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THERMAL EFFECTS

In the broad sense, thermal effects are those caused by a redistribution of internal energy in a system, and they may be grouped in natural and artificial (see [Introduction to Thermodynamics](#)). More often, however, instead of considering a generic compound system out of equilibrium, a system at equilibrium is assumed, and thermal effects are understood as those caused by a temperature variation forced from outside or due to internal processes. Most of the times, both thermal ‘effects’ (i.e. thermal response) and thermal ‘causes’ (i.e. thermal load) are included in the study.

Thermal behaviour of materials is a broader subject, more directly related to their general thermal properties than to thermal effects of specific interest; e.g. heat transfer processes, or the fact that when energy is added to a material it gets hotter, are general thermal behaviour of matter, usually not included in the analysis of thermal effects. Thermal effects on materials may be used advantageously (all kind of [thermometers](#) relay on them), or a nuisance (shape and dimension distortions due to heating or cooling, malfunction of electronic equipment).

Most of the times, thermal effects are understood to focus just on materials (understood as solid materials), and to deal with the effects of a non-comfort working temperature (cold or hot) on some material properties (structural, electronic, etc.), including the thermal processes used to produce, change or dispose of those materials. Sometimes it is also said ‘the effect of heat on materials’, meaning the effect of heating so as to increase the internal energy. Of course, the effects of cooling are also relevant thermal effects.

The traditional thermal effects are:

- Phase change, basically melting and boiling (phase transition temperatures).
- Glass transition temperature.
- Dimensional change, basically thermal expansion (in general, contraction if negative).
- Elasto-plastic changes, due to thermal stresses.
- Brittle/ductile transition temperature.
- Chemical change, decomposition, oxidation, ignition.
- Other physical changes as drying, segregation, outgassing, colour change, etc.
- Thermal effects due to non-thermal causes: frictional heating, electrical heating, chemical heating, nuclear heating.

A general idea to keep in mind is that materials cannot resist very high temperature, say over 1000 K, without decomposition; materials resistant to high temperatures (from 1000 K to 3000 K) are called refractories. On the other hand, the effect of [very low temperatures](#) ([cryogenics](#)) is mainly an increase in fragility (most materials break or even shatter after a knock at cryogenic temperatures), what may help on hard-metals machining; cryogenic cooling of metals increase their resistance to wear.

An overview of some possible classification of thermal effects helps to centre the field, although only a selected mix of topics, in a structured layout but with different levels of detail, is covered below.

MATERIALS. TYPES AND PROPERTIES

Materials are solid bodies with intrinsic properties (apart of the shape) that render them useful, mainly for structures, but also for services (e.g. isolation, piping), electronics, optics, bioengineering, etc... Fluids are treated as intermediate states here (in materials processing). A substance is a chemically identified pure or mixture matter (solid or fluid). Matter is what has mass (i.e. everything except perfect vacuum).

Materials are usually classified in four categories (basically depending on the type of chemical bond):

- Metals (metallic bonds, polycrystalline solids). They are obtained by high-temperature reduction of their ores with carbon (as for iron in a blast furnace), or by high-temperature electrolysis of their molten ores (as for aluminium). They are the materials most used, and amongst them ferrous metals (90%; and non-ferrous being mostly alloys of Al, Cu, Ni and Ti). They are ductile, heavy, and good electrical and thermal conductors.
- Ceramics (ionic bonds, amorphous inorganic solids). They are the most ancient (stones, bricks, glasses), usually made by previous calcination of raw materials (making cement powder) and final curing of composite mixtures, e.g. concrete is made with cement, sand and gravel (plus water). They are resistant to wear (but not to impact), lighter than metals, insulating, porous and fragile (very sensitive to flaws).
- Polymers (covalent bonds, amorphous organic solids). They are organic and non-crystalline soft solids artificially obtained from petroleum in the xx c., by moderate-temperature addition or condensation of organic macromolecules (i.e. very large molecules with very simple composition, as polyethylene, the most used, $-(C_2H_4)_n-$ with n between 100 and 1000 and molar mass $M=10^0..10^3$ kg/mol. Plastics, i.e. mouldable synthetic matter, is often used as a synonym of polymers.
- Composites (a heterogeneous combination of the former three). Examples: wood (lignine in cellulose), bone, adobe (straw in clay), paper (lignine in cellulose), concrete (gravel in cement), reinforced concrete (steel rods in concrete).

There are many types of material properties (see below); Table 1 presents a broad comparison for the three main material types. Traditionally, Material Science and Engineering deals with the microscopic analysis (atoms, molecules and bonds), the microstructure (mesoscale), the macroscopic properties, the processing techniques and the applications, usually divided in the traditional material types: metals, ceramics, polymers and composites.

Table 1. Property comparison for the different types of materials (typical value and range).

Property	Metals	Ceramics	Polymers
Density ρ [kg/m ³]	8000 (2000..22000)	4000 (2000..18000)	1000 (900..2000)
Thermal expansion α [1/K]	$10 \cdot 10^{-6}$ ($1 \cdot 10^{-6}..100 \cdot 10^{-6}$)	$10 \cdot 10^{-6}$ ($1 \cdot 10^{-6}..20 \cdot 10^{-6}$)	$100 \cdot 10^{-6}$ ($50 \cdot 10^{-6}..500 \cdot 10^{-6}$)
Thermal capacity c_p [J/(kg·K)]	500 (100..1000)	900 (500..1000)	1500 (1000..3000)
Thermal conductivity k [W/(m·K)]	100 (10.. 500)	1 (0.1.. 20)	1 (0.1.. 20)
Melting (or yield) point T_m [K]	1000 (250..3700)	2000 (1000..4000)	400 (350..600)
Elastic Young's modulus E [GPa]	200 (20..400)	200 (100..500)	1 ($10^{-3}..10$)
Poisson's ratio	0.3 (0.25..0.35)	0.25 (0.2..0.3)	0.4 (0.3..0.5)
Break strength σ_{break} [MPa]	500 (100..2500)	100 (10..400)	50 (10..150 tensile)

		tensile) (50..5000 compr.)	(10..350 compr.)
Hardness	Medium	High	Low
Machinability	Good	Very poor	Very good
Thermal shock resistance	Good	Poor	Very poor
Thermal creep resistance	Poor to medium	Excellent	Very poor
Electrical conductivity	High	Very low	Very low
Chemical resistance	Low to medium	Excellent	Good

In general, and in what follows, thermal effects on materials usually refer to thermal effects on metallic materials because metals are the back horse of industrial materials. It may be argued also that metals are richer in thermal effects than ceramics, but, in the future, thermal effects on polymers may take the centre of the study, since it is clear that polymers are more sensitive to temperature than metals. However, this thermal sensitivity of polymers is feared nowadays as a handicap (e.g. their low softening temperature, their small thermal conductivity), whereas metals are strong and conducting, and ceramics are strong and insulating. Composites, as most natural materials are, seem to be the most promising.

Polymers usually have low thermal conductivity, but it can be greatly enhanced by adding conductive powders (e.g. bakelite may change from $k=1 \text{ W/(m}\cdot\text{K)}$ to $k=12.3 \text{ W/(m}\cdot\text{K)}$ with 55 % by volume of graphite), and strongly depends on their degree of crystallinity, because the thermal conductivity in polymers is mostly due to so-called phonon transport that is very efficient along the crystallinity axes but substantially reduced by various scattering processes in other directions. In the case of semicrystalline polymers like polyethylene, the thermal conductivity parallel to the orientation increases rapidly with increasing orientation (up to $10 \text{ W/(m}\cdot\text{K)}$), but perpendicular to the orientation it decreases slightly (up to $0.3 \text{ W/(m}\cdot\text{K)}$). For amorphous polymers, as for PVC, PMMA, PS, and PC, the anisotropy ratio remains much lower (typically less than 3).

CLASSIFICATION OF THERMAL EFFECTS ON MATERIALS

Classification by type of substance

- On (solid) materials
- On fluids

Classification by type of effect

- Physical effects (dimensional change, phase change, heating)
- Chemical effects (decomposition, reaction)
- Biological effects (metabolic retardation, sterilisation)

Classification by temperature range

- Cryogenic effects (superconductivity, superfluidity)
- Mid-temperature effects
- High-temperature effects (dissociation, ionisation)

Classification by purpose of its study (study target)

- To know the effects (e.g. expansion, melting, decomposition)
- To avoid the effects (e.g. refractories, ablation, food preservation)
- To know the causes (i.e. thermal analysis; mainly to ascertain substance composition for quantitative analysis).

Classification by stage in the manufacturing of materials

- During materials production
 - Melting temperature of ores, and the influence of fusers
 - Solidification of melts, and the influence of the cooling rate
 - Phase diagrams (most alloys are prepared by melting together and mixing the components).
- During materials shaping (forming)
 - By fusion and solidification (with or without mould, high temperature or chemical bonding)
 - Casting (pouring liquid in a mould at high temperature)
 - Continuous casting (no mould, high temperature)
 - By aggregation at high temperature: soldering (and the like: welding, brazing), accretion (by thermal spray coating), sintering (of powder at high temperature and pressure)
 - Reactive (chemical setting): bonding at low temperature
- On solid phase (by a very high pressure or chemical attack, at low or medium temperature; cold shaping if $T_{\text{work}} < T_{\text{recrystallisation}}$)
 - Pressing (with or without die): Forging, pressing, rolling, bending
 - Machining (with a lathe, drill, mill, abrasive-wheel, sand-blast): cutting, chipping.
 - Thermo-elasto-plastic deformation (heat line technique of plate curving)
 - Reactive (chemical attack)
- During materials finishing
 - Polishing
 - Thermal treatments
- During materials utilisation
 - Heating by friction
 - Brittle-ductile transition
 - Thermal creeping
 - Ablation
- During materials recycling

TYPES OF MATERIAL PROPERTIES

Material properties may be classified according to the material (i.e. metal properties, polymer properties,...) or according to the application; in the latter case, the usual grouping is:

- Mechanical properties (mainly structural): density, elastic modulus (Young's), shear modulus (Poisson's), Poisson's ratio, strength, elongation, $\varepsilon(\sigma)$, rigidity-plasticity, hardness-damping, wear, fatigue, fracture.
- Thermal properties: density, thermal expansion coefficient, thermal capacity (former specific heat), thermal conductivity (or thermal diffusivity), vapour pressure.
- Electrical properties: conductivity (or resistivity), dielectric constant, magnetic permeability, energy bands.
- Chemical properties: composition, material compatibility, oxidation, corrosion, erosion. Environmental attack. Health hazards (safety, exposure limits).
- Optical properties: emissivity ε (hemispherical or normal), absorptance α , transmittance τ , reflectance ρ . Photonics: stimulated emission, fibre optics.

- Acoustic properties: speed of sound, acoustic impedance and sound attenuation.
- Miscellaneous engineering properties: availability (manufacturer), price, ease of manufacture (cutting, joining, shaping), recycling, etc.

REFRACTORY MATERIALS

Refractory materials are basically ceramic materials, mechanically and chemically resistant to high temperature (i.e. thermally resistant), and are used for brick-lining of furnaces, boilers, crucibles, and for high-temperature thermal insulation (including ablation).

Refractory metals (W, Ta, Mo, Nb, Zr) are very expensive, but ceramic-metal composites are in use. Ordinary metals like steels and aluminium cannot resist high temperatures. Aluminium alloys should not be used above 500 K due to loss of strength (but titanium alloys may be used up to 900 K). Low-carbon steels should not be used above 700 K due to quick oxidation and loss of strength; small addition of chrome and/or vanadium in some 1% enhance temperature resistance up to 800 K, by formation of carbides (steam pipes are made of these low-alloy steels); high alloy steels, as stainless steels, may be used up to 850 K. Cr-Ni alloys like 80%Cr-20%Ni may be used up to 1200 K.

Most refractories are consumable materials that wear out, some in less than 10 minutes, but others in more than 20 years. The steel industry is still the major customer of the refractories industry, consuming 50-80% of the total annual refractory production (10..20 kg of refractory per ton of steel produced).

Properties of refractories which can be determined most readily are chemical composition, bulk density, apparent porosity and strength. Properties not only depend on composition but on production details, so they are manufacturer's dependent. The tonnage of monolithic refractories (castables, plastics, gunning/shotcasting mixes, etc.) produced in recent years now exceeds brick-shape refractories.

Classification according to working temperature:

- For <450 K (not proper refractories): pyrex glass (used with boiling water), tempered glass (furnace doors at more than 15 cm from a flame; it lose temper at 600 K).
- For <1000 K: calcium silicate slabs, pyroceram® (transparent ceramic used in cook-tops).
- For <1500 K: fireclay, vycor® (transparent ceramic, Apollo windows), some Ni-Cr alloys used in gas turbine blades.
- For <2000 K: mullite firebricks, metallic carbides.
- For >2000 K: metallic carbides (the highest melting temperatures are 4150 K for HfC, 4100 K for TaC and 3800 K for C).

Classification according to purpose:

- Fired bricks. Ordinary firebricks are made from fireclays (low on soda, potash and lime, high on alumina and silica).
- Mortars and cements for firebricks.
- Monolithic. They are special mixes or blends of dry granular or cohesive plastic materials used to form virtually joint-free linings:

- Castable ceramics. A mixture of a heat-resistant aggregate and a heat-resistant hydraulic cement. For use, it is mixed with water and rammed, cast or gunned into place.
- Plastic refractories.

Classification according to chemical composition:

- Low alumina firebrick (35..40% alumina), 40..45% alumina scotch firebricks, 50% to 80% silica.
- High alumina firebrick (>50% alumina): bauxite, sillimanite, mullite.
- Calcium silicate slabs (for use at 850..1100 °C).
- Magnesite: MgO.
- Silica bricks: porous and dense.
- Metallic carbides (SiC, ZrC, TaC, HfC): arduous wear areas, e.g. skid rails, incinerators.

Classification according to acidity:

- Alkali resistant (basic refractories): magnesite (MgO), dolomite.
- Acid resistant.

HEATING TECHNIQUES

Some energy input is required for heating, most of the times with the intention to rise its temperature, but other times with the aim to force a physical or chemical phase change, or just to maintain a high temperature against heat losses. Different classifications may be established for the study of heating techniques.

According to the extent of the heating:

- Local heating, by means of a hot-air jet, a torch (e.g. propane/air, oxyhydric, oxyacetylene), an electrical resistance, an electrical arc, a laser beam, etc. It may be used for local drying, thawing, cooking, bending, joining (soldering, brazing, welding), cutting, coating (paint removal, tar roof application), ignition. etc.
- Global heating, usually within a furnace, but for small pieces it might be done by sweeping through it with a local heater.

According to the energy source:

- Mechanical heating, usually by friction.
- Electrical heating, using the material itself for energy release (e.g. induction heating), or more commonly by external means with an electrical resistance made of Nichrome (60% Ni, 25% Fe, 15% Cr) or Kanthal (70%Fe, 24%Cr, 5%Al).
- Radiation heating, either with microwaves, infrared radiation from heated wires protected inside a quartz-glass (wires can be made of tungsten, carbon, Kanthal or Nichrome; naked Nichrome coiled wire was also used in the past), or using visible radiation (with a laser).
- Chemical heating, mainly by combustion, but also by hydrogen formation after atomic hydrogen is produced in an electric arc, for instance.

The modern cook-top glass (commercially developed in the 1980s) allows for energy transfer by heat conduction (e.g. from an electrical resistance or gas flame), infrared radiation, and magnetic induction. This ceramic material (68% SiO₂, 19% Al₂O₃, 4% Li₂O, 2% MgO, 2% ZnO), is not amorphous but

polycrystalline (what makes it crack resistant), and has low thermal conductivity (to avoid lateral waste), and good thermal-shock resistance (withstands the sudden cooling due to liquid spills).

THERMAL PROPERTIES

A thermal property is any characteristic of a material defining the substance and related to temperature; e.g. thermal conductivity is said to be a thermal property, but electrical conductivity is not. However, all properties, thermal and non-thermal, are temperature dependent, and in this sense included under thermal properties.

The effect of temperature on thermal properties may be large (what may be used to build good thermometers). Standard values are usually given at 20 °C (comfort lab conditions), but other reference conditions are also traditionally used: 0 °C because its ease of reproducing, 15 °C because it is the average temperature in the Earth surface, 20 °C (human comfort), or 25 °C because it is easier to maintain a bath temperature a little over the oscillating ambient temperature, than below. Fortunately, the influence of all those temperature-standards is minor on property values, but care should be paid to make it explicit.

The effect of pressure on thermal properties is very low on condense substances. The standard value for pressure is 100 kPa, although 101.325 kPa, the average pressure in the Earth surface, is sometimes used.

The effect of uncertainty in composition of the substance is usually small (e.g. properties of tap water, and even of sea water, may be taken as those of pure water, in many instances), except on some sensitive properties, like for the thermo-optical properties of substances, that are heavily dependent on contamination, or the thermal conductivity of metals, that may vary a lot with small alloys, etc.

Traditionally, thermal properties are grouped, with some overlapping) in thermodynamic, thermophysical and thermochemical data.

THERMODYNAMIC

They are further subdivided in gas properties, liquid properties and solid properties, the latter usually found under thermophysical properties, as here below.

Gas

Chemical formula. Used for identification. Although all real gases are mixtures (pure air, humid air, petroleum gases, exhaust gases), only properties of pure gases are usually tabulated (see Gas Data).

Molar mass. It is the mass of a system which contains as many elementary molecules as there are atoms in 0.012 kilogram of carbon-12; e.g. molar mass of air $M=0.029$ kg/mol. The molar mass for a molecule can always be approximated by the sum of the molar mass of its constituents (the difference is the bonding energy divided by the square of the speed of light).

Thermal capacity. It is the energy required to increase the unit mass a unit temperature. It depends on the path (although it is not a path but a state variable), and the thermal capacity at constant pressure is usually given; for condense substances the difference is negligible, but for gases it

is not; e.g. the thermal capacity of air at constant pressure is $c_p=1000 \text{ J/(kg}\cdot\text{K)}$, but at constant volume is $c_v=710 \text{ J/(kg}\cdot\text{K)}$. When the temperature variation is important, polynomial functions $c_p(T)$ are given, usually for the low-pressure limit, instead of for the 100 kPa standard.

Critical point. It is the state at which gas and liquid properties converge. It is usually specified by its temperature and pressure; e.g. the critical point of water is $T_{\text{cr}}=647 \text{ K}$ and $p_{\text{cr}}=22 \text{ MPa}$. Additionally the critical volume, or the critical compressibility factor, is included.

Other properties that may be found on gas tables are thermal conductivity and viscosity (i.e. transport properties). Condensation temperature and vapour pressure are usually included under liquid property data and not under gas properties. When the ideal gas model ($pV=mRT$) needs to be improved for real gases, further $f(p,v,T)$ -correlations, numerical or graphical, are given in analytical form (e.g. Redlich-Kwong equation of state), graphical form (e.g. compressibility-correction diagrams, p - h diagrams), or in tabular form. In particular, for the most common substances, specific diagrams and computer routines are widely available; e.g. for water vapour, humid air, carbon dioxide, other refrigerant fluids, etc.

Liquid

Chemical formula. Used for identification of pure components, but not used for natural liquid mixtures, as for liquid fuels, oils, etc.

Freezing point. It is the temperature at which a liquid solidifies when cooling (at 100 kPa, but the effect of pressure is negligible). If the cooling is rapid, subcooled liquid is obtained below the freezing point (that is why melting is preferred to freezing, to better determine this phase transition). Some liquids, particularly polymers, do not have a well-defined freezing point. Besides the freezing temperature, the freezing enthalpy is tabulated.

Boiling point. It is the temperature at which a liquid vaporises when heating at 100 kPa; the effect of pressure is important and thus the variation of vaporisation temperature (also known as saturation temperature) with pressure must be given, usually as an empirical correlation of the logarithm of vapour pressure with the inverse of temperature. Some liquids, particularly polymers, do not have a well-defined boiling point, or even chemically-decompose before vaporising. Besides the boiling temperature, the boiling enthalpy is tabulated.

Density. It is the mass of the unit volume; e.g. for water $\rho=1000 \text{ kg/m}^3$. When the incompressible-indilatable liquid model needs to be improved, polynomial functions $\rho(T)$ are given, although the linear term, the volumetric thermal expansion coefficient, α , is usually enough. More rarely, the compressibility coefficient, $\kappa \equiv (1/\rho)\partial\rho/\partial p|_T$ is tabulated (or the speed of sound, directly related to the latter). Related to those is the isentropic compression heating coefficient $\partial T \partial p|_s = \alpha/(\rho c)$, that for water is 30 K/GPa at $25 \text{ }^\circ\text{C}$.

Thermal capacity. It is the energy required to increase the unit mass a unit temperature; e.g. the thermal capacity of water is $c=4200 \text{ J/(kg}\cdot\text{K)}$. When the temperature variation is important, polynomial functions $c(T)$ are given.

Other properties that may be found on liquid tables are: transport properties (thermal conductivity, kinematic or dynamic viscosity, species diffusivities, even emissivity and transmissivity), and other physical properties as surface tension with air or with its own vapours.

THERMOPHYSICAL

Thermophysical properties usually refer to thermal properties of (solid) materials, or auxiliary properties of fluid substances used in the manufacture of (solid) materials, as viscosities, mass diffusivities, etc. Other times, Thermophysical refers to transport properties, whereas Thermodynamic refers to equilibrium properties. For thermophysical properties of fluids see just above.

Chemical formula is only relevant for pure chemical substances, what is the exception for ordinary materials: metal alloys, ceramics, polymers and composites. The main thermophysical properties are summarised below, and some special properties are further analysed afterwards.

Melting point. It is the temperature at which a solid melts on heating. Many solids, particularly polymers and ceramics, do not have a well-defined melting point, or even decompose before melting, and a softening temperature or maximum working temperature is given. More rarely, boiling temperatures and phase-change enthalpies are provided.

Density. It is the mass of the unit volume; e.g. for ice $\rho=920 \text{ kg/m}^3$. When the incompressible-indilatable solid model needs to be improved, polynomial functions $\rho(T)$ are given, although the linear term, the linear thermal expansion coefficient, α , is usually enough. More rarely, the compressibility coefficient, $\kappa \equiv (1/\rho)\partial\rho/\partial p|_T$ is tabulated (or the speed of sound, directly related to the latter).

Thermal capacity. It is the energy required to increase the unit mass a unit temperature; e.g. the thermal capacity of iron is $c=420 \text{ J/(kg}\cdot\text{K)}$. When the temperature variation is important, polynomial functions $c(T)$ are given. A simple approximation for thermal capacities of solids is $c=3R$ (Dulong-Petit rule); e.g., for iron, $c=3\cdot 8.3 \text{ J/(mol}\cdot\text{K)}=3\cdot 8.3/0.056 \text{ J/(kg}\cdot\text{K)}=440 \text{ J/(kg}\cdot\text{K)}$.

Thermal conductivity. It is the coefficient in Fourier's law of heat conduction (i.e. heat flux proportional to temperature gradient); e.g. the thermal conductivity of copper is $k=390 \text{ W/(m}\cdot\text{K)}$. When the temperature variation is important, polynomial functions $k(T)$ are given. Sometimes, thermal diffusivity, $a \equiv k/(\rho c)$, is also tabulated. When two metallic parts are in contact, the thermal-joint resistance may drastically deteriorate the heat flow, and a thermal pad or thermal grease is applied to enhance thermal-joint-conductance (e.g. in the contact between the CPU and its board on a computer).

Emissivity. It is the energy radiated per unit area by a one-side surface in all directions and at all wavelengths (what is known as hemispherical bolometric emission, or infrared emission, since not-incandescent materials emit mainly in the infrared), divided by σT^4 (i.e. the energy radiated per unit area by a blackbody surface). The colour-temperature of the emission can be used as a thermometer, as in steel works, where a faint-red indicates some 750 K (in a dark room it is visible above 670 K), a blood-red indicates some 850 K, a cherry-red some 1000 K, a lemon-yellow at 1300 K and a white at 1500 K.

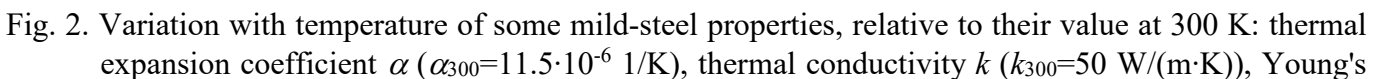
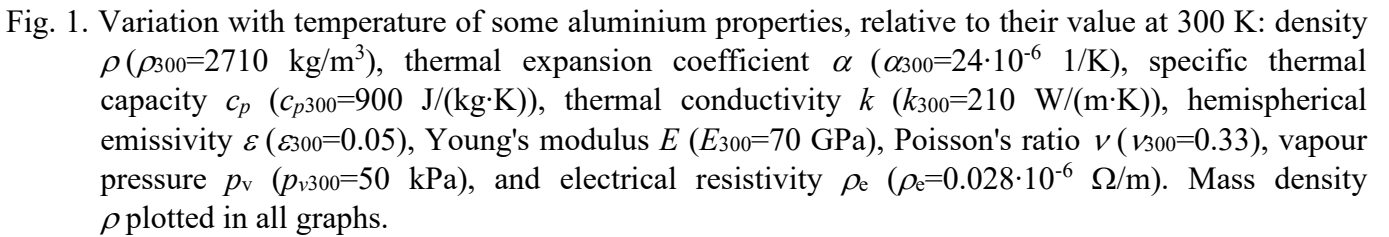
Solar absorptance. It is the energy absorbed per unit surface perpendicular to an incoming radiation with a wavelength distribution similar to the sunshine.

Related to thermal expansion is thermal shock, the stress caused by non-uniform thermal expansions/contractions, mainly affecting poor thermal conductive materials. For instance, when drops of molten window-glass fall into water, they shatter violently because of the large thermal contraction, whereas drops of quartz-glass do not break but get hardened by thermal toughening. Thermal shock resistance is enhanced by high thermal diffusivity, low thermal expansion coefficient, high tensile strength and small size. A simple thermal-shock-resistance measure is the temperature difference between two isothermal layers to yield failure stress: $\Delta T_{\text{break}} = \sigma_{\text{break}}(1-\nu)/(\alpha E)$ (ν being Poisson's ratio, α thermal expansion and E Young's modulus), although a better measure is given by the parameter $D\sigma_{\text{break}}(1-\nu)/(\alpha E)$, D being the thermal diffusivity.

Other thermophysical properties of interest in the study of thermal effects, particularly for thermometry, may be the thermoelectric coefficients and the electrical resistance variation with temperature. Prandtl numbers are often included in the tabulation, although it is just the ratio of momentum diffusivity to thermal diffusivity, $Pr = \nu/a = \mu c_p/k$.

The main interest here is on mechanical properties of materials, so that other thermophysical properties relevant to other fields of Physics are not considered, as the transition temperature between the ferromagnetic-paramagnetic states (Curie temperature), and the transition temperature between the electrical superconductivity and normal conductivity (superconduction temperature).

Most of the times material properties are considered constant but they all depend on temperature; an example of the relative effect of temperature on some thermophysical properties is presented in Fig. 1 for the case of aluminium and Fig 2 for the case of mild steels.



modulus E ($E_{300}=210$ GPa), Poisson's ratio ν ($\nu_{300}=0.29$), and yield stress σ_{yield} ($\sigma_{\text{yield},300}=260$ MPa).

Thermal conductivity of mild steels linearly decreases to a half at 1100 K (from some 50 W/(m·K) at 300 K to some 35 W/(m·K) at 1100 K), increasing afterwards up to 33 W/(m·K).

The electrical conductivity dependence with temperature may be useful (e.g. thermometry) or harmful (thermal runout). Like other thermally-activated processes, this dependence may be modelled with an Arrhenius law: $\sigma=A\exp(-T_a/T)$. The electrical resistance of the wolfram filament in a domestic light bulb increases 16 times from 300 K to 3000 K according to $\rho/\rho_0=(T/T_0)^{1.2}$.

THERMOCHEMICAL

Several different tabulations of thermochemical properties are usually given.

- Thermochemical constants (because they refer to values at a standard temperature and pressure). Besides the formula and molar mass, the standard enthalpy of formation, absolute entropy and Gibbs function of formation are given, although they are redundant and one might be obtained from the others.
- Equilibrium constants (in spite of them being temperature functions). For some simple elementary reactions (mainly dissociation reactions), values of the equilibrium constant relating equilibrium composition to temperature and pressure, are tabulated. Sometimes these data are skipped since a linear approximation of the logarithm of the equilibrium constant in terms of the inverse of temperature, $\ln K=A-B/T$, with A and B obtained from the thermochemical constants above, may be accurate enough.
- Combustion properties. Here, data is related to the fuel (instead of to the combustion reaction), and the amount of information may vary widely: fuel composition, stoichiometry, heating values, flammability limits, autoignition temperature, flash point, laminar deflagration speed, quenching distance, etc.

Other thermochemical data may be used in special topics of thermal effects, as mixing enthalpy, hydration enthalpy, adsorption enthalpy, etc.

MEASUREMENT OF THERMAL PROPERTIES

Common to any thermal property measurement is a precise temperature measurement (thermometry). Notice that more accurate thermometers are not always the best, since many times a very quick response is better. The basic lesson is that there is not a single best thermometer, several thermometers are always needed, and that a trazability of calibrations must be maintained.

Density. Although not a genuine thermal property, density values are often needed to study thermal effects. The basic densimetry method is by weighting and volume measurement (e.g. by water immersion). More accurate meters are based on resonant responses of a sample.

Thermal capacity. The most common technique is by calorimetry, i.e. letting the sample come into equilibrium with a bath at a different initial temperature and measuring the final temperature.

Thermal conductivity. The basic technique is by using Fourier's law through a sample of area A and thickness L , $k = \dot{Q}L / (A\Delta T)$, while maintaining a temperature difference ΔT between thermal blocks (e.g. a heated copper block and a water cooling stream). For poor thermal conductors a thin plate is used (i.e. $L^2/A \ll 1$), whereas for good conductors a laterally insulated bar is preferred. If a reference sample of a known-conductivity material of analogue value is put in series with the test sample, the uncertainty is decreased. Accuracy, however, is not great, and transient methods are often preferred, as when a sudden heating is performed (e.g. with a laser) and the temperature response of a nearby point is analysed (e.g. with an infrared radiometer). In reality, those transient meters measure thermal diffusivity $a \equiv k/(\rho c)$. When heat must flow through the contact surface of two metals, imperfections in the finishing give way to the so-called thermal contact resistance, an empirical value difficult to characterise.

Heat flux. The fundamental measure of heat is based on energy balances (e.g. $Q = \Delta E - W$ for a fixed mass); heat rates are computed by small time increments. The easiest practical way is by electrical energy dissipation by Joule effect at steady rate ($\dot{Q} = -\dot{W} = -I^2 R$) or in a small resistor ($Q = -W = -I^2 R t$), measuring electrical voltages and intensities (helped by Ohm's law $V = IR$). General purpose surface heat meters are thin devices where the temperature loss through a reference layer of known conductivity gives a measure of the heat flux. The layer must be very thin and conductive (dielectric polymer sheets some 0.1 mm thin are used) to not alter the original heat flux, but not so much as to render the measuring of the temperature jump by a series of thermocouples (a thermopile) inaccurate. High conductivity adhesives are used to mount the sensor on the testing surface to enhance thermal joint conductance.

TEMPERATURE EFFECTS ON MECHANICAL PROPERTIES

Materials working outside room temperatures are exposed to thermal loads that may arise from different sources:

- Hot sources: from hot gasses, fire, proximity to heat sources such as boilers, incinerators and engines, hot process fluids, or belonging to heat generating equipment such as heat engines.
- Cold sources: from low temperature process fluids, cold storage, or cold winter temperatures.

And the temperature change not only affects mechanical behaviour as an additional load, but modifying all material properties. Let start the study by considering small reversible effects on the mechanical properties, i.e. thermoelasticity.

THERMOELASTICITY

Thermoelasticity is an extension of elasticity that includes thermal effects, i.e. the study of the stress field originated by thermal strains in a constrained solid (if the stress overpass the elastic limit, it is thermoplasticity).

Traditionally, the goal of thermoelasticity was to predict the stress, strain or deformations caused by a measurable thermal load, but recently, thermoelasticity is also been used to measure stress fields based on the minute temperature changes (some tenths of a degree) their rapid change causes (adiabatic

compression forces a heating, and expansion a cooling), although only applicable to periodic loads, to have a reasonable signal-to-noise ration in infrared thermography.

Elasticity, fluid mechanics, heat transfer, etc., are different parts of continuous media mechanics. The evolution of a continuum is governed by the general balance equations of mass, momentum and energy, completed with material constitutive relations and with initial and boundary conditions (space-time constraints). Material constitutive relations can further be grouped in equilibrium constitutive relations (the realm of Thermodynamics, here extended with reversible stress-strain relations), and transport constitutive relations, the realm of mass diffusion, rheology (including newtonian fluid mechanics and plasticity), and heat transfer.

We here restrict the analysis to linear thermoelasticity, i.e. small deformations and small temperature-differences with slow time-variation. In this case the heat-transfer problem gets decouple and it is solved first (on the undisturbed solid):

$$\frac{\partial T}{\partial t} = a \nabla^2 T + \frac{\phi}{\rho c} \quad (1)$$

(with $a \equiv k/(\rho c)$ the thermal diffusion coefficient and ϕ the energy source), and later the thermoelastic problem is solved assuming known temperatures, that should not depart a lot from the initial value in order to assume constant (temperature-independent) elastic properties. A brief introduction to elasticity, including thermal effects) follows.

Displacement

A material particle can be displaced to other position by an overall motion or by a relative motion to the rest of the material, forced by mechanical, thermal, hygroscopic, or chemical forces. Overall motion maintains the shape but relative motion causes a shape deformation.

When a body deforms, a generic particle centred around point P at position \vec{r}_p in time t , goes to position $\vec{r}_p + d\vec{r}_p$ at time $t+dt$; we call $\int d\vec{r}_p \equiv \vec{u}_p$ its displacement (sometimes, due to the smallness of displacements, it is written $d\vec{r}_p = \vec{u}_p$, incorrectly). Notice that $d\vec{r}_p$ is in a Lagrangian frame (it refers to body-fitted particle P) whereas \vec{u} is to be in a Eulerian frame (field variable at position \vec{r}). In the rigid-solid motion, $d\vec{r}_p = (\dot{\vec{r}}_O + \vec{\Omega} \times \vec{r}_p) dt$. Notice that the displacement is a vector field, $\vec{u} = u_i(x,y,z)$. In the study of deformations, what matters is the differential displacements in the neighbourhood of a point.

Strain

What matters in the study of deformations is not displacements but differential displacements in the neighbourhood of a point, i.e. the differential displacement tensor $\nabla \vec{u}$ such that $\vec{u}(\vec{r} + d\vec{r}) = \vec{u}(\vec{r}) + (\nabla \vec{u}) d\vec{r}$, that can be further split in its symmetric and antisymmetric components:

$$\nabla \vec{u} = \frac{\nabla \vec{u} + (\nabla \vec{u})^T}{2} + \frac{\nabla \vec{u} - (\nabla \vec{u})^T}{2} = \bar{\bar{\epsilon}} + \bar{\bar{\omega}} \quad (2)$$

where $\bar{\varepsilon} = \varepsilon_{ij} = (\nabla u_j / \nabla x_i + \nabla u_i / \nabla x_j) / 2 = (\varepsilon_x, \varepsilon_y, \varepsilon_z, \gamma_{xy}/2, \gamma_{xz}/2, \gamma_{yz}/2)$ is named the strain tensor and $\bar{\omega}$ the rotation tensor, the latter corresponding to rigid-solid motion, such that $\bar{\omega} d\vec{r} = (1/2)(\nabla \times \vec{u}) \times d\vec{r}$. Notice that the 6 components of the (symmetric) strain tensor cannot be independent since they come from just the three components of the displacement vector, what implies the so-called compatibility relations.

The interpretation of one-dimensional strain may be as $\varepsilon = \lim(\Delta L/L)$ with $L \rightarrow 0$, and that of shear as the angular deformation of an initially square body element $(\pi/2 - \gamma)$. Metals can bear a small elastic strain (usually smaller than 0.5%; beyond which they deform permanently and ultimately break), ceramics even smaller values (usually smaller than 0.1%, beyond which they break), and polymers may sustain large elastic strains.

Stress

The stress, τ (sometimes named σ) is the force per unit area applied to a body externally or as a result of the actions of other parts of the body. A body is under stress if, thinking we cut it, we would have to apply external forces and moments to avoid displacements.

There are normal and tangential stresses, and at any point in a three-dimensional body there are nine ordered components τ_{ij} (the first index referring to the facet, and the second to the direction of the applied force), forming the stress tensor, $\bar{\tau}$ (Euler 1776), that is symmetrical (only 6 components independent, usually named $\bar{\tau} = (\sigma_x, \sigma_y, \sigma_z, \tau_{xy}, \tau_{xz}, \tau_{yz}$ with $\sigma_i = \tau_{ii}$). Sometimes the elastic problem can be drastically reduced, as when there are only uniaxial stresses (the tensor reduces to a scalar, σ), or when there are only planar stresses (only σ_x , σ_y , and τ_{xy} exist).

Mechanical equilibrium applied to a differential tetrahedral element implies that the stresses in any facet are $\vec{f}_A = \bar{\tau} \cdot \vec{n}$ (force or translational equilibrium), and that the stress tensor is symmetric (moment or rotational equilibrium), and the differential equilibrium of an elementary hexahedral element gives the relation between stresses (surface forces) and volume forces, $\vec{f}_V + \nabla \cdot \bar{\tau} = 0$, where \vec{f}_V is the applied force per unit volume (e.g. weight).

Constitutive relations

The material constitutive relations in elasticity relate stresses and strains. A simplified first-look to the uniaxial load case (where the tensors fields become simple scalars), helps to a better understanding.

Uniaxial load. Hook's law

R. Hook establishes in 1678 that “ut tensio sic vis” (i.e. as the extension, so the force), or in today's nomenclature:

$$\sigma = E\varepsilon \quad (\text{Hooke's law}), \text{ or its inverse } \varepsilon = \frac{\sigma}{E} \quad (3)$$

the factor, E , is named Young's modulus (or rigidity, or elasticity modulus) in honour of T. Young that identified shear stress, and distinguished it from tensile stress, in 1807. This is only applicable to an ideal elastic solid (Euler's solid), i.e. that do not sustain any irreversibility. Table 2 presents some values of

Young's modulus for different materials; they can be measured in a traction-machine test (using $\sigma=E\varepsilon$), what is not very accurate, or better by measuring the speed of sound c (of order $c=5000$ m/s for steels) and applying $E=\rho c^2$, or even from the coefficient of compressibility, usually under isothermal conditions, $\kappa=3(1-\nu)/E$ (its inverse $K=1/\kappa=-\Delta p/(\Delta V/V)$ is the bulk modulus), or from a known response to a known loading (e.g. eigenfrequency of a cantilever beam).

Table 2. Typical values of the elastic properties of materials at room temperature.

	E [GPa]	ν	$\sigma_{\text{fluency}=0,2\%}$ [MPa]	$\varepsilon_{\text{fluency}=0,2\%}$ [%]	σ_{break} [MPa]	$\varepsilon_{\text{break}}$ [%]	$\alpha \cdot 10^6$ [1/K]	ρ [kg/m ³]
<u>Metals</u>								
Aluminium	74	0.33	40	0,35	200..500	50	24	2710
Alu. alloys	69..72	0.33	300		90..500	5..40	23..25	2720
Alu. alloy 2024-T4 (Al, 4.5%Cu, 1.5%Mg)	73	0.32	330		470		23	2770
Brass	92	0.33	100..300		300..500		18..20	8780
Bronze	100	0.31	150..500		350..500		17..19	8800
Copper	120	0.34	70		400..500		17	8910
Iron (Cast iron)	70..140	0.36	200..600		100..800	2..20	9..12	7300
<u>Steels</u>								
Carbon steel	207	0.30	200..1000	0,30	400..1500	20	12	7900
Carbon steel AISI 1018 (0.18%C, 0.8%Mn)	198	0.30	390		500	27	12	7800
Carbon steel EN-335 (0.24%C, 1.7%Mn)	199	0.32	335	0,10	490..630	20	12	7860
Invar steel (36%Ni)	140	0.30					1.7	8000
Stainless steel	193..204	0.30	200..1500		400..1400	20	10..17	7900
Platinum	150	0.38			240		9	21470
Titanium	110	0.32	700		800..900		9	4530
<u>Ceramics</u>								
Concrete	25..45	0.20	NA	0	30..50*	0.1	10..14	2300
Glass	70	0.23	NA	0	20..40**	0.1	7..9	2470
Glass (Pyrex)	70		NA	0			3..4	2230
Fused quartz	75	0.17	NA	0	100*	0.2	0.5	2650
Granite	80	0.27	NA	0	70..140*		6..10	3000
<u>Polymers</u>								
Elastomer (rubber)	0,1 a 0,01	-	30	500	30	500	200..300	1100
Kevlar (aramide)	124				2800		-2	1400
PE (Polyethylene)	0.2..0.9		1		10..20	100..800	200	930
PET	9.0				160			
PMMA	3.0				70	2.6	60..80	1190
Polyester	3.4				40..60			1380
Polyurethane	0.1				1	100	150	1100
PP (Polypropylene)			2		40		110	
PS (Polystyrene)	3.4		3		45..55	2.4	70	1040
PVC	2.4..4.1				50	40..80	90..150	1400
Nylon	2.5..3.0		45		80		80	1140
Teflon (PTFE)	0,4 a 0,55	0.46			20..35	200..300	130..200	2250
<u>Composites***</u>								
CFRP 60/40 unidirect.	150						10 ^L , -1 ^T	200
Wood (balsa)	4				20			200
Wood (pine and fir)	16				70		4 ^L , 70 ^T	550

*Flexural or bending strength for ceramics; tensile strength is typically half of that, and compressive strength typically ten times that.

**For annealed soda glass; tempering produces a three or four time increase. Compression strength is 1000 MPa.

***For fibrous materials, properties vary with orientation: ^L, Longitudinal; ^T, Transversal to the fibres.

Hooke's law defines the so-called linear elastic model. Real solids do show a linear elastic behaviour for small loads, but an actual stress-strain diagram, $\sigma(\varepsilon)$, is as shown in Fig. 3 for a brass alloy. The σ - ε diagram should coincide locally with the molecular force-distance-diagram, $F(d)$, around $F=0$ (the slope at this point is E). The Lennard-Jones model of inter-molecular forces predicts a maximum force of attraction at $d=1.25d_0$, what would imply a maximum allowable stress (the strength) of $\sigma_{\max}=E\varepsilon_{\max}=0.25E$, a value that is only approached in some brittle materials; it is several orders in magnitude smaller in metals (e.g. $\sigma_{\text{break}}=500$ MPa for mild steels, against $E=200$ GPa).

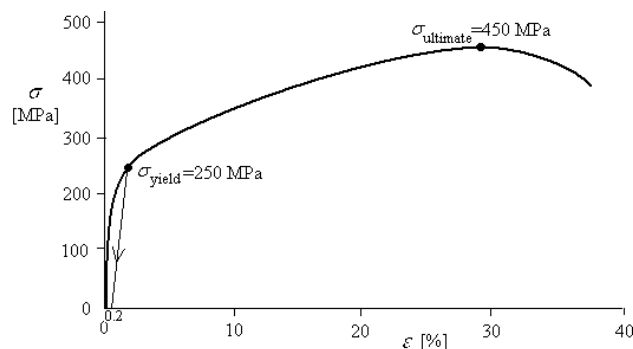


Fig. 3. Tensile test of a typical brass alloy.

Mechanical properties depend on temperature. The general rule is that all of them decrease with a temperature increase, as shown in Fig. 4 for the case of mild steels, but there are exceptions, as for shape-memory alloys, that are soft at low temperature and stiff at high temperature, although the ultimate behaviour is always a tendency to creep (see below) at very high temperatures up to the melting point.

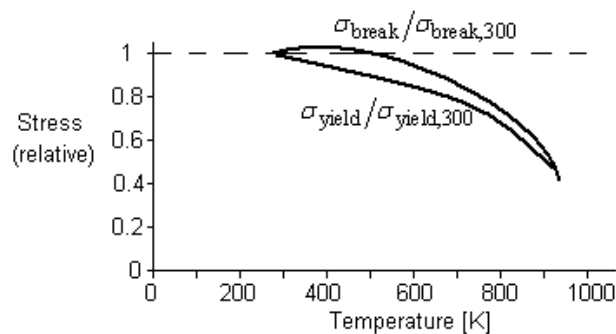


Fig. 4. Variation of yield stress and ultimate strength of mild steels with temperature.

It was also discovered that a uniaxial stress σ not only produces a uniaxial strain $\varepsilon=\sigma/E$, but also transversal strain in the amount $\nu\varepsilon$, ν being Poisson's ratio, i.e. the ratio between the transversal deformation due to an axial load and the axial deformation. If volume were preserved, Poisson's ratio should be $\nu=0.5$; ideal molecular models predict a value $\nu=0.25$; real values are between 0.2 and 0.4 as shown in Table 2.

Similar to the axial stress-strain behaviour, tangential or shear loads give rise to transversal deformations, and a transversal rigidity modulus, G (shear modulus) is defined such that $t=G\gamma$. It was also found that only two elastic properties are independent for an isotropic solid, and that $G=E/(2(1-\nu))$.

A comparison of the stress-strain behaviour of an ideal elastic body, with other possible behaviours, as sketched in Fig. 5, is much helpful (other plots, as the time-evolution of strain for a given stress pattern, step load, sinusoidal load, are most illustrative).

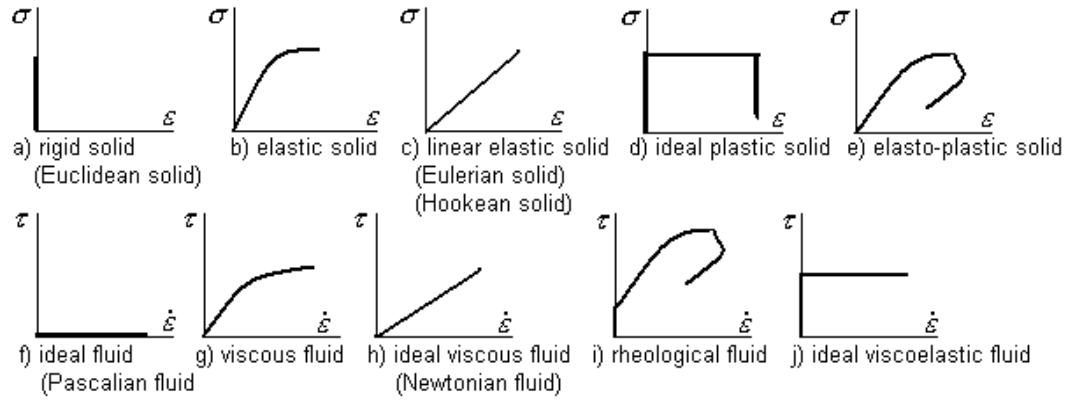


Fig. 5. Stress-strain relations (for solids) and stress-flux relations (for fluids). Solids show similar behaviour for normal and for tangential loads, but fluids show an elastic behaviour to normal stress (case c) but unbound strain for any tangential stress ($\varepsilon \rightarrow \infty$ for $\tau > 0$).

Many real elastic solids show a quasi-reversible linear stress-strain behaviour for small loads, but they start to irreversibly deform at high loads (what is named fluency or yield). Some solids only show this behaviour for compression loads, being unable to support sizeable tension loads, like concrete. There are some special materials that show a kind of superelasticity, i.e. they deform non-linearly (like in case c in Fig. 5) but fully recover the initial shape after load removal.

For a given material, other characteristic parameters are tabulated besides the linear slope E : a limit for linear elasticity (usually defined as the point with 0.1% or 0.2% of fluency, or yield), and the absolute limits, σ_{\max} (and the corresponding strain), and ε_{\max} (and the corresponding stress). Some typical values are presented in Table 2.

When thermal effects are considered, Hooke's law becomes:

$$\sigma = E(\varepsilon - \alpha \Delta T) \quad \text{or the inverse} \quad \varepsilon = \frac{\sigma}{E} + \alpha \Delta T \quad (4)$$

where α is the coefficient of linear thermal expansion (positive for the majority of cases, and of value around 10^{-5} K^{-1} , see Table 2).

Example 1. Breakage by constrained expansion of a rod.

Q. Find the temperature change that would break a glass rod held between rigid supports at the ends.

Sol.: Hooke's law shows that $\sigma = E(\varepsilon - \alpha\Delta T)$, and for $\varepsilon=0$ (strain fully restricted), the maximum ΔT would correspond to the maximum σ (from Table 2, $\sigma_{\text{break}}=50$ MPa), and thus $\Delta T_{\text{max}}=\sigma_{\text{break}}/(\alpha E)=50\cdot 10^6/(9\cdot 10^{-6}\cdot 70\cdot 10^9)=80$ K, where worst-case values are taking (from Table 2). Notice that the temperature change is probably beyond the linear range and might affect the E -value. A flexible rod might buckle (elastically) or suffer some latic deformation, instead of breaking.

For a compound rod, i.e. for uniaxial stress along two axially joined rods, the equilibrium at the common interface is $\sigma_{\text{mat1}}A_{\text{mat1}}=\sigma_{\text{mat2}}A_{\text{mat2}}$ (A being their cross-section area), whereas the overall displacement is $u_{\text{total}}=\varepsilon_{\text{mat1}}L_{\text{mat1}}+\varepsilon_{\text{mat2}}L_{\text{mat2}}$ (L being their length),

Example 2. Breakage by constrained expansion of a compound rod.

Q. A given fire sprinkler is activated when the thermal expansion of an aluminium rod breaks an adjacent glass rod that blocks the water outlet, the compound rod being constrained to move by a massive cast-iron holder. The aluminium piece has 5 mm in diameter and 25 mm in length, and the glass rod has 5 mm in diameter and 5 mm in length. The device is exposed to hot gases at 800 °C from a fire. Consider the unsteady heating from the already hot gases with a heat convection of $h=20$ W/(m²·K), and find the stresses being developed until breakage.

A. First of all, the temperature history must be known. From the energy balance, $mc dT/dt=hA(T_{\infty}-T)$, we know that the rod temperature grows exponentially as $(T-T_0)/(T_{\infty}-T_0)=1-\exp(-t/t_c)$, with a characteristic time $t_c=mc/(hA)=(\rho L\pi D^2/4)c/(h\pi DL)=(2700\cdot 0.025\cdot 3.14\cdot 0.005^2/4)\cdot 900/(20\cdot 3.14\cdot 0.005\cdot 0.025)=150$ s.

Second, the thermoelastic problem is solved, forcing a zero overall displacement, i.e., $u_{\text{total}}=\varepsilon_{\text{mat1}}L_{\text{mat1}}+\varepsilon_{\text{mat2}}L_{\text{mat2}}=0$, with equal stresses because of the same area ($\sigma_{\text{mat1}}=\sigma_{\text{mat2}}$). Substituting Hooke's law for each material in the displacement equation one gets:

$$\left(\frac{\sigma}{E_{\text{mat1}}} + \alpha_{\text{mat1}}\Delta T\right)L_{\text{mat1}} + \left(\frac{\sigma}{E_{\text{mat2}}} + \alpha_{\text{mat2}}\Delta T\right)L_{\text{mat2}} = 0 \rightarrow \Delta T_{\text{max}} = \frac{\sigma_{\text{break,min}}}{E_{\text{mat1}}\alpha_{\text{mat1}}} \frac{1 + \frac{L_{\text{mat2}}/E_{\text{mat2}}}{L_{\text{mat1}}/E_{\text{mat1}}}}{1 + \frac{\alpha_{\text{mat2}}L_{\text{mat2}}}{\alpha_{\text{mat1}}L_{\text{mat1}}}}$$

where the minimum of the breaking stresses corresponds to glass. Substituting values, one gets $\Delta T_{\text{max}}=50$ K. Notice the effect of the aluminium rod; without it, the glass rod would break with $\Delta T_{\text{max}}=80$ K (see Example 1); if only the aluminium rod were used, the corresponding value would be $\Delta T_{\text{max}}=120$ K obtained by just changing values of glass to aluminium in Example 1. According to the heat transfer result, the elapsed time is (a linear approximation is adequate) $\Delta t=t_c(\Delta T_{\text{max}}/\Delta T_{\text{fire}})=150(50/800)=9$ s.

Three-dimensional load. Generalised Hook's law

For general non-uniaxial loads, the already generalised Hooke's law, $\sigma = E(\varepsilon - \alpha\Delta T)$, is further generalised to:

$$\bar{\bar{\tau}} = \frac{E}{1+\nu} \left(\bar{\bar{\varepsilon}} + \frac{\nu}{1-2\nu} \text{tr}(\bar{\bar{\varepsilon}}) \bar{\bar{I}} - \frac{1+\nu}{1-2\nu} \alpha \Delta T \bar{\bar{I}} \right), \quad \text{or} \quad \bar{\bar{\varepsilon}} = \frac{1+\nu}{E} \left(\bar{\bar{\tau}} + \frac{\nu}{1-2\nu} \text{tr}(\bar{\bar{\tau}}) \bar{\bar{I}} \right) + \alpha \Delta T \bar{\bar{I}} \quad (5)$$

that reduces to the former for uniaxial stress (where $\text{tr}(\bar{\bar{\varepsilon}}) \equiv \varepsilon_x + \varepsilon_y + \varepsilon_z = \varepsilon - \nu\varepsilon - \nu\varepsilon = \varepsilon(1-2\nu)$ and $\text{tr}(\bar{\bar{\tau}}) \equiv \sigma_x + \sigma_y + \sigma_z = \sigma$).

Navier's equation

In practice, some external loads and surface displacements are given that determine the problem at hand. In theory, the general problem of thermoelasticity is to find at each location point and time the 15 unknowns $(\bar{\bar{\tau}}, \bar{\bar{u}}, \bar{\bar{\varepsilon}})$ with the 15 equations:

- The three local mechanical equilibrium:

$$\bar{\bar{f}}_V + \nabla \cdot \bar{\bar{\tau}} = 0, \quad \text{or} \quad f_{Vi} + \sum_j \frac{\partial \tau_{ji}}{\partial j} = 0 \quad (i,j=x,y,z) \quad (6)$$

- The six definitions of strain components in terms of displacement components:

$$\bar{\bar{\varepsilon}} = \frac{\nabla \bar{\bar{u}} + (\nabla \bar{\bar{u}})^T}{2}, \quad \text{or} \quad \varepsilon_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial j} + \frac{\partial u_j}{\partial i} \right) \quad (i,j=x,y,z) \quad (7)$$

- The six generalised Hooke's relations:

$$\bar{\bar{\tau}} = \frac{E}{1+\nu} \left(\bar{\bar{\varepsilon}} + \frac{\nu}{1-2\nu} \text{tr}(\bar{\bar{\varepsilon}}) \bar{\bar{I}} - \frac{1+\nu}{1-2\nu} \alpha \Delta T \bar{\bar{I}} \right), \quad \text{or} \quad \tau_{ij} = \frac{E}{1+\nu} \left(\varepsilon_{ij} + \frac{\nu}{1-2\nu} \delta_{ij} \sum \varepsilon_{ii} - \frac{1+\nu}{1-2\nu} \alpha \Delta T \delta_{ij} \right) \quad (8)$$

with known values of the elastic constants (E, ν) and the temperature field $(T(t,x,y,z)-T_0)$.

But the general thermoelastic problem may be formulated in other terms, because the linearity of the equations allow for the elimination of some unknowns and equations. For instance, the problem may be reduced to solve the 3 equations with 3 unknowns named Navier equations:

- Navier equations (substituting Hooke's relations and the strain definition in the local mechanical equilibrium):

$$\nabla^2 \bar{\bar{u}} + \frac{1}{1-2\nu} \nabla (\nabla \cdot \bar{\bar{u}}) + \frac{2(1+\nu)}{E} \bar{\bar{f}}_V - \frac{2(1+\nu)}{1-2\nu} \alpha \nabla T = 0 \quad (9)$$

and from the displacement field the strain field (by its definition) and the stress field (by Hooke's law).

The general three-dimensional elastic problem may be drastically reduced in some cases, as for planar problems, corresponding to uniform thickness systems without normal loads, i.e. $L_z = \text{constant}$ and $f_z = 0$, what implies $t = t(x,y)$ and $\mathbf{e} = \mathbf{e}(x,y)$. Two special cases are of interest:

- Planar stresses, if $L_z \ll (L_x, L_y)$, what implies $\mathbf{s}_z = 0$ ($\mathbf{e}_z^1 0$).
- Planar deformations, if $L_z \gg (L_x, L_y)$, what implies $\mathbf{e}_z = 0$ ($\mathbf{s}_z^1 0$).

Thermoelastic deformation and bending

Small temperature variations always cause some elastic deformation on free-standing materials (expansion/contraction, bending, torsion), that disappears when the initial temperature is recovered. This

is advantageously used in many thermometer devices, like liquid-in-glass and vapour-pressure devices. If the material is constrained to move, internal elastic stresses develop to accommodate the imposed boundary conditions, as in bimetallic strips, but they also fade away when the initial temperature is recovered.

The basic rules are:

- A uniform heating on an isotropic material free to move, produces a uniform stress-free expansion (contraction in some rare cases).
- Holes expand or contract as if they were filled with surrounding material (i.e. a hole in a coin expands proportionally to the expansion of the whole coin).
- Linear temperature fields, $T=ax+by+cz+d$, on free isotropic bodies are also compatible with a stress-free material (although they produce a quadratic displacement field). Non-linear temperature fields or boundary constraints in the material give way to a thermoelastic stress field.
- The stress due to constrained expansion/contraction is the same as for unconstrained expansion/contraction followed by external loading to achieve the former size.
- Thermal effects on linear elastic solids are equivalent to the effect of two additional forces on an isothermal body (Duhamel's theorem):
 - a volumetric force:

$$\vec{f}_V = \frac{-E\alpha}{1-2\nu} \nabla T \quad (10)$$

- and a surface force normal to the external boundary:

$$\vec{f}_A = \frac{E\alpha(T-T_0)}{1-2\nu} \vec{n} \quad (11)$$

Example 1. Thermoelastic expansion in a prismatic piece.

Q. Find the stress field and the strain field in a stainless-steel piece of $L_x=0,2$ m, $L_y=0,1$ m and $L_z=0,3$, when heated 30 °C, on the two following cases: a) clamped on one side ($x=0$), and b) clamped on both sides ($x=0$ and $x=L_y$), and free on the other directions.

Sol.: Case a). Substituting in $\sigma=E(\varepsilon-\alpha(T-T_0))$ $\varepsilon=0$, $E_{\text{steel}}=200 \cdot 10^9$ Pa, $\alpha_{\text{steel}}=13 \cdot 10^{-6}$ K⁻¹ and $\Delta T=30$ °C, one gets $\sigma_x=-0,78$ MPa. With the general equations one gets, additionally (with $\nu=0.3$), $\sigma_y=0$, $\sigma_z=0$, $\varepsilon_x=0$, $\varepsilon_y=0,56 \cdot 10^{-3}$, $\varepsilon_z=0,56 \cdot 10^{-3}$.

Case b). Substituting in $\sigma=E(\varepsilon-\alpha(T-T_0))$ $\varepsilon=0$, $E_{\text{steel}}=200 \cdot 10^9$ Pa, $\alpha_{\text{steel}}=13 \cdot 10^{-6}$ K⁻¹ and $\Delta T=30$ °C, one gets $\sigma_x=-0,78$ MPa. With the general equations one gets, additionally (with $\nu=0.3$), $\sigma_y=0$, $\sigma_z=0$, $\varepsilon_x=0$, $\varepsilon_y=0,56 \cdot 10^{-3}$, $\varepsilon_z=0,56 \cdot 10^{-3}$.

Example 2. Thermoelastic bending of a plate.

Q. Find the deflection at the tip of a bimetallic strip of $L_x=200$ mm, $L_y=10$ mm and $L_z=1$ mm, made half and half in depth of invar and copper, when subjected to a uniform $\Delta T=100$ K.

Sol.: The bimetallic device is based on the difference in thermal expansion of the two metals ($\alpha_{\text{invar}}=1,7 \cdot 10^{-6}$ K⁻¹ and $\alpha_{\text{Cu}}=17 \cdot 10^{-6}$ K⁻¹, from data tables). If there were no bonding between the strips, the displacement at the free end would be $u=\Delta L=L\alpha\Delta T=0,2 \cdot 1,7 \cdot 10^{-6} \cdot 100=34 \cdot 10^{-6}$ m for

invar and $340 \cdot 10^{-6}$ m for copper. But the bonding forces a common displacement, creating flexural stresses that bend the strip towards the less dilatable solid. The neutral curve in each beam has no stress, so the former displacements apply. To the first approximation, the deformed shape can be taken as a circular arc of radius R and arc-angle θ ; the neutral line in the invar is at $r=R-L_z/4$, and that of the copper at $r=R+L_z/4$, and the displacements are (Fig. 6):

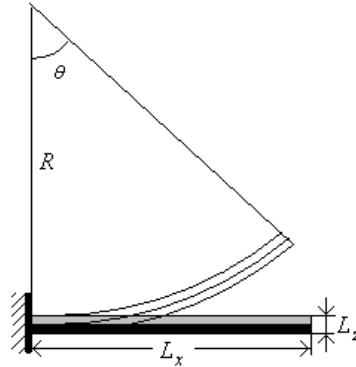


Fig. 6. Sketch of the bimetallic strip.

$$L + \Delta L_{\text{invar}} = (R - L_z/4)\theta$$

$$L + \Delta L_{\text{copper}} = (R + L_z/4)\theta$$

from where the radius R can be deduced:

$$R = \frac{L_z}{2} \frac{1 + \frac{\alpha_{\text{Cu}} + \alpha_{\text{inv}}}{2} \Delta T}{(\alpha_{\text{Cu}} - \alpha_{\text{inv}}) \Delta T} = \frac{10^{-3}}{2} \frac{1 + \frac{17 \cdot 10^{-6} + 1.7 \cdot 10^{-6}}{2} 100}{(17 \cdot 10^{-6} - 1.7 \cdot 10^{-6}) 100} = 0.327 \text{ m}$$

The transversal deflection at the tip is:

$$\Delta y = R(1 - \cos \theta) = R \frac{\theta^2}{2} = \frac{L^2}{2R} = \frac{0.2^2}{2 \cdot 0.327} = 0.061 \text{ m}$$

Notice that the approximation of the deflected shape by a circle may be too coarse.

Temperature-dependant shape-memory materials

Shape-memory materials have the ability to return from a deformed state (temporary shape) to their original (permanent) shape induced by an external stimulus (trigger), such as temperature change. These materials can be grouped as:

- Shape-memory alloys (**SMA**), based on a martensitic/austenitic transitions. They are strong, and can be an alternative to conventional actuators.
- Shape-memory polymers (**SMP**), based on a glass transitions. They are softer, and may retain two or sometimes three shapes; the transition is usually induced by temperature, but sometimes by electric or magnetic fields.

There are some alloys that show strange shape-memory effects when a certain phase-transition takes place, that may be classified according to Fig. 7.

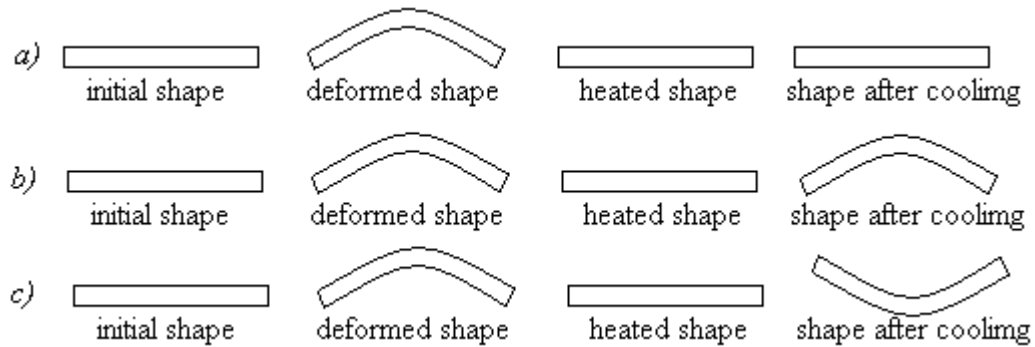


Fig. 7. Types of shape-memory allows (SMA): a) one-way, b) two-way, reverse-way.

- **One-way shape-memory:** heating removes the deformation, and cooling has no effect. It occurs in martensitic alloys (notably equimolar Ni-Ti-alloys with some Fe). Martensite is very soft and elastic for small loads (like an elastomer, up to a strain of 8% or 10%, above which is stiff), but the relaxation time upon load removal is very large at low temperatures. At higher temperature (depending on the alloy; some 100 °C), a reversible martensite-austenite phase-transition occurs, greatly increasing the stiffness and immediately recovering the initial shape by relaxation of the stress field, that elastically recovers the initial shape, and so remains even after cooling. For some alloys the martensitic phase requires temperatures below the ambient; they are deformed when cold (e.g. in dry ice) and recover the shape on attaining room temperature (they are used a lot for coupling of small pipes; a memory-shape tube expands on cooling and tightens at room temperature).
- **Two-way shape-memory:** heating removes the deformation, but cooling recovers it. It occurs on some alloys that suffer a thermoplastic (irreversible) deformation above the phase transition.
- **Reverse-way shape-memory:** heating removes the deformation, but cooling reverses it. It occurs on some alloys that suffer a thermoplastic (irreversible) deformation well above the phase transition (e.g. soaked at 400 °C), but without full relaxation of the stress field, that upon cooling give way to a shape reversal.

Shape-memory alloys (SMA) were discovered in the 1930s on Au-Cd alloys, but nowadays most of them are Ni-Ti-alloys. They show very large anisotropic thermal expansion coefficients, sometimes negative. They are good electrical conductors and can be used as sensors or as actuators (passive or active, e.g. by Joule heating). Besides Ni-Ti alloys, some Cu-Zn-Al-alloys have been developed, but with higher transition temperatures. Superelasticity, or more appropriately non-linear elasticity is related to shape-memory alloys. It occurs when the martensite-austenite phase-change takes place induced by the stress field at room temperatures. These alloys are used in orthodontic pre-stressed wires (they behave as metal elastomers that avoid frequent tightening).

Shape-memory polymers show several advantages over shape-memory alloys, among which the much lower cost and much broader variety of materials stand out.

PLASTICITY. PLASTIC DEFORMATION AND BENDING

Small stresses or a temperature change cause elastic deformations that disappears when the stresses cease or the initial temperature is recovered, but large stresses or temperature variations (particularly on heating), give way to inelastic (plastic, non-recoverable) deformations on either free-standing or constrained materials. Yield stress is the stress required to have a sizeable plastic deformation (agreed to be 0.2% residual strain, usually). Greater temperatures produce melting, with large mobility and easy rearrangement of matter that, after solidification, establish new solid bonds, what is used locally in welding and globally in casting.

Materials that can sustain large plastic deformations are ductile (extensible), malleable (thinneable) and tough (absorb a lot of energy before breaking), whereas brittle material break before any plastic deformation.

Plastic deformation is due to slippage at the atomic level, with bond-breakage and bond-formation processes, favoured by dislocations and imperfections in general, that tend to smooth out the elastic-to-plastic transition (pure monocrystals show a sharp transition).

Laser writing of compact discs (CD-RW) is by thermoplastic deformation of a 0,6 μm thin Al_2O_3 layer underneath a thicker (3 μm) transparent glass protective layer, causing minute fusion at 1900 K of a 0.1 mm spot (with a laser beam of 10^9 W/m^2).

Thermoplastic shrinkage. Heat line technique or line heating method

When a plate is locally heated, there is an elastic convex deformation at first (that fades out if left to cool), and a plastic concave permanent deformation (after cooling, if the temperature has been hot enough). The permanent bending is caused by material shrinkage due to plastic strains from the heated zone (see Fig. 8).

The process is known as heat line technique or line heating method of plate bending; it is applied mainly to mild-steel plates, and was started in the 1970s in shipbuilding. It consists on the following steps (Fig. 8):

1. Initial heating. It forces the heated mass to expand against the rest of material, creating great stresses and a very-small convex elastic-deformation due to the temperature gradient.
2. High heating. Up to 1200 K (but usually limited to $<995 \text{ K}$ to avoid the mild-steel phase-transition). It lowers so much the strength of the heated mass, that plastic-yield takes place, the side material forcing the heated mass to bulge in the hottest region.
3. After cooling. Forced cooling (usually by water) increases the temperature gradient that forces the heated mass to recover its original strength but not its original shape, because the plastic deformation is not reversible, causing a shrinkage that pulls-in from the rest of the material (i.e. in the whole it is not a thermal push but a thermal pull), causing a concave bending (and perhaps some cracks), and minor in-plane deformations due to the point-wise application (instead of the whole line at a time).

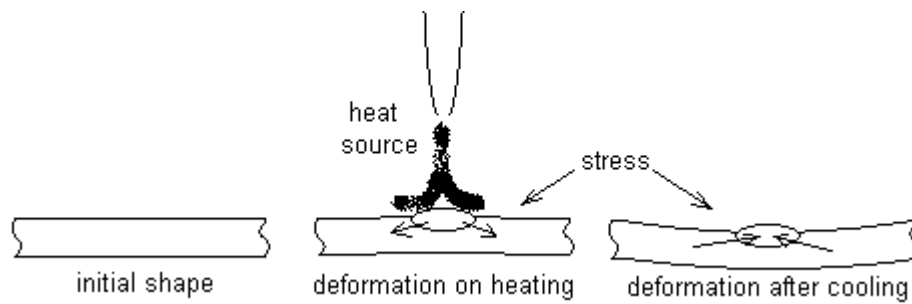


Fig. 8. Heat line technique.

Its main characteristics are:

- Advantages: applicable to heavy plates without heavy equipment (no die, no press, no rolls), cheap (an oxyacetylene handheld torch is enough), and the bend gets thicker (more resistant) and not thinner as when rolling or hammering. The trend however is towards large automated heating-line equipment, with a heat source (preferably a laser) mounted on a gantry crane.
- Handicaps: demands manual skill, high-temperature causes material degradation (grain growth, allotropic changes, species diffusion, surface reactions: carburization, nitration, oxidation, combustion).
- Materials: usually applied to thick mild-steel plates; the heating is below the transition temperature (995 K) to avoid hysteresis problems.
- Geometrical parameters. The initial shape is a thick plate ($D \approx 10..20$ mm), and the location of lines, their quantity, breath ($b \approx 10..20$ mm) and depth (depending on the heating method), must be selected (up to now empirically).
- Heating parameters. Heat-source input is a Gaussian profile with a global power of some 5 kW, and a size at the surface $qI = q_0 \exp(-r^2/R^2)$. The oxyacetylene torch is the cheapest source, but requires gas-flowrate-control and automated travelling (clearance distance, $L_T \approx 40$ mm, and speed, $v \approx 10$ mm/s) for constancy. Laser beam offers best control and inert atmosphere, but is more expensive. High-frequency induction depends a lot on the material, and its penetration is frequency-dependent. The welding arc is no good because the low penetration causes surface melting.
- Cooling parameters. A water jet following the heat source at a distance $L_C \approx 100$ mm is used, producing some hardening by quenching.

Heat joining. Welding distortions

Joining two materials may be achieved by removable or by more permanent means; amongst the latter one may quote chemical adhesives, and heat techniques: soldering, brazing and welding. Soldering is a low-temperature process (60..400 °C) that uses a low-melting metal (a base of tin combined with lead, silver, antimony, bismuth, indium) to join similar or dissimilar metals; it is mainly used in electronic boards. Brazing is a mid-temperature process (450..1200 °C) that uses a high-melting metal (a base of silver combined with nickel, copper, zinc) to join similar or dissimilar metals; it is mainly used in copper piping and jewellery. Welding is a high-temperature process (800..2000 °C) that uses a powerful heat source to locally melt and join similar metals; it is mainly used in iron and steel work.

In all heat-joining methods, a flux material (dependent on the materials to join) is used to get rid of surface metal oxides, to protect against re-oxidation, to enhance thermal contact, and to assist the flow of filler material, if any.

It was well-known that welding produces distortion in the piece, due to differential shrinking, phase transformations and residual stress effects. This deformation, usually unwanted, can be used advantageously to bend heavy metal plates just by hand, as explained above.

Laser welding using high-power diode lasers of 1..5 kW in the infrared at 0.808 μm , focused to a 3x2 mm² spot, has ameliorated those unwanted distortions, in comparison with the traditional torch welding, because the energy is absorbed directly at the material surface instead of by heat transfer from the flame gases, what facilitates a quick cooling of the surrounding area by a compressed-air jet, a water jet (some 20 times better than air, but floods), a liquid nitrogen jet (some 100 times better than air), or by condensed carbon dioxide (snow cooling, some 200 times better than air). A CO₂ cooling-jet following some 3 cm behind the welding spot may lower the temperature of the join to <100 °C in less than 10 mm distance after the laser spot, practically eliminating any distortion. The additional cooling can be extremely beneficial in the case of welding ferritic stainless steels where grain growth in the post-weld cooling phase can have significantly detrimental effects on the ductility and corrosion resistance in the solidified weld and heat affected zones. On the other hand, using increased weld cooling rates in some alloys can potentially increase the hardness and reduce ductility. Laser welding is also used to weld aerospace alloys.

Welding ferrous metals (low absorptivity) requires $>10^6 \text{ W/m}^2$ to reach $>1000 \text{ °C}$ (but $<10^{11} \text{ W/m}^2$ to avoid ablation). If $>10^6 \text{ W/m}^2$, the molten depth is larger than the molten width. CO₂-lasers are the most powerful ($10^{10}.. 10^{11} \text{ W/m}^2$); they work with $\lambda=10 \mu\text{m}$ (far infrared).

A special welding technique is by using thermite, a mixture of aluminium powder and iron oxide, in the way $\text{Al} + (3/8)\text{Fe}_3\text{O}_4 \rightarrow (1/2)\text{Al}_2\text{O}_3 + (9/8)\text{Fe} + 418 \text{ MJ/mol}$.

Heat cutting

Related to welding (a heat-joining technique) is material cutting by local melting and jet-blowing (a heat-disjoining technique). As for welding, the heat source may be a flame (coarse cutting, $\pm 2 \text{ mm}$ tolerance), laser beam (fine cutting, using CO₂ lasers, $\pm 0.5 \text{ mm}$ tolerance), plasma cutting (thin, precision cutting, accelerating the gasses in an electric arc). Water abrasive jet cutting is not heat-based (no thermal deformation, perfect finishing).

In flame cutting, the material must be combustible (metals, polymers and some ceramics), and a conventional gas torch (e.g. oxyacetylene, butane, methane) is used for ignition, the combustion proceeding afterwards with the oxygen supplied by a third pipe in the torch. Oxycutting is used in ferrous alloys in the 3..300 mm thickness range. An electrical arc may be also used for ignition. There is no need to melt the material; for mild steels above 650 °C, the quick oxidation $\text{Fe} + (2/3)\text{O}_2 = (1/3)\text{Fe}_3\text{O}_4 + 1130$

J/mol takes place; stainless steel and cast iron however must be melted because they have higher ignition temperatures.

An iron-oxygen lance is used to cut through very thick walls (e.g. 0.5 m concrete bunkers), establishing the same exothermic reaction but supplying the fuel (Fe) in the form of the hollow lance (consumable) through which liquid oxygen is supplied.

If a flame is used to melt the material, and for laser and plasma cutting, any gas-jet may be used to expel the melt (N_2 , CO_2 , He), and any material can be cut.

Heat treatment

The solid state, because of its low mobility, is prone to hold metastable states, and thermal treatment may transform a metastable state to a more stable state by thermal soaking, or may transform an equilibrium state to a metastable state by quick cooling.

Metals can be made more ductile, softer and machineable by annealing, and some metals can be made harder and more resistant to wear by quenching. Usually some properties are improved at the expense of others (e.g. hardening increases brittleness).

Annealing consists of heating a metal to a specific temperature, holding it at that temperature for a set length of time (heat soaking), and then slowly cooling the metal to room temperature. Annealing relieves internal stresses, softens the material, makes it more ductile, and refines the grain structure. Normalising is a kind of annealing done on ferrous metals at higher temperature than annealing and with air cooling; it leaves a harder material.

Tempering is a hardening process applied to ferrous metals that, once heated, are quenched (quickly cooled) and then heated below the annealing temperature to eliminate the brittleness.

Heat treatment is not exclusive of metals; ceramics are sometimes heated to harden them (notice that metals soften when heated). For instance, the mechanical properties of some kind of grounds can be changed, to get better structural foundations, to decrease its thermal sensitivity (swelling and compressibility) and to increase shear strength and stiffness (soil stabilisation). At approximately 200 °C soil plasticity begins decreasing until it is reduced to zero at around 500 °C. Swelling is reduced to zero at temperatures above 750 °C and shear strength rises continuously throughout this range of temperatures. At temperatures above 900 °C the soil begins to fuse into brick-like material. Finally, the soil melts and later hardens in a rock-like material (similar to obsidian) at temperatures above 1100 °C.

Recrystallisation temperature

When heating a metal, well before its melting point, the grain limits disappear by interdiffusion (recrystallisation), disappearing dislocations, with an increase of ductility and a decrease in resistance. The recrystallisation temperature is approximately $T_{\text{recryst}} \approx 0.4T_m$ (in kelvins; see Table 3).

Table 3. Recrystallisation temperatures (decreases with cold working).

	$T_{\text{recryst}} [^{\circ}\text{C}]$	$T_m [^{\circ}\text{C}]$
Zn	$<T_{\text{amb}}$	420
Al	150	660
Mg	200	650
Ag	200	960
Cu	200	1090
Fe	450	1540
Ni	600	1450

Thermal creeping

Creeping of a material is the slow visco-plastic deformation that grows with time under a constant load at a given temperature (e.g. it is the cause of springs getting loose with time). Notice the importance of slowness: quick creeping is flowing, and unnoticeable-slow creeping is shape memory (elasticity). The load and the temperature are also of importance; everybody knows that

Creeping usually happens above $0.3T_m$ (T_m being the melting point or the glass-transition temperature), and is shown by polymers at moderate temperatures and by metals at higher temperatures. But loading promotes creeping; creeping is the combined effect of strain and temperature (Fig. 9).

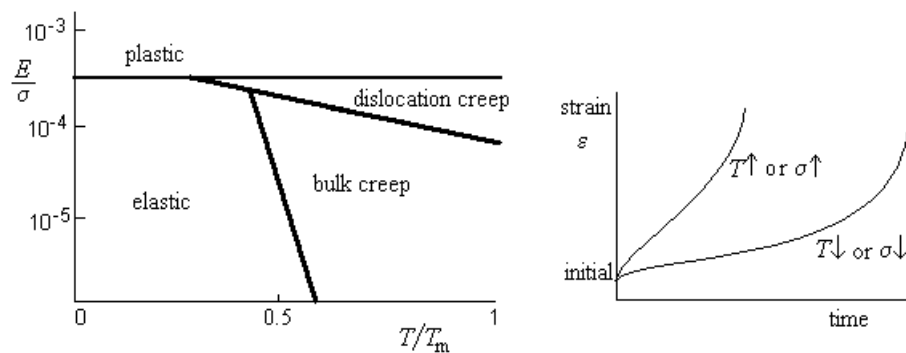


Fig. 9. Creeping regions in the temperature-stress diagram, and sketch of the combined effect of temperature and stress.

There has been a controversy about whether a glass is a solid or a highly-viscous liquid, but it is just a matter of nomenclature. Everything flows (the ‘panta rei’ of Heraclitus, 500 b.C.), but we know that solids take aeons to change shape, and they do it more readily by wear and evaporation than by bulk flow. A standard test to classify creeping substances as either solid or liquid is as follows: a 1 litre can is filled with the substance (perhaps previously softened or molten to facilitate the filling); under an equilibrium temperature of 38 °C (100 °F), the lid (if any) is removed, the can inverted, positioned 50 mm above a plate (half of the can diameter), and 3 minutes waited; if the substance touches the plate it is termed a liquid, otherwise a solid.

Table 4. Softening (heat deflection) temperatures of some polymers at a load of 2 MPa (decrease under load).

	$T_{\text{soft}} [\text{K}]$
Nylon	370
PET	490
PC	400
PMMA	370
Polyester	540

Polyethylene	320
Polypropylene	340

Thermoplastics, e.g. PE and PVC used in most new piping networks, quickly reduce their stiffness with temperature. Exposed PVC (grey) and PE (black) pipes under sunshine in summer may reach near 70 °C.

Creeping speed, and thus time-until-breakage, t_{break} , follows an Arrhenius law with temperature: $t_{\text{break}} = a\sigma^b \exp(T_a/T)$, where σ is the applied stress, and a , b and T_a are empirical factors for a given material.

Thermal creeping usually refers to creeping at moderate and high temperatures, but sometimes it refers to another problem unrelated to the mechanical properties of materials, namely to the flow induced in rarefied gases by a temperature gradient.

FRACTURE

A material fractures when it becomes suddenly disjoined; i.e. when the stress in a material is increased, there is a point when it cannot keep bonded and breaks apart. The failure behaviour can be measured by the ultimate stress (σ_{break} ; notice that the yield stress only refers to the elastic-to-plastic transition), the ductility or ultimate strain (not corresponding to the ultimate stress), and the toughness or ultimate deformation energy. Tensile tests are made on traction machines, measuring elongation of a standard specimens versus applied force (traction curve), or just the yield point and the fracture point.

Materials can fail in other ways, e.g. by creeping, but two fracture modes are traditionally considered: brittle fracture (due to crack propagation), and ductile fracture (due to dislocation propagation). Metals usually show ductile fracture (i.e. after a large plastic strain; but some cast irons are brittle), ceramics usually show a brittle fracture (i.e. with a negligible plastic strain) and polymers may show any of both (polystyrene is fragile). Ductile fracture produces a necking (that starts when at the maximum stress and continuous until the ultimate stress).

Brittle-ductile transition

Some metals and polymers show a fracture behaviour strongly dependent on temperature (and somehow on the stress); at low temperature they show a brittle fracture, and at high temperature a ductile one. The transition, however, is not very sharp; e.g. for a low-carbon steel (<0.05%C), the fracture energy in the Charpy pendulum test, that is 75 J for $T > 30$ °C, falls to 40 J at 10 °C, 10 J at –10 °C, and approaches 0 J for < -30 °C.

Body-centred-cubic (bcc) crystals, and amorphous materials, show a thermal brittle-ductile transition (e.g. carbon steels, polymers), whereas stainless steels have face-centred-cubic (fcc) crystals and do not show a thermal brittle-ductile transition. Brittle-ductile transition temperature in amorphous solids corresponds to the glass transition temperature. Brittleness may also be enhanced by inclusions, dissolved gases, neutron irradiation, etc.

Table 5. Brittle-ductile transition temperatures (decrease with cold working).

	T_{bd} [K]
Low carbon steel, <0.05%C, coarse grain (60 μm)	270
Carbon steel, 0.2%C, fine grain (<10 μm)	270
Carbon steel, 0.2%C, coarse grain (60 μm , Titanic*)	310
Kevlar (Aramide)	800
Nylon	480
PMMA (Methacrylate)	360..380
Polyester	530
PE (Polyethylene)	370
PP (Polypropylene)	440
PS (Polystyrene)	370
PVC (Polyvinyl chloride)	350..380
PTFE (Teflon)	600

*with high sulfur content (0.07%) due to MnS inclusions.

The general behaviour for polymers is that they have brittle fracture if their glass-transition temperature is above room temperature (as for PMMA and many epoxies), and ductile fracture if they are near room temperature (as for PE); elastomers have their glass-transition temperature below room temperature.

Surface cracks on anodised metals

Anodising is a surface-protection process based on increasing the thickness of the natural oxide layer on a metal in an electrolytic cell. It is mostly used to protect aluminium, forming an Al_2O_3 layer that grows on both sides of the original surface (the overall dimensions may increase some micrometres). This layer is well adhered to the metal (better than paints), and is harder than the metal, but more brittle because the oxide has a much lower thermal conductivity and coefficient of linear expansion than aluminium, producing cracks under thermal stress (e.g. under changes of $\Delta T > 50^\circ\text{C}$), although without peeling, due to the high bonding to the substrate. This high-melting-point oxide layer makes welding anodised aluminium difficult.

THERMAL EFFECTS DUE TO MANUFACTURING OR USE

PHASE DIAGRAMS

Pure chemical compounds (e.g. Al or Al_2O_3) are rarely used as engineering materials, which are commonly mixtures, either because mixing enhances their properties, or because they are so found in nature (for that same reason). Even for pure materials, traditional p - T phase diagrams (indicating the regions of solid, liquid and vapour phases) have little relevance for engineering materials, since either their vapour phase is outside the interesting temperature range, or they chemically decompose before being heated to the vapour phase (or even to the liquid phase).

Phase change diagrams for pure materials are usually restricted to the solid allotropic transformations and the liquid region, e.g. to show the 9 phases of SiO_2 , the 3 phases of $\text{Al}_{12}\text{SiO}_5$, the 5 phases of carbon, the 5 phases of Fe, etc. Although many materials are many-component mixtures, the study of binary mixtures already provides most of the understanding of materials behaviour. Because of the variance of the system, a two-dimensional p - T diagram is used to show the whole thermodynamic information for a pure substance, but for binary systems a T - x diagram only applies to a given pressure, and for ternary systems a triangular x_A - x_B - x_C phase diagram only applies to a given temperature and pressure.

Phase changes in solid state (allotropic transformations) are of great importance in thermal treatments on materials, as explained below. Writing data on CD and DVD discs is based on a solid-state phase change that changes optical reflectance, what is accomplished with a laser pulse (reading is done with a less powerful laser beam).

Phase diagrams for binary mixtures of interest in engineering materials are not simple because they only deal with condensed phase mixtures; the ideal solution model is only applicable to some liquid-vapour binary mixtures (usually of interest to other engineering fields, as petrochemistry or cryogenics). Full mixing at any proportion is the exception in engineering materials; Cu-Ni alloys, Ag-Au alloys, and Bi-Sb alloys, for instance, show complete mixing at any composition (Fig. 10a); the ceramic mixture NiO-MgO behaves ideally too. The basic binary phase diagram for materials is the partial miscibility one, Fig. 10b, where solid solutions are formed only for low-alloys, one named alpha (to the left) and the other beta (to the right), and an eutectic point, E (best melting alloy) appears where the two solid solutions coexist with the liquid solution. An heterogeneous liquid / solid solution transforming into a single solid solutions, i.e. a peritectic point, P in Fig. 10c (where α +liquid cools to ϵ), is also common, as well as eutectoids and peritectoids points, similar to the previous but all solid phases. This basic partial mixing diagram of Fig. 10b applies to Ag-Cu alloys, Al-Si alloys, Sn-Bi alloys and Sn-Pb alloys amongst others, although in many cases one of the solid solution regions disappear. Some of the most important engineering alloys have however much complicated phase diagrams, as for Fe-C alloys, Cu-Zn alloys and Cu-Sn alloys.

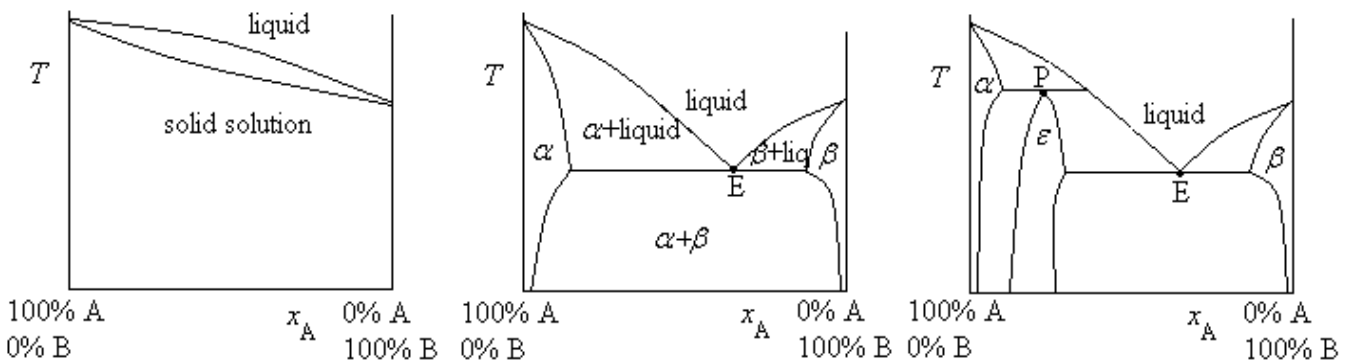


Fig. 10. a) Perfect miscibility in the solid phase (one solid solution, as for Cu-Ni alloys, Ag-Au alloys, Bi-Sb alloys); b) Partial miscibility (two solid solutions and heterogeneous mixtures of them, as for Ag-Cu alloys, Al-Si alloys, Sn-Bi alloys and Sn-Pb alloys). Other alloys have more complicated phase diagrams, as for Fe-C alloys, Cu-Zn alloys and Cu-Sn alloys.

Phase change kinetics, nucleation and segregation

Tendency to a phase change corresponds to the decrease in the Gibbs function of the system, $\Delta G = \Delta H - T\Delta S$; i.e., all thermodynamic systems tend to lower their Gibbs function G in their evolution in the presence of an environment. For instance, solidification occurs because, below the melting point, the Gibbs energy of the solid is lower than the Gibbs energy of the liquid. For a small subcooling below the melting temperature T_m , ΔH and ΔS can be taken as constant, and thus:

$$\Delta G = \Delta H - T\Delta S \approx \Delta H - T \frac{\Delta H}{T_m} = \Delta H \left(1 - \frac{T}{T_m} \right)$$

But the speed not only depends on the undercooling force (growing almost linearly with the temperature departure ($T_m - T$)), but also on the ease at which particles can rearrange for the change, i.e. on the diffusion coefficient, that can be modelled by an Arrhenius factor, $A \exp(-E_A/(RT))$, as for any other physico-chemical reaction, A being a preexponential factor, E_A an activation energy and R the gas constant. This exponential factor, sketched in Fig. 11, combines with the linear driving force to give a maximum speed somewhere below the transition temperature (Fig. 11).

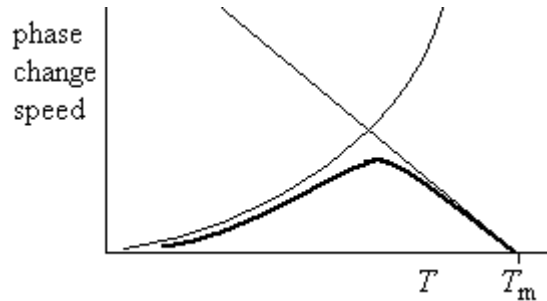


Fig. 11. Phase change speed in the case of solidification; the linear term is due to the thermodynamic driving force, and the exponential term is due to the kinetics (Arrhenius factor).

The actual mechanism through which the phase transition takes place is usually by molecular diffusion (i.e. the random movement of the particles), a slow process going at speed D_i/L , D_i being the diffusion coefficient and L the characteristic length, but in some special instances (in solid transformations, notably the martensitic transformation, see below), the mechanism may be by coherent displacement of the atoms at the speed of sound (similar to plastic deformation and crack propagation). The phase change speed is analogous to that of Fig. 11 but much more pronounced (infinite in comparison).

The growth of a solid phase at the expense of another solid or liquid phase (as the growth of droplets from vapours), requires atoms being attached to the growing crystal, but that is assuming an existing crystal seed; but nucleation must occur at the first place. Small nuclei, however, are unstable, so that a large fluctuation driven by a high undercooling is required for homogeneous nucleation, or, most of the times, the crystal growing starts over already-existing nuclei on the walls or at dispersed contaminants (heterogeneous nucleation).

The kinetics of phase change above-explained for solidification of a pure component equally applies to other phase transitions in mixtures. Mixtures, however, generally change composition when they suffer a phase change (eutectics and azeotropes not), what is used to purify, concentrate, dilute or modify the properties of a mixture. Full equilibrium segregation by interdiffusion of species, partial segregation during more rapid cooling, and sudden displacive transformations, are advantageously used in materials science and technology. The reason why ice cubes (these refreshing commodities related to arctic materials engineering) are white and not transparent, is because of the segregation of dissolved air in the liquid, that can hold up to 0.0038%wt of air, upon solidification (the solid phase can only hold 0.0002%wt of air).

An example of the kinetics of phase changes is presented for the case of pure iron (Fe with say less than 0.03%wtC) to illustrate these different mechanisms.

Pure iron solidifies at 1810 K into a body centred crystal (bcc) structure named δ -Fe that readily transform to a face centred crystal (fcc) structure named γ -Fe or austenite below 1680 K (because of the quick diffusion at these high temperatures). If the cooling is continued, below 1180 K there is a fcc-to-bcc phase transition that is diffusive for slow cooling (producing the stable phase named α -Fe or ferrite), but displacive for quick cooling (producing the metastable phase named martensite), as represented in a typical temperature-time-transformation diagram (TTT-diagram) in Fig. 12. Instead of the linear cooling represented as parabolic dashed-lines because of the logarithmic time scale in Fig. 12, one can imagine a sudden cooling to a given temperature and then look at the transformations as time passes (that is the way TTT-diagrams are built).

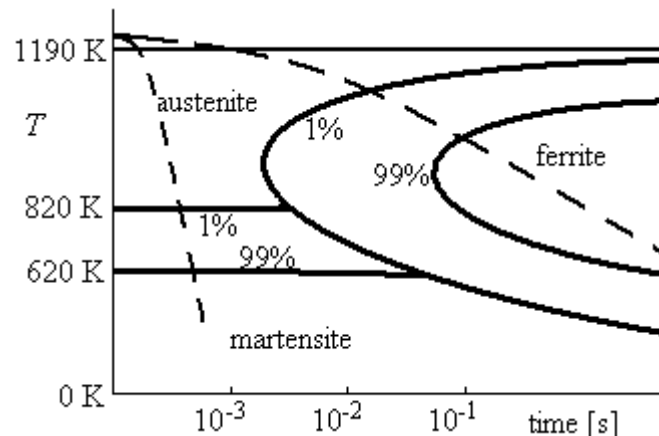


Fig. 12. TTT-diagram for fcc-to-bcc transformation in pure iron; The two dashed lines represent a slow cooling (austenite transforming into ferrite by atom diffusion) and a quick cooling (austenite transforming into martensite by atom displacement).

The martensitic transformation is difficult to get in pure iron due to the large cooling rates required (some 10^5 K/s), but much easier to get in alloys because the foreign atoms already add some distortion to the crystal structure; e.g. a cooling rate of 10^2 K/s is enough for an eutectoid steel (i.e. 0.8%wtC) to already skip the ferrite nose (now much to the right than in Fig. 12) and yield martensite. The behaviour complicates in alloy steels; an addition of >13%wtCr completely removes the austenitic γ -Fe phase, but subsequent addition of >7%wtNi brings back an stable austenitic γ -Fe phase. As the austenitic microstructure is more readily hardenable, the most common stainless steel has 18%wt of chrome (to be protected from oxidation) and 8%wt of nickel (to be austenitic).

SHRINKAGE ON CASTING

Raw metals and finished metal and polymer pieces are easily produced by letting a molten material to solidify inside a mould, i.e. by casting (there exist also mouldless casting). In this material-shaping technique, the raw material is melt in a furnace, put on a 'spoon' for transportation, and drop into a mould, where the material solidifies and takes its shape; the mould is taken off and the piece is ready (perhaps after some thermal or surface finishing). Care must be paid to the problem of inclusions, i.e. to the structural defects in metals caused by oxide particles some 10..100 μm in size, kept in the molten matrix because oxides have a higher melting temperatures. They are less dense and would form a slag if time allows while the metal is molten (it helps a lot to stir with argon bubbles for coalescence of the smaller particles and agglomeration at the upper slag layer).

It is important to take into account the shrinkage on the solidification process, mainly due to the density change on solidification most materials show, with smaller contributions from the thermal expansion in the solid phase and in the liquid phase; see Table 6 for the typical shrinkage range (actual values depend on impurities).

Table 6. Shrinkage on solidification from above melting (T_m+150 K) to room temperature.

Material	%shrinking
Aluminium	5..7
Steel (mild)	5..7
Steel (inox)	8..10
Iron (cast)	4..6
Brass	6..7
Copper	4..5
Magnesium	4..5

HEATING DURING SOLID FRICTION

Solid friction, wear, abrasion, chipping and cutting, may be viewed as incremental steps in the elasto-plastic cold-deformation of a material, with dissipation of mechanical energy that transforms to internal thermal energy and ultimately to heat transfer to the environment.

The Coulomb model for solid friction is just a tangential force, F , proportional to the normal force, N : $F=\mu N$, where μ is the coefficient of friction. Aerodynamic or hydrodynamic levitation ($\mu\approx 0.001$), friction bearings ($\mu\approx 0.01$), normal friction ($\mu\approx 1$) and contact welding (seizure, $\mu N\approx \sigma_{\text{yield}}A$), might be viewed as incremental steps in materials-contact approaching. Soft bearing materials (Pb, Sn, Zn and their alloys) deform and partially melt, making a paste that lubricates the contact (shears easily) and holds debris.

Heating or heat-dissipation by solid friction is very important not only in intended heat applications (e.g. in brakes), but most of the times as an undesirable effect in all moving joints and drag mechanisms, as pistons, clutches, tyre-wheels, pulleys, gears, shafts, etc.

A temperature transition sometimes appears on solid friction, as for the traditional waxed-wood skis, that have $\mu\approx 0.02$ above -10 °C but $\mu\approx 0.4$ below, as observed by polar explorers and sledged airplanes. The reason for that is that below -10 °C friction-heat dissipation is most effective and there is no time to melt the snow in contact (that is also why metal skis are worse than wood skis and have higher frictional temperature-transitions). Teflon and polyethylene, however, have such a low coefficient of friction ($\mu\approx 0.05$) and thermal conductivity that it only grows, smoothly, to $\mu\approx 0.1$ at -30 °C.

Fluid friction really means viscous dissipation (since there is no slip in the solid-fluid contact-interface. Heating due to viscous dissipation is usually negligible except on very-high-viscous fluids, like polymer solutions and polymer melts.

HEATING DURING MACHINING

Machining a material (piece cutting, chip cutting, abrading, eroding, or any other material-removal process) causes great energy dissipation, and problems associated to the temperature field in the tool and the work-piece: heat transfer, dimensional deformations, and even chemical transitions.

In the machining process, chemical changes, phase transitions, plastic deformation, and residual stresses are usually restricted to the immediate vicinity of the cutting edge, and do not affect the work-piece (the chips removed absorb most of the energy). The temperature increase softens the work-piece material, what is an advantage, but softens also the cutting tool, what is most detrimental to the process, thus, intermediate fluids are added (cutting fluids or taladrines) to decrease the heating effect (by heat convection) and to decrease the heating source (by lubrication).

The American-born British engineer Benjamin Thompson (later Count Rumford of Bavaria) was the first, in 1798, to study thermal effects on iron machining (making cannons by boring cylinders of iron immersed in water). The American engineer Frederic Taylor was the first, in 1906, to realise the relevance of tool-tip temperature on tool life, and invented a tungsten carbide tool-steel (18%W-4%Cr-1%Va-0.75%C, notice that $T_f(W)=3680$ K) that kept sharp even hot-red without refrigeration (Paris Exhibition).

Machining is an intermediate or final manufacturing process; the raw piece may have been obtained by casting or by rough-cutting from a plate (with a saw, a high-pressure water-jet, a plasma jet, or an oxy-acetylene cutting torch).

Cutting energy

From the thermodynamics point of view, cutting energy is the variation in Gibbs energy from the initial solid to its final two-pieces state (or the piece and the chip). Figure 11 shows an intermediate step, similar to the problem of crack propagation and fracture in a stressed solid, first studied by Griffith in 1920. Irwin in the 1940s made great progress in crack growth theory.

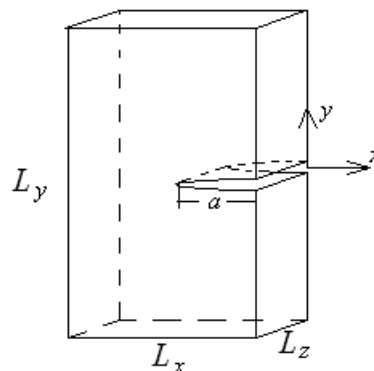


Fig. 13. Crack-propagation as a model of cutting.

For a thin infinite plate, initially subjected to a constant one-dimensional and uniform stress σ , with a crack of width $2a$ normal to the stress, the elastic problem has an analytical solution (Kolosov & Inglis, 1907; the first to model stress concentration was Kirsch in 1898 in a circular hole) that for $y=0$ is:

$$\begin{aligned} \text{for } |x| < a \quad \sigma_x = \sigma_y = \tau_{xy} = 0 \quad u_x = 0, \quad u_y = \pm \sigma \frac{(1+\nu)(1+\chi)}{2E} \sqrt{a^2 - x^2} \\ \text{for } |x| > a \quad \sigma_x = \sigma_y = \sigma \frac{x}{\sqrt{a^2 - x^2}}, \quad \tau_{xy} = 0 \quad u_x = 0, \quad u_y = 0 \end{aligned}$$

where $\chi=(3-\nu)/(1+\nu)$ for planar stresses and $\chi=(3-4\nu)$ for planar strains (Guiu-1997-CSIC). Note that the displacements in the crack correspond to an ellipse.

The change in (potential) energy (Gibbs' function) has two contributions: a positive one due to the increase in interfacial energy, $\Delta G=4\gamma aL_z$ (where the 4 is for the two faces and the $2a$, and γ is the free-energy per unit area $\gamma=(1/2)\partial G/\partial A$), and a negative one due to a modification of the stress field, $\Delta G= -\pi\sigma^2 a^2 L_z/E$. The variation of this energy with a , $\partial G/\partial a=4\gamma L_z-2\pi\sigma^2 aL_z/E$ measures the work to be done (if positive) or the irreversible propagation of the crack if it is negative.

Two practical problems, the sharp edge needed for cutting, and the high solid friction among piece and tool, can be alleviated if the cut is superficial (meaning not small but near the surface of the piece) because the chip can deform and get out of the way.

Cutting power. Geometry and variables

Figure 12 shows the main geometry and variables in orthogonal chip cutting (i.e. with tool edge perpendicular to cutting direction; most machining is oblique), applicable to machining on the lathe, drill, mill, broach, etc. A two-dimensional model is used, since the width of the tool has just a proportional effect (i.e. the analysis is by unit width).

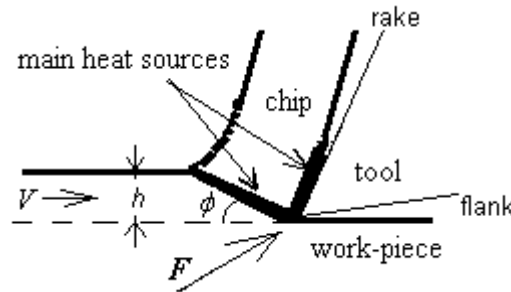


Fig. 14. Cutting geometry (orthogonal).

The tool is edge-shaped and its two sides forming the cutting edge (edge angle α) are named rake (that in contact with the chip) and flank (that in contact with the work-piece). The tool is tilted a bit relative to the (local) plane of cutting, to avoid too much tool-piece friction, what is known as angle of incidence or contact angle β (some 5°). The angle between the tool rake and the perpendicular to the cutting plane is the rake angle, γ (*desprendimiento* in Spanish). Of course $\alpha+\beta+\gamma=\pi/2$. But 'shear plane' refers to that joining the inner edge and outer corner where the main plastic deformation occurs, and its angle with the cutting plane is known as shear angle ϕ .

The piece geometry is just characterised by the depth of the non-deformed chip, h (actual chip thickness is always larger), that is the nominal depth of cut, and the cutting power depends somehow on it (it is

also proportional to the width of cut, w). The power is not proportional to h because there is the same cutting interface area for any h , and only the 'wall effect' counts.

The chip geometry is characterised by the chip ratio, $r=h/h_{ch}$, i.e. the width of the non-deformed chip relative to the actual chip. There are several types of chips: continuous (ductile materials at high rake angles), discontinuous (cast iron, bronze, ductile metals at high speed and deep cutting), or corrugated (material builds up on the tool before breaking)..

The force required for cutting has two components (in this two-dimensional model): the force of advancing, F (the only one that consumes work), and the force of thrust, F_{\perp} (perpendicular to the cutting plane and against the piece). The specific force of cutting $k=F/(hw)$ or cutting pressure is the usual variable for analysis.

The cutting speed, V , is another key variable; typical values are from 0.5 m/s in finishing to 3 mm in rough chipping.

A first approximation to the required cutting power, \dot{W} , is as follows. The cutting power is the cutting the force times the cutting speed (the moment times the angular speed in rotating machines), and all this work degrades to thermal energy (equivalent heat) in the chip (some 80%), the piece (some 15%) and the tool (some 5%), that ultimately will flow as heat to the environment (after several minutes up to one hour, depending on size). The amount of energy stored elastically in the solids is negligible.

$$\dot{W} = FV = kVA = \dot{Q}_{chip} + \dot{Q}_{piece} + \dot{Q}_{tool} \approx \sigma_{break}VA$$

For example, for fine chip cutting on a steel, say with $h=0.5$ mm, $w=3$ mm ($A \equiv hw=1.5$ mm²) and $\sigma_{break}=700$ MPa, a force $F=(700 \cdot 10^6)(0.5 \cdot 10^{-3})(3 \cdot 10^{-3})=1000$ N results, and a required power for a cutting speed of $V=1$ m/s of $\dot{W} = FV = 1$ kW. Somehow larger values are usual in practice, since, besides the breaking of the material, some energy is spent on solid friction (typical values of the power contribution may be 60% for plastic deformation and breaking, 30% for chip-tool friction at the rake and 10% for piece-tool friction at the flank).

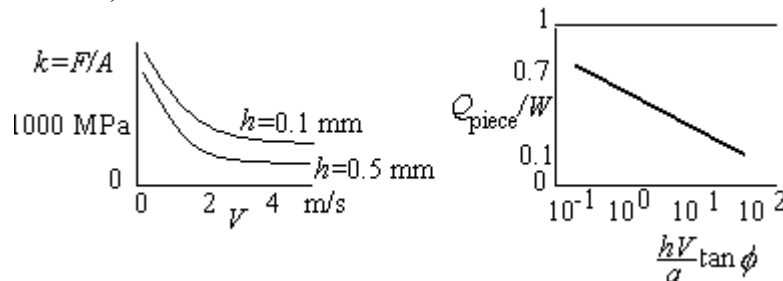


Fig. 15. Variation of the specific force of cutting with cutting speed, and fraction of energy going to the work-piece.

Cutting temperature

A bound for temperatures is obtained assuming that all the energy goes to the chip, that is the mayor sink. The energy balance is then:

$$\dot{W} \approx \dot{Q}_{\text{chip}} = \rho V A c \Delta T_{\text{chip}} \rightarrow \Delta T_{\text{chip}} = \frac{k}{\rho c} \approx \frac{\sigma_{\text{break}}}{\rho c} = \frac{700 \cdot 10^6}{7800 \cdot 500} = 200 \text{ }^{\circ}\text{C}$$

what is representative of measurements in the bulk chip (extremely difficult to carry out on the actual chip); the hottest point is found at a few millimetres along the rake face (some 700 K have been measured when finishing mild steels at 0.5 m/s, and up to 1500 K on rough chipping at 2.5 m/s). In copper work the temperatures are much lower because the high thermal conductivity quickly spreads the energy out (the hottest point rarely surpasses 500 K).

The best technique for thermometry is infrared imaging, taking care that metals may have low emissivities (if not painted). Other techniques have been also used, as thermochromic paints, embedded thermocouples, etc.

Dimensional effects of machining

The heating on both the piece and the tool may have undesired deformations in the finished piece, since the cutting variables and kinematics are fixed at room temperature, and the thermal expansion of the work-piece or the tool would force some over-cutting of material (of course, the initial and final measurements are assumed to be correctly done at a reference temperature, e.g. 20 °C, or appropriately compensated).

The problem is not so serious in traditional machining helped with cutting fluids, since the deformations due to the dynamic expansion are of order of 0.01 mm, but may be important in high precision work and when the use of cutting fluids is not appropriate. The first era on precision machining started in the 1840s with the introduction of the calliper and interchangeable pieces for fire arms. In the Metre Conference in 1890 all industrial nations adopted that unit, but nothing was stated on tolerances (the first norms were introduced by Germany in 1903; DIN), in spite of being a requisite for all kind of mechanical assembly processes (nowadays all components are assumed to be reproducible and built in series of interchangeable units). Dimensional tolerances in ISO norms are specified by a letter (capital for holes and container-pieces and small-case for axes and contained-pieces) designating the position (diameter increase relative to the base line) and a number designating the quality (equal to $16i$, with $i/[\mu\text{m}] = 0,45(D/[\text{mm}])^{1/3} + 0,001(D/[\text{mm}])$; e.g. H7/h7 means quality 7 ($7 \cdot 16i$, e.g. for a $D=50$ mm, $7 \cdot 16i=0.19$ mm) in position H (slipping).

Cutting fluids

Cutting fluids are used in metal machining for improving tool life, reducing thermal deformations, and decreasing solid friction. They are natural oils (best lubrication, worst cooling), oil/water stabilised emulsions (best cooling, worst lubrication) or synthetic fluids (usually inorganic; more expensive).

THERMAL MANUFACTURING

Thermal manufacturing is the application of thermo-fluid sciences and material science to the design and control of manufacturing and to materials processes. The aim can be diverse:

- To understand and control the thermal field in traditional machining.

- To understand and control thermal processes used in manufacturing: casting, hot rolling, thermal spraying.
- To model process equipment such as electric-arc furnaces, laser welding, etc.

Thermal manufacturing is based on:

- Thermal actuators: flame, electrical resistance, arc, plasma, electron, laser, ultrasound.
- Thermal sensors: expansion, resistance, thermoelectric, infrared.
- Thermal process applications: cutting, joining, deposition (e.g. spraying molten material with compressed air), heat treatment.

THERMAL DEGRADATION

Degradation may be a subjective term (e.g. hardening of ceramics by heat, or of metals by tempering, is degradation or enhancement of the material?).

Thermal degradation may be due to a mild sustained heating (giving rise to discolouration, increased creeping, thermal ageing) or to a wild heating as in fire exposure. Thermal ageing of materials is particularly important in the case of austenitic stainless steels, because chromium-carbide precipitation might occur at grain boundary, depleting the adjacent zones in chromium and hence reducing corrosion resistance.

The effect of fire on materials is a key issue in building (e.g. aluminium cannot be used as a structural building material because its collapse at high temperature). As for many of the thermal effects problems, first a purely thermal model is designed and solved, producing the input to the subsequent structural analysis; both models may be established and solved with the same tool (e.g. a finite element analyser for structures and heat transfer), or by independent tools (what may be cheaper and more versatile, at the expense of entangling the data interfacing).

THERMAL PROTECTION. ABLATION

Thermal protection is the part of thermal control aiming at thermally-separating the system to protect from a hostile environment, usually restricted to protection from the hot (protection from the cold is termed thermal shielding, and realised by means of evacuated blankets or multi-layer insulation, MLI).

At high temperatures, thermal radiation is very important, so the first thermal protection measure is a radiation shield.

In spacecraft re-entry, high-speed hypersonic flow produces such huge energy dissipation that the surrounding gas converts to plasma, with a temperature increase of a few thousand kelvins, much higher than the melting temperature of vehicle-frames and skins currently used (steel, aluminium, graphite epoxy). To protect the craft, one method is to place a suitable coat of refractory material (e.g. Shuttle tiles are made of a pure silica-fibre compound to withstand the 1900 K re-entry surface temperature; metal carbides have even better thermal protection properties, but are very fragile), and another method is to place a consumable ablative material like in Apollo capsules..

Refractory coatings are needed in many parts of advanced heat engines (e.g. nozzles), and are grown by chemical vapour deposition (CVD) from gaseous compounds of the refractory materials (e.g. W(s) from $\text{WF}_6(\text{g})$ by reduction with hydrogen, Ta(s) from $\text{TiCl}_5(\text{g})$, etc.).

The main characteristics of a thermal protection system are: high melting point, high emissivity, low thermal diffusivity, and low thermal expansion. There are some ceramic matrix composites (carbon fibre-reinforced silicon carbide hafnium carbide) capable of working at 2000 K while the other side of a 10 mm thick panel stays at 300 K with good mechanical properties and minimum ablation.

Ablation, the process of vaporising a solid surface by intense heat, is also used in medicine to get rid of undesired tissue (e.g. corneal defects, tumours), by laser beams, radiofrequency, ultrasounds, etc.

THERMAL EFFECTS AS FORENSIC EVIDENCE

Some thermal effects are routinely used to investigate fires and explosion accidents. Charring and soot extents, spalling (chipping of masonry due to extreme heat), glass and metal melting, and structural deformation, are examples of thermal effects caused by fire.

Molten chunks of aluminium, silver or iron, indicate that their melting temperatures were locally exceeded. Charred wood depth indicates the duration of the fire. V-shaped soot deposition in walls point to the origin of fire. Plastic deformation of a lamp bulb due to internal gas pressure may indicate not only the temperature level to soften the glass, but the direction of the hot focus, since a uniform bulb will bump towards the weakest (hottest) side.

On increasing temperature, materials change surface colour, outgas, char or melt, vaporise and disappear (in the sense that they dissociate or get ionised, as when an electrical wire explodes on a short-circuit, or upon lightning).

THERMAL ANALYSIS

Thermal analysis is the study of thermal effects, either aiming at identifying material properties (and thus the material itself), or aiming at solving a thermal problem (thermomechanical or thermofluid). We only deal here with the former case.

Thermometry and calorimetry are the basic techniques in thermal analysis methods, but gravimetry, dilatometry and electrometry are also used. As for thermal effects, it is usually understood that thermal analysis applies to solid materials (in a gaseous atmosphere). The effect of pressure is usually irrelevant except for volatile materials, but the effect of the atmosphere composition can be important due to humidity and oxidation problems, so that an inert atmosphere of dry N_2 is the standard, and the output gas stream is usually analysed to detect evolved gases from dehydration or decomposition (or from reaction with a non-inert gas supply).

The most important milestones in thermal analysis are summarised in Table 7.

Table 7. Some milestones in thermal analysis.

1704	Fahrenheit manufactures the first precision thermometers
1760	J. Black develops the ice calorimeter
1826	Becquerel develops the thermocouple, based on the Seebeck effect (1822)
1871	Siemens develops the resistance thermometer
1899	Austen-Roberts develop the differential thermal analysis (DTA)
1965	The International Conference on Thermal Analysis (ICTA) is created (in 1992 Calorimetry was added, changing to ICTAC)

THERMAL ANALYSIS TECHNIQUES

When matter is heated or cooled by controlled means, the thermodynamic changes (or related physical changes) provide information about the sampled substance's composition.

- Differential thermal analysis (DTA). It is the basic and most used technique. The sample and a reference-material are subjected to the same thermal law inside a furnace (i.e. same boundary temperature, and the difference in temperature, ΔT (sample minus reference), is plotted versus the temperature of the reference (or that of the heating block). Endothermic and exothermic processes produce a temporary temperature departure which shows as an area (in the $\Delta T(T)$ plot) proportional to the enthalpy change.
- Differential scanning calorimetry (DSC). Similar to DTA but with precision local-heating at the sample and reference, aiming to compensate the thermal process at the sample by additional heating to maintain the temperature difference at zero. The difference in heating power supplied is plotted versus the temperature of the reference; the area departure from the base-line is proportional to the enthalpy change
- Thermogravimetry (TG or TGA) measures changes in sample weight with temperature or time due to volatility dehydration, oxidation... The sample-holder hangs from a balance and is placed in a furnace. For calibration, small pieces of ferromagnetic materials are hung from the sample-holder and attracted by a magnet in the furnace, suddenly losing the attractive force when their respective Curie points are reached.
- Thermomechanical analysis (TMA) is used to measure changes in the physical dimensions (length or volume), of a sample as a function of temperature and/or time. TMA is commonly used to determine thermal expansion coefficients and the glass transition temperature of polymer or composite materials, either at zero stress, or under static or dynamic stress. Other thermoelastic properties (e.g. hardness, elastic module..) may be measured instead of thermal expansion.
- Thermal offgassing (by desorption, decomposition or reaction). Mass spectrometry (MS) and Fourier transform infrared spectroscopy (FTIR) are used to analyse the evolved gases, gas chromatography (GC) being used only to separate highly complex mixtures for later MS or FTIR analysis. This is essential for chemical reaction kinetics data.
- Thermo-magnetometry. Magnetic properties of the sample are measured while varying its temperature.
- Thermo-electrometry (TE). Measuring the dielectric properties of the sample while varying its temperature.

- Thermo-optometry (TO). Measuring an optical characteristic of a substance (absorption, emission, index of refraction...) as a function of temperature while the substance is subjected to a controlled temperature programme. There are many photo-thermal effects:
 - Thermo-luminescence. The emitted light from a sample is measured while varying its temperature.
 - Photo-acoustics. When light (or any other non-ionizing radiation) goes through a sample (solid, liquid, or gas), in a chopped pattern (usually a solid-state laser pulsed in the kHz range), the rapid thermo-elastic process creates pressure waves (usually ultrasounds, in the MHz range) with a spectrum characteristic of sample composition. Absorbed radiation creates the sound, which transmits through the medium and is detected with a microphone, usually in the gas phase (i.e. outside the sample if condensed). Related to this analytical technique (the photo-acoustic effect was discovered in 1888 by Bell) is the direct interaction between heat and sound (thermoacoustics), used to build thermal sirens, acoustic engines, refrigerators and heat pumps. Notice that thermoacoustic imaging refers to the photo-acoustic technique but using radio waves instead of light.
 - Thermal lensing. When a laser beam goes through a transparent sample (solid, liquid, or gas), a small amount of energy is absorbed and heats the sample along the beam path, causing some thermal expansion and a corresponding decrease in refractive index, n (which is proportional to density). This radial n -dependence creates a divergent lens (i.e. with negative focal length). Thermal inertia in the sample (heating and subsequent lens formation is not instantaneous) causes a time-dependent decrease in the light power detected at the centre of the beam which may be correlated to sample composition.

REFERENCE POINTS IN THERMAL ANALYSIS

Melting points (and transition temperatures on heating) are better than solidification points (and transition temperatures on cooling), because they have much lower metastable excursions (subcooling may be very large). The melting temperature is not the peak in the DTA or DSC analysis but the extrapolation to the base line of the departing curve (DT in DTA, or DQ in DSC).

Table 8. Some reference points in thermal analysis.

Melting temperature		Melting enthalpy	Substance	
[K]	[°C]	[kJ/kg] or [J/g]		
234.29±0.03	-39	11.469±0.008	Hg	Mercury
273.16±0.0001	0	334±0.5	H ₂ O	Water
302.915±0.001	30	80.1±0.5	Ga	Gallium
353.4±0.1	80	147.6±0.2	C ₁₀ H ₈	Naphthalene
429.76±0.02	157	28.71±0.08	In	Indium
505.06±0.02	232	60.2±0.2	Sn	Tin
933.48±0.03	660	401±1	Al	Aluminium
1234.93±0.01	962	110±1	Ag	Silver

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