THERMAL EXPANSION COEFFICIENT (start)

- Describes the change in length L or volume $\mathcal{V}$ of a material with changes in temperature:

    - ***Linear*** thermal expansion coefficient: $$\alpha_L \equiv \frac{1}{L}\frac{dL}{dT}$$

    - ***Volume*** thermal expansion coefficient: $$\alpha_V \equiv \frac{1}{V}\frac{dV}{dT}$$

- Units: $°C^{-1}$

- For isotropic[†] substances, $\alpha_{\mathcal{V}}$ $3\alpha_L$

- A ubiquitous property of matter (liquids & gases as well as solids)

- Is the root cause of most thermal stresses

[†]) "Isotropic" means having the same value of physical properties in all directions through the material. With regard to thermal expansion, all materials with cubic crystal structures and inorganic glasses are normally isotropic. Liquids and gases are isotropic.

THERMAL EXPANSION COEFFICIENT (end)

- For solids, thermal expansion has its origins in the nature of the bonding between atoms
  - Add thermal energy
    atoms ***oscillate*** around eq'm spacing
  - Potential is ***asymmetric***
    atoms spend more time at separations $r > r_o$
    (where r_o is their spacing at absolute zero)

  material ***expands**** as T ↑

Interatomic potentials (Callister Fig. 20.3)

- ***Narrow*** potential ***low*** thermal expansion

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* There are a few examples of materials that contract on heating, *e.g.* certain polymers and some lithium aluminosilicate feldspar minerals.

CAUSES OF THERMAL STRESSES (start)

1) Temperature gradients

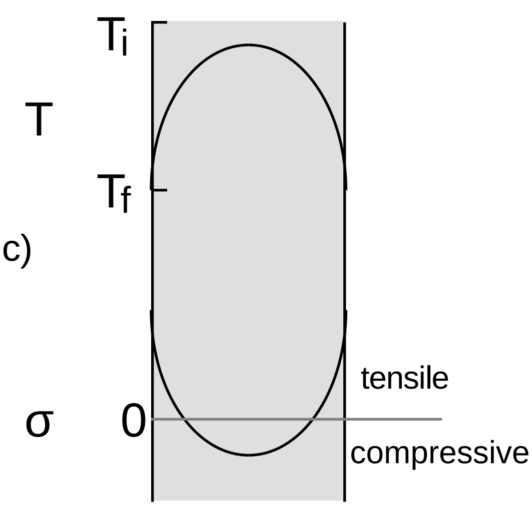
Recall that α, the thermal expansion coefficient, is usu. positive → solids *expand* on heating, *contract* on cooling.

If $T_{surf} < T_{int}$, the interior will *constrain* the surface from contracting

thermal stresses: $\left\{ \begin{array}{l} \text{tensile on surface} \\ \text{compressive on interior} \end{array} \right\} \left(\begin{array}{l} \text{during} \\ \text{cooling} \end{array} \right)$

Example — infinite solid slab initially at T_i, cooled quickly to T_f

(schematic)



Note:

net force ΣF (= ma) = 0 (mechanical eq'm)

(area under ***tensile*** portion of profile)

exactly balances

(area under ***compressive*** portion of profile)

Maximum thermal stress possible on surface is

$$\boxed{\sigma = \frac{E\alpha}{1-\nu}(T_i - T_f)}$$

E: Young's modulus [Pa]

α: linear thermal expansion coeff. [°C^{-1}]

ν: Poisson's ratio [unitless]

CAUSES OF THERMAL STRESSES (cont.)

with ***or without*** a T-gradient…

2) Thermal expansion mismatch between dissimilar materials in…

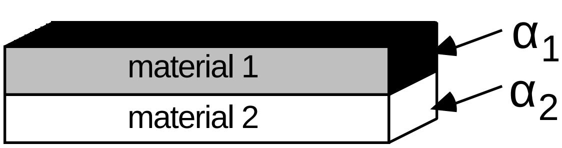
- Composites
- Multiphase microstructures

Example:

Layered composite of two materials, $\alpha_1 > \alpha_2$,

initially at uniform temperature T_i,

initially at zero stress throughout.



Heat composite to T_f.

If interface bond holds, then ***mat'l 2*** will be in ***tension*** & ***mat'l 1*** will be in ***compression***

For $\Delta T \equiv (T_f - T_i)$, the upper bounds on stress at the interface* will be:

Case I (assuming interface strain is $\alpha_2 \Delta T$):	σ_1	$E_1(\alpha_2 - \alpha_1)\Delta T$
Case II (assuming interface strain is $\alpha_1 \Delta T$):	σ_2	$E_2(\alpha_1 - \alpha_2)\Delta T$

* The actual stress at any point in the composite will depend on 1) the distance of that point from the interface and 2) the actual strain of the composite

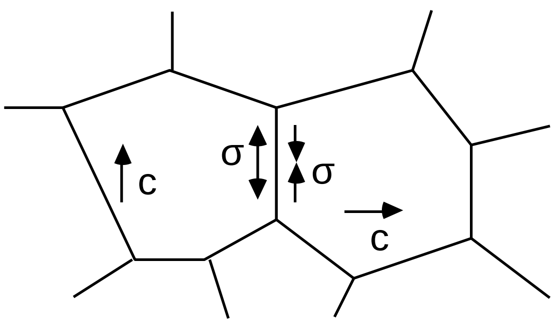
CAUSES OF THERMAL STRESSES (cont.)

with ***or without*** a T-gradient…

3) Anisotropy of α

For a material with crystal symmetry lower than cubic, α can differ along different crystal directions

Example: tetragonal or hexagonal crystal, $\alpha_{||c} > \alpha_{\ c}$



On cooling, stresses develop at grain boundaries: ***microcracks*** can occur between or within individual grains of brittle materials

Microcracks are…

- Not readily detectable
- Rarely fatal, but weaken the material
- Usually permanent
- Not always undesirable (!)

CAUSES OF THERMAL STRESSES (end)

4) Phase transformations (⇒ volume changes)

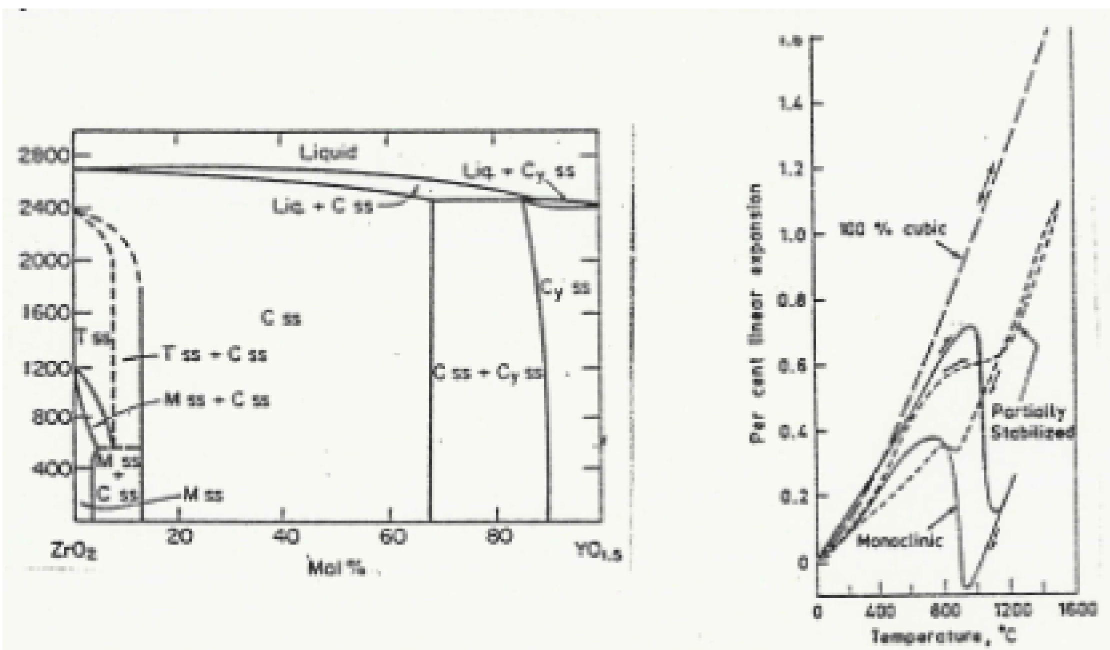
Example (§10.7)***:*** austenite → martensite $\Delta\mathcal{V}>0$
large pcs. of austenitic steel may crack on quenching

Example: Pure ZrO_2 vs. "stabilized" (*i.e.*, doped) zirconia

- Pure ZrO_2 transforms on cooling (see phase diagram):

  cubic $\xrightarrow{\sim 2370°C}$ tetragonal $\xrightarrow{\sim 1200°C}$ monoclinic

  each with abrupt $\Delta\mathcal{V}$ crystals shatter



- Add several mol% Y_2O_3*:
  - Cubic phase stable to low T
  - Overall $\alpha = \frac{1}{3V}\frac{dV}{dT}$ still large, but ***no discontinuities***

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* Or MgO, CaO, or rare earth oxides

SUMMARY OF THERMAL STRESSES

Can stresses from…	Occur in…			
	thermal eq'm?	a single crystal?	a one-phase material?	a multi-phase material?
T gradients	No	Yes	Yes	Yes
α mismatch	Yes	No	No	Yes
Anisotropy	Yes	No	Yes	Yes
Phase transfor-mations	Yes	Yes	Yes	Yes

THERMAL SHOCK RESISTANCE (TSR)

- A material's ability to ***withstand abrupt changes in temperature*** without fracturing

- A combination of ***thermal*** and ***mechanical*** properties

If heat transfer is limited by conduction through solid…

$$TSR \quad \frac{\sigma_f\, \kappa}{E\, \alpha}$$

TSR: thermal shock resistance parameter

σ_f: fracture stress

E: Young's modulus

κ: thermal conductivity

α: linear therm. exp. coeff.

Rationalizing this empirical relationship: TSR ↑ as…

- α ↓ : ***smaller thermal dimensional changes*** occur, and hence smaller strain gradients, for a given temperature gradient in material

- E ↓ : the thermal ***stress*** from a given thermal ***strain*** will be reduced ($\sigma = E\varepsilon$)

- κ ↑ : thermal ***conduction*** through material will ***reduce internal temperature gradients***

- σ_f ↑ : material withstands high thermally-generated stress before fracture

THERMAL CONDUCTIVITY (start)

Macroscopic description of 1-D heat transfer (Fourier's law):

$$\frac{\dot{Q}}{A} = -\kappa \frac{dT}{dx}$$

term	definition	generic units	SI units
$\frac{\dot{Q}}{A}$	heat flux per unit area	$\frac{\text{energy}}{\text{length}^2\ \text{time}}$	$\frac{W}{m^2}$
κ	thermal conductivity	$\frac{\text{energy}}{\text{length time temp}}$	$\frac{W}{m\ K}$
$\frac{dT}{dx}$	temperature gradient	$\frac{\text{temp}}{\text{length}}$	$\frac{K}{m}$

What "carries" heat in solids?

- Free electrons
- Phonons
- Photons

The net thermal conductivity is:

$$\kappa = \kappa_{el} + \kappa_{phon} + \kappa_{phot}$$

- $\kappa_{el} = 0$ for insulators
- κ_{phon} $0.01\kappa_{el}$ for metals
- κ_{phot} significant only in…
  - Transparent materials (glasses, ceramic single crystals)
  - At moderately high T (>~700 K)

THERMAL CONDUCTIVITY (cont.)

Goal of a “microscopic” description: to understand what determines κ and its temperature dependence

For each mode of thermal conduction:

$$\kappa = \frac{1}{3}\, c_{\nu}\, v\, \delta$$

c_{ν}: ***heat capacity*** of the “thermal carriers” per unit volume

v: ***velocity*** of the carriers

δ: ***mean free path*** — distance between carrier collisions

$\kappa \left[\frac{W}{m\,K}\right]$	$c_{\nu} \left[\frac{J}{m^3\,K}\right]$	$v \left[\frac{m}{s}\right]$	δ [m]
κ_{phon}	heat capacity of the solid per unit volume; $= C_P d$	velocity of sound in solid;* $\sqrt{E/d}$	phonon mean free path (see p. 15.11)
κ_{el}	heat capacity of electrons per unit volume; $= \frac{\pi^2 n k_B{}^2 T}{2E_F}$	velocity of electrons at Fermi level; $= \sqrt{\frac{2E_F}{m_e*}}$	electron mean free path (see p. 15.11); $= v\tau$
κ_{phot}	$\frac{16\sigma_{S\text{-}B}\eta^3 T^3}{c}$	c/η	photon mean free path

C_P: specific heat capacity; d: density; n: concentration of conduction electrons; k_B: Boltzmann’s constant; T: temperature; E_F: Fermi energy; τ: time between collisions; m_e*: effective mass of electrons in the solid; $\sigma_{S\text{-}B}$: Stefan-Boltzmann radiation constant; η: refractive index; c: speed of light in vacuum

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* More precisely, $v = \sqrt{\frac{E(1-\nu)}{d(1+\nu)(1-2\nu)}}$ where ν = Poisson’s ratio; $v \;\; 1.1\sqrt{\frac{E}{d}}$ for a typical ν of 0.25.

THERMAL CONDUCTIVITY (cont.)

- ***Mean free path,*** δ

  Phonons and electrons are scattered by
  disruptions in the periodicity of the lattice:

  - Other ***phonons*** — δ_{phon}

  - ***Intrinsic defects*** (vacancies, self-interstitials) — δ_{int}

$$\delta_{int} \quad \frac{1}{[\text{intrinsic defects}]^{1/3}}$$

  - ***Impurities*** — δ_{imp}

$$\delta_{int} \quad \frac{1}{[\text{impurities}]^{1/3}}$$

  - Line defects (***dislocations***) — δ_{dis}

$$\delta_{dis} \quad \frac{1}{[\quad]^{1/2}}$$

  - Planar defects (*e.g.* ***grain boundaries***) — δ_{gb}

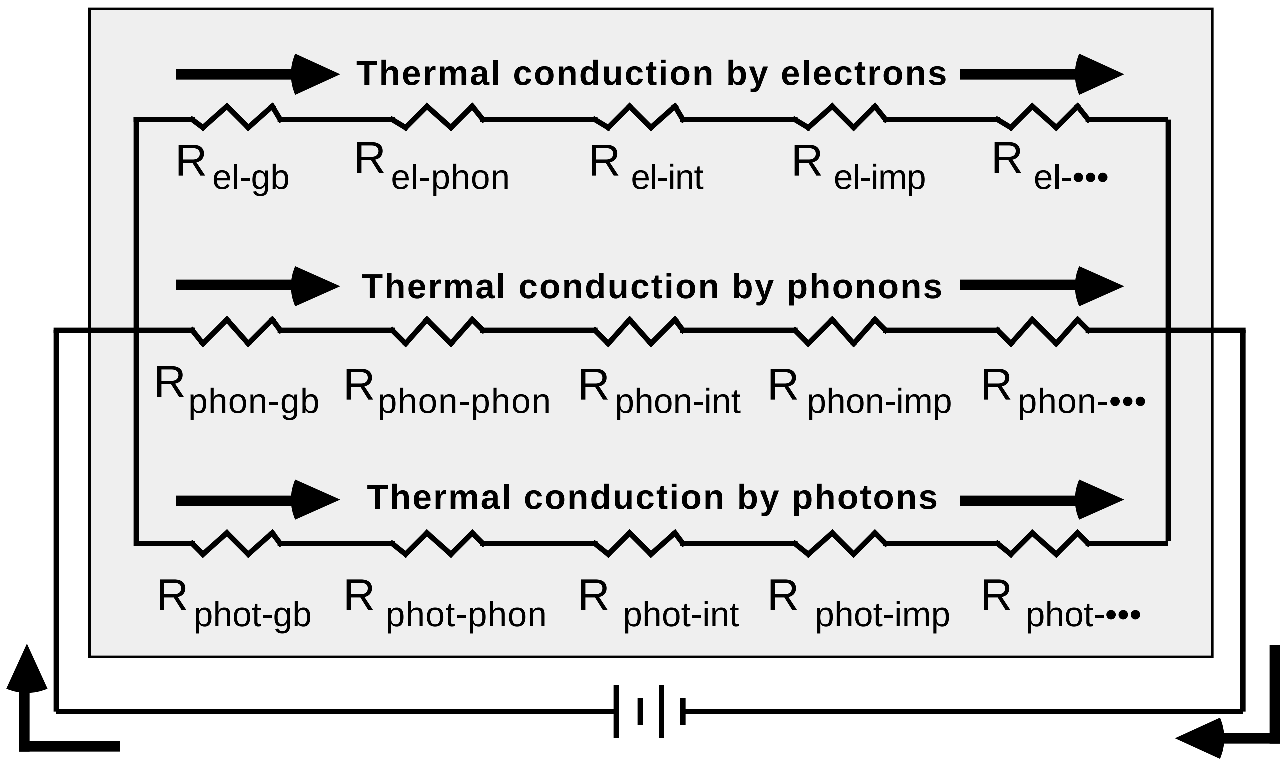
$$\delta_{gb} \quad \text{grain size}$$

- Each scattering mechanism presents its own resistance to heat flow

$$\frac{1}{\delta} = \sum_i \frac{1}{\delta_i} = \frac{1}{\delta_{phon}} + \frac{1}{\delta_{int}} + \frac{1}{\delta_{imp}} + \frac{1}{\delta_{dis}} + \frac{1}{\delta_{gb}}$$

"Thermal resistance" $\left(\frac{1}{\delta}\right)$ is dominated by ***smallest*** δ_i

ELECTRICAL ANALOGY TO THERMAL CONDUCTION (start)



current density ~ heat flux

electric field ~ temperature gradient

- In general, there are three ***parallel*** paths for heat flow

$$\kappa = \kappa_{el} + \kappa_{phon} + \kappa_{phot}$$ (parallel flows add)

- Each path presents resistances (R 1/δ) to flow from several sources ***in series***

$$\frac{1}{\delta} = \sum_i \frac{1}{\delta_i} = \frac{1}{\delta_{phon}} + \frac{1}{\delta_{int}} + \frac{1}{\delta_{imp}} + \frac{1}{\delta_{dis}} + \frac{1}{\delta_{gb}}$$

series R's add

ELECTRICAL ANALOGY TO THERMAL CONDUCTION (end)

flux = [material property] × [gradient in potential]

Fourier's law: $\frac{\dot{Q}}{A} = -\kappa \frac{dT}{dx}$	Ohm's law: $\mathcal{J} = \sigma \mathcal{E}$
heat flux: $\frac{\dot{Q}}{A} \left[\frac{J}{m^2\ s}\right]$	charge flux (current density) $\Big\}$: $\mathcal{J} \equiv \frac{\dot{q}}{A} \left[\frac{C}{m^2\ s}\right]$
thermal conductivity: $\kappa \left[\frac{J}{s\ m\ K}\right]$	electrical conductivity: $\sigma \left[\frac{C}{s\ m\ V}\right]$
temperature gradient: $\frac{dT}{dx} \left[\frac{K}{m}\right]$	electric field (voltage gradient) $\Big\}$: $\mathcal{E} = \frac{dV}{dx} \left[\frac{V}{m}\right]$

Note similarities as well to Fick's first law:

diffusive flux, $J = -D \frac{dC}{dx}$

THERMAL CONDUCTIVITY (cont.)

- For κ_{el}: $$\frac{1}{3}\, c_V\, v\, \delta = \frac{\pi^2 n k_B^2 T \tau}{3 m_e^*}$$ …a useful result for later

  (Note: T in numerator, but $\tau \downarrow$ as $T \uparrow$
  T-dependence is not simple)

- For κ_{phon}: sonic v generally ↓ slightly as T ↑

- For κ_{el} and κ_{phon}: c_V not strongly temperature dependent

- Glasses lack structural periodicity δ small low κ
  - Polymers
  - Inorganic glasses

- Porosity: like a composite with air as a second phase greatly reduces net κ of material

  (gases have very low κ at RT— 0.002 $\frac{\text{W}}{\text{m K}}$)
  - Styrofoam
  - Porous ceramics
    - Firebrick: 0.25 $\frac{\text{W}}{\text{m K}}$
    - Fiberglass blankets: 0.4 $\frac{\text{W}}{\text{m K}}$, more if compacted
    - Other bubbled, fibrous, or low-density structures

THERMAL CONDUCTIVITY (end)

Typical values of κ for various materials at room T, in $\frac{W}{m\,K}$

Metals		Ceramics		Carbon	
Silver (c.p.)	428	BeO	220-300	C (diamond)	1450-4650
Copper C11000	388	AlN	100-220	C (graphite)	1.7-520
1100 aluminum	222	SiC	63-160	**Polymers**	
Cartridge brass	120	Alumina, 99.5%	36	HD polyethylene	0.48
1020 steel	52	Alumina, 90%	16	LD polyethylene	0.33
Gray cast iron	46	Silicon nitride	9-33	6,6 Nylon	0.25
304 stainless	16	Cubic zirconia	1.7	Polyimide	0.2
Ti (c.p.)	16	Glasses	0.4-1.7	Epoxy	0.19

Refs.: W. D. Callister, Jr., Materials Science and Engineering: an Introduction, 5th Ed.; W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, Introduction to Ceramics, 2nd Ed.; *Adv. Ceram. Mater.* **2** [1] 24-30 (1987); CRC Handbook of Chemistry and Physics, 60th Ed.; company literature from Advanced Refractory Technologies and BrushWellman Engineered Materials.