Material Science

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Chapter 15. Thermal properties

Engineering materials are important in everyday life because of their versatile structural properties. Other than these properties, they do play an important role because of their physical properties. Prime physical properties of materials include: electrical properties; thermal properties; magnetic properties; and optical properties. Selection of materials for use at elevated temperatures and/or temperature changes require an engineer to know and understand their thermal properties. This chapter deals with the thermal properties of materials. Physical property of a solid body related to application of heat energy is defined as a thermal property.

This chapter shall describe thermal properties like heat capacity, thermal expansion, thermal conductivity, and thermal stresses. It is important to know and understand the concept of thermal expansion which is the root cause for thermal stresses. Thermal stresses are stresses leading to failure of engineering structures at elevated temperatures.

15.1 Heat capacity

Many engineering solids when exposed to heat experiences an increase in temperature i.e. it absorbs heat energy. This property of a material i.e. material's ability to absorb heat energy is called its *heat capacity*, *C*. It is defined as the energy required to change a material's temperature by one degree. Mathematically, it is expressed as:

$$C = \frac{dQ}{dT}, \qquad \text{J/mol-K or Cal/mol-K}$$

where *dQ* is the energy required to produce a temperature change equal to *dT*.

Heat capacity is not an intrinsic property i.e. total heat a material can absorb depends on its volume / mass. Hence another parameter called *specific heat*, *c*, it defined as heat capacity per unit mass (J/kg-K, Cal/kg-K).

With increase of internal energy, geometrical changes may occur. Accordingly, heat capacity is measured either at constant volume, C_v, or at constant external pressure, C_p. The magnitude of C_p is always greater than C_v but only marginally.

Heat energy absorption of a (solid, liquid or gaseous) material exists in mode of thermal energy vibrations of constituent atoms or molecules, apart from other mechanisms of heat absorption such as electronic contribution. With increase of energy, atoms vibrate at higher frequencies. However, the vibrations of adjacent atoms are coupled through atomic bonding, which may lead to movement of lattices. This may be represented as elastic waves (phonon) *or* sound waves. Vibrational contribution of heat capacity of solids varies with temperature according to the following relation at low temperatures:

$$C_v = AT^3$$

C_v is equal to zero at 0 K, but increase rapidly with temperature. It represents increased ability of atomic vibrations or enhanced energy of lattice waves with ascending temperature. Above a temperature called Debye temperature, θ_d, dependence of volumetric heat capacity value reaches saturation. This saturation values if approximately equal to 3R ($\approx$ 6 cal/mol-K), R being the universal gas constant. For many solids, value of θ_d is below room temperature.
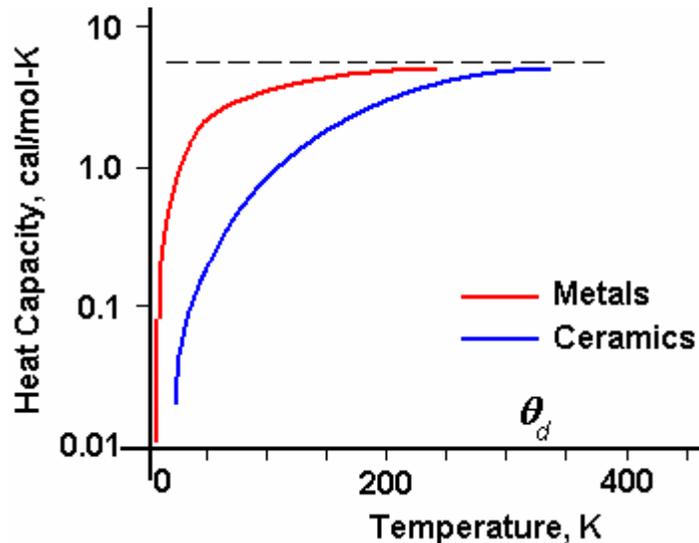
Figure 15-1: Heat capacity as a function of temperature.

15.2 Thermal expansion

After heat absorption, vibrating atoms behaves as though they have larger atomic radius, which leads to increase in materials dimensions. The phenomenon is called thermal expansion. It is quantified in terms of thermal expansion coefficient. Linear coefficient of

thermal expansion (α) defined as the change in the dimensions of the material per unit length, and is expressed as:

$$\alpha = \frac{l_f - l_0}{l_0 (T_f - T_0)} = \frac{\Delta l}{l_0 \Delta T} = \frac{\varepsilon}{\Delta T}$$

where T_0 and T_f are the initial and final temperatures (in K), l_0 and l_f are the initial and final dimensions of the material and ε is the strain. α has units as $(°C)^{-1}$. For most metals α is the range of $5\text{-}25\times10^{-6}$, for ceramics $0.5\text{-}15\times10^{-6}$, and for polymers $50\text{-}400\times10^{-6}$.

A volume coefficient of thermal expansion, α_v ($=3\alpha$) is used to describe the volume change with temperature.

$$\alpha_v = \frac{\Delta v}{v_0 \Delta T}$$

An instrument known as dilatometer is used to measure the thermal expansion coefficient. It is also possible to trace thermal expansion using XRD.

At microscopic level, thermal expansion can be attributed to the increase in the average distance between the atoms. Thus, the coefficient of thermal expansion of a material is related to the strength of the atomic bonds. The relation between inter-atomic distance and potential energy is shown in the *figure 15.2*. As shown in the figure, the potential energy curve has trough and is characterized by a minimum. This minimum corresponds to the equilibrium inter-atomic distance ay 0 K. With increase in temperature of the material, vibrational amplitude increase, and the mean of it represents the average inter-atomic distance. Because of asymetric nature of the potential energy trough, rather than the increase in atomic vibration amplitude, the average inter-atomic distance increases with the temperature of a material.
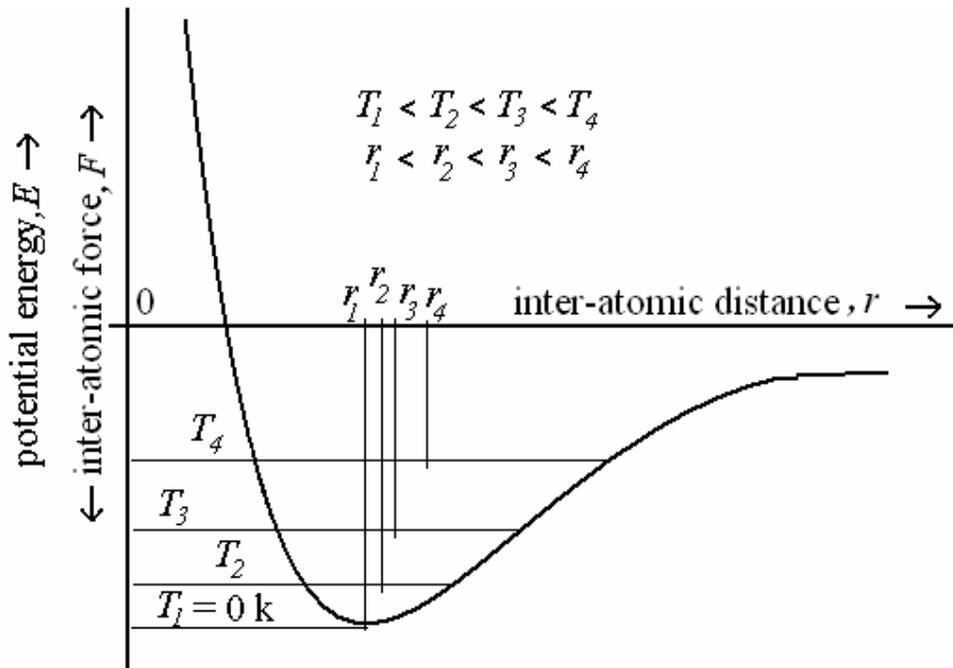
Figure 15.2: *Change if inter-atomic distance with temperature.*

If a very deep energy trough caused by strong atomic bonding is characteristic of the material, the atoms separate to a lesser and the material has low linear coefficient of thermal expansion. This relationship also suggests that materials having a high melting temperature – also due to strong atomic bonds – have low thermal expansion coefficients. Most ceramics having strong atomic bonds, thus, have low thermal expansion coefficients compared with metals and polymers. However, as a consequence of non-uniform dimensional changes, brittle materials like ceramics may experience fracture, known as *thermal shock*. The capacity of material to withstand this failure is known as thermal shock resistance. (TSR).

$$TSR \cong \frac{\sigma_f k}{E \alpha}$$

where σ_f – fracture strength.

Thermal shock behavior is affected by several factors: thermal expansion coefficient – a low value is desired; thermal conductivity – a high value is desired; elastic modulus – low value is desired; fracture strength – high value is desired; phase transformations. Thermal shock may be prevented by altering the external conditions to the degree that cooling or heating rates are reduced and temperature gradients across the material are minimized. Thermal shock is usually not a problem in most metals because metals normally have sufficient ductility to permit deformation rather than fracture. However, it is more of a problem in ceramics and glass materials. It is often necessary to remove thermal stresses in ceramics to improve their mechanical strength. This is usually accomplished by an annealing treatment.

15.3 Thermal conductivity

The ability of a material to transport heat energy from high temperature region to low temperature region is defined as thermal conductivity. Similar to diffusion coefficient, thermal conductivity is a microstructure sensitive property. The heat energy, Q, transported across a plane of area A in presence of a temperature gradient $\Delta T/\Delta l$ is given by

$$Q = kA\frac{\Delta T}{\Delta l}$$

where k is the thermal conductivity of the material. It has units as W/m.K. Metals have k values in the range 20-400, ceramics 2-50, while polymers have in order of 0.3.

Heat energy in solids in transported by two mechanisms: lattice vibrations (phonons) and free electrons. However, usually only one or other predominates the proceedings. Valence electrons gain energy, move toward the colder areas of the material, and transfer their energy to other atoms. The amount of energy transported depends on number of excited electrons, their mobility i.e. type of material, lattice imperfections, and temperature. The thermal energy associated with phonons is transported in the direction of their motion.

In metals, since the valence band is not completely filled, with little thermal excitation number of electron move and contribute to the transfer of heat energy. Thus thermal conduction I metals is primarily due to movement of electrons. It is the same for electrical conduction. Both conductivities are related through the following relation:

$$\frac{k}{\sigma T} = L$$

where L – Lorentz constant, 5.5×10^{-9} cal.ohm/sec.K^2 *or* 2.44×10^{-8} W.ohm/ K^2. The relation is termed as *Wiedemann-Franz law*. Lorentz constant is supposed to be independent of temperature and the same for all metals if the heat energy is transported entirely by free electrons. Thus, the relationship is followed to a limited extension in many metals.

With increase in temperature, both number of carrier electrons and contribution of lattice vibrations increase. Thus thermal conductivity of a metal is expected to increase. However, because of greater lattice vibrations, electron mobility decreases. The combined effect of these factors leads to very different behavior for different metals. For example: thermal conductivity of iron initially decreases then increases slightly; thermal conductivity decreases with increase in temperature for aluminium; while it increases for platinum.

In ceramics, phonons are primarily responsible for thermal conduction. Since the electronic contribution is absent, the thermal conductivity of most ceramics is lower than

that of metals. However, main reason for experimentally observed low conductivity of ceramics is the level of porosity, as phonons are effectively scattered by imperfections. The scattering of phonons becomes more pronounced with rising temperature. Hence, the thermal conductivity of ceramic materials normally diminishes with increasing temperature. Advanced ceramic materials like AlN, SiC are good thermal conductors, they are also electrical insulators. Therefore these materials are useful as electronic packaging substrates where heat dissipation is needed.

Thermal conductivity of polymers is even low, compared with ceramic materials. Vibration and movement/rotation of molecular chains transfer heat energy. In these materials thermal conductivity depends on degree of crystallinity; a polymer with highly crystalline and ordered structure will have higher conductivity than amorphous polymer.

15.4 Thermal stresses

Apart from thermal shock, another instance of problem exists with thermal expansion of a material where there is no scope of dimensional changes. Thus due to temperature changes, material may experience thermal stresses ($\sigma_{thermal}$).

$$\sigma_{thermal} = \alpha E \Delta T$$

where E – elastic modulus of the material. Thermal stresses in a constrained body will be of compressive nature if it is heated, and vice versa.

Another source for thermal stresses is thermal gradient within the body when a solid body is heated or cooled. It is because temperature distribution will depend on its size and shape. These thermal stresses may be established as a result of temperature gradients across a body, which are frequently caused by rapid heating or cooling.

Engineering materials can be tailored using multi-phase constituents so that the overall material can show a zero thermal expansion coefficient. For example: Zerodur – a glass-ceramic material that consists of 70-80% crystalline quartz, and the remaining as glassy phase. Negative thermal expansion coefficient of glassy phase compensates for the positive thermal expansion coefficient of the crystalline base, leading to a zero thermal expansion. This material has many applications like parts of telescopes in astronomy. Many ceramic materials for critical thermal applications are developed based on sodium-zirconium-phosphate (NZP) that have a near-zero thermal expansion coefficient.

References

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