precipitation strengthening titanium and nickel based alloys retain strength at temperatures above room temperature, allowing them to be used in gas turbines and in chemical engineering.

Precipitation hardened alloys
2000, 6000 and 7000 series aluminum alloys
AZ series magnesium alloys
Ti-6Al-X titanium alloys
Copper-beryllium and copper-cobalt alloys
Precipitation hardened stainless steels
Tool steels
Nickel-based super-alloys
Particulate metal-matrix composites



Microstructure. Precipitates in an age-hardening aluminum alloy

Applications of precipitation and dispersion hardened alloys

Precipitation-hardened aluminum and magnesium alloys are used in aerospace for airframe and undercarriage components. Titanium and nickel-based precipitation hardened alloys have useful strength at high temperatures, giving them a key role in gas turbine design. The automotive sector, seeking to reduce weight, makes increasing use of aluminum and magnesium alloys for panels, suspension and transmission parts. Makers of sports equipment (cycling, motor sport, water sport), always seeking higher performance, also make extensive use of precipitation-hardened light alloys.

Links at Level 2 to:

- Materials – Age-hardened wrought aluminum alloys; Wrought magnesium alloys; Titanium alloys
- Processes – all Heat Treatments
- Phase diagram – Aluminum-copper
- Property-process profiles - 3. Alloying and heat treatment: stainless steels; 4. Alloying and heat treatment: aluminum alloys

Further Reading

Askeland, D.R., Phulé, P.P. and Wright W.J. (2010) *The Science and Engineering of Materials*, 6th edition, Ch. 11.

Callister, W.D. and Rethwisch, D.G. (2014) "Materials Science and Engineering", 9th Edition Ch. 11.9

Shackelford, J.F. (2014) "Introduction to materials science for engineers", 8th edition, Ch. 10.

4. Grain-size strengthening

Grain size strengthening

Almost all metals are polycrystalline, made up of tiny, randomly oriented, crystals, or *grains*, meeting at grain boundaries. The grain size, D , is typically 1–100 μm . The grain boundaries obstruct dislocation motion. A dislocation in one grain – call it grain 1 – can't just slide into the next – grain 2 – because the slip planes don't line up. Instead, new dislocations have to nucleate in grain 2 with slip vectors that, if superimposed, match that of the dislocation in grain 1 so that the displacements match at the boundary. This mismatch obstructs dislocation motion, giving a contribution to strength. Not surprisingly, the smaller the grains, the greater the area of grain boundaries and the greater this contribution. The figure¹ shows how the strength of a stainless steel changes with grain size. It is plotted like this to illustrate a general finding: that the contribution to strength, σ_{gb} scale as $D^{-1/2}$, giving

$$\sigma = \sigma_o + \frac{k}{\sqrt{D}} \quad (1).$$

where σ_o is the strength when the grain size is very large and k is called the Petch constant, after the man who first measured it. For normal grain sizes the grain-size contribution to strength is small, but for materials that are micro-crystalline ($D < 1 \mu\text{m}$) or nano-crystalline (D approaching 1 nm) it becomes large. The table lists values for the constants in equation (1).

Material with very small grains are made by very rapid cooling from the melt, by extreme deformation followed by controlled recrystallization, by electro-plating, vapor deposition or laser surface treatment, or by compaction of nano-scale particles. They are difficult to make and not easy to keep – the energy associated with nano-scale grains means that, given a little thermal energy, they grow.

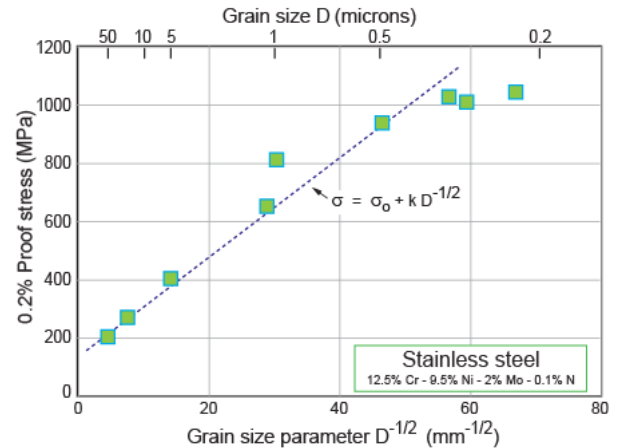
The mechanism of grain size strengthening

There is room in a single grain for more than one dislocation. When a stress is applied, the dislocations within one grain move, piling up against the boundary that obstructs its passage into the next grain in their path. Suppose an array of n identical dislocations pile up against a grain boundary under the effective shear stress,

$$\tau_{eff} = \tau - \tau_o$$

where τ is the applied shear stress and τ_o is the sum of other contributions to the shear strength. The pile-up magnifies the stress acting on the front dislocation by the factor n :

$$\tau_{pu} = n\tau_{eff}$$



Hall–Petch constant		
Material	σ_o [MPa]	k [MPa $\text{m}^{1/2}$]
Copper	25	0.11
Titanium	80	0.40
Mild steel	70	0.74
Stainless steel	150	0.54
Ni ₃ Al	300	1.70

¹ Data from K.Tomimura, S.Takagi and Y.Tominaga: Iron and Steel Institute of Japan, (1991), p.105

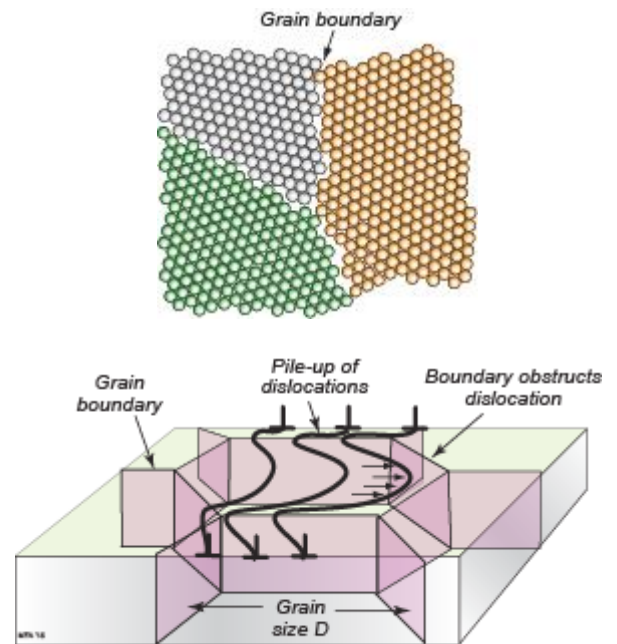
If the pile-up has length, D , the number of dislocations it contains is also determined by the effective stress, and is

$$n \approx \frac{C D \tau_{eff}}{E b}$$

where E is the modulus and C is a geometric factor of order unity. Yield occurs when the stress on front dislocation in the pile-up exceeds that needed to nucleate slip across the grain boundary, τ_c , giving the contribution of grains to the strength:

$$\tau_{gb} = \tau_o + \sqrt{\frac{E b \tau_c}{C}} \frac{1}{\sqrt{D}}$$

Replacing shear strengths by axial strength using $\sigma \approx 2\tau$ gives an equation with the same form as the empirical equation (1) above.

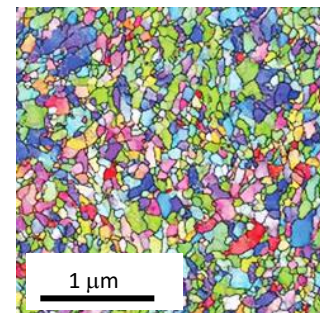


Grain-size hardening

Examples of materials that rely on grain boundary strengthening

Bulk materials with ultra-small grains are difficult to make. Making them as thin layers, wires or surface coatings is rather easier. For this reason, grain size strengthening is exploited most commonly as surface deposits to increase wear and fatigue resistance.

Grain size strengthened alloys
Electro-less and electro-deposited metal coatings
Steels subjected to extreme deformation
Mechanically alloyed metal-ceramic composites
Burnished and shot-peened metal surfaces
Vapor-deposited thin films



Microstructure. Nano-scale stainless steel. <http://www.ebsd.com/solving-problems-with-ebsd/material-analysis-at-the-nano-scale>

Applications of grain boundary hardened alloys

Grain boundary strengthening raises strength while leaving thermal and electrical conductivity almost unchanged.

Links at Level 2 to:

- Materials – Stainless steels
- Processes – Electroless plating; Electroplating; Metal flame spray; Vapor metallizing

Further Reading

Askeland, D.R., Phulé, P.P. and Wright W.J. (2010) *The Science and Engineering of Materials*, 6th edition, Ch. 4.
 Callister, W.D. and Rethwisch, D.G. (2014) "Materials Science and Engineering", 9th Edition Ch. 7.8.
 Shackelford, J.F. (2014) "Introduction to materials science for engineers", 8th edition, Ch. 4.

5. Toughening

Toughness.

The two most important properties for mechanical design are strength and crack-resistance. The energy required to propagate a crack of unit length by unit distance is called the *toughness*, symbol G_c . Its units are J/m^2 or, more usually, kJ/m^2 . It should not be confused with the *fracture toughness*, K_{Ic} , units $\text{MPa}\cdot\text{m}^{1/2}$, which is a measure of the intensity of stress at the crack tip when the crack propagates. The two are related approximately by

$$G_c \approx \frac{K_{Ic}^2}{E}$$

where E is Young's modulus. The chart opposite shows all three of these properties for metals, polymers and ceramics. The toughness spans a wide range, from as little as 3 J/m^2 for the most brittle glasses and ceramics to as much as $300,000 \text{ J/m}^2$ for the toughest metals.

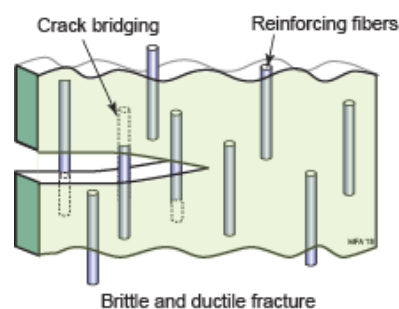
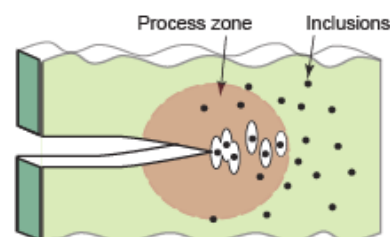
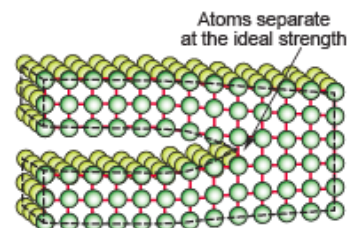
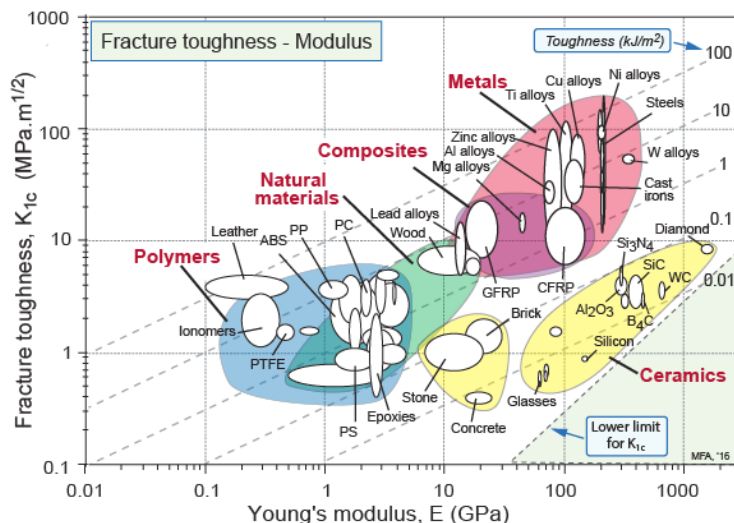
The surface energy, γ , of a solid (units J/m^2) is the energy it costs to make a square meter of new surface. Think of taking a 1 m cube of a material and cutting it in half to make two new surfaces, each of area 1 m^2 . To do so we have to provide the cohesive energy associated with the bonds that previously connected across the cut. The atoms are bonded on all six sides so the surface atoms lose $1/6$ of their bonds when the cut is made. This means that we have to provide $1/6$ of the cohesive energy H_c to a slice $4r_o$ thick and thus to a volume $4r_o \text{ m}^3$, where r_o is the atom radius. So, the surface energy should be:

$$2\gamma \approx \frac{1}{6} H_c \cdot 4r_o \quad \text{or} \quad \gamma \approx \frac{1}{3} H_c \cdot r_o$$

Typically, $H_c \approx 3 \times 10^{10} \text{ J/m}^3$ and $r_o \approx 10^{-10} \text{ m}$, so surface energies are around 1 J/m^2 . The toughness G_c cannot be less than 2γ . As we have seen, the toughness of most materials is hundreds of times larger than 2γ . Where is the extra energy going? That depends on the mechanism.

Mechanisms of toughening

To understand how cracks propagate in ductile materials, think first of pulling a sample with no crack. Ductile metals deform plastically when loaded above their yield strength, work-hardening until the tensile strength is reached. If ultra-pure, the metal may simply thin down until the cross-section goes to zero. Engineering alloys are not ultra-pure; almost all contain inclusions – small, hard particles of oxides, nitrides, sulphides, intermetallics and the like. As the material deforms stress builds up at the inclusions, which act as stress concentrations. These separate from the matrix or fracture, nucleating tiny holes. The holes grow as strain increases, linking and weakening the part of the specimen in which they are most numerous until they finally coalesce to give a *ductile fracture*. Many polymers, too, are ductile. They don't usually contain inclusions but when stretched they *craze* – tiny cracks



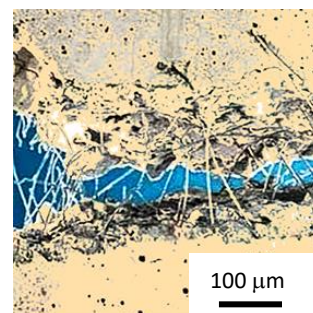
open up in the most stretched regions, whitening them if the polymer is transparent. The details differ but the results are the same: the crazes nucleate, grow and link to give a ductile fracture.

Return now to the cracked sample. The stress rises as the crack tip is approached, but at the point that it exceeds the yield strength the material yields and a process (plastic) zone develops. Within the process zone the same sequence takes place: voids nucleate, grow and link to give a *ductile fracture*. The crack advances and the process repeats itself. The plasticity blunts the crack, and the stress concentrating effect of a blunt crack is less severe than that of a sharp one, so that at the crack tip itself the stress is just sufficient to keep plastically deforming the material there. This plastic deformation absorbs energy, increasing the toughness G_c .

How increase this energy? Removing the inclusions ("Clean steels") means fewer voids which then have to grow more before they link. High work hardening (martensitic stainless steels) and other tricks for inducing a deformation-triggered phase change at the crack tip (yttria toughened zirconia) expands the process zone, dissipating more energy. Reinforcement with fibers provides crack bridging that both reduces the stresses at the crack tip and – through stretching and pull-out of the fibers, creates additional energy-dissipating mechanisms.

Examples of materials that exploit toughening mechanisms

Tough materials
Low alloy steels
Stainless steels
Titanium alloys
Nickel based alloys
Copper alloys
Metal matrix composites
Fiber-reinforced polymers
Yttria-toughened ceramics



Microstructure. Crack bridging in fiber reinforced concrete.

<http://www.readymadeseminar.com/2015/06/fibre-reinforced-concrete.html>

Applications of toughened materials.

High toughness is a design priority for pressure vessels, chemical engineering equipment, aircraft landing gear; crash protection and armor-plate, for which a failure can have catastrophic consequences.

Links at Level 2 to:

- Materials – Low alloy steels; Titanium alloys; Metal matrix composites; GFRP, CFRP, SMC and DMC
- Processes – Composite forming
- Property-process profiles - 2. Heat treatment of carbon steels; 3. Alloying and heat treatment: Stainless steels; 4. Alloying and heat treatment: Aluminum alloys; 5. Filling and reinforcing of polymers.

Further Reading

Askeland, D.R., Phulé, P.P. and Wright W.J. (2010) *The Science and Engineering of Materials*, 6th edition, Ch. 7.
 Callister, W.D. and Rethwisch, D.G. (2014) "Materials Science and Engineering", 9th Edition Ch. 8.
 Shackelford, J.F. (2014) "Introduction to materials science for engineers", 8th edition, Ch. 8.

6. Electron scattering

Free electrons.

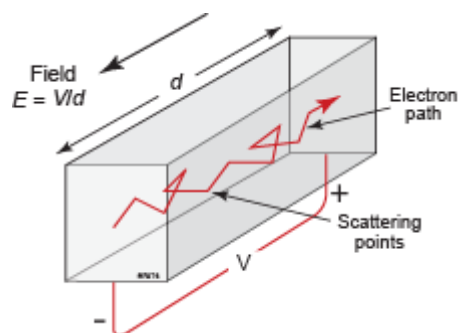
“Free” electrons are electrons that are not bound to a single atom but can move between atoms when an electric field is applied to the solid containing them. Some metals (copper, silver, aluminum) have many free electrons all of which can move with very little resistance. Others (stainless steels, titanium alloys) have many free electrons but their “freedom” is restricted by scattering from the many solute atoms they contain. Yet others (semiconductors) have free electrons but not many of them – they have to be created by thermal energy or by deliberate doping with electron-donating impurities.

Mechanisms of electron scattering.

An electric field E exerts a force Ee on a conduction electron (one free to move through the material), accelerating it. Why does it not accelerate forever, giving a current that continuously increases with time? This is not what happens; instead, switching on a field causes a current i that almost immediately reaches a steady value such that the current density i/A is proportional to the field E (Ohm’s law):

$$\frac{i}{A} = \frac{E}{\rho_e} = \sigma_e E$$

where ρ_e is the resistivity and σ_e , its reciprocal, is the electrical conductivity.



Broadly speaking, the explanation is this. The thermal energy of conduction electrons, kT (k = Boltzmann’s constant, T = absolute temperature) causes them to move like gas atoms in all directions. In doing this they collide with *scattering centers*, bouncing off in new directions. Impurity or solute atoms are particularly effective scattering centers (which is why alloys always have a higher resistivity than pure metals), but electrons are scattered also by imperfections such as dislocations and by the thermal vibration of the atoms themselves. When there is no field, there is no *net* transfer of charge in any direction even though all the conduction electrons are moving freely. A field imposes a drift velocity $v_d = \mu_e E$ on the electrons, where μ_e is the electron mobility and it is this that gives the current. The drift velocity is small compared with the thermal velocity; it is like a breeze in air – the thermal motion of the air molecules is far greater than the “drift” that we feel as the breeze. The greater the number of scattering centers, the shorter is the mean-free path, l_e , of the electrons between collisions, and the slower, on average, they move. Both the electrical the thermal conductivity depends on mean free path, on the density of carriers (the number n_v of mobile electrons per unit volume) and the charge ($e = 1.6 \times 10^{-19}$ coulombs) that they carry. Thus, the current density, i/A , is given by

$$\frac{i}{A} = n_v e v_d = n_v e \mu_e E$$

Comparing this with the previous equation gives the conductivity:

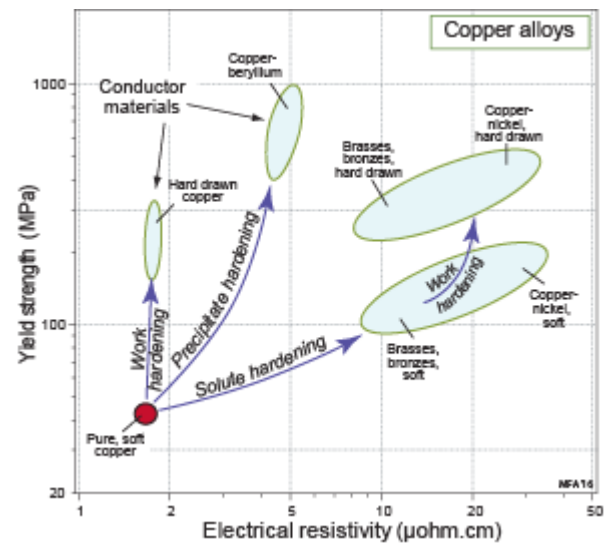
$$\kappa_e = n_v e \mu_e$$

Thus, the electrical conductivity is proportional to the density of free electrons and to the drift velocity, and this is directly proportional to the mean-free path through the following expression:

$$\sigma_e = \frac{e^2 n_v l_e}{m v_0}$$

where v_0 and m are, respectively, the initial velocity and the mass of the electrons.

Metals are strengthened by solid solution strengthening, work hardening or precipitation strengthening. All of these change the resistivity too. The features of the microstructure that obstruct dislocation motion (increasing strength) also scatter electrons. The figure shows how the strength and resistivity of copper change alloying and working. A solid solution introduces closely spaced scattering centers, greatly reducing the mean free path λ_{mfp} of free electrons. Precipitates are more widely spaced so restrict the mean free path less. The stored dislocations responsible for work hardening and the grain boundaries that give grain-size strengthening, too, scatter electrons, though much less than solute. Thus, precipitation strengthening, work hardening or grain size strengthening (or some combination of them) are the best ways to strengthen conductors. The figure shows that commercial conductor alloys have much greater strength and only slightly greater resistivity than pure copper.



Resistance decreases as temperature falls because the reduced thermal vibration scatters electrons less. As absolute zero is approached most metals retain some resistivity, but a few suddenly lose all resistance and become superconducting between 0 and 10 K. The resistivity of semiconductors, by contrast, decreases as temperature increases because thermal energy allows more electrons to escape into the conduction band, increasing the number n_v of carriers.

Compared to other materials, metals are very good conductors of both electricity and heat because electronic thermal conductivity dominates in metals. By considering that electrons behave as a perfect gas, one can express the electronic thermal conductivity as:

$$\kappa_e = \frac{1}{3} C_e v l_e$$

where C_e is the electronic specific heat, v the electron velocity and l_e the electron mean free path.

By developing the expression of the specific heat and by using the above expression for the electric conductivity, one obtains the well-known Wiedemann-Franz law:

$$\kappa_e = L_0 T \sigma$$

where L_0 is the Lorentz factor ($2.45 \cdot 10^{-8} \text{ V}^2 \text{K}^{-2}$).

Examples. The table lists materials that exploit electron scattering.

Conductor materials (minimum scattering)
Pure copper
Pure silver
Pure aluminum
Resistor materials (maximum scattering)
Nichrome (Ni 15%Cr 25%Fe)
Kanthal (Fe 25%Cr 6%Al)
Carbon composite (a mix of graphite and clay)



Nichrome resistor wire

Applications of electron-scattering materials.

Resistor materials are used for resistance elements in electrical circuits and as heating elements of all types.

Links at Level 2 to:

- Materials – Copper, Silver, Aluminum, Nickel-chromium alloys
- Processes – Swaging
- Phase diagrams – Copper-zinc, Copper-tin
- Property-process profiles – 1. Alloying and working: Copper alloys

Further Reading

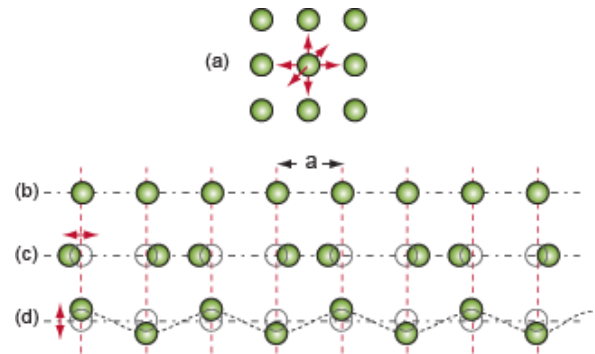
Callister, W.D. and Rethwisch, D.G. (2014) “Materials Science and Engineering”, 9th Edition Ch. 19.

Shackelford, J.F. (2014) “Introduction to materials science for engineers”, 8th edition, Ch. 15.

7. Phonon scattering

Phonons

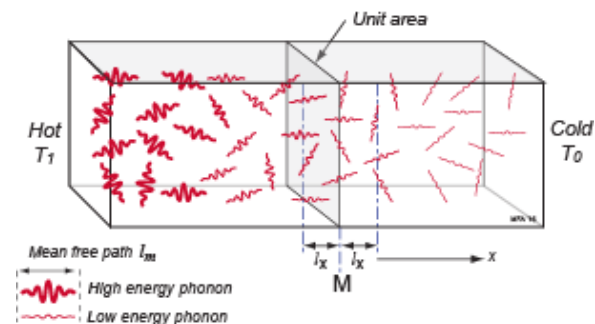
The atoms of a solid vibrate but because they are bonded to their neighbours they do not do so independently. The coupling means that energy is transmitted through solids as waves called *phonons*, with one longitudinal and two transverse modes. The figure shows the modes with the shortest wavelength. Thermal energy propagates as short-wavelength phonons; sound propagates as phonons of much greater wavelength.



Phonons are scattered by discontinuities in density, modulus or imperfections of order; the scattering is strongest when the scale of the discontinuity is comparable with the phonon wavelength. Thus, thermal phonons (wavelengths 0.2 – 200 nm) are scattered by solute atoms, grain boundaries, precipitates and dislocations; sound waves (wavelengths 20 – 20,000 nm) are scattered by internal and external surfaces of the material in which they propagate. At high temperature, phonon scattering is dominated phonon-phonon interactions (umklapp process), decreasing the phonon mean free path. At low temperature, the phonon mean free path is limited by the crystal dimensions. Because of this the lattice thermal conductivity falls with increasing temperatures at high temperatures, but independent of temperature at low temperatures.

Mechanism of phonons scattering

Like any elastic wave, phonons move with the speed of sound, c_o ($c_o = \sqrt{E/\rho}$). If this is so, why does heat not diffuse at the same speed? It is because phonons travel only a short distance, their *mean free path* ℓ_m , typically less than 0.01 microns (10^{-8} m), before they are scattered by the slightest irregularity in the lattice of atoms through which they move, even by other phonons.



Phonon conductivity is modelled using a *net flux model*, much as you would calculate the rate at which cars accumulate in a car park by counting the rate at which they enter and subtracting the rate at which they leave. The figure shows a rod with unit cross section carrying a uniform temperature gradient dT/dx between its ends. Phonons within it have 6 degrees of freedom of motion (they can travel in the $\pm x$, the $\pm y$ and the $\pm z$ directions). Focus on the mid-plane M-M. On average $1/6$ of the phonons are moving in the $+x$ direction; those within a distance ℓ_m of the plane will cross it from left to right before they are scattered, carrying with them an energy $\rho C_p (T + \Delta T)$ where T is the temperature at the plane M-M and $\Delta T = (dT/dx)\ell_m$. Another $1/6$ of the phonons move in the $-x$ direction and cross M-M from right to left carrying an energy $\rho C_p (T - \Delta T)$. Thus, the energy flux q J/m².sec across unit area of M-M per second is

$$q = -\frac{1}{6}\rho C_p c_o \left(T + \frac{dT}{dx} \ell_m \right) + \frac{1}{6}\rho C_p c_o \left(T - \frac{dT}{dx} \ell_m \right) = -\frac{1}{3}\rho C_p \ell_m c_o \frac{dT}{dx}$$

Comparing this with the definition of thermal conductivity λ

$$q = -\lambda \frac{dT}{dx}$$

we find the conductivity to be

$$\lambda = \frac{1}{3} \rho C_p \ell_m c_o$$

This is the well-known Debye relationship for the lattice thermal conductivity.

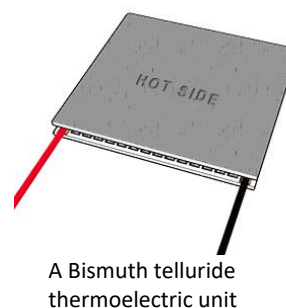
Anything that reduces the mean free path ℓ_m limits phonon conduction. As already said, discontinuities of density, modulus or order on the scale of the phonon wavelength do this, meaning – for thermal phonons – solute, particles, dislocations and other phonons.

Two classes of applications require exceptional combinations of thermal and electrical conductivity. Heat sinks must conduct heat well but be electrical insulators. No free electrons means that there is no thermal transport by electrons. The answer is to minimize the phonon scattering by choosing materials with high Debye temperature, with as high a purity and as perfect a lattice as possible. The chart shows materials which achieve this – they are the ones at the upper right.

The other class is that of thermoelectric materials. These require (semi)conduction but with as low a thermal conductivity as possible to maintain a steep temperature gradient between the hot and the cold face of the device. For a given electron carrier concentration thermal conduction is minimized by maximizing phonon scattering – the materials at the lower left of the chart such as Bi-Te, Ph-Te and Si-Ge meet this requirement.

Examples

Heat sink materials with low phonon scattering
Aluminum nitride
Alumina
Silicon carbide
Diamond
Thermoelectric materials with high phonon scattering
Bismuth telluride
Lead telluride
Silicon-Germanium



Applications of phonon-scattering materials.

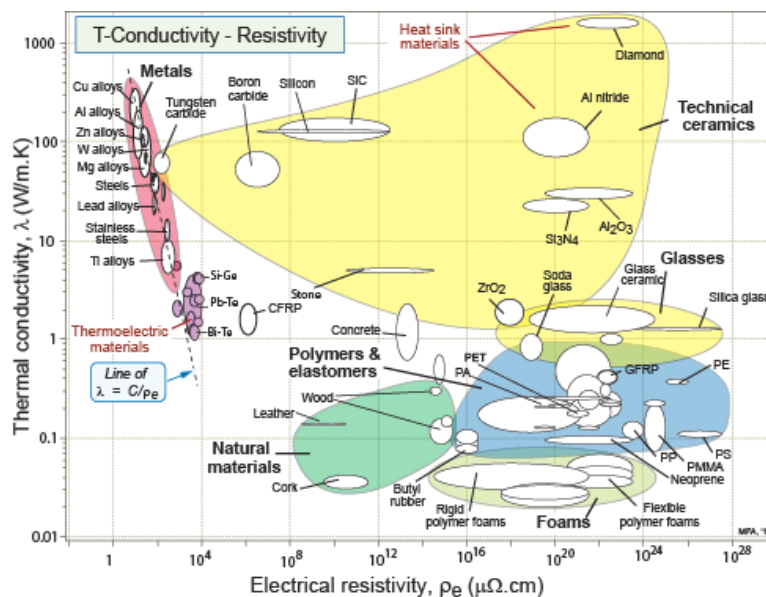
Ceramics with low phonon scattering such as aluminum nitride, silicon carbide and alumina are used as heat sinks. Semiconductors with high phonon scattering are used as elements of thermoelectric devices.

Links at Level 2 to:

- Materials – Aluminum nitride; Alumina; Bismuth telluride, Lead telluride

Further Reading

Callister, W.D. and Rethwisch, D.G. (2014) “Materials Science and Engineering”, 9th Edition Ch. 19.
Shackelford, J.F. (2014) “Introduction to materials science for engineers”, 8th edition, Ch. 7.

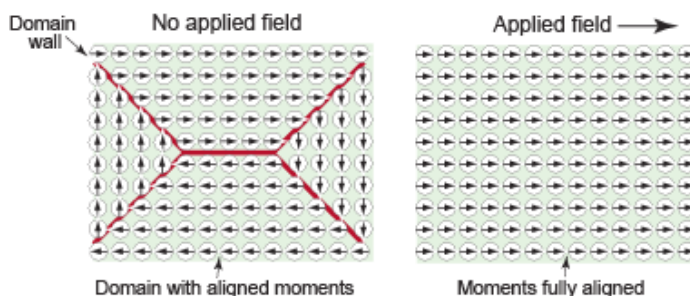


8. Domain wall pinning

Domains in Ferromagnetic and Ferroelectric materials.

The spin of unpaired electrons of an atom in a material generates a magnetic dipole. In ferromagnetic materials, these dipoles spontaneously align to give a permanent magnetization. In a similar way, molecules with an asymmetric crystal structure carry an electric dipole moment; in ferroelectric materials these dipoles align to give a permanent polarization.

A uniformly magnetized or polarized rod creates a magnetic or electric field that has an energy associated with it. This energy is reduced if the material splits up into *domains* within which the atomic or molecular moments are parallel, but with a switch of direction of 90° or 180° between mating domains to minimize the external field. The domains meet at *domain walls*, regions a few atoms thick in which the moments swing from the orientation of one domain to that of the other. The result is that most ferromagnetic and ferroelectric materials, unless manipulated in some way, adopt a domain structure with minimal external field.



When placed in a magnetic or electric field the domains already aligned with the field have lower energy than those aligned against it. The domain wall separating them feels a pressure pushing it in a direction to make the favourably oriented domains grow at the expense of the others. As they grow, the magnetization or polarization of the material increases until it saturates when the entire sample is a single domain.

Domain wall pinning. Domain walls move easily in soft magnetic materials. To make hard magnets or polar materials the domain walls must be pinned to stop them moving. Impurities, foreign inclusions, precipitates and porosity all interact with domain walls, tending to pin them in place. They act as obstacles to dislocation motion too so magnetically hard materials are mechanically hard as well. And there are subtler barriers to domain-wall motion. One is *magnetic or polar anisotropy*, arising because certain directions of magnetization or polarization in the crystal are more favorable than others. Small, single-domain magnetic particles are particularly resistant to having their magnetism reversed, which is why they can be used for information storage.

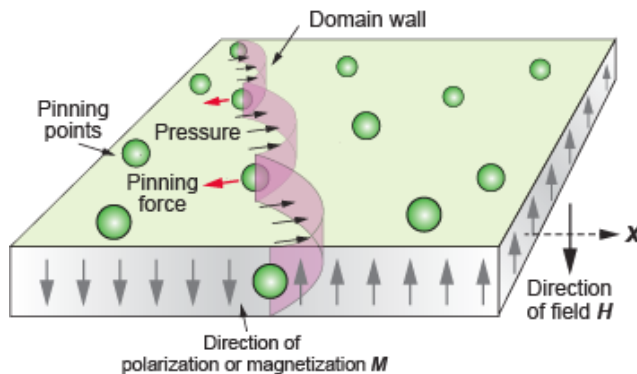
When a magnetic field H is applied to a ferromagnetic material, a domain wall within it experiences a pressure P per unit area pushing it in the direction that enlarges the favourably-aligned domain and contracts that which is unfavorably aligned. The energy per unit volume of a domain with (saturation) magnetization M_s when subject to a field H is

$$E_H = -\mu_0 M_s H$$

where μ_0 is the permeability of vacuum ($4\pi \times 10^{-7}$ henry/meter). Thus, the energy change when an area A of a 180° domain wall (like that in the schematic) advances through a distance Δx is

$$\Delta E_H = -2\mu_0 M_s H A \Delta x$$

and the pressure on the domain wall is



$$P = -\frac{1}{A} \frac{dE_H}{dx} = 2\mu_0 M_s H$$

Domain walls have energy E_{dom}^0 per unit area. A non-magnetic solute, particle or other obstacle interacts with a domain wall, “screening out”, so to speak, an area πr^2 where r is the effective radius of the obstacle. If a volume fraction f_v of obstacles each of radius r interacts with a domain wall, the number of pinning points per unit area is $N_A = f_v / \pi r^2$ and the energy that is screened out is $N_A \pi r^2 E_{dom}^0$. This energy has to be recreated if the domain wall advances by a distance r so the effective pinning pressure exerted by the obstacles is

$$P_{obs} = \frac{1}{r} N_A \pi r^2 E_{dom}^0 = \frac{f_v}{r} E_{dom}^0$$

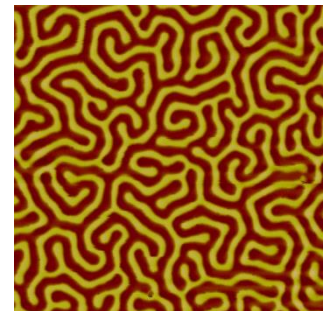
Equating this to the pressure exerted by the applied field gives the critical field, H_c , to tear the domain wall free as

$$H_c = \frac{1}{2\mu_0 M_s} \frac{f_v}{r} E_{dom}^0$$

Thus, the greater the volume fraction of obstacles and the smaller their size, the greater is the critical field.

Examples: with high or low domain wall pinning.

Hard magnetic materials (maximum pinning)
Alnico (Al-Ni-Co-Fe alloys)
Neodymium-iron-boron
Samarium cobalt
Soft magnetic materials (minimum pinning)
Permalloy
Silicon iron transformer alloy



Magnetic domains in an Fe-Gd alloy.
<http://www.iith.ac.in/~jmohanty/research.html>

Applications of domain pinning.

Hard magnets are used in permanent-magnet motors, dynamos and generators, headphones and speakers. Soft magnets are used in transformer and solenoid cores, magnet read heads and magnetic shielding.

Links at Level 2 to:

- Materials – Iron; Alnico; Neodymium iron boron; Samarium cobalt; Perm alloy 45%; Perm alloy 75%; Silicon iron transformer alloy
- Processes – Sand casting; Investment casting; Forging; Rolling; Powder pressing and sintering; Hot isostatic pressing
- Phase diagrams – Iron-nickel

Further Reading

Askeland, D.R., Phulé, P.P. and Wright W.J. (2010) *The Science and Engineering of Materials*, 6th edition, Ch. 20.
 Callister, W.D. and Rethwisch, D.G. (2014) “Materials Science and Engineering”, 9th Edition Ch. 20.
 Shackelford, J.F. (2014) “Introduction to materials science for engineers”, 8th edition, Ch. 18.

Author

Professor Mike Ashby
University of Cambridge, Granta Design Ltd.
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