

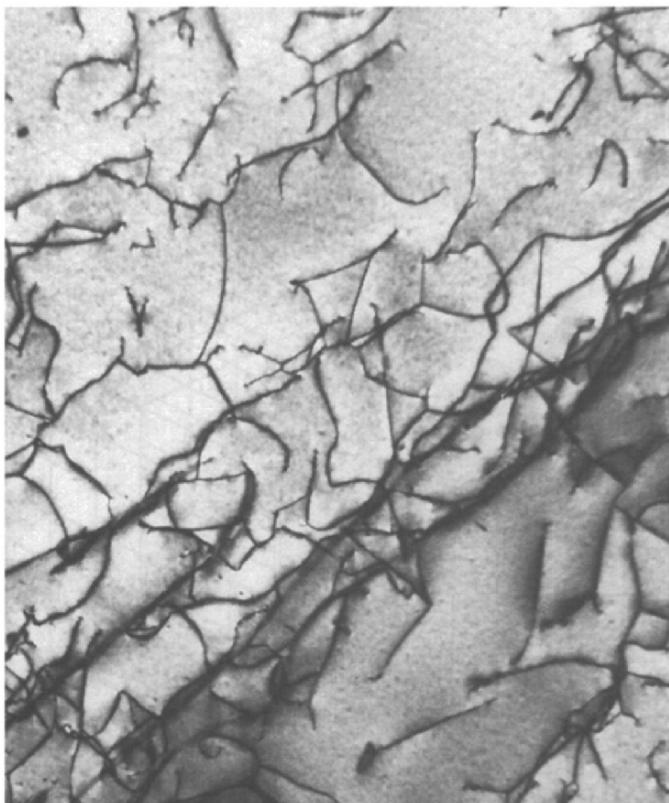
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CHARACTERIZATION OF MATERIALS — I



A transmission electron micrograph of a titanium alloy in which dark lines are dislocations. Courtesy of M.R. Plichta, Michigan Technological University. Reprinted with permission from Callister (2000). Copyright © 2000, Wiley.

The characterization of materials is an important step to be taken before utilizing the materials for any purpose. Depending on the purpose one can subject the material to mechanical, thermal, chemical, optical, electrical, and other characterizations to make sure that the material under consideration can function without failure for the life of the final product. We will consider only mechanical, thermal, and surface properties in this chapter, while in the next chapter we will study electrical, optical, and diffusive properties.

3.1. MECHANICAL PROPERTIES

Among the most important properties for the application of materials in medicine and dentistry are the mechanical properties. We will study the fundamental mechanical properties that will be used in later chapters.

3.1.1. Stress–Strain Behavior

For a material that undergoes a mechanical deformation, the *stress* is defined as a force per unit area, which is usually expressed in Newtons per square meter (Pascal, Pa) or pounds force per square inch (psi):

$$\text{Stress } (\sigma) = \frac{\text{force}}{\text{cross-sectional area}} \left[\frac{\text{N}}{\text{m}^2} \right] \text{ or } \left[\frac{\text{lbf}}{\text{in}^2} \right]. \quad (3-1)$$

A load (or force) can be applied upon a material in *tension*, *compression*, and *shear* or any combination of these forces (or stresses). Tensile stresses are generated in response to loads (forces) that pull an object apart (Figure 3-1a), while compressive stresses squeeze it together (Figure 3-1b). Shear stresses resist loads that deform or separate by sliding layers of molecules past each other on one or more planes (Figure 3-1c). The shear stresses can also be found in uniaxial tension or compression since the applied stress produces the maximum shear stress on planes at 45° to the direction of loading (Figure 3-1d).

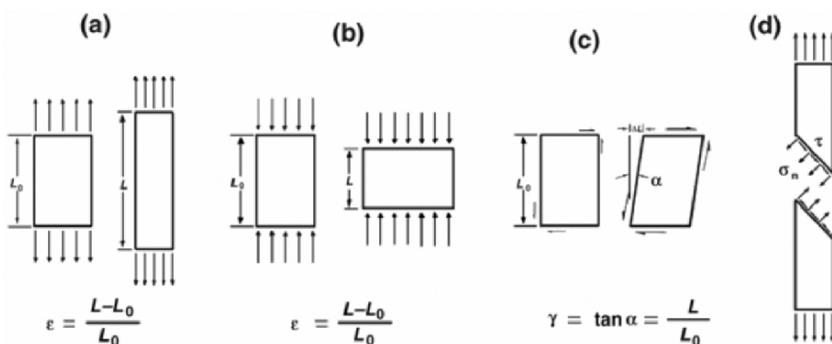


Figure 3-1. Three different modes of deformation: (a) tension, (b) compression, (c) shear, and (d) shear in tension. The shear stresses can be produced by tension or compression as in (d).

The deformation of an object in response to an applied load is called *strain*:

$$\text{Strain } (\sigma) = \frac{\text{deformed length} - \text{original length}}{\text{original length}} \left[\frac{\text{m}}{\text{m}} \right] \text{ or } \left[\frac{\text{in}}{\text{in}} \right]. \quad (3-2)$$

It is also possible to denote strain by the stretch ratio, i.e., deformed length/original length. The deformations associated with different types of stresses are called tensile, compressive, and shear strain (cf. Figure 3-1).

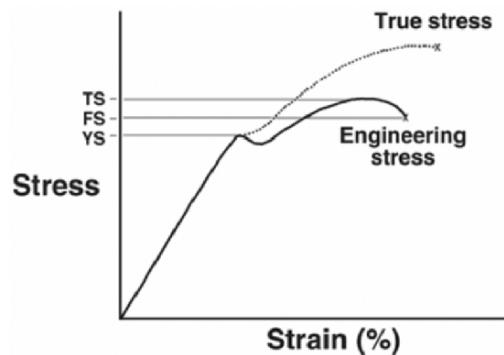


Figure 3-2. Stress–strain behavior of an idealized material.

If the stress–strain behavior is plotted on a graph, a curve that represents a continuous response of the material toward the imposed force can be obtained, as shown in Figure 3-2. The stress–strain curve of a solid sometimes can be demarcated by the yield point (σ_y or YP) into elastic and plastic regions. In the elastic region, the strain ϵ increases in direct proportion to the applied stress σ (Hooke's law):

$$\sigma = E\epsilon : \text{stress} = (\text{initial slope}) \times (\text{strain}). \quad (3-3)$$

The slope (E) or proportionality constant of the tensile/compressive stress–strain curve is called *Young's modulus* or the *modulus of elasticity*. It is the value of the increment of stress over the increment of strain. The stiffer a material is, the higher the value of E and the more difficult it is to deform. Similar analysis can be performed for deformation by shear, in which the *shear modulus* (G) is defined as the initial slope of the curve of shear stress versus shear strain. The unit for the modulus is the same as that of stress since strain is dimensionless. The shear modulus of an *isotropic* material is related to its Young's modulus by

$$E = 2G(1 + v), \quad (3-4)$$

in which v is the *Poisson's ratio* of the material. Poisson's ratio is defined as the negative ratio of the transverse strain to the longitudinal strain for tensile or compressive loading of a bar. Poisson's ratio is close to $1/3$ for common stiff materials, and is slightly less than $1/2$ for rubbery materials and for soft biological tissues. For example, stretch a rubber band by 10% of its original length and the cross-sectional dimensions will decrease by about 5%.

In the *plastic region*, strain changes are no longer proportional to the applied stress. Further, when the applied stress is removed, the material will not return to its original shape but

will be permanently deformed which is called a *plastic deformation*. Figure 3-3 is a schematic illustration of what will happen on the atomic scale when a material is deformed. Note that the individual atoms are distorted and stretched while part of the strain is accounted for by a limited movement of atoms past one another. When the load is released before atoms can slide over other atoms, the atoms will go back to their original positions, making it an elastic deformation. When a material is deformed plastically the atoms are moved past each other in such a way they will have new neighbors, and when the load is released they can no longer go back to their original positions.

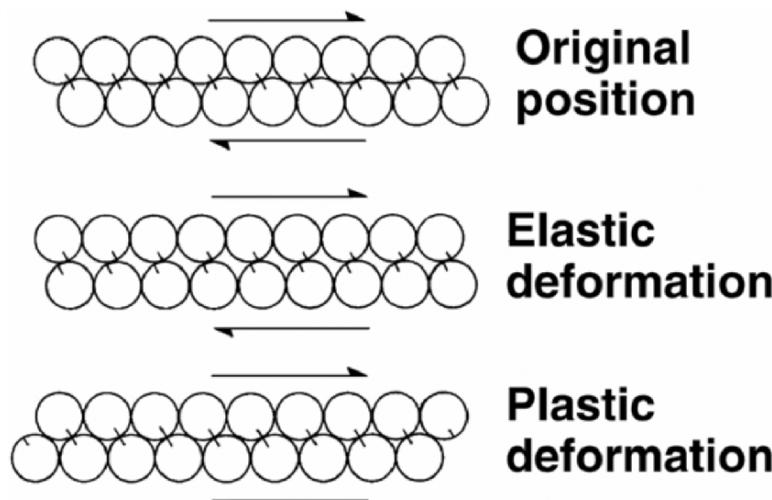


Figure 3-3. Schematic diagrams of a two-dimensional atomic model after elastic and plastic deformation.

Referring back to Figure 3-2, a peak stress can be seen that is often followed by an apparent decrease until a point is reached where the material ruptures. The peak stress is known as the *tensile* or *ultimate tensile strength* (TS); the stress where failure occurs is called the *failure* or *fracture strength* (FS).

In many materials such as stainless steels, definite yield points occur. This point is characterized by temporarily increasing strain without a further increase in stress. Sometimes it is difficult to decipher the yield point since the deviation from linear behavior may be obscured by noise in the data. Therefore, an *offset* (usually 0.2 to 1.0%) yield point is used in lieu of the original yield point. Specifically, the offset-based yield point is the stress at which a 0.2% (or 1%) residual strain occurs after removal of the load.

Thus far we have been examining the *engineering stress-strain* curves, which differ from the *true stress-strain* curves since the former curve is obtained by assuming a constant cross-sectional area over which the load is acting from the initial loading until final rupture. This assumption is not correct, which accounts for the peak seen at the ultimate tensile stress. For example, as a specimen is loaded under tension, sometimes *necking* (Figure 3-4) occurs, which reduces the area over which the load is acting. If additional measurements are made of the changes in cross-sectional area that occur, and the true area is used in the calculations, then a dotted curve like that in Figure 3-2 is obtained.

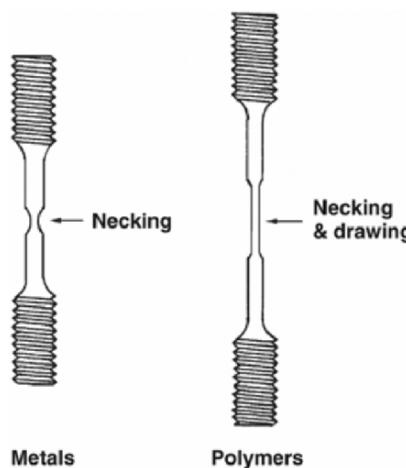


Figure 3-4. Deformation characteristics of metals and plastics under stress. Note that metals rupture without further elongation after necking occurs; by contrast, in plastics the necked region undergoes further deformation, called drawing.

Example 3.1

The following data were obtained for an aluminum alloy. A standard tensile test specimen with a 2-inch gauge length and 0.505 inch diameter was used:

- Plot the engineering stress-strain curve.
- Determine the Young's modulus, yield strength (0.2% offset), and tensile strength.
- Determine the engineering and true fracture strength. The diameter of the broken pieces was 0.4 in.

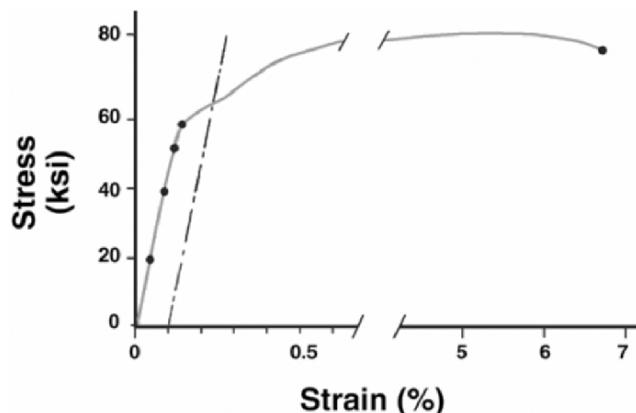
Load (kilo-lbf)	Gauge length (in)
2	2.002
4	2.004
8	2.008
10	2.010
12	2.011
13	2.014
14	2.020
16	2.050
16 (maximum)	2.099
15.6 (fracture)	2.134

Answer

- See the plot from the calculations based on cross-sectional area = $\pi \text{ (diameter)}^2/4 = 0.2 \text{ in}^2$.

Stress (ksi)	Strain (%)
20	0.2
40	0.4
50	0.5
60	0.6
65	0.7
70	1.0
80	2.5
80	5.0
78	6.7

- b. Young's modulus = $40 \text{ ksi}/0.004 = 1 \times 10^7 \text{ psi}$ (69 GPa)
 0.2% yield stress: from graph: 62,000 psi (428 MPa)
 Tensile strength: 80,000 psi (560 MPa)
- c. Engineering fracture strength = $15,600 \text{ lbs}/0.2 \text{ in}^2 = 78,000 \text{ psi}$ (538 MPa)
 True fracture strength = $15,600 \text{ lbs}/\pi(0.2 \text{ in})^2 = 124,140 \text{ psi}$ (856 MPa)



Stress versus strain for an aluminum alloy.

3.1.2. Mechanical Failure

3.1.2.a. Static failure

Mechanical failure usually occurs by fracture. The fracture of a material can be characterized by the amount of energy per unit volume required to produce the failure. The quantity is called **toughness** and can be expressed in terms of stress and strain:

$$\text{toughness} = \int_{\varepsilon_0}^{\varepsilon_f} \sigma d\varepsilon = \int_{l_0}^{l_f} \sigma \frac{dl}{l}. \quad (3-5)$$

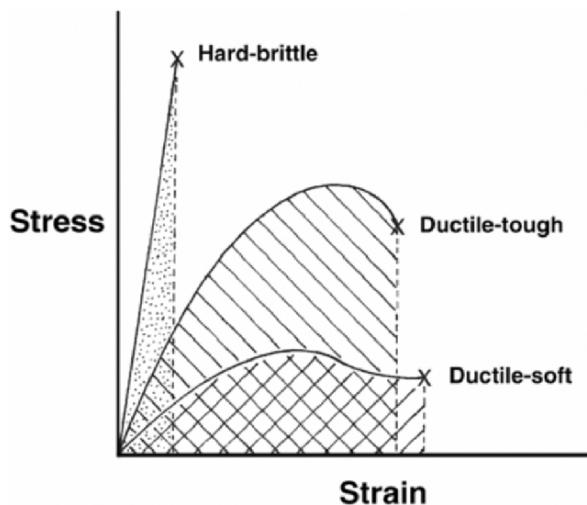


Figure 3-5. Stress-strain curves of different types of materials. The areas underneath the curves are the measure of toughness.

Expressed another way, toughness is the summation of stress times the normalized distance over which it acts (strain) taken in small increments. The area under the stress-strain curve provides a simple method of estimating toughness, as shown in Figure 3-5.

A material that can withstand high stresses and can undergo considerable plastic deformation (*ductile-tough* material) is tougher than one that resists high stresses but has no capacity for deformation (*hard-brittle* material) or one with a high capacity for deformation but can only withstand relatively low stresses (*ductile-soft* or plastic material).

Brittle materials exhibit fracture strengths far below the theoretical strength predicted based on known atomic bond strengths. Moreover, there is much variation in strength from specimen to specimen, so that the practical strength is difficult to predict. These facts, along with the comparative weakness of ceramics in tension, are the major reasons why ceramic and glassy materials are not used extensively for implantation despite their excellent compatibility with tissues.

The comparative weakness of brittle materials is explained as follows. The stress on a brittle material is not uniformly distributed over the entire cross-sectional area if a crack or flaw is present, as shown in Figure 3-6. If the crack is a narrow elliptic hole in a specimen subjected to a tensile stress, the maximum stress (σ_{\max}) acting at the ends of the hole is given by

$$\sigma_{\max} = \sigma_{\text{app}} \left(1 + \frac{2a}{b} \right), \quad (3-6)$$

where σ_{app} is the applied (or nominal) tensile stress experienced away from the crack. One can rearrange Eq. (3-6):

$$\frac{\sigma_{\max}}{\sigma_{\text{app}}} = \left(1 + \frac{2a}{b} \right), \quad (3-7)$$

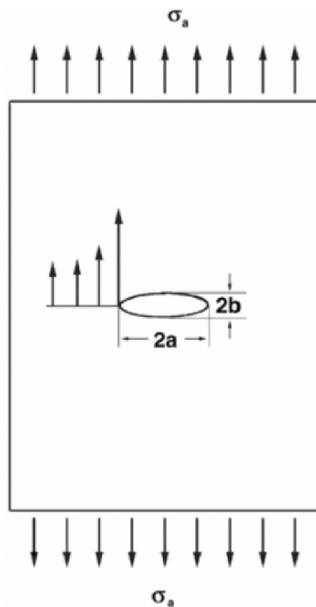


Figure 3-6. An elliptic microcrack inclusion in a brittle material.

where the ratio $\sigma_{\max}/\sigma_{\text{app}}$ is called the *stress concentration factor* (scf), which can be substantial if ratio a/b is high, i.e., a sharp crack. If the crack tip has a radius of curvature $r (= b^2/a)$, then Eq. (3-6) can be rewritten:

$$\sigma_{\max} = \sigma_{\text{app}} \left[1 + 2 \left(\frac{a}{b} \right)^{1/2} \right]. \quad (3-8)$$

Since $a \gg r$ for a crack,

$$\sigma_{\max} \approx 2\sigma_{\text{app}} \left(\frac{a}{r} \right)^{1/2}. \quad (3-9)$$

Equation (3-9) indicates that the stress concentration becomes very large for a sharp crack tip as well as for long cracks. Thus, the propagation of a sharp crack can be blunted if one increases the crack tip radius. For example, progression of a crack in a large glass window can be halted or slowed by drilling a hole in the glass at the crack tip.

Griffith proposed in 1920 an energy approach to fracture. The elastic energy stored in a test specimen of unit thickness is

$$\sigma \times \varepsilon = \pi a^2 \sigma \left(\frac{\sigma}{E} \right) = \frac{\pi(a\sigma)^2}{E}. \quad (3-10)$$

Observe that the elastic energy for a brittle material is twice the area under the stress-strain curve. The elastic energy is used to create two new surfaces as the crack propagates. The surface energy, $4\gamma a$ (γ is the surface energy) should be smaller than the elastic energy for the

crack to grow. Thus, the incremental changes of both energies for the crack to grow can be written as

$$\frac{d}{da} \left(\frac{\pi}{(a\sigma)^2} \right) = \frac{d}{da} (4\gamma a). \quad (3-11)$$

Hence,

$$\sigma = \sigma_f \sqrt{\frac{2\gamma E}{\pi a}}. \quad (3-12)$$

Since for a given material E and γ are constants,

$$\sigma_f = \frac{K}{\sqrt{\pi a}}. \quad (3-13)$$

In this case, K has the units of psi $\sqrt{\text{in}}$ or MPa $\sqrt{\text{m}}$ and is proportional to the energy required for fracture. K is also called *fracture toughness*. Stress concentrations also occur in ductile materials, but their effect is usually not as serious as in brittle ones since local yielding that occurs in the region of peak stress will effectively blunt the crack and alleviate the stress concentration.

Example 3.2

Estimate the size of the surface flaw in a glass whose modulus of elasticity and surface energy are 70 GPa and 800 erg/cm², respectively. Assume that the glass breaks at a tensile stress of 100 MPa.

Answer

From Eq. (3-12), and keeping in mind the transformation from cgs to SI units,

$$\begin{aligned} a &= \frac{2\gamma E}{\pi\sigma_f^2} \\ &= \frac{2 \times 800 \text{ dyne/cm} \times 70 \text{ GPa}}{\pi(100 \text{ MPa})^2} \\ &= \underline{3.6 \text{ } \mu\text{m}}. \end{aligned}$$

[Note that if the crack is on the surface its length is a ; if it is inside the specimen it is $2a$. Remember that 1 dyne = 10^{-5} N, 1 cm = 10^{-2} m, and 1 erg = 1 dyne cm.]

3.1.2.b. Dynamic fatigue failure

When a material is subjected to a constant or a repeated load below the fracture stress, it can fail after some time. This is called static or dynamic (cyclic) fatigue respectively. The effect of cyclic stresses (Figure 3-7) is to initiate microcracks at centers of stress concentration within the material or on the surface, resulting in the growth and propagation of cracks, leading to failure. The rate of crack growth can be plotted in a log-log scale versus time, as shown in Figure 3-8. The most significant portion of the curve is the crack propagation stage, which can be estimated as follows:

$$\frac{da}{dN} = A(\Delta K)^m, \quad (3-14)$$

where a , N , and ΔK are the crack length, number of cycles, and range of stress intensity factor (cf. Eq. (3-13)), $\Delta K = \Delta\sigma \sqrt{\pi a}$. A and m are the intercept and slope of the linear portion of the curve. This is called the Paris equation.

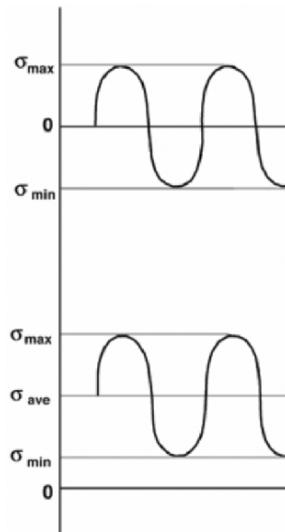


Figure 3-7. Cyclic stresses. σ_{\min} and σ_{\max} are the maximum and minimum values of the cyclic stresses. The range of stresses $\Delta\sigma = \sigma_{\min} - \sigma_{\max}$ and average stress $\sigma_{\text{ave}} = (\sigma_{\max} + \sigma_{\min})/2$. The top curve is fluctuating, and the bottom curve is for reversed cyclic loading.

Another method of testing the fatigue properties is to monitor the number of cycles to failure at various stress levels, as shown in Figure 3-9. This test requires a large number of specimens compared with the crack propagation test. The *endurance limit* is the stress below which the material will not fail in fatigue no matter how many cycles are applied. Normally 10^7 cycles is considered as a representative limit for normal fatigue failure. Not all materials exhibit an endurance limit. Since implants are often flexed many times during a patient's life, the fatigue properties of materials are very important in implant design.

3.1.2.c. Friction and wear failure

Wear properties of an implant material are important, especially for various joint replacements. Wear cannot be discussed without some understanding of friction between two materials. When two solid materials contact, they touch only at the tips of their highest asperities (microscopic protuberances). Therefore, the real contact area is much smaller than the apparent surface area. It is found that the true area of contact increases with applied load (P) for ductile materials. Ductile materials can be pressure welded due to the formation of plastic junctions, as shown in Figure 3-10. The plastic junctions are the main source of an adhesive friction when two materials are sliding over each other with or without a lubricating film. The

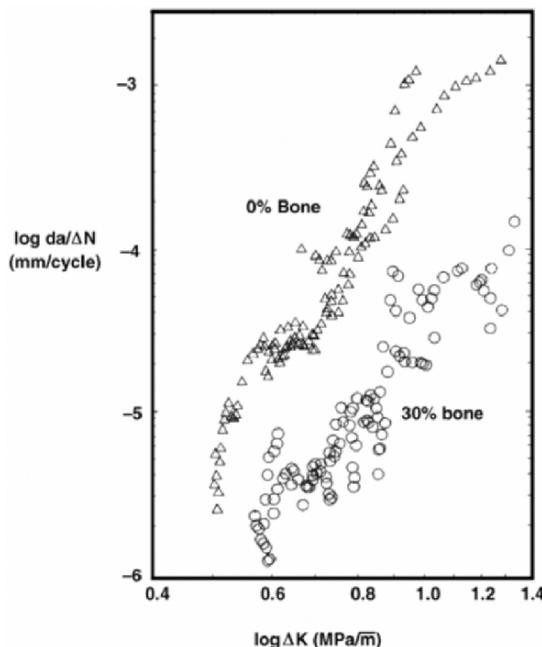


Figure 3-8. Log da/dN versus $\log \Delta K$ for polymethylmethacrylate bone cement. Reprinted with permission from Liu et al. (1987). Copyright © 1987, Wiley.

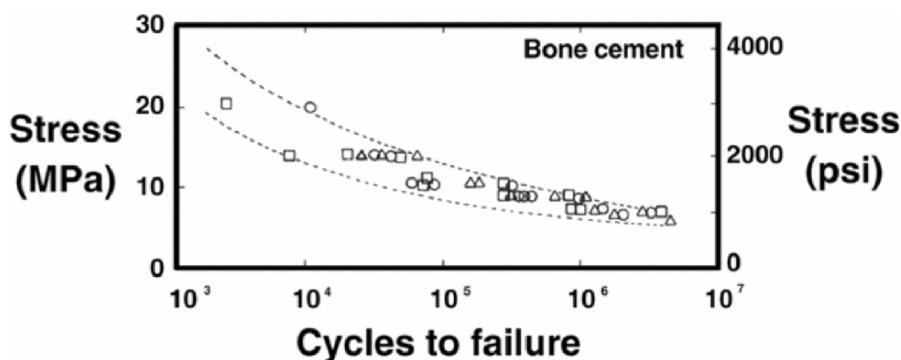


Figure 3-9. Stress versus $\log N$ (number of cycles) of PMMA bone cement. The Simplex P bone cement test specimens were fabricated at pressures between 5 and 50 psi and tested in air at 22°C. Reprinted with permission from Freitag and Cannon (1977). Copyright © 1977, Wiley.

resistance to the shear failure of the plastic junction results in a frictional force. Therefore, the sliding force F will be simply proportional to the shear yield strength k of the junctions and the contact area A :

$$F = Ak. \quad (3-15)$$

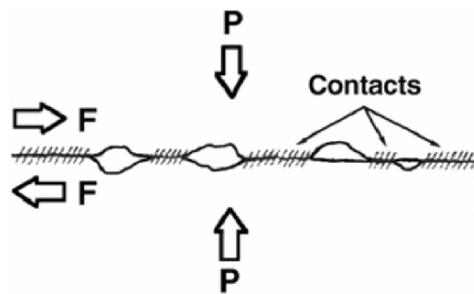


Figure 3-10. Schematic representation of two surfaces under pressure. Plastic junctions are formed when ductile materials are pressed together between asperities.

Since for ductile materials the area of contact increases with P ,

$$P = HA, \quad (3-16)$$

where H is the penetration hardness or yield pressure. If we combine Eqs. (3-15) and (3-16), the coefficient of sliding friction μ can be obtained:

$$\mu = F / P = k / H. \quad (3-17)$$

This equation implies that the friction coefficient is merely the ratio of two plastic strength parameters of the weaker material and is independent of the contact area, load, sliding speed including surface roughness, and geometry. Figure 3-11 shows an example of the effect of contact area changes on the friction coefficient. Note that there are no significant variations in friction coefficient with wide variations of the contact area.

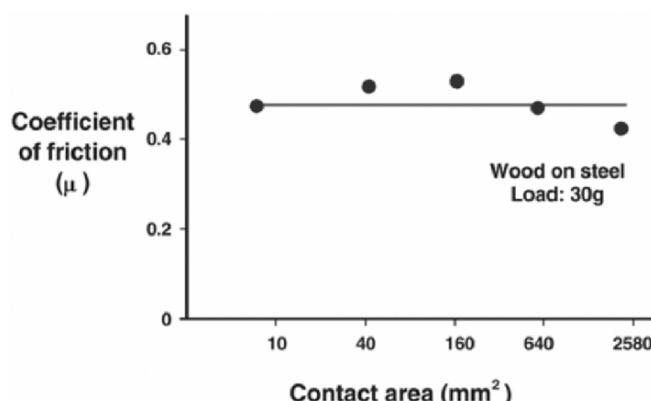


Figure 3-11. Friction coefficient versus sliding contact area, wood on steel. Modified with permission from McClintock and Argon (1966). Copyright © 1966, Addison-Wesley.

Wear is surface damage or material removal from surfaces in contact and in motion with respect to each other. Material may be damaged at the surface, broken loose as a wear particle, or it may be transferred from one surface to another. The rate of wear tends to increase with the applied load P and, for metals in contact, to decrease with the hardness H of the surface that is worn. An empirical relation for the wear volume ΔV of wear debris as it depends on the distance x moved by the sliding surfaces is as follows:

$$V = k(Px/H), \quad (3-18)$$

with k as a dimensionless *wear coefficient* or *constant* that depends on the materials in contact and the presence or absence of lubrication. The hardness H can be considered as the yield strength of the material being worn. Indeed, the above equation can be derived via a model in which asperities (microscopic protuberances) experience yield and failure during the wear process.

If metals in contact are similar, wear is higher than if they are dissimilar. Specifically, the lower the mutual solid solubility of the metals, the lower the wear. Typical wear coefficients for various conditions are listed in Table 3-1.

Table 3-1. Typical Values of Wear Coefficients k (in 10^{-6}) for Various Conditions

Condition	Similar metals	Dissimilar metals	Nonmetal–metal
No lubrication	1500	15–500	1.5
Poor lubrication	300	3–100	1.5
Average lubrication	30	0.3–10	0.3
Excellent lubrication	1	0.03–0.3	0.03

In the context of biomaterials, dissimilar metals are problematic in view of the fact that corrosion occurs when dissimilar metals are placed in an aqueous, saline environment such as the body. Moreover, wear of metals in a corrosive environment is exacerbated.

Polymer–metal interfaces can exhibit relatively low friction and wear, but low friction does not guarantee low wear. For example, Teflon® (PTFE, polytetrafluoroethylene) offers a low coefficient of friction, but it undergoes severe wear. Teflon® was tried in early implants but was not successful due to excess wear. Currently, UHMWPE (ultrahigh-molecular-weight polyethylene) is favored for use in joint replacement implants. Polymers cannot withstand as much contact stress as metals, but they are adequate in this regard for use in joint replacements.

Wear debris in hip replacement implants can cause tissue reactions, including proliferation of local fibroblast-like cells and activated macrophages. While PMMA and UHMWPE are inert in the bulk, small particles of these materials act as cellular irritants. Tissue reaction to wear debris is a contributing factor to bone resorption and implant loosening, a major cause of joint implant failure. In joint replacement implants, metal-on-metal designs offer reduced wear rates in comparison with metal-on-polymer ones, and are therefore considered an alternative. However, since the new designs and better congruent head and socket designs are relatively new, only early and midterm clinical results are available, and no long-term results. Elevated levels of metal ions due to wear debris have been observed in patients with these implants, but it is not yet known if there is a health risk. Diamond coatings have been explored in the labora-

tory in an effort to achieve wear-free surfaces. Alumina ceramic surfaces have been used clinically to achieve low wear.

3.1.3. Viscoelasticity

3.1.3.a. Viscoelastic material behavior

Viscoelastic materials are those for which the relationship between stress and strain depends on time. In such materials the stiffness will depend on the *rate of application* of the load. In addition, mechanical energy is dissipated by conversion to heat in the deformation of viscoelastic materials. All materials exhibit some viscoelastic response. In metals such as steel or aluminum at room temperature, as well as in quartz, the response at small deformation is almost purely elastic. Metals can behave plastically at large deformation, but ideally plastic deformation is independent of time. Also, plastic deformation occurs only if a threshold stress is exceeded. By contrast, materials such as synthetic polymers, wood, and human tissue display significant viscoelastic effects, and these effects occur at small or large stress.

3.1.3.b. Characterization of viscoelastic materials

Creep is a slow, progressive deformation of a material under constant stress. Suppose the history of stress σ as it depends on time t is a step function beginning at time zero:

$$\sigma(t) = \sigma_0 H(t), \quad (3-19)$$

where $H(t)$ is the unit Heaviside step function defined as zero for t less than zero, and one for t equal to zero. The step function is normally defined to be 1/2 at zero. The strain $\varepsilon(t)$ will increase, as shown in Figure 3-12. The ratio

$$J(t) = \frac{\varepsilon(t)}{\sigma_0} \quad (3-20)$$

is called the creep compliance. In linear materials, it is independent of stress level. If the load is released at a later time t_s , the strain will exhibit recovery, as shown in Figure 3-12. For linear materials we may invoke the *Boltzmann superposition principle*, which states that the effect of a compound cause is the sum of the effects of individual causes. The stress may then be written as a superposition of a step up followed by a step down:

$$\sigma(t) = [H(t) - H(t - t_1)], \quad (3-21)$$

so the strain is, assuming superposition,

$$\varepsilon(t) = \sigma_0 [J(t) - J(t - t_1)]. \quad (3-22)$$

The strain may or may not recover to zero, depending on the material.

Stress relaxation is the gradual decrease of stress when the material is held at constant extension. If we suppose the strain history to be a step function beginning at time zero — $\varepsilon(t) = \varepsilon_0 H(t)$ — the stress $\sigma(t)$ will decrease as shown in Figure 3-13. The ratio

$$E(t) = \frac{\sigma(t)}{\varepsilon_0} \quad (3-23)$$

is called the *relaxation modulus*. In linear materials it is independent of strain level.

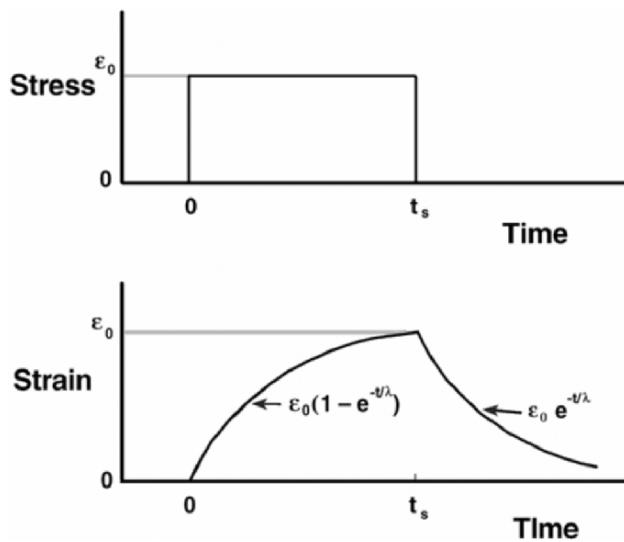


Figure 3-12. Creep and creep recovery of an idealized viscoelastic material.

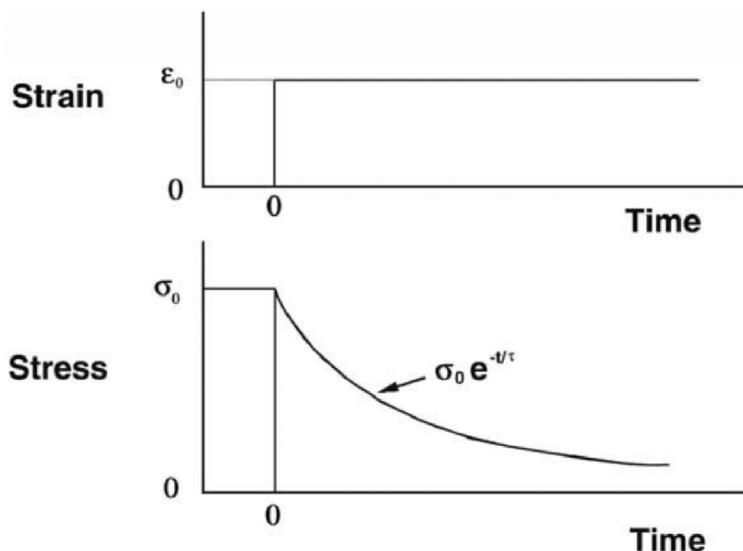


Figure 3-13. Stress relaxation of an idealized viscoelastic material.

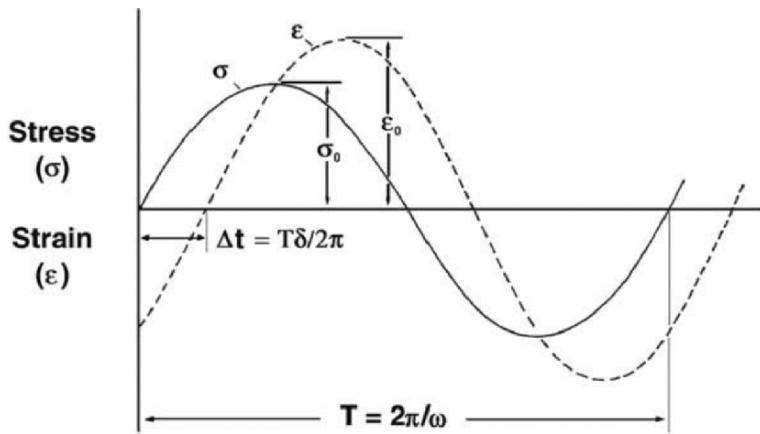


Figure 3-14. Loss angle δ for oscillatory loading of viscoelastic material.

If a sinusoidally varying stress,

$$\sigma(t) = \sigma_0 \sin(2\pi ft), \quad (3-24)$$

of frequency f is applied to a linearly viscoelastic material, the strain

$$\varepsilon(t) = \varepsilon_0 \sin(2\pi ft - \delta) \quad (3-25)$$

will also be sinusoidal in time but will lag the stress by a phase angle δ , as shown in Figure 3-14. The loss angle δ is a measure of the viscoelastic damping of the material. Both the loss angle and the dynamic stiffness E ($= \sigma_0/\varepsilon_0$) depend on frequency. The tangent of the loss angle is referred to as the *loss tangent*, $\tan \delta$.

For a given material, viscoelastic damping, creep, and stress relaxation are not independent. For example, the creep and relaxation functions are related by a convolution; the dynamic properties are related to the creep or relaxation behavior by Fourier transformation; and the loss angle and dynamic stiffness are related by the Kramers-Kronig relations. We remark that the larger the value of the loss tangent, the more rapidly the dynamic stiffness changes with frequency, and the more rapidly the relaxation modulus and creep compliance change with time. An approximate correspondence between the frequency scale, f , for dynamic behavior and the time scale, t , for creep and relaxation is the relation

$$t = \frac{1}{2\pi f}. \quad (3-26)$$

Furthermore, the viscoelastic properties of a material in tension need not follow the same time or frequency dependence as those in shear.

3.1.3.c. Prediction of the response

Viscoelastic materials may be used under conditions of complex loading. It is possible to predict the response of such materials based on the material properties discussed above. The

Boltzmann superposition principle for linear materials is applied to decompose the load history into a series of differential creep and recovery episodes. Summing the effects of these, one obtains the Boltzmann superposition integral:

$$\varepsilon(t) = \int_0^t J(t-\tau) \frac{d\sigma(\tau)}{d\tau} d\tau, \quad (3-27)$$

or conversely,

$$\sigma(t) = \int_0^t E(t-\tau) \frac{d\varepsilon(\tau)}{d\tau} d\tau, \quad (3-28)$$

in which τ is a time variable of integration. Consequently, if the response of a material to step stress or strain has been determined experimentally, the response to *any* load history can be found for the purpose of analysis or design.

3.1.3.d. Mechanical models

Simple mechanical models may be considered as an aid for visualizing viscoelastic response. The models consist of springs, which are purely elastic, and dashpots, which are purely viscous. In a spring, the stress is proportional to the strain:

$$\sigma = k\varepsilon \quad (3-29)$$

(cf. Eq. 3-3). The constant of proportionality k is the spring constant. By contrast, in a dashpot the stress is proportional to the time derivative of the strain (the strain rate):

$$\sigma = \eta \frac{d\varepsilon}{dt}. \quad (3-30)$$

The constant of proportionality η is a viscosity. For example, the Kelvin (Voigt) model consists of a spring in parallel with a dashpot. The strain is the same in both elements, but the stress in the Kelvin model is the sum of the spring and dashpot stresses. After some reductions, one may obtain a differential form of the stress-strain relation:

$$\eta \frac{d\varepsilon}{dt} + k\varepsilon = \sigma. \quad (3-31)$$

The solution of this differential equation for a step stress input gives the creep compliance:

$$J(t) = \frac{[1 - e^{-\frac{kt}{\eta}}]}{k}. \quad (3-32)$$

Real materials, both synthetic and natural, exhibit behavior that cannot be described by simple mechanical models. In a two- or three-element model, the creep or relaxation is completed within about one logarithmic decade [a factor of ten in time] while in real materials the creep or relaxation is distributed over many decades.

Although the simple Eq. (3-3) can describe the elastic behavior of many materials at low strains, as represented by a spring in Figure 3-15, it cannot be used to characterize the polymers and tissues that are some of the major concerns of this book. The fluid-like behavior of a

material (such as water or oil) can be described in terms of (shear) stress and (shear) strain as in the elastic solids, but the proportionality constant (viscosity, η) is derived from the relationship given in Eq. (3-30). It is noted that the stress and strain are shear in this case rather than tensile or compressive, although the same symbols are used to avoid complications.

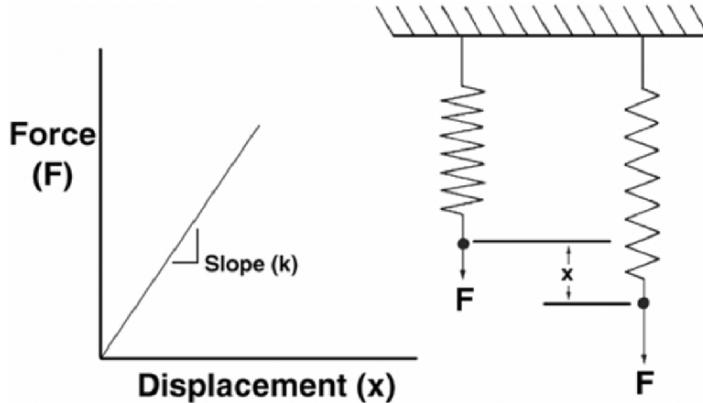


Figure 3-15. Force versus displacement of a spring.

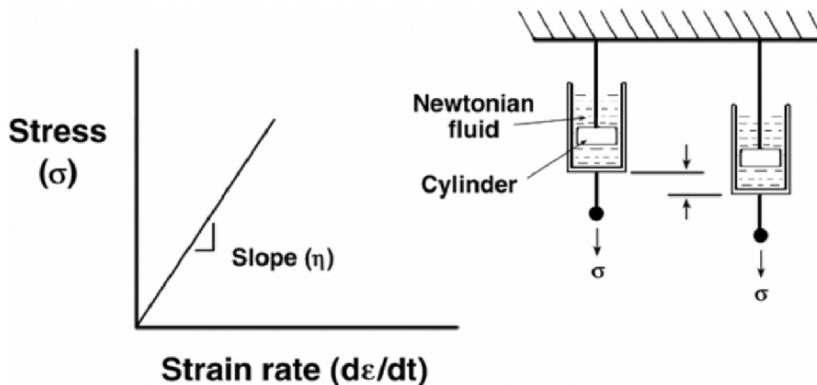


Figure 3-16. Stress-versus-strain rate of a dashpot.

A mechanical analog (dashpot) can be used to model the viscous behavior of Eq. (3-30), as shown in Figure 3-16. An automobile shock-absorbing cylinder that contains oil as the damping fluid has a similar construction. By examining Eq. (3-30) one can see that the stress is time-dependent, i.e. if the deformation is accomplished in very short time ($t \approx 0$) then the stress becomes infinite. On the other hand, if the deformation is achieved slowly ($t \Rightarrow \infty$) the stress approaches zero regardless of the viscosity value.

Real materials that have both elastic and viscous aspects to their behavior are known as *viscoelastic* materials. Simple equations (3-29) and (3-30), when combined together as if the material is made of springs and dashpots, can describe, in principle, the viscoelastic behavior of an idealized material. The stress-strain behavior of a spring and dashpot combination can be

represented as shown in Figure 3-17. If the spring and dashpot are arranged in series and parallel they are called Maxwell and Voigt (or Kelvin) models, respectively. Remember that Eq. (3-29) does not involve time, implying the spring acts instantaneously when stressed. Hence, if the Maxwell model is stressed suddenly the spring reacts instantaneously, while the dashpot cannot react immediately since the piston of the dashpot cannot move abruptly due to the infinite stress that would be required by the surrounding fluid, following Eq. (3-30). However, if we hold the Maxwell model after instantaneous deformation, the dashpot will react due to retraction of the spring, and this will take time ($t = \text{finite}$). The foregoing description can be expressed concisely by a simple mathematical formulation. The deformation response to stress by the Maxwell model is the sum of deformations, since the displacements are additive:

$$\varepsilon_{\text{total}} = \varepsilon_{\text{spring}} + \varepsilon_{\text{dashpot}}. \quad (3-33)$$

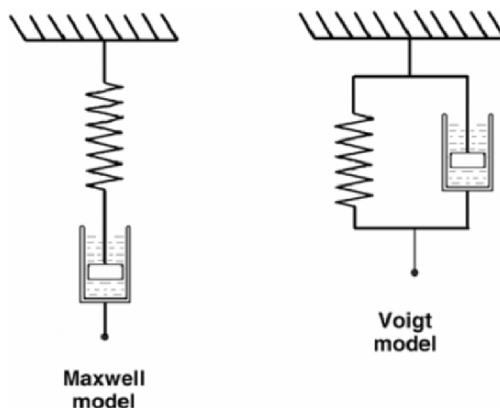


Figure 3-17. Two-element viscoelastic models.

Differentiating both sides and using Eqs. (3-29) and (3-30) will result in Eq. (3-31). Replacing the spring constant k with Young's modulus E to express the relationship in the context of material rather than structural properties, we obtain

$$\frac{d\varepsilon}{dt} = \frac{1}{E} \frac{d\sigma}{dt} + \frac{\sigma}{\eta}. \quad (3-34)$$

Equation (3-34) can be applied easily to a simple mechanical test such as stress relaxation in which the specimen is strained instantaneously and the relaxation of the load is monitored while the specimen is held at constant length, as shown in Figure 3-18. Thus, the strain rate becomes zero ($d\varepsilon/dt = 0$) and at $t = 0$ and $\sigma = \sigma_0$, in $\sigma_0 = \text{constant}$; hence,

$$\frac{\sigma}{\sigma_0} = \exp\left(-\frac{E}{\eta}t\right). \quad (3-35)$$

Constant η/E has dimension of time and is defined as the *relaxation time* τ , and Eq. (3-35) becomes

$$\sigma = \sigma_o e^{-\frac{t}{\tau}} = \frac{\sigma_o}{e^{\frac{t}{\tau}}} \quad (3-36)$$

Examining Eq. (3-36), one can see that if the relaxation time is short in comparison to the present time t , then the stress σ at a given time becomes small. On the other hand, if the relaxation time is long, then the stress σ is nearly the same as the original stress σ_o , as shown in Figure 3-18.

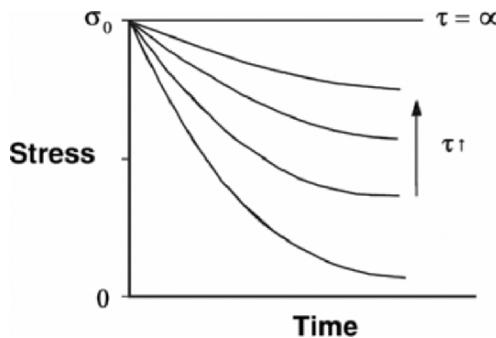


Figure 3-18. Relaxation curve for Maxwell model with different values of relaxation time (τ).

Example 3.3

A stress of 1 MPa was required to stretch a 2-cm aorta strip to 2.3 cm. After an hour in the same stretched position, the strip exerted a stress of 0.75 MPa. Assume the mechanical property of the aorta did not vary appreciably during the experiment.

- What is the relaxation time, assuming a simple exponential decay model?
- What stress would be exerted by the aorta strip in the same stretched position after five hours?

Answer

- From Eq. (3-32):

$$\sigma = \sigma_o e^{-t/\tau}, \quad \frac{0.75}{1} = \exp\left(-\frac{1}{\tau}\right).$$

Therefore, $\tau = \underline{3.48 \text{ hour}}$

- Substituting the relaxation time

$$\sigma = 1 \exp\left(-\frac{5}{3.48}\right) = \underline{0.24 \text{ MPa.}}$$

In comparison, window glass has a distribution of relaxation times including very large relaxation times of many years; minimal stress relaxation occurs over short times. By contrast, water

and oil have short relaxation times. Thus, when stressed their shape changes immediately to relieve the applied stress (instantaneous stress relaxation).

Similar analysis can be made with the Voigt model (Figure 3-17, right). In this case the strain of the spring and dashpot are equal since both are assumed to deform together, in parallel:

$$\varepsilon_{\text{total}} = \varepsilon_{\text{spring}} = \varepsilon_{\text{dashpot}} = \varepsilon. \quad (3-37)$$

The total stress is the summation of that in the spring and dashpot:

$$\sigma_{\text{total}} = \sigma_{\text{spring}} = \sigma_{\text{dashpot}} = \sigma. \quad (3-38)$$

The reason is that the forces in this parallel system are additive.

Substituting Eqs. (3-29) and (3-30) into (3-38), with E again substituted for k :

$$\sigma = E\varepsilon + \eta \frac{d\varepsilon}{dt}. \quad (3-39)$$

The creep behavior of the Voigt model is given by a compliance $J(t) = \varepsilon(t)/\sigma$. In terms of retardation time, λ , the creep behavior can be expressed as

$$J(t) = \frac{1}{E} (1 - e^{-t/\lambda}).$$

If a stress is applied and maintained for a long time, and if the stress is removed, then the strain recovers with time in a way that can be derived from Eq. (3-39):

$$\varepsilon(t) = \varepsilon_0 \exp\left(-\frac{E}{\eta} t\right), \quad (3-40)$$

where ε_0 is the strain at the time of stress removal. The constant η/E is termed the *retardation time* λ for this *creep recovery* process. Since the strain is being recovered from the original strain ε_0 , Eq. (3-40) can be rewritten as

$$\varepsilon_{\text{recovery}} = \varepsilon_0 - \varepsilon_0 \exp\left(-\frac{t}{\lambda}\right) = \varepsilon_0 \left[1 - \exp\left(-\frac{t}{\lambda}\right)\right]. \quad (3-41)$$

Therefore, the pattern of recovery of a creep strain follows the same pattern as the original creep, provided the material is linearly viscoelastic (stress and strain proportional for each time or frequency). Figure 3-19 shows the creep response of a Voigt model with varying retardation times.

Example 3.4

A piece of polyethylene is stretched to 20% of its length. When the stress was released it recovered 50% of its strain after one hour at room temperature.

- What is the retardation time assuming a single exponential model?
- What is the amount of strain recovered after 5 hours at room temperature?

Answer

- a. From Eq. (3-41):

$$\varepsilon = \varepsilon_0 [1 - \exp(-t/\lambda)], \quad \frac{\varepsilon}{\varepsilon_0} = 0.5 = 1 - \exp\left(-\frac{1}{\lambda}\right).$$

Therefore, $\lambda = 1.443$ hour

- b. $\varepsilon = 0.2 [1 - \exp(-5/1.443)] = 0.194$ [or 19.4%, which is 96.9% recovery of the strain since the original strain is 20%].

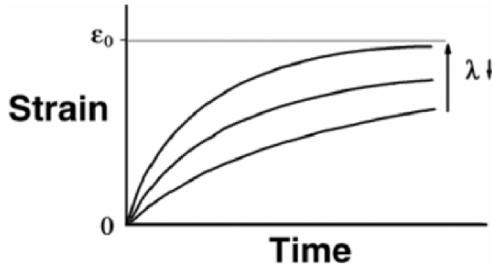


Figure 3-19. Retarded elastic deformation (creep and recovery) curves for Voigt model with various retardation time (λ).

3.1.3.e. Behavior of viscoelastic materials

The viscoelastic behavior of various materials is shown in Figure 3-20. The dynamic stiffness (Figure 3-20a) and loss tangent (Figure 3-20b) are shown since they are the properties most easy to conceptualize. Observe that the scales are logarithmic. The very low frequencies correspond to very long times in creep: $t = 1/2\pi f$. The behavior of a three-element spring–dashpot model is also shown in Figure 3-20b for comparison. Observe that the glass-to-rubber transition in polymers is associated with a large peak in the loss tangent in the frequency domain. Crosslinked polymers exhibit a nonzero limit to the stiffness at low frequency; the stiffness of uncrosslinked polymers tends to become zero at sufficiently low frequency or sufficiently long time. Such materials are viscoelastic liquids. Some such materials may superficially appear solid; the excess creep becomes apparent only after months or years. Blood is also a viscoelastic liquid.

3.1.3.f. Applications

There are a variety of consequences of viscoelastic behaviors that influence the application of viscoelastic materials. For example, in those applications for which a steady-state stress is applied, the creep behavior is of greatest importance. The expected service life of implant materials may be very long; consequently, attention to the long-term creep behavior is in order. Blood vessels experience a steady-state internal pressure that gives rise to circumferential stress, so creep in blood vessel materials is important. Creep also occurs in the polyethylene

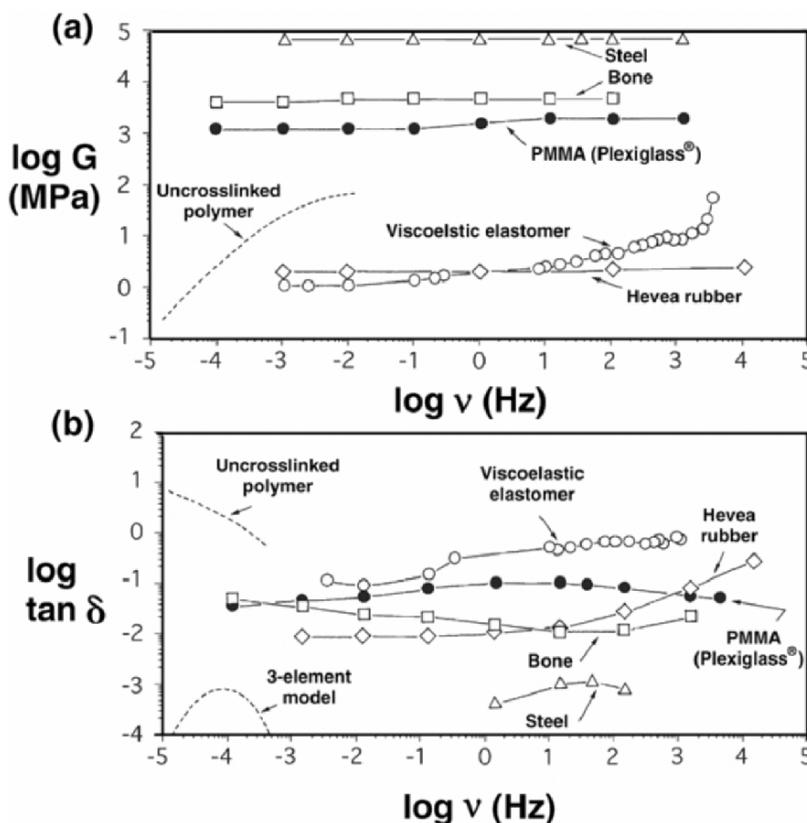


Figure 3-20. Viscoelastic behavior of various materials: (a) stiffness, (b) loss.

socket component of the total hip replacement. This creep gives rise to an indentation of the socket component by the ball joint. Wear and loosening are usually more important than creep in these implants. Stress relaxation is relevant to such situations as the loosening of screws that have been tightened to a specified extension. Bone screws are an example. In applications involving vibration, the width of the vibration amplitude-versus-frequency curve is proportional to the loss tangent. The maximum vibration amplitude at resonance is inversely proportional to the loss tangent. Vibrations damp out more rapidly for higher loss tangent values. Viscoelastic materials may therefore be used to reduce vibration in machinery or to protect the body from vibration or from mechanical shock. At higher frequency, sound or ultrasound waves are attenuated in proportion to the loss tangent. Diagnostic ultrasound is therefore absorbed in tissues, and will not penetrate far into a body composed of highly viscoelastic materials.

3.2. THERMAL PROPERTIES

The most familiar thermal properties are the melting and freezing (solidification) temperatures. These are phase transformations that occur at specific temperatures. These transformation tem-

peratures depend on the bond energy, e.g., the higher the bonding strength, the higher the melting temperature. If the material is made of different elements or compounds, then it may have a range of melting or solidification temperatures, that is, the liquid coexists with solid over a range of temperatures, unlike a pure material.

The thermal energy spent on converting one gram of material from solid to liquid is called the heat of fusion. The unit is Joules per gram, where one Joule is equivalent to one Newton meter. The heat of fusion is closely related to the melting temperature (T_m), i.e., the higher is T_m , the higher the heat of fusion, although there are many exceptions (Table 3-2).

Table 3-2. Thermal Properties of Materials

Substance	Melting temp. (°C)	Specific heat (J/g)	Heat of fusion (J/g)	Thermal conductivity (W/mK)	Linear thermal expansion coeff. ($\times 10^{-6}/^{\circ}\text{C}$)
Mercury	-38.87	0.138	12.7	68	60.6
Gold	1,063	0.13	67	297	14.4
Silver	960.5	0.2345	108.9	421	19.2
Copper	1,083	0.385	205.2	384	16.8
Platinum	1,773	0.134	113	70	—
Enamel	—	0.75	—	0.82	11.4
Dentine	—	1.17	—	0.59	8.3
Acrylic	70*	1.465	—	0.2	81.0
Water	0	4.187	334.9 (ice)	—	—
Paraffin	52	2.889	146.5	—	—
Beeswax	62	—	175.8	0.4	350
Alcohol	-117	2.29	104.7	—	—
Glycerin	18	2.428	75.4	—	—
Amalgam	480	—	—	23	22.1–28
Porcelain	—	1.09	—	1	4.1

*Softening temperature (T_g).

The thermal energy spent on changing the temperature of a material by 1°C per unit mass is called *specific heat*. Traditionally, water is usually chosen as a standard substance, and 1 calorie is the heat required to raise 1 gram of water from 15 to 16°C , but now the standard unit of energy including energy associated with heat is the Joule. Thus, the specific heat is in units of J/g. (1 calorie is equivalent to 4.187 J. The calorie used to represent food or metabolic energy is actually a kilocalorie, or 1000 calories.)

The change in length Δl for a unit length l_0 per unit temperature is called the *linear coefficient of expansion* (α), which can be expressed as

$$\alpha = \frac{\Delta l}{l_0 \Delta T}. \quad (3-42)$$

The thermal expansion may depend on the direction in a single crystal or composite, and it may depend on temperature. If the material is homogeneous and isotropic, then the *volumetric* thermal expansion coefficient (V_{exp}) can be approximated:

$$V_{\text{exp}} \approx 3\alpha. \quad (3-43)$$

Another important thermal property is the *thermal conductivity*, which is defined as the amount of heat passed for a given time, thickness, and area of material. The unit is Watt/mK, where one Watt is equivalent to one J per second. Generally, the thermal conductivity of metals is much higher than ceramics and polymers due to the free electrons in metals that act as energy conductors.

Example 3.5

In order to fill a cavity, a cylindrical hole with $r = 2$ mm is made in a molar tooth, the remaining thickness of which is 1 mm. The length of the hole is $L = 4$ mm. Consider that it is filled with amalgam; then consider it to be filled with acrylic resin. Assume the temperature variation is 50°C . The modulus of elasticity of the amalgam and resin are $E_{\text{amalgam}} = 20 \text{ GPa}$ and $E_{\text{resin}} = 2.5 \text{ GPa}$, respectively. Moreover, $E_{\text{dentin}} = 14 \text{ GPa}$, $E_{\text{enamel}} = 48 \text{ GPa}$. The thermal expansions are $\alpha_{\text{amalgam}} = 25 \times 10^{-6}/^\circ\text{C}$, $\alpha_{\text{resin}} = 81 \times 10^{-6}/^\circ\text{C}$, $\alpha_{\text{enamel}} = 11 \times 10^{-6}/^\circ\text{C}$. Assume that Poisson's ratio for all the materials is $\nu = 1/3$.

- Calculate the volume changes for the fillings.
- Calculate, based upon an elementary one-dimensional model and neglecting any remaining dentin, the force developed between the enamel and fillers.
- Calculate the force between the filling and the remaining enamel tooth structure, considered as a cylindrical shell in a more realistic two-dimensional model, considering the filling as a cylinder. Also determine the stress at the interface and the stress in the enamel and discuss the results.

Answer

- Since the volume expansion coefficient can be defined as in Eq. (3-39),

$$\frac{\Delta V}{V_0 \Delta T} = 3\alpha;$$

therefore, $\Delta V = V_0 \times 3\alpha \times \Delta T$

The net volume change after the filling will be

$$\Delta V_{\text{amalgam}} = \pi (1 \text{ mm})^2 \times 4 \text{ mm} \times 3(25 - 8.3) \times 10^{-6} \times 50 = 0.03 \text{ mm}^3,$$

$$\Delta V_{\text{resin}} = \pi (1 \text{ mm})^2 \times 4 \text{ mm} \times 3(81 - 8.3) \times 10^{-6} \times 50 = 0.14 \text{ mm}^3.$$

- First, it is necessary to choose a simple model for the thermal mismatch. If we have two dissimilar rods end to end, then they expand freely and do not generate mismatch stress. If they are constrained at the ends, they generate thermal strains even if there is no mismatch in thermal expansion. Two dissimilar bars or plates bonded together over their long surfaces will bend when heated, but this geometry is not representative of a tooth filling.

Consider the elementary analysis for a cylindrical pressure vessel of radius r and thickness t containing a pressure P . The circumferential stress is $\sigma = Pr/t$. This solution may be used to analyze the tooth modeled as a thin outer ring (the remaining tooth structure) bonded to an inner ring representing the filling. The strain is $\varepsilon = \sigma/E + \alpha\Delta T$, with σ as stress, E as Young's

modulus, α as thermal expansion, and ΔT as temperature change. The strain in the tooth and the strain in the filling are the same since they are modeled as bonded layers. So,

$$\sigma_f / E_f + \alpha_f \Delta T = \sigma_t / E_t + \alpha_t \Delta T.$$

Here f represents the filling and t represents the tooth. Rearranging,

$$\sigma_t / E_t - \sigma_f / E_f = (\alpha_f - \alpha_t) \Delta T.$$

But the contact pressures P are equal but the filling and tooth stresses are opposite in sign. So

$$\sigma_t = (\alpha_f - \alpha_t) \Delta T / [1/E_f + 1/E_t].$$

But $\sigma = Pr/t$. The force is $F = PA$, with $A = 2\pi rL$ as the contact area. So

$$F = (t/r) 2\pi r L (\alpha_f - \alpha_t) \Delta T / [1/E_f + 1/E_t].$$

Substituting values given above for an amalgam filling, $F = 248$ N.

In reality, the filling is solid, not hollow. A more realistic analysis is given in the following.

- c. Consider the remaining tooth structure to be a hollow cylindrical shell of thickness t , length L , and radius R . The filling occupies the inside of this shell.

Calculate the strain in the filling ε_f , in terms of the stresses σ in different directions, Poisson's ratio v , the coefficient of thermal expansion α , and the temperature change ΔT .

First, write the three-dimensional constitutive equation relating stress, strain, and temperature change:

$$\varepsilon_{fx} = [\sigma_x - v(\sigma_y + \sigma_z)]/E + \alpha \Delta T.$$

Similarly, in the y direction,

$$\varepsilon_{fy} = [\sigma_y - v(\sigma_x + \sigma_z)]/E + \alpha \Delta T.$$

Let us neglect stress in the z direction. Moreover, the stresses should be equal in the x and y directions in view of the cylindrical geometry assumed. So the radial and tangential strain in the filling (subscript f) are given by:

$$\varepsilon_f = \sigma(1-v_f)/E_f + \alpha_f \Delta T.$$

Since Poisson's ratio is about 1/3, neglect of the elementary three-dimensional aspect of this problem would generate an error of about 30%. This would perhaps be acceptable in view of the other simplifications involved in this problem.

The surrounding tooth (represented by subscript t) may be thought of as a thin-walled pressure vessel in this approximation, so the tangential stress is much less than the radial stress. The tangential strain is given by

$$\varepsilon_t = \sigma_t / E_t + \alpha_t \Delta T.$$

If no gap opens up between the filling and tooth (since the filling expands more than the tooth), the tangential strains will be equal, so

$$\sigma_f(1-v_f)/E_f + \alpha_f/E_t + \alpha_t\Delta T.$$

Now consider the radial force F . Stress is force per area, so for the filling we consider equal radial and tangential stresses, so

$$\sigma_f = F/2\pi RL.$$

For the tooth, represented as a thin cylindrical shell with pressure P from within (radial stress), the tangential stress is given by

$$\sigma_t = PR/t = [R/t][F/2\pi RL] = F/2\pi Lt.$$

Substituting the stresses above, simplifying, and recognizing if the filling is in compression, the shell of tooth structure is in tension:

$$F = [2\pi(\alpha_f - \alpha_t)\Delta TL]/[(1/E_t t) + ((1-v_f)/ER)].$$

Observe that the force between filling and tooth is a result of the *difference* in thermal expansion. Of course, the actual geometry of a filled tooth is more complex than we have assumed here. A more accurate result would be obtained by finite-element analysis involving the true geometry.

We obtain, after substituting appropriate values, forces of 547 N for a resin filling and 459 N for an amalgam filling. Moreover, we calculate the tangential tensile stress in the enamel with an amalgam filling to be 18 MPa. This is in the neighborhood of the fracture stress of enamel. Ordinarily, the dentist would avoid having such a thin layer of tooth structure remaining. Moreover, the filling is placed at a temperature between room temperature (20°C) and body temperature (37°C). Even though a range of 50°C can occur in the mouth, a portion of that range is below ambient, as in the eating of ice cream. Cooling of the filling can result in a gap forming between the filling and tooth, and leakage can occur in that gap. Leakage of oral fluids can give rise to tooth sensitivity or further decay of the tooth.

3.3. PHASE DIAGRAMS

When two or more metallic elements are melted and cooled they form an intermetallic compound or a *solid solution* or, more commonly, a mixture thereof. Such combinations are called “alloys.” The alloys can exist as either a single phase or a blend of multiple phases depending on temperature and composition. A *phase* is defined as a physically homogeneous part of a material system. Thus, a liquid and gas are both single phase, but there can be more than one phase for a solid, such as fcc iron and bcc iron, depending on pressure and temperature. Among multiphase metals, steels are iron-based alloys containing various amounts of a carbide (usually Fe₃C) phase. In this case, the carbon atoms occupy the interstitial sites of the iron atoms (cf. Figure 2-9); this is called an *interstitial* solid solution. Most metal atoms are too large to exist in the interstitial sites. If the two metal atoms are roughly the same size, have the same bonding tendencies, and tend to crystallize in the same types of crystal structure, then a *substitutional* solid solution may form. This structure is composed of a random mixture of two different atoms, as shown in Figure 3-21. Unless the elements are very similar in properties, such a solution will exhibit a limited solubility, i.e., as more substitutional atoms are added into the

matrix, the lattice will be more and more distorted until phase separation occurs at the solubility limit. In some systems, such as Cu–Ni, as shown in Figure 3-21, complete solid solubility exists.

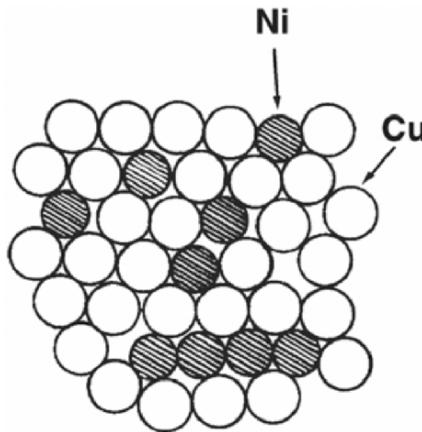


Figure 3-21. Substitutional solid solution of a Cu–Ni system.

The phase diagram is constructed first by preparing known compositions of Cu–Ni, and then melting and cooling them under thermal equilibrium. During the cooling cycle one has to determine at what temperatures the first solid phase (α) appears and all of the liquid disappears. These points will determine the *liquidus* and *solidus* line in the phase diagram. From this phase diagram one can determine the types of phase and amount of each element present for a given composition and temperature. Thus, if we cool a 40 w/o Ni–60 w/o Cu liquid solution, from Figure 3-22;

Temperature (°C)	Phase (relative amount)	Composition of each phase
above 1270	liquid (all)	40 Ni – 60 Cu
1250	liquid (63%)	33 Ni – 67 Cu
	α (37%)	52 Ni – 48 Cu
1220	liquid (5%)	26 Ni – 74 Cu
	α (95%)	43 Ni – 57 Cu
below 1210	α (all)	40 Ni – 60 Cu

The relative amount of each phase present at a given temperature and composition is determined by the *lever rule* after making a horizontal isothermal (tie) line at the temperature of interest. Let C_A and C_B be the composition of element A (Ni) and B (Cu) in the two-phase region met by the tie line (say 1240°C) with the same composition given above (40 w/o Ni = C_A); then the amount of liquid (L) phase can be calculated as follows:

$$\frac{L}{\alpha + L} = \frac{C_l - C_A}{C_l - C_\alpha} = \frac{52 - 40}{52 - 33} = \frac{12}{19} = 0.63, \quad (3-42)$$

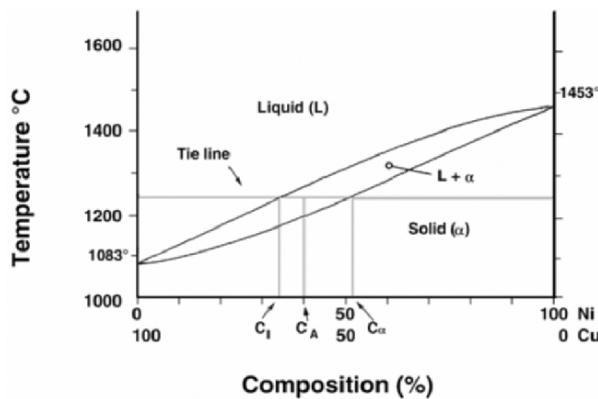
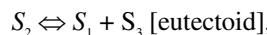


Figure 3-22. The Cu–Ni phase diagram: an example of complete solid solubility. See text for an explanation of the tie line.

where C_A is the original composition of element A. This principle can be applied in more complicated systems such as Ag–Cu (eutectic) or Fe–C (eutectic + eutectoid) systems, as shown in Figures 3-23 and 3-24. The eutectic and eutectoid reactions are defined as



where L refers to liquid, S refers to solid phases, and the numbers indicate the relative amount of phases. There is a relatively larger amount of one of the components at those temperatures. For example, the copper content increases from 8.8% (S_1 or α), 28.1% (L), and 92% (S_3 or β) for the Cu–Ag alloy at 779.4°C, as can be deduced from Figure 3-23. Note that the last liquid will disappear at eutectic temperature and composition (cf. Figure 3-23).

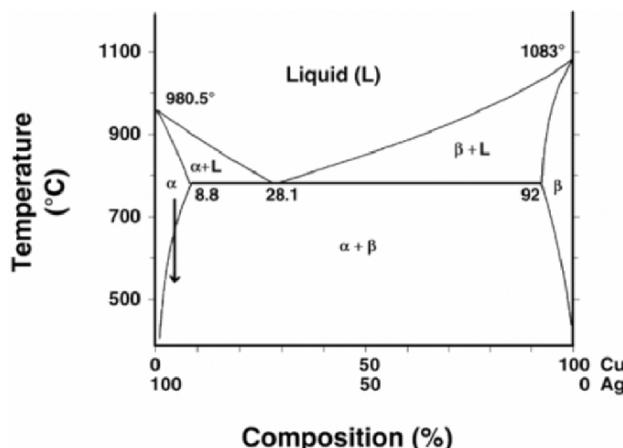


Figure 3-23. The Cu–Ag phase diagram: the dotted vertical line indicates precipitation hardening by quenching of the α phase.

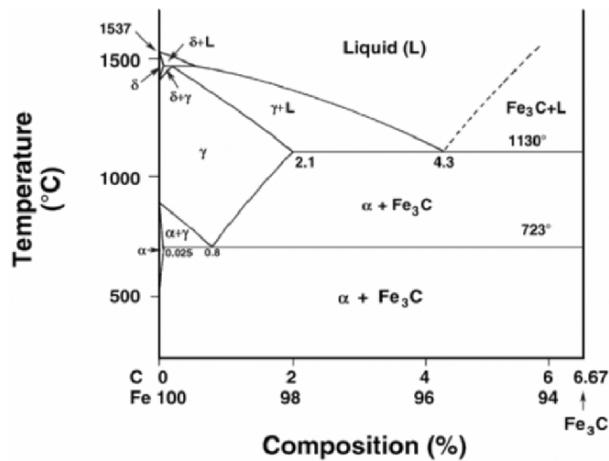


Figure 3-24. Fe–C phase diagram.

Example 3.6

Copper and silver metal are mixed thoroughly in powder form, in proportions 80 w/o Cu and 20 w/o Ag and heated to well above the melting temperature of the alloy. The liquid metal is then cooled and allowed to reach thermodynamic equilibrium. Give the composition of each phase and the relative amount of each phase:

- At 1,000°C.
- At 780°C.
- At 700°C.

Answer

From Figure 3-23:

- At 1,000°C, all liquid (80 w/o Cu + 20 w/o Ag).
- At 780°C, β (92 w/o Cu + 8 w/o Ag) 81 w/o.
 L (28.1 w/o Cu + 71.9 w/o Ag) 19 w/o.

$$\frac{\beta}{\beta + L} = \frac{28.1 - 80}{28.1 - 92} = 0.81.$$

- At 700°C, a (6 w/o Cu + 94 w/o Ag); 15 w/o.
 b (93 w/o Cu + 7 w/o Ag); 85 w/o.

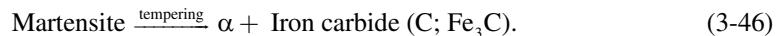
$$\frac{\alpha}{\alpha + \beta} = \frac{93 - 80}{93 - 6} = \frac{13}{87} = 0.15.$$

3-4. STRENGTHENING BY HEAT TREATMENTS

3.4.1. Metals

One of the strengthening processes is precipitation (or age) hardening of alloys by heat treatments. This is accomplished by rapidly cooling (quenching) a solid solution of decreasing solubility, as shown in Figure 3-23 along the dotted vertical line. If quenching is done properly, there will not be enough time for the second phase (β) to form. Hence, a quasi-thermal equilibrium exists, but depending on the amount of thermal energy (related to temperature) and time, the second phase (β) will form (precipitation). If the β phase particles are small and uniformly dispersed throughout the matrix, their presence can increase the strength greatly. It is important that they be dispersed within a grain as well as at grain boundaries, so that the dislocations can be impeded during the deformation process, as in the case of cold-working.

In relation to the precipitation process, the diffusionless *martensitic* transformation process is another mechanism of strengthening steel and other alloys. When fcc iron or steel is quenched from the austenitic temperature range (γ phase in Figure 3-24), there is no time for carbon and other alloying elements to form $\alpha + \text{C}$ phases. Almost all the carbon atoms must diffuse to form carbide (C) as well as the carbide formers (Cr, Mo, and V), which should concentrate in the carbide, whereas ferrite formers (Ni and Si) must diffuse into the ferrite (α). These reactions take time at low temperature (below 400°C). Since the fcc structure of austenite is not in equilibrium, a driving force develops and at low enough temperatures this driving force becomes sufficient to force transformation by shear. The resulting structure is a *tetragonal martensite* instead of the body-centered cubic ferrite. The martensite is extremely hard because it is non-cubic (has fewer slip systems than bcc structure) and the interstitially entrapped carbon prevents slip. Martensite is the hardest iron-rich phase material but is extremely brittle. Hence, tempering by heating (600°C) and slow cooling is necessary to make the material tough and strong. Martensite crystal structures are also of interest in the context of shape memory materials such as nickel-titanium alloys:



3.4.2. Ceramics and Glasses

As mentioned earlier, ceramics and glasses are hard and brittle due to their *non-yielding* character during deformation, which in turn is due to their bonding characteristics. Because of this brittleness they are subject to stress concentration effect at the microcracks present in the material when in tensile deformation mode (cf. §3.1.2). Therefore, if we want to increase their strength we can employ means to overcome these problems by (1) introducing surface compression that has to be overcome before the net stress becomes tensile, and (2) reducing stress concentration by minimizing sharp cracks on the surface and in the bulk.

We can accomplish surface compression by thermal treatment (quenching from high to low temperature and surface crystallization) or by chemical treatment (ion exchange). In the latter process, a small ion such as Na^+ is exchanged with a larger ion such as K^+ . Reduction of the number of microcracks for glasses can be accomplished by a simple fire-polishing process that will also concomitantly introduce surface compression, making the glass very strong (this can increase its strength up to 200-fold). Strong glass can also be achieved by drawing the glass into fibers. The fibers have good surface quality, and they are smaller in size than the typical distance between defects such as microcracks. Therefore, such fibers can be essentially defect-free and are very strong. Such fibers are used in composite materials.

3.4.3. Polymers and Elastomers

Polymers and elastomers cannot be heat treated to increase their strength in general. The strengths of these materials are sensitive to the chemical composition, side group, branching, molecular weight, polydispersity, and degree of crosslinking. Considerable strength increase can be achieved by substituting the main chain repeating unit of polyamide (nylon) with a benzene ring. The resulting polymer is called aramid (Kevlar®). This fiber is stronger than piano wire if compared in terms of specific strength (see §7.3.1). Drawing and annealing indeed involve a thermal process but usually are used to increase the strength of fibers or thin sheets. We will consider this topic in chapter 8.

3.5. SURFACE PROPERTIES AND ADHESION

Surface properties are important since all implants interface with the tissues at their surfaces. The surface property is directly related to the bulk property since the surface is the discontinuous boundary between different phases. If ice is being melted, then there are two surfaces created between three phases: liquid (water), gas (air and water vapor), and solid (ice).

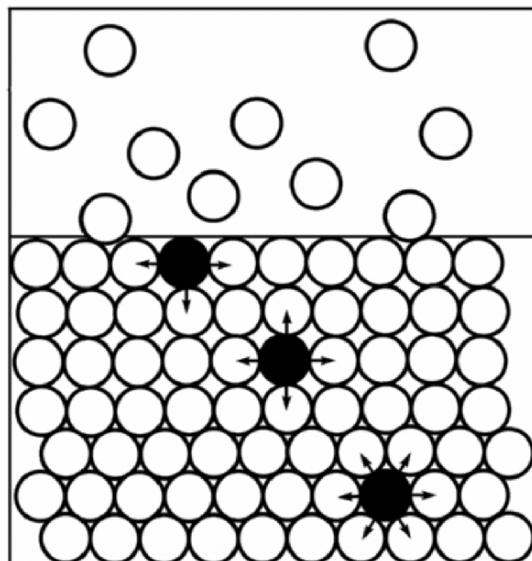


Figure 3-25. Two-dimensional representation of a surface. Surface molecules are not subject to balanced forces from surrounding atoms in the solid, and are therefore more reactive.

The *surface tension* develops near the phase boundaries since the equilibrium bonding arrangements are disrupted, leading to an excess energy that will minimize the surface area, as shown in Figure 3-25. Other means of minimizing the surface energy is to attract foreign materials (*adsorption*) and bonding with adsorbent (*chemisorption*). The surface free energy (dG) can be expressed as,

$$dG = dw - \gamma dA, \quad (3-47)$$

where w is work done on the surface area change dA , and γ is the surface energy of the material.

The conventional units used to describe surfaces are dynes per cm or ergs per cm^2 for surface energy (or tension), but these units are exactly the same since one erg is one dyne cm. The SI unit is N/m, as given in Table 3-3.

Table 3-3. Surface Tension of Materials

Substances	Temperature (°C)	Surface tension (N/m)
Mercury	20	0.465
Lead	327	0.452
Zinc	419	0.785
Copper	1131	1.103
Gold	1120	1.128

$$1 \text{ N/m} = 10^3 \text{ ergs/cm}^2 = 10^3 \text{ dynes/cm}$$

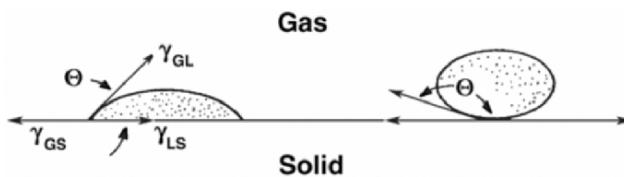


Figure 3-26. Wetting and non-wetting of a liquid on the flat surface of a solid. Note the contact angle.

If a liquid is dropped on a solid surface, then the liquid droplet will spread or make a spherical globule, as shown in Figure 3-26. At equilibrium the sum of surface tensions (γ_{GS} , γ_{LS} , and γ_{GL}) among the three phases (gas, liquid, and solid) in the solid plane should be zero since the liquid is free to move until force equilibrium is established. Therefore,

$$\gamma_{GS} - \gamma_{LS} - \gamma_{GL} \cos\theta = 0, \quad \cos\theta = \frac{\gamma_{GS} - \gamma_{LS}}{\gamma_{GL}}, \quad (3-48)$$

where θ is called the contact angle. The wetting characteristic can be described as

$$\begin{aligned} \theta &= 0 && (\text{complete wetting}), \\ 0 < \theta < 90^\circ & && (\text{partial wetting}), \\ \theta > 90^\circ & && (\text{non-wetting}). \end{aligned} \quad (3-49)$$

Note that Eq. (3-48) gives only ratios rather than absolute values of surface tension. Some values of contact angle are given in Table 3-4.

The lowest surface tension of a liquid (γ_{GL}) in contact with a solid surface with a contact angle (θ) greater than zero degrees is termed *critical surface tension* (γ_c). The critical surface

tension can normally be used as the surface tension of a solid, as given in Table 3-5, for some polymers. The critical surface tension can be measured by measuring contact angles with various liquids of known surface energy. Extrapolating the curve to a zero contact angle would be equivalent to the surface energy of the substrate material. The plot is called a *Zisman plot*, as given in Figure 3-27.

Table 3-4. Contact Angle Values

Liquid	Substrate	Contact angle(°)
Methylene iodine (CH_2I_2)	Soda-lime glass	29
Water	Fused quartz	33
Mercury	Paraffin wax	107
	Soda-lime glass	140

Table 3-5. Critical Surface Tension of Polymers

Polymer	γ_c (dyne/cm)
Polyhexamethylene adipamide, nylon 66	46
Polyethylene terephthalate	43
Poly(6-amino caproic acid), nylon 6	42
Polyvinyl chloride	39
Polyvinyl alcohol	37
Polymethylmethacrylate	33–44
Polyethylene	31
Polystyrene	30–35
Polydimethyl siloxane	24
Poly(tetrafluoroethylene)	18.5

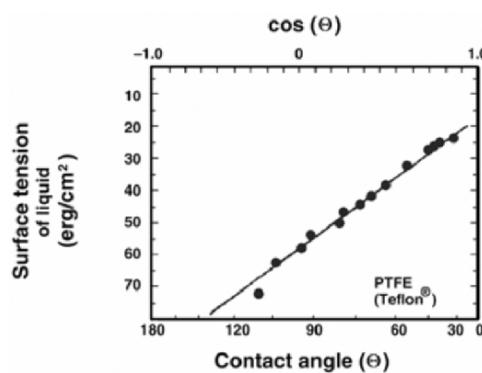


Figure 3-27. Zisman plot of contact angles: the PTFE substrate with various liquids (Baier, 1980).

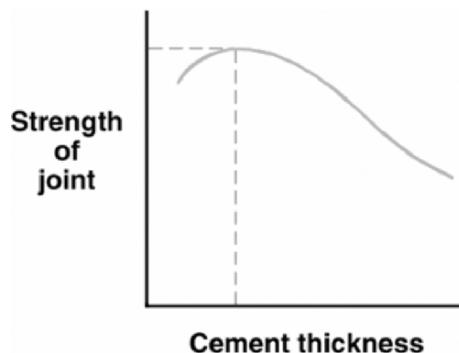


Figure 3-28. Variation of the strength of a joint versus the thickness of the cement between adherends.

When two surfaces are bonded together it is called adhesion if the two materials are different and cohesion if the same. All surfaces cemented with a cementing agent are bonded by adhesion; hence, the cementing agent is an adhesive. For the maximum interfacial strength the thickness of the adhesive layer must be optimal, as shown in Figure 3-28.

In dental and medical applications the adhesives should be considered a temporary remedy since the tissues are living, replacing the old cells with new ones, and thus destroying the initial bonding. This problem led to the development of porous implants, which allows tissues to grow into the interstices (pores), creating a viable, interlocking system between implants and tissues.

PROBLEMS

- 3-1. Which of the following materials will be best described by the three stress-strain curves of Figure 3-5?
- Ceramics and glasses.
 - Plastics (polymers) such as polyethylene.
 - Glassy polymers such as Plexiglas® (polymethylmethacrylate).
 - Soft tissues such as skin, blood vessel walls, etc.
 - Hard mineral tissues of bone and teeth.
 - Copper.
 - Rubber band.
- 3-2. Poisson's ratio (ν) is defined by the following expression:

$$\nu = -\varepsilon_x / \varepsilon_z,$$

where ε is strain; the load is applied in the z direction in simple tension or compression.

Silicone rubber has a Poisson's ratio of 0.4. Consider a silicone rubber drain hose for a surgical procedure; the hose has an outer diameter of 4 mm and a wall thickness of 0.5 mm. How much does the lumen (interior space) of the catheter constrict if the hose is stretched by 20%?

- 3-3. The following data were obtained using a stainless steel tensile specimen:

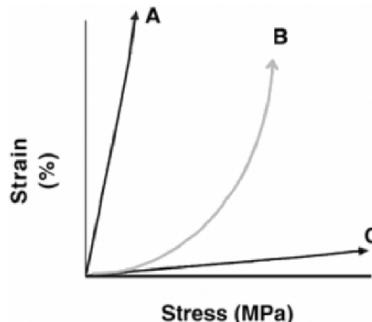
Stress (MPa)	Strain (%)	Stress (MPa)	Strain (%)
98	0.06	700	0.50
160	0.10	770	0.60
280	0.16	830	0.70
350	0.20	870	0.80
500	0.30	920	0.90
620	0.40	930	1.00

- a. Plot the stress-strain curve.
 - b. Determine the modulus of elasticity, 0.2% offset yield strength, fracture strength and the toughness.
- 3-4. A piece of suture is tested for its stress relaxation properties after cutting a 3-cm long sample with a diameter of 1 mm. The initial force recorded after stretching 0.1 cm between grips was 5 Newtons. Assume the suture material will behave as if it has one relaxation time. The gauge length was 1 cm.
- a. Calculate the initial stress.
 - b. Calculate the initial strain.
 - c. Calculate the modulus of elasticity of the suture if the initial stretching can be considered as linear and elastic.
 - d. Calculate the relaxation time if the force recorded after 10 hours is 4 Newtons.
- 3-5. The following data were obtained using unknown liquids and a polyethylene sheet.

Liquid	γ (erg/cm ²)	Contact angle (°)
A	75	96
B	40	63
C	30	15
Polyethylene	29	—

- a. Plot the interfacial surface tension versus contact angle.
 - b. Obtain a linear relationship between interfacial surface tension and contact angle.
 - c. What conclusions can you draw regarding γ_{GL} and γ_{SL} ?
- 3-6. Surface properties change after a material is implanted inside the body.
- a. Explain how properties will be changed as a result of adsorption of protein, or as a result of diffusion of water into the material.
 - b. What methods should be used to understand the interaction between the tissue and implant. Can you use the data obtained from in vitro surface experiment in vivo?
- 3-7. From the data given in Figure 3-9:
- a. Estimate the endurance limit of bone cement.

- b. If a tooth implant is made of this material with a 4-mm diameter and is cylindrical in shape, how long will it last? Assume the maximum force of chewing is 100 N in compression.
- 3-8. From the data given in Table 3-2:
- Plot melting temperature (T_m) versus specific heat, heat of fusion, thermal conductivity, and linear thermal expansion coefficient.
 - What conclusions can you draw?
- 3-9. Show that the maximum (resolved) shear stress operates on a 45° angle with respect to the force (stress) being applied. Hint: the shear stress $\tau = F/A_s$ can be resolved into a component upon a slip direction which has an angle of λ and a force normal to the slip plane. The slip plane has an angle of ϕ ; then $\tau = \sigma \cos \lambda \cos \phi$, where σ is the applied stress on the cross-sectional area A .
- 3-10. Prove the lever rule.
- 3-11. A 70 w/o Cu and 30 w/o Ag alloy was made and cooled from liquid. From the Cu–Ag phase diagram (Figure 3-23).
- At what temperature does the solid phase start to appear?
 - What phases exist at 780°C ?
 - What are the compositions of the phases in b?
 - What is the weight of Cu in the solid phase and liquid phase in b if we started with 100 g of alloy?
 - Can this alloy be solution hardened?
- 3-12. From the following general stress–strain curves, answer the following. Observe the axis labels carefully.



- Which curve represents the lowest Young's modulus material?
- Which curve represents the toughest material?
- Which curve represents alumina (Al_2O_3)?
- Which curve represents aluminum?
- Which curve represents polyethylene $[-\text{CH}_2\text{CH}_2-]_n$?
- Which curve represents material with the lowest Poisson's ratio?

- 3-13. The plastic was stretched from 100.00 cm to 120.00 cm and released at room temperature. The length changes with time were obtained as the following. Assume the Voigt model can be applied for this mechanical behavior.

Time (hr)	Length (cm)
0	120.0
1	110.0
3	103.0
6	100.4
20	100.1

- a. What is the retardation time(hours)?
- b. What is the percent strain at 15 minutes based on the original length of the sample?
- c. What is the amount of strain (%) recovered after 15 minutes?
- d. If the test was made at body temperature, would the recovery be faster, slower, or the same compared to the room temperature test.

SYMBOLS/DEFINITIONS

Greek Letters

- α : Linear thermal expansion coefficient, amount of length change per unit length per unit temperature.
- δ : Loss angle, the phase angle between stress and strain in oscillatory loading of viscoelastic materials; it is zero in an elastic material.
- ϵ : Strain, change in length per unit length.
- γ : Surface energy. See definitions of words.
- γ_c : Critical surface tension that is the lowest surface energy a solid exhibits.
- η : Viscosity, measure of the flow characteristic of a material [Pa * s or Poise].
- λ : Retardation time at which the strain level is reduced to its original value by $1/e$ at constant stress.
- ν : Poisson's ratio — the ratio of lateral contraction to longitudinal extension in simple tension.
- θ : Contact angle which is formed between liquid and solid substrate due to the partial or non wetting nature of the surface.
- σ : Stress (tensile, compressive, or shear), force per unit cross-sectional area.
- κ : Yield stress of the softer material between two sliding materials that can wear.
- τ : Relaxation time at which the stress level is reduced to its original value by $1/e$ at constant strain.
- μ : Friction coefficient.

Latin Letters

- a : Surface crack length of an elliptic crack ($2a$ if the crack is in the bulk).
- b : One half-width of an elliptic crack.
- C : Iron carbide (Fe_3C).

E: Young's modulus or modulus of elasticity; slope of the stress-strain curve in the elastic portion.

FS: Failure or fracture strength of a material.

H(t): Heaviside step function; 0 for $t < 0$, 1 for $t > 0$.

J(t): Creep compliance, ratio of time-varying strain to constant stress, $\varepsilon(t)/\sigma_0$.

K: Fracture toughness derived from the micromechanics of crack propagation. Units are [MPa $\sqrt{\text{m}}$ or psi $\sqrt{\text{in}}$]

r: Crack tip radius.

scf: Stress concentration factor, the ratio of the stress at a tip of a crack or hole to nominal stress away from the tip.

TS: maximum or ultimate tensile strength of a material.

ΔV : wear volume.

YS: yield point or stress beyond which the material will be permanently deformed.

Words

Adhesion: Joining of two different materials.

Adsorption: Physical attachment of foreign material (usually gas) on a surface.

Boltzmann superposition principle: Effect of a compound cause is the sum of the effects of individual causes. This is the statement of linearity for viscoelastic materials.

Chemisorption: Chemical attachment of foreign material (usually gas) on a surface.

Cohesion: Joining of identical materials.

Contact angle (θ): Angle made when a drop of liquid spreads over a solid surface. It is governed by the balance of surface tension at various interfaces.

Convolution: Type of integral equation used in the analysis of viscoelastic materials.

Creep: Increase of strain with time in viscoelastic materials under constant stress.

Endurance limit: Stress level below which the material will not fail by cyclic fatigue loading no matter how many cycles (a practical limit is often chosen as 10^7 cycles).

Engineering stress: Stress calculated based on its original cross-sectional area.

Fourier transform: Integral transform equation involving sinusoids. In the context of viscoelastic materials, Fourier transforms relate the time and frequency domains.

Griffith theory: Energy approach to the fracture of a (brittle) material in which the fracture strength in tension is inversely proportional to the square root of the crack length. The intrinsic properties of surface energy and Young's modulus are directly related to the strength.

Heaviside step function: Unit step function; has a value of zero for arguments less than zero, and one for arguments greater than zero. It is used in analysis of viscoelastic materials.

Hooke's law: Stress is linearly proportional to strain. Most materials follow this law at low strains.

Isotropic: Properties of material are the same in every direction. Materials such as steel and glassy polymers are usually isotropic, but composite materials and biological materials are not.

Kramers-Kronig relations: Relationships between the compliance and loss functions of frequency in viscoelastic materials.

Limited solubility: Results when only a maximum amount of solute material can be dissolved in a solution (solid).

Martensite: Iron carbon alloy (steel) obtained by quenching from austenite (γ); has a body-centered tetragonal crystal structure. Other similar crystal structures such as those occurring in shape memory alloys (e.g., nickel–titanium) are also called martensite.

Maxwell model: Mechanical analog model consisting of a spring and a dashpot in series for describing viscoelastic material properties.

Necking: Unstable irreversible flow of material locally during tensile deformation, resulting in a neck-like shape.

Phase: Having the same (atomic or micro) structure and properties throughout.

Relaxation modulus: Stress relaxation of viscoelastic materials is the decrease in stress that occurs under constant strain. The relaxation modulus is the ratio of stress to strain during stress relaxation.

Solid solution: Solid phase that contains more than two elements that are mixed uniformly everywhere in the phase.

Surface tension (surface energy): Amount of free energy exhibited at the surface of a material.

Tempering: Toughening of martensite by heat treatment; the structure becomes more stable by converting to ferrite (α) and carbide microstructure.

Thermal conductivity: Amount of heat (thermal energy) passed for a given thickness, time, and cross-sectional area of a material.

Toughness: amount of energy expended before its fracture or failure.

True stress: Stress calculated based on a specimen's true cross-sectional area.

Voigt or Kelvin model: Mechanical analog model describing material properties by arranging a spring and a dashpot in parallel.

Yield point: Point of the stress–strain curve where transition takes place from elastic to plastic deformation, i.e., the curve deviates from initial linear portion.

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