Chapter 22

Thermal Properties of Materials

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Heat Capacity

Heat capacity

(Limit of the) ratio of heat change (i.e.,, release/gain) for a material due to the corresponding temperature change, often at constant pressure, for unit mass or unit mole

Mass heat capacity or
Specific heat
(at constant pressure)

$$C_{p\_mass} = \frac{\lim_{\Delta T \to 0} \frac{\Delta Q}{\Delta T}}{m}$$

Molar heat capacity
(at constant pressure)

$$C_{p\_mol} = \frac{\lim_{\Delta T \to 0} \frac{\Delta Q}{\Delta T}}{n}$$

ΔQ Heat change
ΔT Temperature change
m Mass for the material
n Mole for the material

Specific Heat for Selected Materials at RT (298 K)

Material	Specific Heat $\left(\frac{J}{K \cdot g}\right)$	Material	Specific Heat $\left(\frac{J}{K \cdot g}\right)$
Al	0.90	Al_2O_3	0.84
Cu	0.38	C (diamond)	0.51
Fe	0.44	Si	0.71
Mg	1.02	SiC	1.05
Ni	0.44		
Pb	0.13	HDPE	1.84
Ti	0.52	Polystyrene	1.17
W	0.13		
Zn	0.39	H_2O	4.18
		N_2	1.04

Molar Heat Capacity for Selected Materials at RT (298 K)

Material	Molar Heat Capcity $\left(\frac{J}{K \cdot mol}\right)$	Material	Molar Heat Capcity $\left(\frac{J}{K \cdot mol}\right)$
Al	24.3	Al_2O_3	78.8
Cu	24.5	C (diamond)	6.6
Fe	25.1	Si	20.0
Mg	24.8	SiC	26.7
Ni	26.0		
Pb	26.8	HDPE	
Ti	25.2	Polystyrene	
W	24.3		
Zn	25.4	H_2O	75.4
		N_2	29.1

Many pure elementals have molar heat capacity of $\sim 3R$ at ambient temperature

Example Showing Use of (Average) Heat Capacity

How much heat is needed for 200 g of aluminum to raise its temperature from 25^{o}C to 125^{o}C? Assuming average specific heat is 0.93 J/(K•g)

$$\Delta Q = m \cdot C_{p\_mass} \cdot \Delta T = 200\ g \cdot 0.93 \frac{J}{K \cdot g} \cdot (125 - 25)K = 18{,}600\ J$$

Notes:

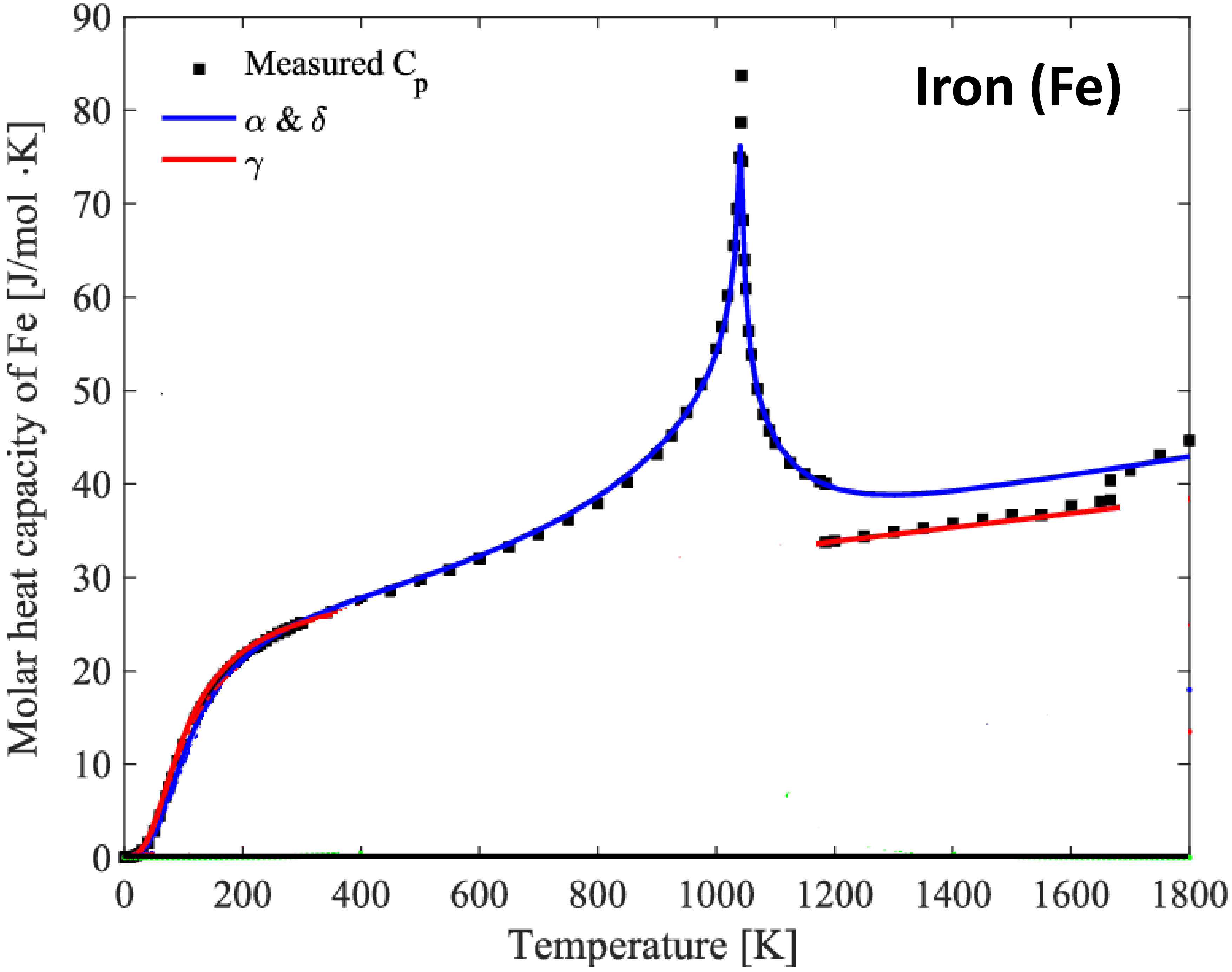
- Such value is the minimum amount of heat needed to raise the material's temperature, assuming no heat loss.
- In reality, depending on the set-up, more heat/energy is often needed, to overcome heat loss or maintain the surrounding temperature

Factors Influencing Heat Capacity

- Heat capacity is NOT a constant
- C_p, whether normalized by mass or by mole, changes with temperature, crystal structure, and even magnetic behavior
- C_p for iron (Fe) example
  - Increase from 0 from 0 K
  - ~$3R$ at ~RT
  - Peak at ~770°C (1043 K) from ferro- to para- magnetic behavior
  - Discontinuity at phase changes

    $\alpha_{\text{(BCC)}} \rightarrow \gamma_{\text{(FCC)}}$ at 912°C (1185K)

    $\gamma_{\text{(FCC)}} \rightarrow \delta_{\text{(BCC)}}$ at 1394°C (1667K)



Lindgren et al., J Thermal Stresses, v42(6), 725-743

Thermal Expansion

- **Linear coefficient of thermal expansion (CTE)** $\alpha = \frac{\Delta L}{L_0 \Delta T}$

Material	CTE $\left(\frac{10^{-6}}{℃}\right)$	Material	CTE $\left(\frac{10^{-6}}{℃}\right)$
Al	25	Al2O3	6.7
Cu	17	Fused silica (SiO_2)	0.55
Fe	12	SiC	4.3
Ni	13	Soda-lime glass	9.0
Pb	29		
Si	3	Polyethylene (PE)	100
W	4.5	Polystyrene	70
Invar (Fe-36% Ni)	1.5	Nylon 6, 6	80
Brass	19	Nylon 6, 6 – 33 % glass fiber	20

- Low melting point metals (e.g., Pb) have high CTE, and polymers have highest CTE!

Thermal Expansion Example

A steel rod has length of 20 cm at room temperature (i.e., 25°C). Please calculate its length at 300°C. Knowing average linear thermal expansion coefficient for steel is 12×10^{-6}/°C. What if the original length is 10 m?

Absolute change in length due to temperature increase:

$$\Delta L = \alpha L_0 \Delta T = 12 \times 10^{-6}\ \frac{1}{°\mathrm{C}} \times 20\ cm \times (300 - 25)°\mathrm{C} = 0.066\ cm$$

Final length after reaching 300°C:

$$L = L_0 + \Delta L = 20\ cm + 0.066\ cm = 20.066\ cm$$

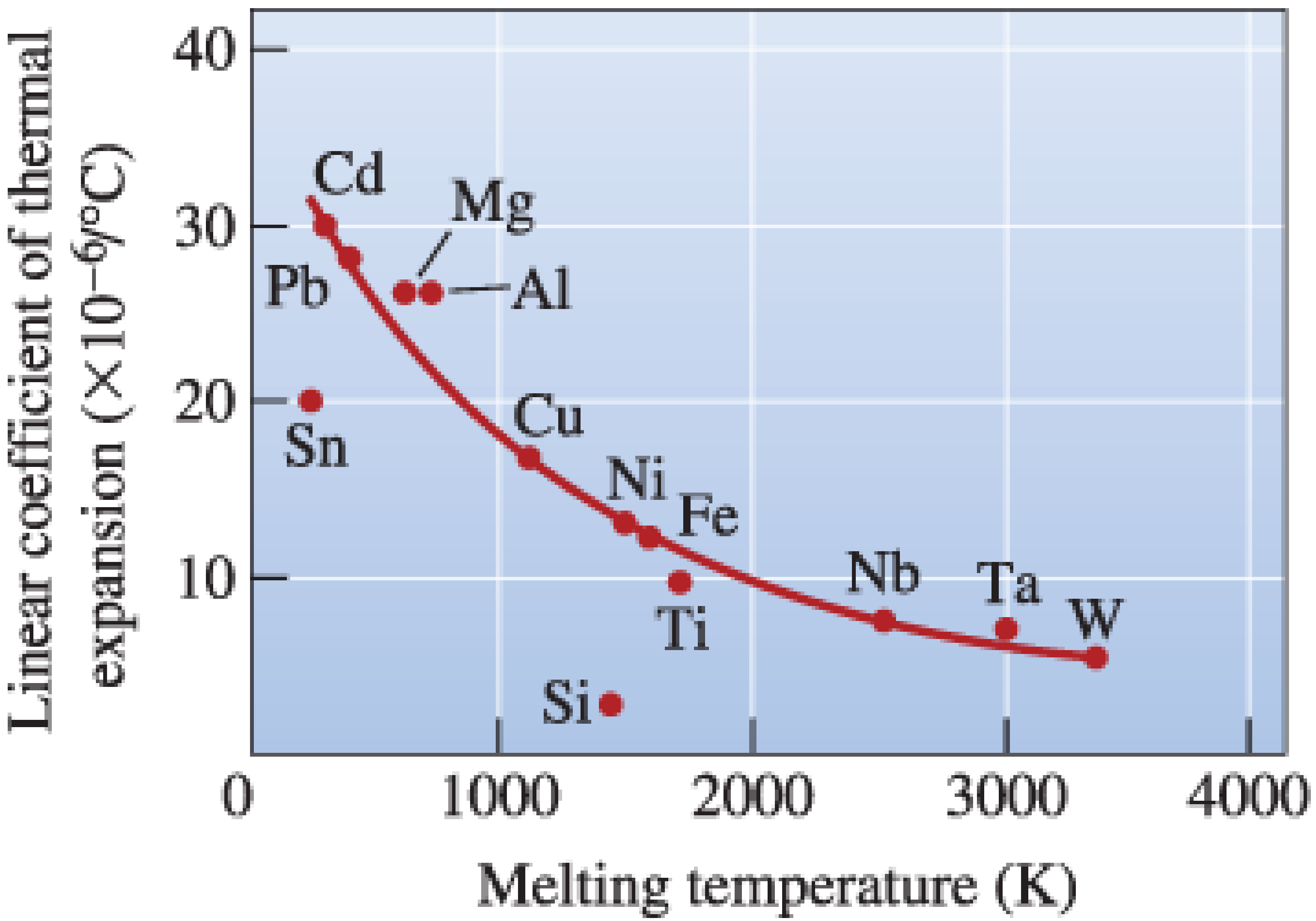
If the original length is 10 m, change in length would be

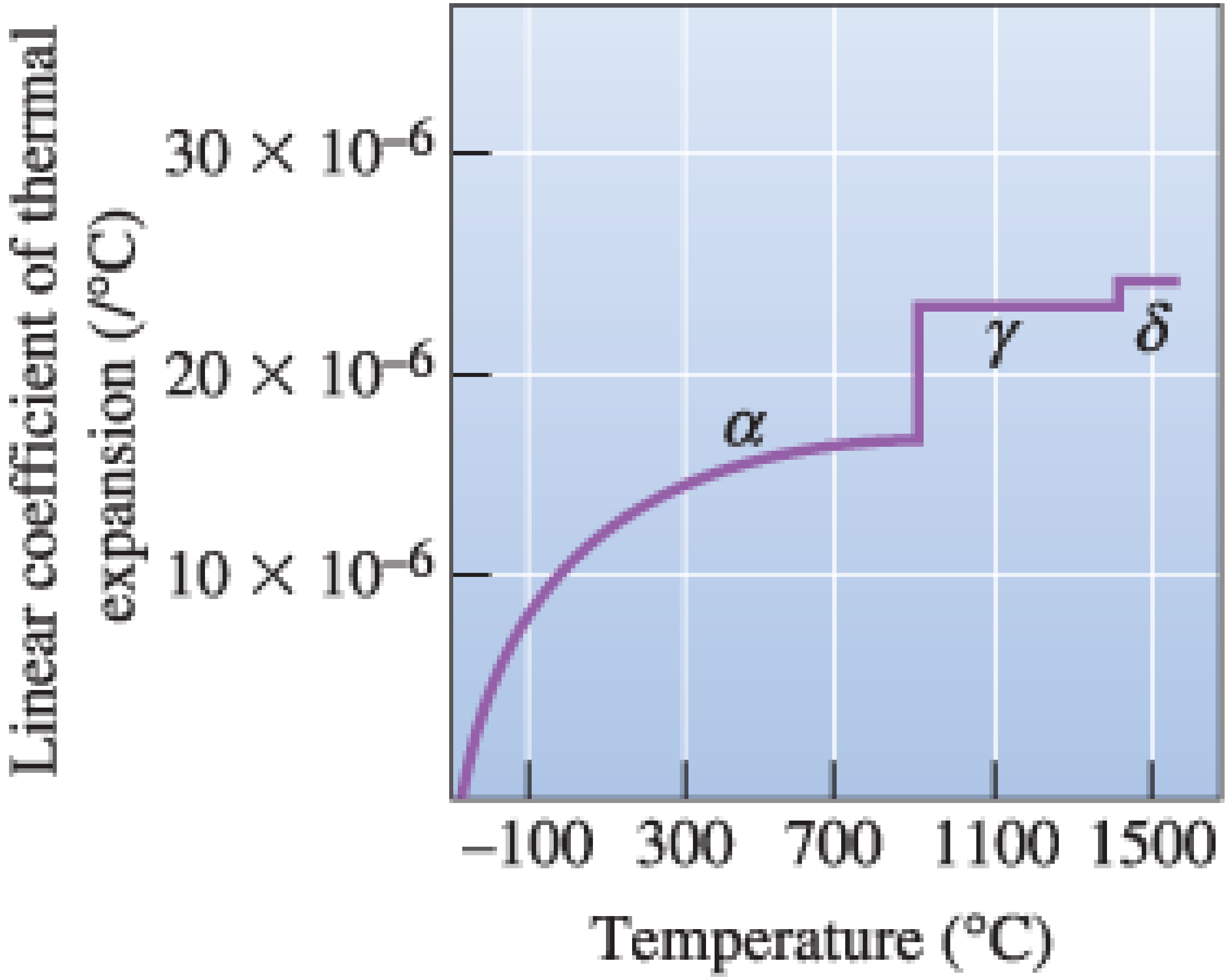
$$\Delta L = \alpha L_0 \Delta T = 12 \times 10^{-6}\ \frac{1}{°\mathrm{C}} \times 10\ m \times (300 - 25)°\mathrm{C} = 0.033\ m = 3.3\ cm$$

Final length:

$$L = L_0 + \Delta L = 10\ m + 0.033\ m = 10.033\ m$$

Factors Influencing Thermal Expansion Coefficient



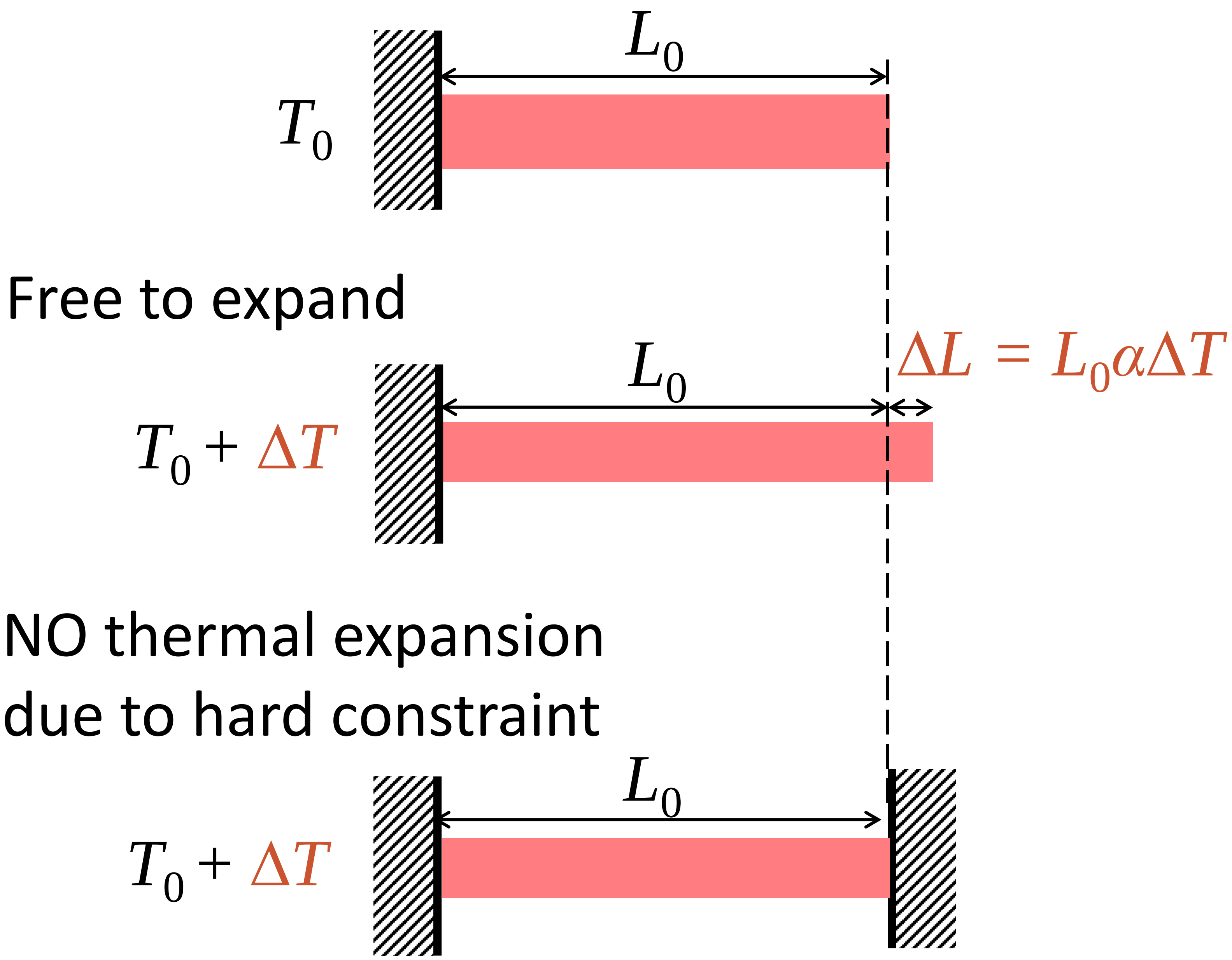


- ➢Lower melting point indicates weaker bonding, and, as a result, higher CTE

- ➢CTE increases from 0, as T increases
- ➢CTE shows discontinuity when phase changes

Thermal Stress

If a material is confined/restricted from thermal expansion, stress will develop within it, which is called thermal stress.



Assume no expansion due to hard mechanical constraint

Resulting thermal strain:

$$\varepsilon_{thermal} = \frac{-\Delta L}{L_0} = -\alpha \Delta T$$

Negative for compression

Assuming constant elastic modulus E, resulting thermal stress (absolute value):

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

Thermal Stress Examples

1. Calculate the thermal stress for a hard-confined steel part (i.e., no expansion) if the steel part is subject to a temperature change of 100°C. Assuming constant elastic modulus of 200 GPa and steel CTE of $12\text{x}10^{-6}$/°C

   Thermal stress

$$\sigma_{thermal} = \alpha \Delta T E = 12 \times 10^{-6} \frac{1}{℃} \times 100℃ \times 200 \times 10^{9} Pa = 2.4 \times 10^{8} Pa = 240\ MPa$$

2. A ceramic coating (called enamel) is applied onto a steel plate. The ceramic has a fracture strength of 3000 psi, a elastic modulus of $10\text{x}10^{6}$ psi, and a CTE of $8\text{x}10^{-6}$/°C. The steel has CTE of $12\text{x}10^{-6}$/°C. Please estimate the maximum temperature the coated steel part can be used without cracking the ceramic coating.

   Thermal stress due to **<u>mismatch</u>** in CTE

$$\Delta\alpha = \alpha_{steel} - \alpha_{ceramic} = 12 \times 10^{-6}\ ℃^{-1} - 8 \times 10^{-6}\ ℃^{-1} = 4 \times 10^{-6}\ ℃^{-1}$$

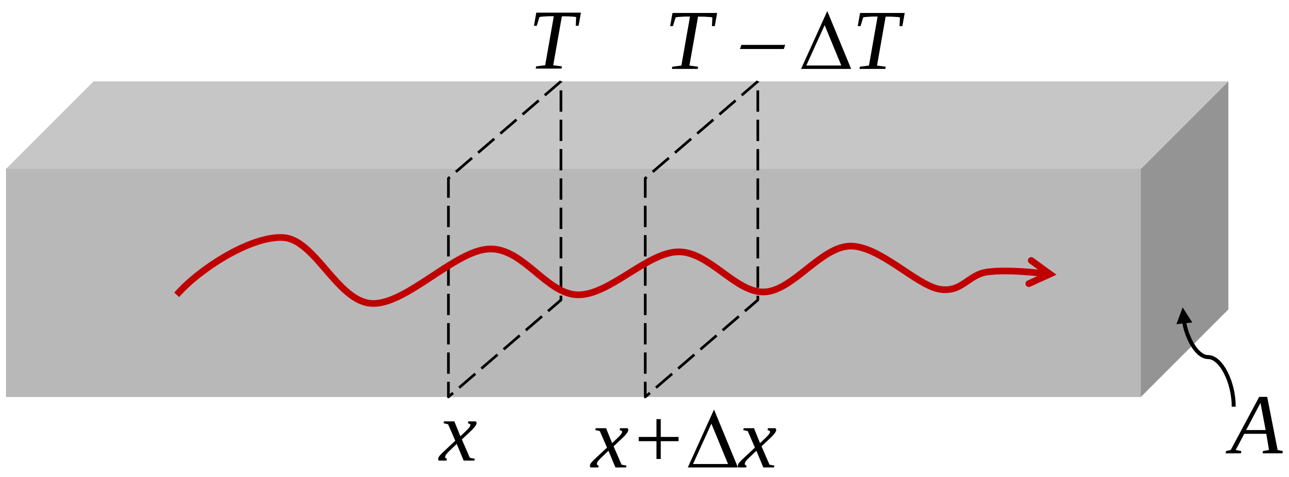
Thermal stress smaller than ceramic fracture strength $\sigma_{thermal} = \Delta\alpha \cdot \Delta T \cdot E_{ceramic} < 3000\text{ psi}$

$$\Delta T < \frac{3000\text{ psi}}{\Delta\alpha \cdot E_{ceramic}} = \frac{3000\text{ psi}}{4 \times 10^{-6}\ ℃^{-1} \times 10 \times 10^{6}\text{ psi}} = 75℃$$

Heat Conduction & Thermal Conductivity

Heat conduction

Flow of heat or thermal energy within one material or between material in contact through diffusional motion, i.e., atom/molecule kinetic energy exchange



Heat flux

Flow of heat per unit area per unit time is proportional to temperature gradient:

$$q = \frac{\Delta Q/\Delta t}{A} = -k\frac{\Delta T}{\Delta x}$$

q Heat flux, unit of J/(m^2·s) or W/m^2

$\frac{\Delta T}{\Delta x}$ Temperature gradient, unit of K/m

k Thermal conductivity, unit of W/(m·K)

Thermal Conductivity for Selected Materials at RT (298 K)

Material	$k\left(\frac{W}{m \cdot K}\right)$	Material	$k\left(\frac{W}{m \cdot K}\right)$
Al	238	AlN	~270
Cu	400	Al_2O_3	16-40
Fe	79	Diamond	~2000
Mg	100	SiC	270
Ni	90	Soda lime glass	~1
Pb	35	ZrO_2	2-3
W	171		
Zn	117	Polyethylene (PE)	0.3
		Polystyrene	0.1
Brass	221	Polystyrene foam/Air	0.03

- Metals have high thermal conductivity; polymers have very low thermal conductivity
- Ceramics' thermal conductivity vary from very high (diamond, AlN) to low (ZrO_2)

Heat Conduction Example

A house has 10 windows, with average size of 1.5 m x 2 m each. The window glass is 4.4 mm thick. If the inside temperature is 22^{o}C, while the outside temperature is 0^{o}C.
(1) Please estimate the total heat loss from the windows in a day (24 h), in kwh. Knowing thermal conductivity for the window glass is 1 W/(m·K).
(2) What if a double-pane glass window with an air gap of 13 mm is used? (Assume heat loss is determined by the air gap, and air thermal conductivity is 0.025 W/(m·K).

Total area: $A = 10 \times (1.5\, m \ \times 2\, m) = 30\, m^2$ Total time: $\Delta t = 24 \times 3600\, s = 86{,}400\, s$

(1) If 4.4 mm glass, total heat loss (absolute value):

$$\Delta Q = k \frac{\Delta T}{\Delta x} \cdot A \cdot \Delta t = 1 \frac{W}{m \cdot K} \times \frac{(22-0)\, K}{0.0044\, m} \times 30 m^2 \times 86{,}400\, s = 1.3 \times 10^{10} J = \mathbf{3600}\, kwh$$

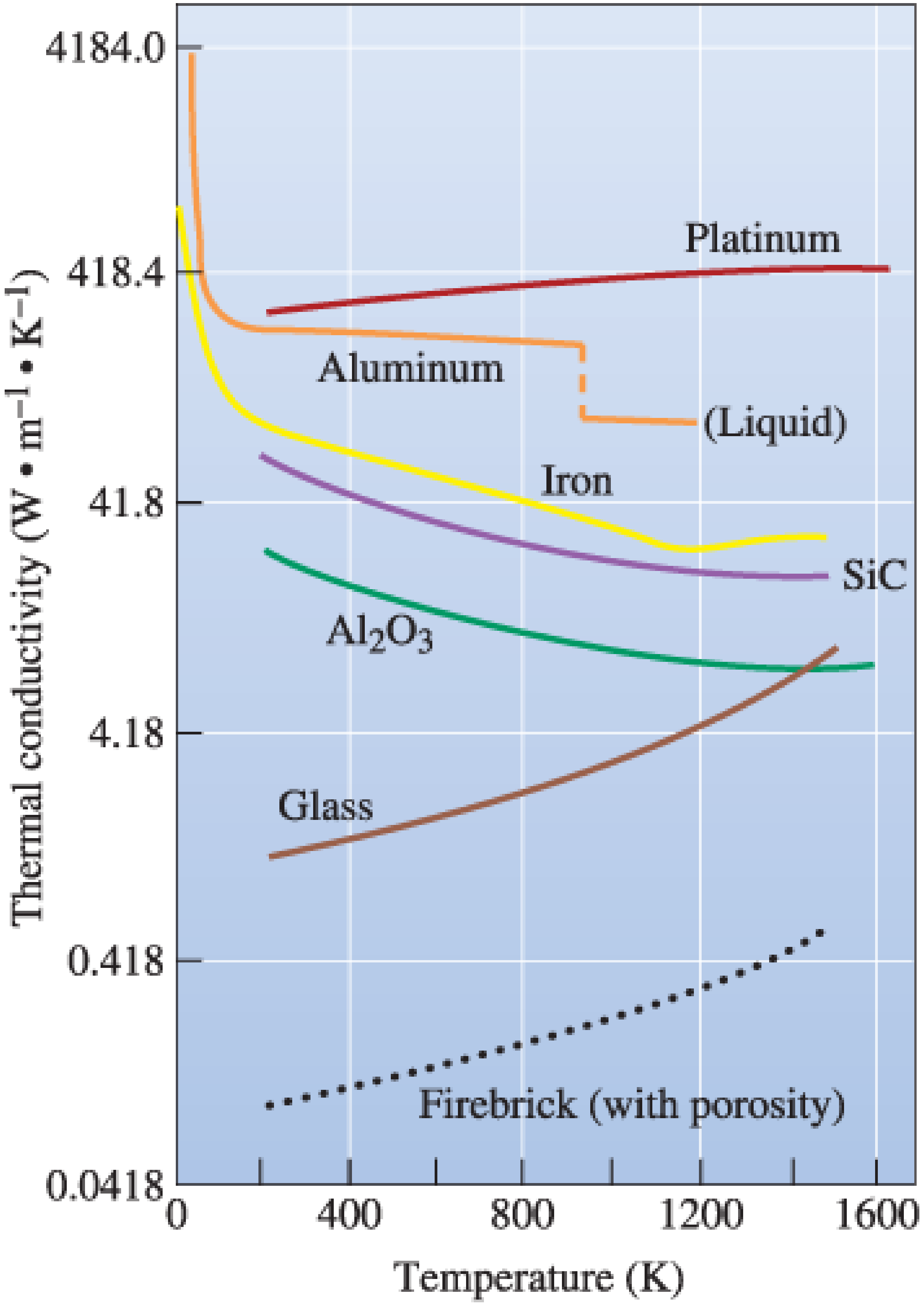
(*Actual heat loss from single-pane glass window is MUCH LOWER than the above value, ~60 kwh, probably due to temperature gradient inside and outside, which slows down heat conduction*)

(2) If 12 mm air gap, total heat loss (absolute value):

$$\Delta Q = k \frac{\Delta T}{\Delta x} \cdot A \cdot \Delta t = 0.024 \frac{W}{m \cdot K} \times \frac{(22-0)\, K}{0.013\, m} \times 30 m^2 \times 86{,}400\, s = 1.05 \times 10^{8} J = 29\, kwh$$

Change of Thermal Conductivity with Temperature

- Thermal conductivity changes with temperature & crystal structure
- From 0K, thermal conductivity drops with increasing T for crystalline materials
- Complex behaviors, e.g.,
  - Pt vs. Fe
  - Al_2O_3 vs. glass



Thermal Shock & Thermal Shock Resistance

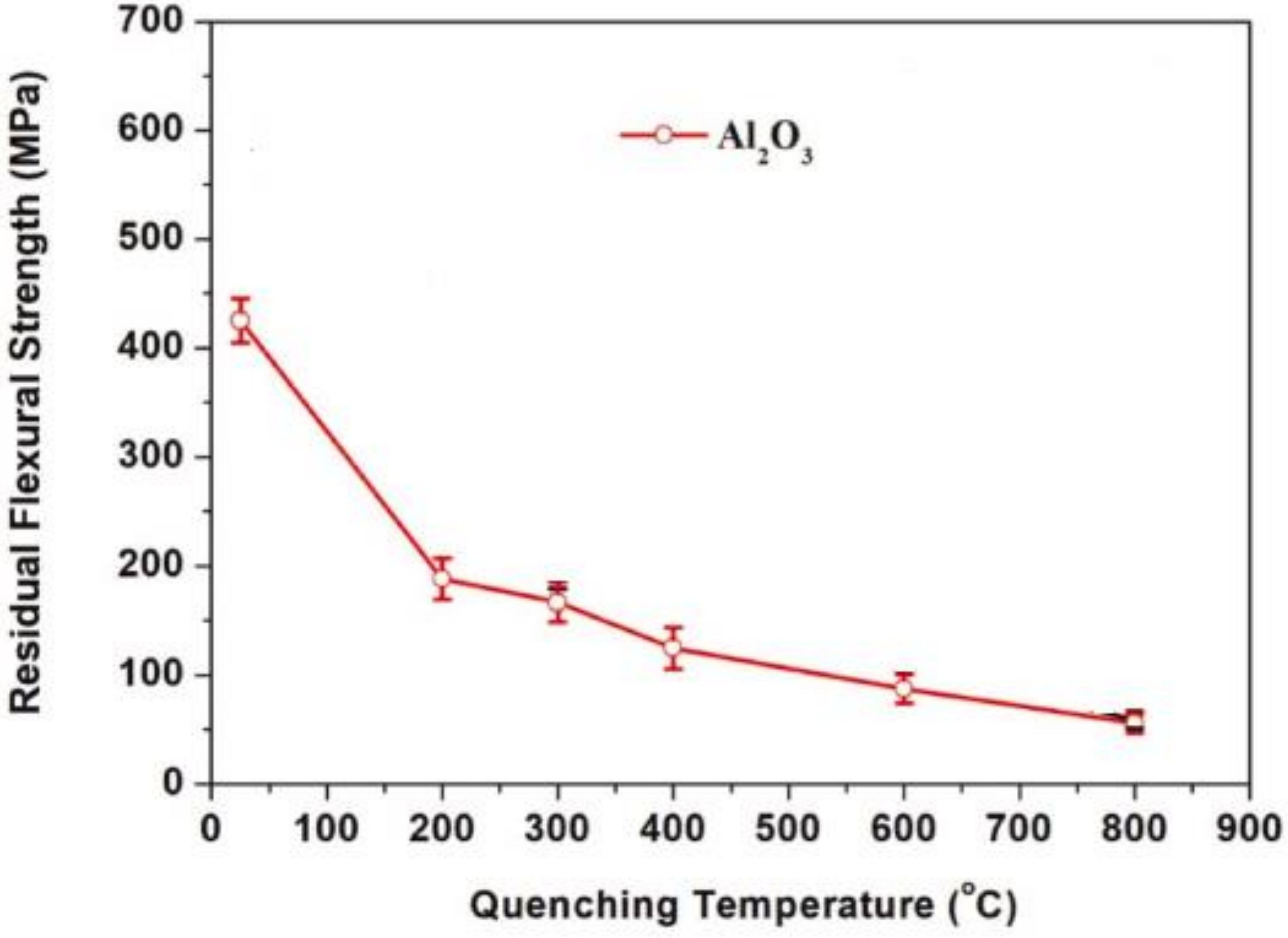
- Thermal shock
  Failure (fracture or cracking) of a material due to sudden temperature change

- Thermal shock resistance depends on multiple factors:
  - Thermal conductivity
    Higher the better – more uniform T
  - Fracture stress
    Higher the better – difficult to crack
  - Elastic modulus
    Lower the better – lower stress
  - CTE
    Lower the better – less strain
  - Others

https://upload.wikimedia.org/wikipedia/commons/thumb/3/31/Broken_glass_through_thermal_shock_-_3rd_of_3.jpg/1200px-Broken_glass_through_thermal_shock_-_3rd_of_3.jpg

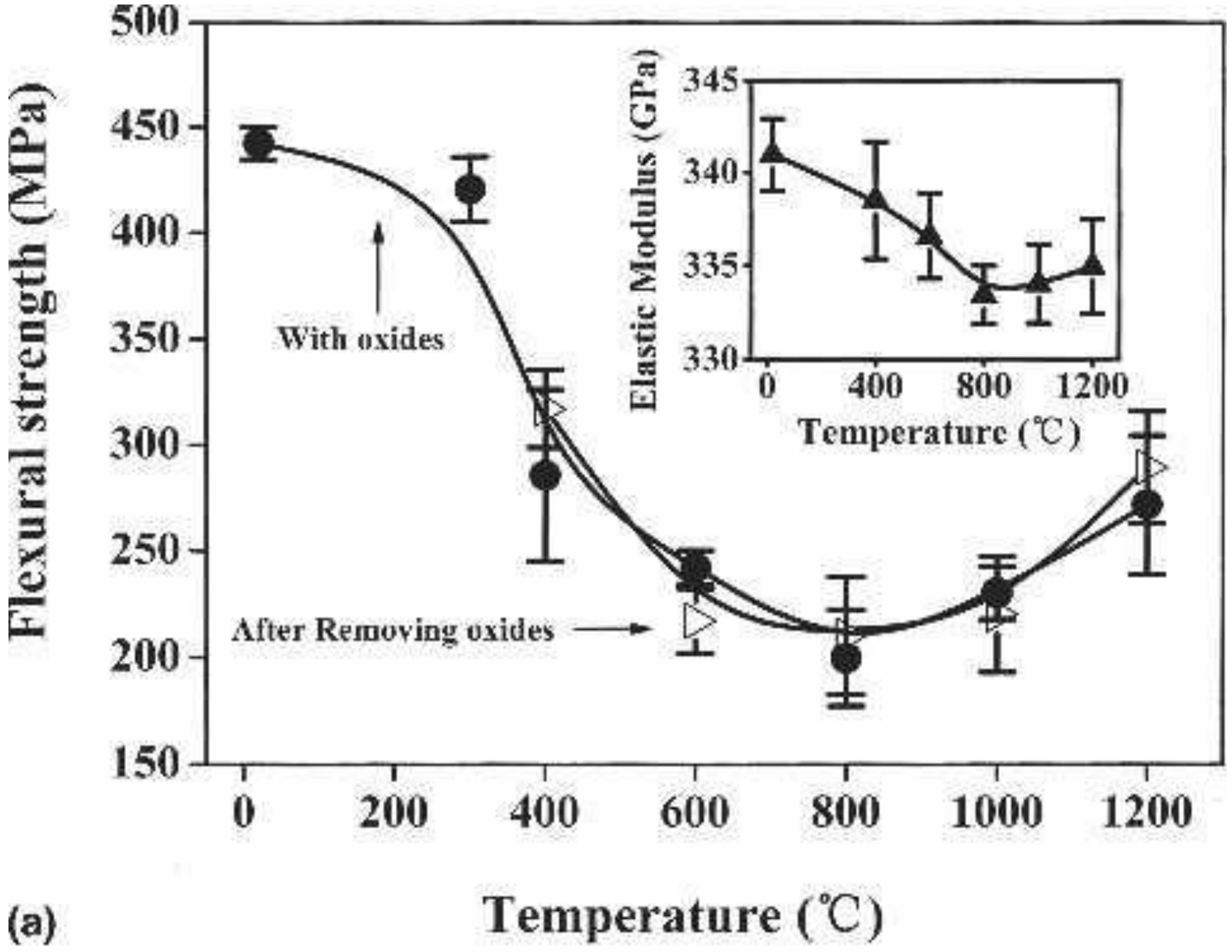
Change of Flexural Strength vs. Temperature Difference

Al_2O_3



Li et al., Ceramics International, v48(19), Part A, p28745 (2022)

Ti_3SiC_2



Zhang and Zhou et al., J Materials Research, v21(9), p2401 (2006)

- Generally, flextural strength decreases as temperature difference increases
- Change (drop) in elastic modulus much less significant

END

Homework 22.0

Carefully review chapter 22 lecture slides and, if time allows, read textbook sections of Askeland 22.1 - 22.4 and give an honor statement confirming the reading

Homework 22.1

Calculate the increase in temperature for 100 g of samples of the following when 1000 J of heat is supplied to the following materials at 25^oC: (a) Al; (b) Cu; (c) Al_2O_3. The specific heat (mass heat capacity) is 0.90, 0.38, and 0.84 J/(K•g), respectively

Homework 22.2

A 100 g aluminum sample is heated to 300^{o}C and then quenched into 1500 cc water at 25^{o}C. Calculate the water/Al equilibrium temperature after reaching the system's thermal equilibrium. Assume no heat loss from the system and specific heat for Al and H_2O is 0.90 and 4.18 J/(K•g), respectively.

Homework 22.3

A 1 m long soda-lime glass rod is produced at 1325^oC. Determine its length after cooling to 25^oC. Specify the assumptions made. Suppose soda-lime glass CTE is $9x10^{-6}/^oC$.

Homework 22.4

A thick nickel part is coated with thin SiC film to inhibit high temperature corrosion of Ni. If no residual stress at 25^oC, please determine the stress developed in the SiC coating when the part is heated to 225^oC. Knowing CTE for Ni and SiC is 13x10^{-6}/^oC and 4.3x10^{-6}/^oC, respectively, and elastic modulus for **silicon carbide** is 420 GPa.

Homework 22.5

Temperature for a 0.5 m long copper rod is maintained at 200^{o}C at one end and 0^{o}C at the other end. Knowing copper has a thermal conductivity of 400 W/(m*K),

(1) Please calculate the heat flow per unit area per unit time through the copper rod.

(2) If the copper rod has diameter of 1 cm, please calculate the total heat flow in 1 hour.