## Creep

At elevated temperatures, permanent deformation of components over a period of time under constant applied load/stress is known as creep.

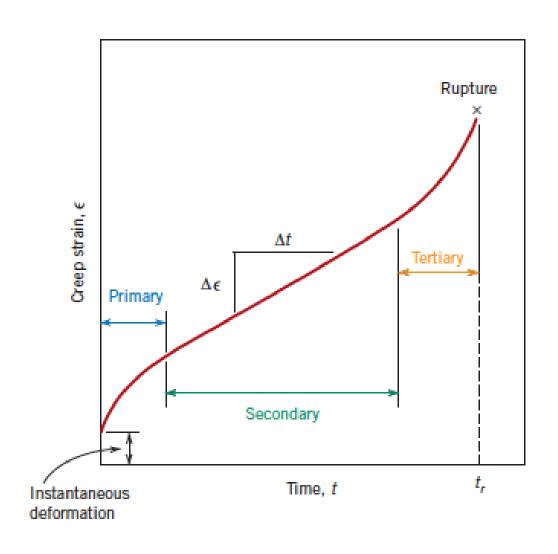
- ightharpoonup Creep is important only at temperatures > 0.4T<sub>m</sub>, where T<sub>m</sub> is the absolute melting temperature.
- Normally the stress level is significantly below the room temperature tensile yield strength of the material.
- ➤ Both crystalline and amorphous materials undergo creep deformation.

## Generalized creep behavior

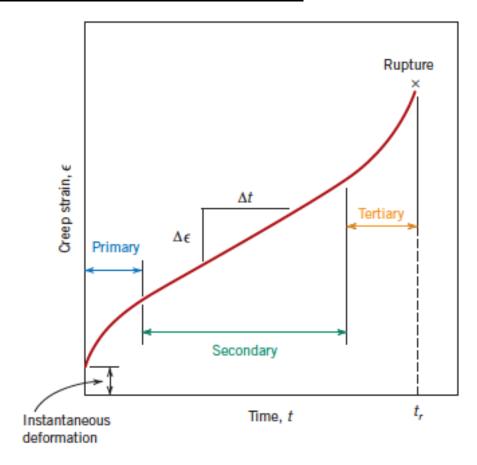
#### Creep test

The specimen is subjected to a constant load or stress at constant temperature.

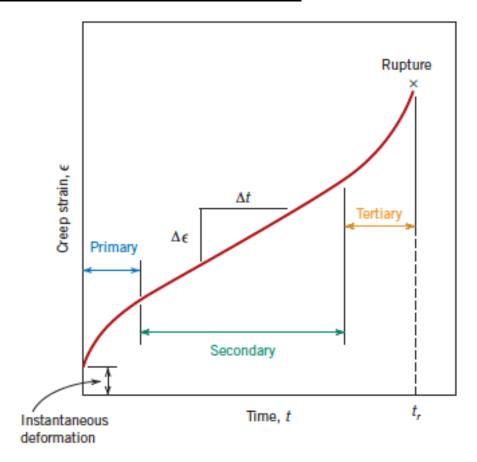
Deformation or strain is measured and plotted as a function of time until sample failre



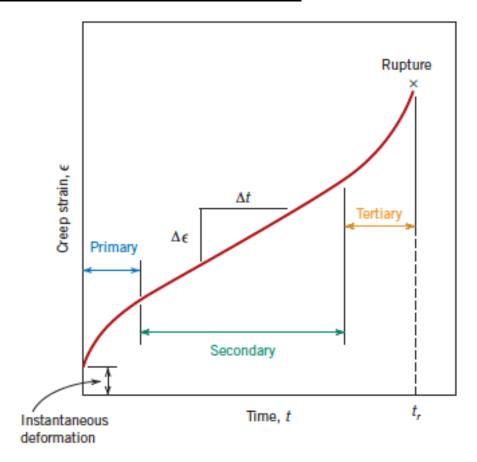
Typical creep curve at constant load



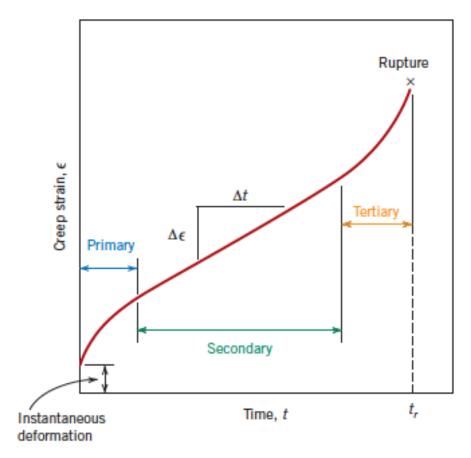
Instantaneous deformation upon application of load. This deformation is totally elastic.



Stage I: Primary or transient creep. Constantly decreasing creep rate. Creep resistance of the material increases in this stage → Strain hardening

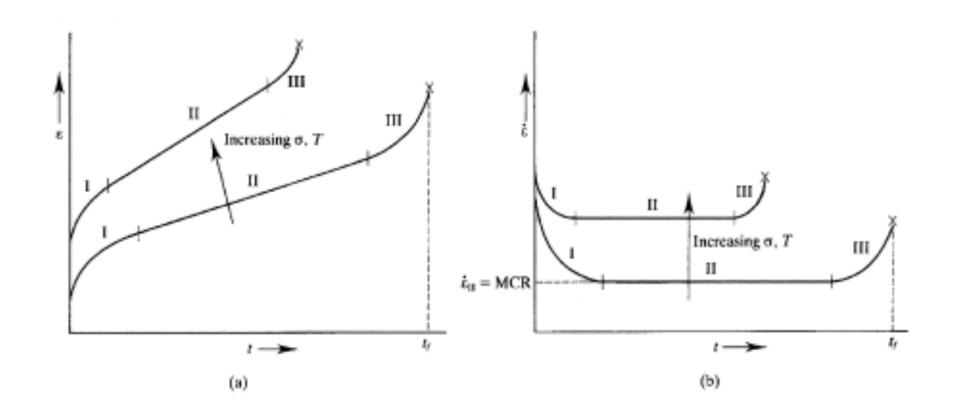


Stage II: Secondary or steady state creep. Creep rate is constant → Balance between competing processes of strain hardening and recovery.



Stage III: Tertiary state creep. Creep rate increases continuously finally culminating into material failure by rupture.

# Effect of stress and temperature



Increasing stress and temperature raises the overall level of the creep curve and also results in higher creep rates.

# Steady state creep

- Stage II of creep curve is known as steady state creep
- This is the most important state of creep deformation from engineering design point of view.
- ➤ Slope of the creep curve (i.e. strain rate) in this steady state region is known as the minimum creep rate (MCR)
- MCR or steady state creep rate is typically defined as:

$$\varepsilon_{II}^{\cdot} = A\sigma^m exp\left[\frac{-Q_c}{RT}\right]$$

A, m: Material constants

Q<sub>c</sub>: Activation energy for creep

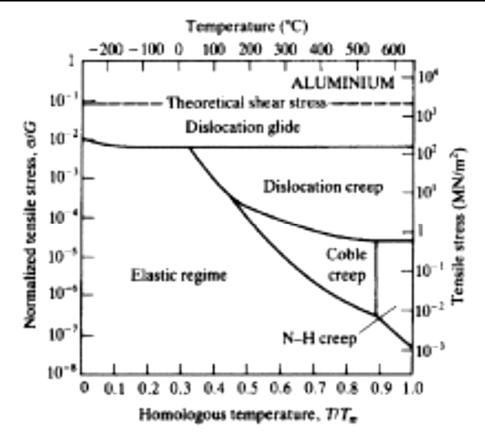
## <u>Deformation mechanism maps</u>

Mechanisms involved in creep deformation of materials include:

- Dislocation glide and climb
- > Stress induced vacancy diffusion
- Grain boundary diffusion
- Grain boundary sliding

Deformation mechanism maps are diagrams which indicate the operating deformation mechanisms at different stresstemperature combinations.

## <u>Deformation mechanism maps</u>



- Ordinate or stress axis is typically normalized by shear modulus (G) and plotted in logarithmic scale
- Abscissa or temperature axis is normalized by absolute melting temperature.  $(T/T_m) \rightarrow Homologous temperature$

## Material design for creep

Creep rates vary with stress, material diffusivity & grain size.

- Reduction of diffusion rate reduces creep rate. As diffusivity decreases with increasing melting point, high melting point materials have higher creep resistance.
- Because of their more open structure than FCC metals (and correspondingly higher diffusivity), BCC metals are generally less creep resistant.
- An increase in grain size reduces the total grain boundary area. This subsequently reduces creep rate as both grain boundary sliding and diffusion become more difficult.
- Dispersed second phase particles at grain boundaries reduce creep rate by hindering grain boundary sliding

# Thermal properties

Two thermal properties of materials will be discussed:

- Coefficient of thermal expansion (CTE)
- > Thermal conductivity (k)

# Coefficient of thermal expansion (CTE)

Linear coefficient of thermal expansion ( $\alpha$ ) is defined as the fractional increase in the linear dimension of a material with increase in temperature at unit pressure.

$$\alpha_l = \frac{\left(l_f - l_0\right)}{l_0 \left(T_f - T_0\right)}$$

 $I_0$  and  $I_f$  are the sample lengths at temperatures  $T_0$  and  $T_f$ .

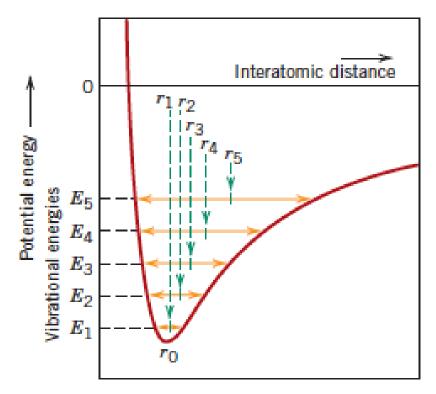
Unit of CTE is (°C)<sup>-1</sup> or (°F)<sup>-1</sup>

Temperature change causes a volume change of material. Volume coefficient of thermal expansion (av) is defined as

$$\alpha_{v} = \frac{\Delta V}{V_{0} \cdot \Delta T}$$
 For isotropic materials,  $\alpha_{v} = 3\alpha_{l}$ 

# Coefficient of thermal expansion (CTE)

From an atomistic perspective, thermal expansion is reflected by an increase in interatomic distance.

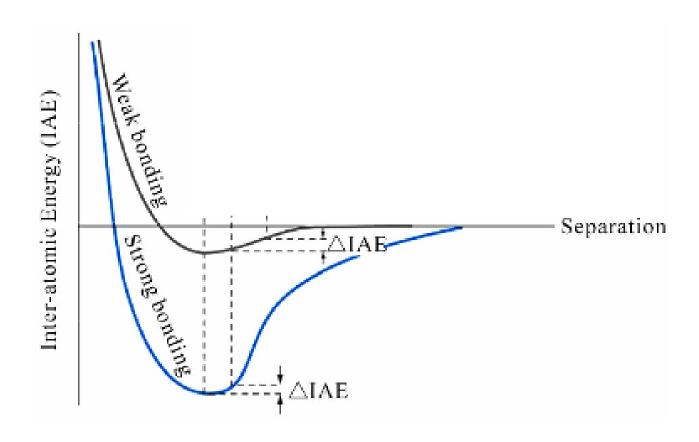


Potential energy vs.
Interatomic energy curve
for a solid

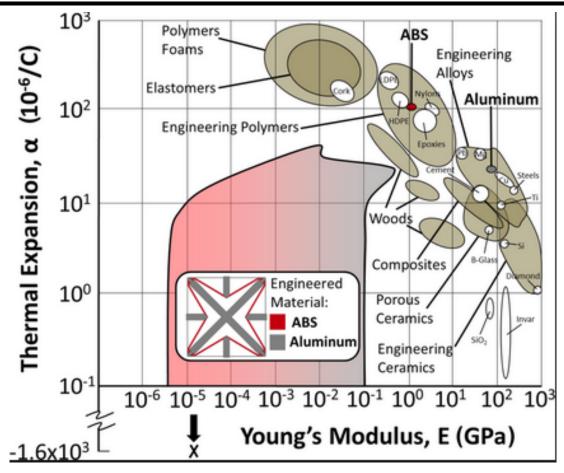
- ightharpoonup At OK  $r_o$  is the equilibrium interatomic spacing
- $\triangleright$  Heating to  $T_1, T_2,...$  Raises vibrational energy to  $E_1, E_2,...$
- Average interatomic distance at  $T_1$ ,  $T_2$  etc. are  $r_1$ ,  $r_2$  etc.
- Due to the asymmetric shape, the interatomic spacing changes with temperature and thermal expansion results

# Coefficient of thermal expansion (CTE)

For each class of material, the higher the atomic bonding energy, the deeper and narrower the potential energy trough → the lower will be the CTE

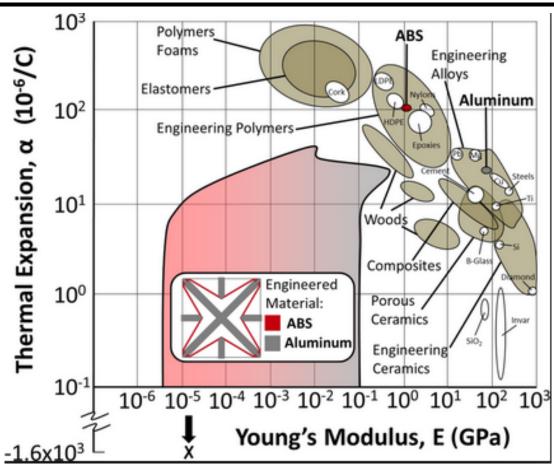


#### CTE & different classes of materials



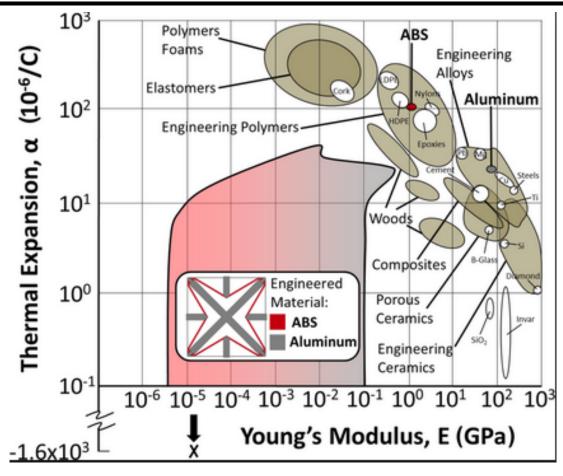
CTE of metals are intermediate between those of ceramics and polymers

#### CTE & different classes of materials



Because of very strong interatomic bonds, CTE of ceramics are inherently low

#### CTE & different classes of materials



Because of weak intermolecular bonds, CTE of polymers are very high. With increased crosslinking, the CTE of polymers decreases.

#### Thermal stresses

Thermal stresses are developed in a body if the axial movement resulting from temperature changes ( $\Delta T$ ) is constrained by rigid supports.

The magnitude of thermal stress ( $\sigma$ ):

$$\sigma = E \cdot \alpha_l \cdot \Delta T$$

- The magnitude of thermal stress scales with the CTE of the material
- As ceramics are very brittle, for them to be used at different temperatures, the CTE needs to be very small. Otherwise the generated thermal stresses may fracture the component.

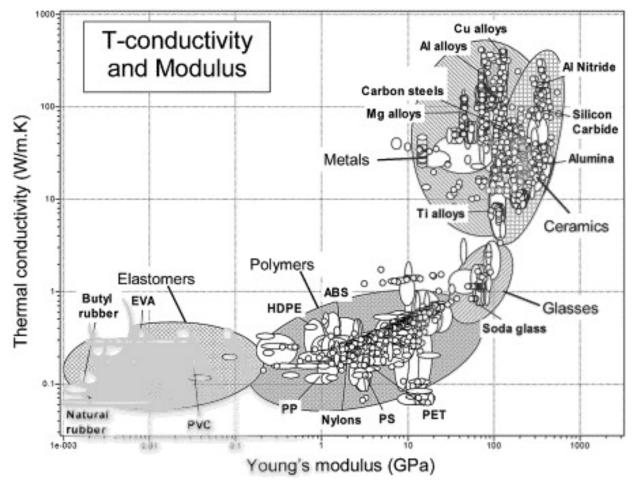
# Thermal conductivity

The property that characterizes the ability of a material to transfer heat from high- to low-temperature regions is known as thermal conductivity (k).

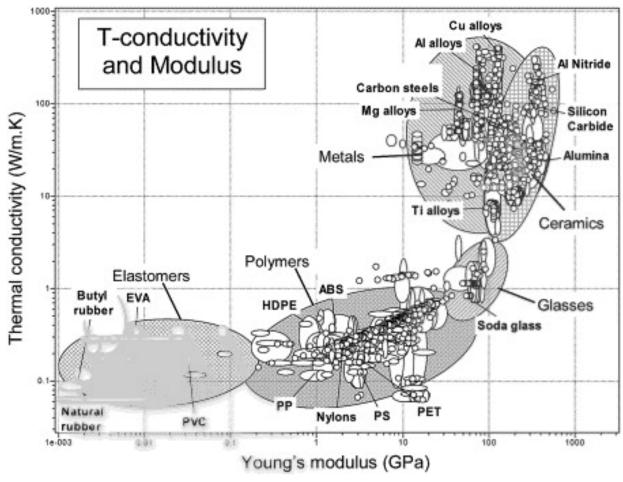
$$q = -k \cdot \frac{dT}{dx}$$
 q denotes the heat flux.

Unit of thermal conductivity is W/m.K

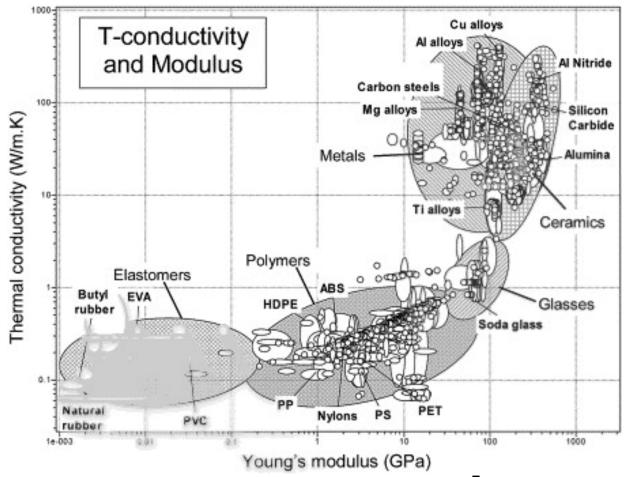
- Heat is transported in solids by i) free electrons and ii) lattice vibration waves (phonons)
- With increasing free electron concentration in materials, the relative contribution from them to thermal conductivity increases



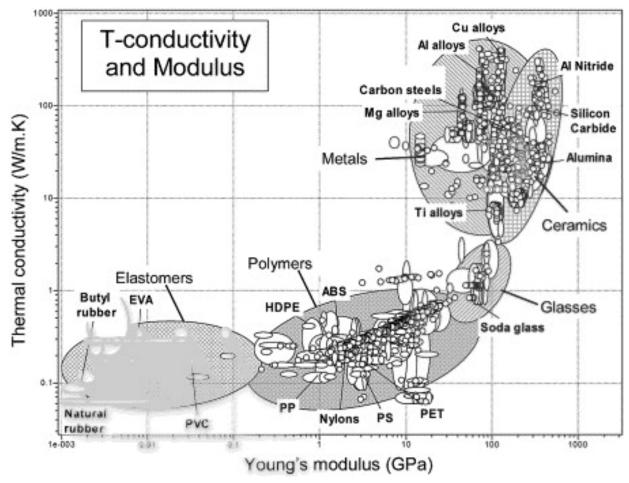
- Because of the presence of large number of free electrons, metals have high thermal conductivity
- Alloying metals with impurities reduces conductivity



Ceramics lack free electrons. Due to the lesser contribution of phonons to thermal conduction than free electrons, thermal conductivity of ceramics are low



With  $\uparrow$  porosity, thermal conductivity  $\checkmark$ , because heat transfer across pores is slow and air contained in the pores has very low thermal conductivity.



- > Thermal conductivity of polymers are also very low
- With increasing crystalinity in polymers, generally the thermal conductivity also increases.

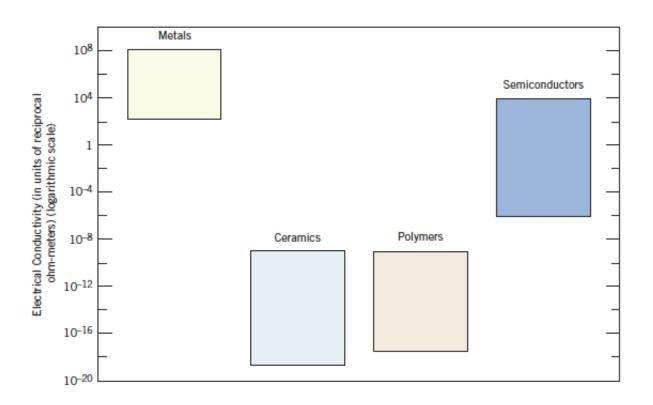
#### **Lecture 4**

# Electrical properties

#### **Electrical conductivity**

It is indicative of the ease with which a material is capable of conducting electric current.

The unit of electrical conductivity is mho/m.



#### Basics of electronic conduction

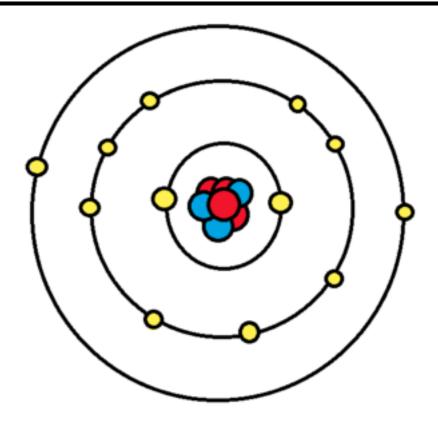
- The magnitude of electrical conductivity is strongly dependent upon the number of electrons available to participate in the conduction process.
- ➤ Electrical properties of solids are consequence of its electron band structure.

Valence band: Band of electron orbitals that electrons can jump out of, when excited.

Conduction band: Band of electron orbitals that electrons can jump up into from valence band when excited.

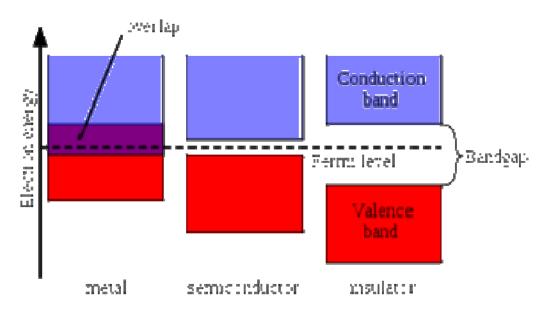
Band gap: Energy difference between the highest occupied energy state of the valence band and lowest unoccupied state of the conduction band

#### Basics of electronic conduction



Valence electrons are the electrons orbiting the nucleus in the outermost atomic shell of an atom. Electrons that are closer to the nucleus are in filled orbitals and are called core electrons.

#### Basics of electronic conduction



Fermi level is the highest energy occupied electron orbital at abolute zero.

Metals: Valence and conduction bands overlap. Electrons readily jump to the conduction vand → high conductivity

Semiconductors: The energy band gap is narrow

Insulators: The energy band gap is large

The larger the band gap, the lower is the electrical conductivity at any given temperature.

## Electrical resistivity of materials

- > It is a fundamental material property that quantifies how strong a material opposes the flow of electric current.
- Resistivity is the reciprocal of conductivity
- Unit of resistivity is ohm.m

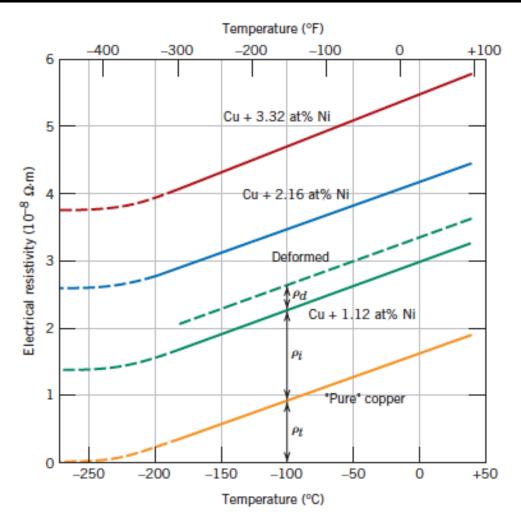
Factors affecting electrical resistivity

Crystal defects: Increase of vol. fraction of crystal defects increases the electrical resistivity

Temperature: Temperature increase increases the lattice vibrations. These serve as electron scattering points and increase the resistivity

Plastic deformation: Raises the electrical resistivity by increasing dislocations which scatter electrons.

## Factors affecting electrical resistivity



Electrical resistivity of pure copper increases with increasing alloying, temerature and plastic deformation.

# Chemical property

- Almost all engineering materials come into contact either with other materials and/or environment.
- Chemical characteristics of materials determine their extent of degradation

The deterioration and loss of a material and its critical properties due to chemical, electrochemical and other reactions of the exposed material surface with the surrounding environment is known as corrosion

#### Fundamentals of corrosion

Corrosion is an electrochemical process in which electrons are transferred from one chemical species to another.

The characteristic process in which a metal loses or gives up its electrons is called an oxidation process.

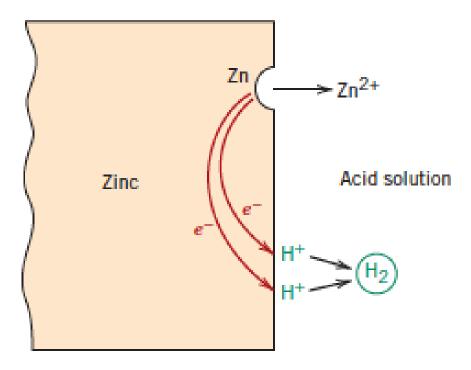
$$M \rightarrow M^{n+} + ne^{-}$$

The sites at which oxidation occurs are called anode.

Electrons generated from oxidation process are consumed to become part of another chemical species. This process is called reduction.

The sites at which reduction occurs are called cathode.

#### Fundamentals of corrosion



- ➤ An overall electrochemical reaction must consist of at least one axidation and one reduction reaction
- ➤ The total rate of oxidation must equal the total rate of reduction
- All electrons generated through oxidation must be consumed by reduction

# Electrode potentials

- Not all metallic materials oxidize to form ions with the same degree of ease.
- When two metals are electrically connected in an electrolyte, wherein one acts as anode and corrodes and the other acts as cathode, it is called galvanic couple
- Metallic materials may be rated in terms of their tendency to oxidize when coupled to other metals in solution of their respective ions.



Standard electromotive force (emf series)

# Standard emf series

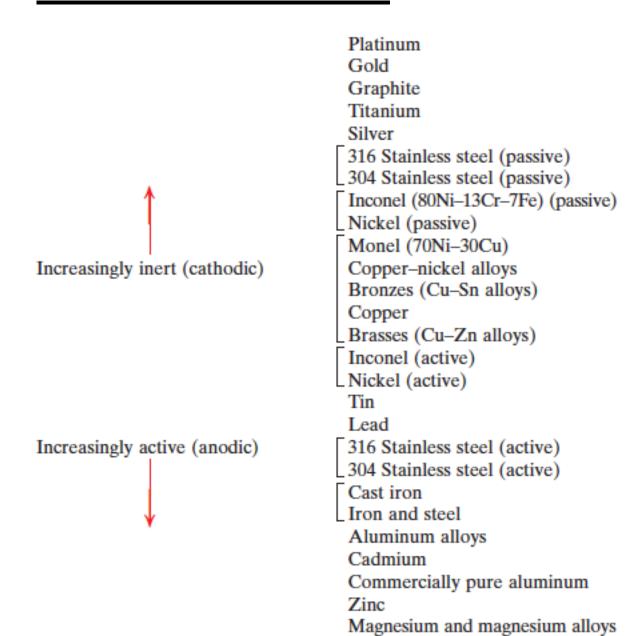
	Electrode Reaction	Standard Electrode Potential, V <sup>0</sup> (V)
	$Au^{3+} + 3e^{-} \longrightarrow Au$	+1.420
1	$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	+1.229
	$Pt^{2+} + 2e^{-} \longrightarrow Pt$	~ +1.2
	$Ag^- + e^- \longrightarrow Ag$	+0.800
Increasingly inert	$Fe^{3+} + e^{-} \longrightarrow Fe^{2+}$	+0.771
(cathodic)	$O_2 + 2H_2O + 4e^- \longrightarrow 4(OH^-)$	+0.401
	$Cu^{2+} + 2e^{-} \longrightarrow Cu$	+0.340
	$2H^+ + 2e^- \longrightarrow H_2$	0.000
	$Pb^{2+} + 2e^{-} \longrightarrow Pb$	-0.126
	$Sn^{2+} + 2e^{-} \longrightarrow Sn$	-0.136
	$Ni^{2+} + 2e^{-} \longrightarrow Ni$	-0.250
	$Co^{2+} + 2e^{-} \longrightarrow Co$	-0.277
	$Cd^{2+} + 2e^{-} \longrightarrow Cd$	-0.403
	$Fe^{2+} + 2e^{-} \longrightarrow Fe$	-0.440
Increasingly active	$Cr^{3+} + 3e^{-} \longrightarrow Cr$	-0.744
(anodic)	$Zn^{2+} + 2e^{-} \longrightarrow Zn$	-0.763
	$Al^{3+} + 3e^- \longrightarrow Al$	-1.662
	$Mg^{2+} + 2e^{-} \longrightarrow Mg$	-2.363
	$Na^+ + e^- \longrightarrow Na$	-2.714
	$K^+ + e^- \longrightarrow K$	-2.924

### Standard emf series

- Metals at the top of the emf series are most noble, while those at the bottom are most active
- ➤ When standard half cells (a pure metal electrode immersed in a 1M solution of ist own ions at 25 °C) are coupled together, the metal lying lower in the emf series will corrode.

Example: If nickel (Ni) and cadmium (Cd) standard half cells are coupled together, cadmium will be corroded, as it is located below nickel in emf series.

- emf series has been generated under highly idealized conditions and has limited practical value
- Galvanic series provides a more practical and realistic ranking of materials
- While emf series lists only metals, both metals and alloys are included in galvanic series
- While for emf series the potentials are calculated from thermodynamic principles, for galvanic series the potentials are measured vs. reference electrode in a specific environment

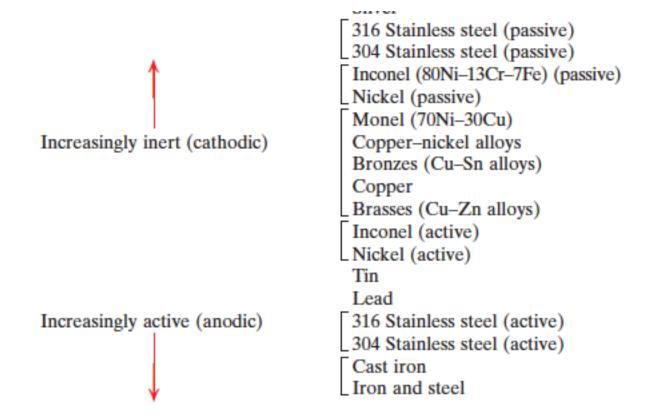


Galvanic series of metals and alloys in seawater

- ➢ Galvanic series plays a key role in predicting galvanic corrosion → corrosion that occurs when two different metals immersed in an electrolyte are connected
- Metals located towards the top of the series are cathodic (i.e. unreactive) while those at the bottom are anodic (i.e. they undergo corrosion)
- When two metals far apart in the galvanic series come to contact in an electrolyte, the metal that is anodic will corrode at an increased rate.
- To avoid possible corrosion, metals lying close to each other should be considered

#### **Typical application:**

An unprotected couple made of passive stainless steel and low-carbon steel in seawater will result into accelerated corrosion of the low-carbon part.



# Some important forms of corrosion

- Galvanic corrosion
- Uniform corrosion
- Crevice corrosion
- Pitting corrosion
- Erosion-corrosion
- Intergranular corrosion (will be discussed later in the course)
- Stress corrosion cracking

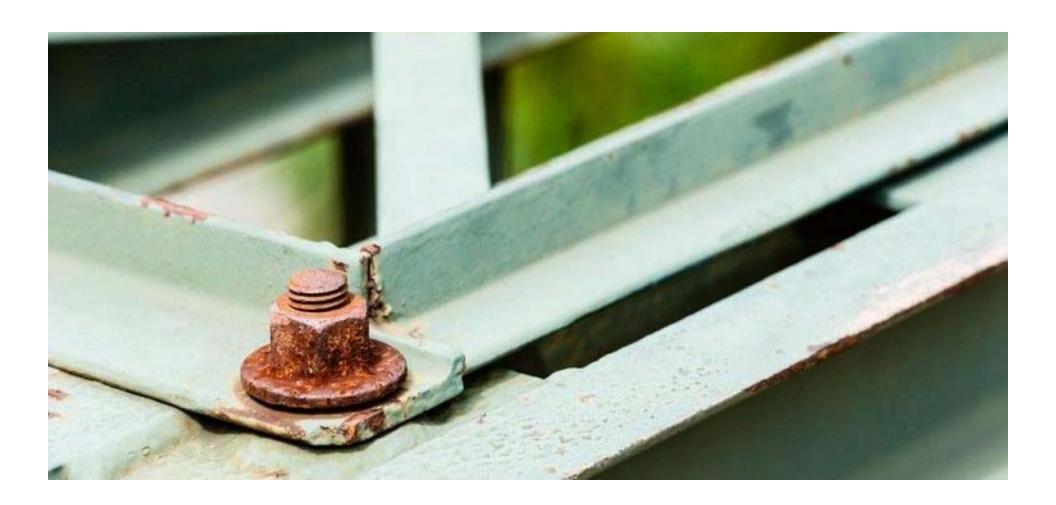
### **Galvanic corrosion**

- Refer to the discussion related to galvanic series
- Rate of galvanic attack depends upon the relative anodeto-cathode surface areas exposed to the electrolyte
- A smaller anode will (e.g. plain carbon steel screw) will corrode more when in contact with a large cathode in an electrolyte due to the larger corrosion current density

#### Prevention of galvanic corrosion

- For coupling dissimilar metals, choose two lying close in the galvanic series
- Use as large an anode area as possible
- > Electrically insulate dissimilar metals from each other
- ➤ Electrically connect a third more anodic metal to the other two → cathodic protection

# Real world galvanic corrosion



# Uniform corrosion

- Almost uniform intensity over the entire exposed surface area
- This often leaves behind a scale or deposit as corrosion product.
- Typical example is rusting of plain carbon steel

This form of corrosion attack is of least concern, as it can be measured easily and as progression of attack is visible, preventive action can be taken.

### Crevice corrosion

- Localized attack on a metal surface at, or immediately adjacent to the gap or crevice between two joining surfaces
- The gap must be wide enough for solution to penetrate, yet narrow enough for stagnancy
- ▶ Depletion of dissolved oxygen and build up of aggressive ions like Cl<sup>-</sup> are chief causes of crevice corrosion

#### Prevention of crevice corrosion

- Use welded instead of bolted or riveted joints
- Remove accumulated deposits frequently
- Design to avoid stagnant areas and proper drainage.

# Real world crevice corrosion



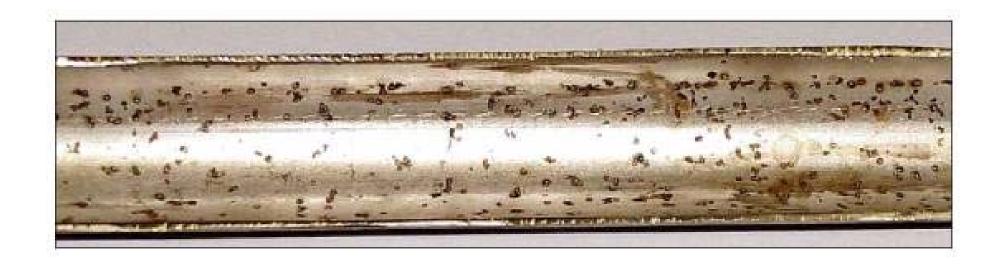
### Pitting corrosion

- Form of localized corrosion which produces attack in the form of spots or pits in normally passive metals like stainless steels and aluminum alloys
- Occurs when the ultrathin passive film is locally damaged and not immediately re-passivate
- Liquid mediums containing high concentration of Cl- ions (e.g. seawater) are most insidious
- Depth of pits in materials can be very large and may result in fast catastrophic failure without notice
- ➤ It is one of the most damaging forms of corrosion, as the extent of pit growth in components is generally not easily discerned.

# Prevention of pitting corrosion

- Proper selection of materials with appropriate alloying elements
- ➤ Control of environment in terms of Cl<sup>-</sup> ion concentration pH, temperature etc.

# Real world pitting corrosion



### **Erosion-corrosion**

- Caused by combined action of chemical attack and mechanical action caused by fluid flow
- Particularly harmful in metals passivated by ultrathin films e.g. stainless steels, Al alloys etc.
- Increasing fluid velocity normally enhances corrosion rate
- Presence of bubbles and suspended particles also enhance the corrosion rate

#### Prevention of erosion-corrosion

- ➤ Proper pipe design to reduce turbulent fluid flow → eliminate bends, elbows, abrupt changes in pipe diameter
- Removal of particulates and bubbles from liquid

# Real world erosion-corrosion



# Stress corrosion cracking

- Results from the combined action of operating tensile stress and the particular corrosive environment
- Materials virtually inert in an environment may become susceptible to corrosive attack when tensile stress is present
- Most alloys are susceptible to stress corrosion in specific environments
- The tensile stress may be applied, residual stress or generated due to temperature changes
- Even for inherently ductile materials the fracture is brittle like

# Prevention of stress corrosion cracking

- ➤ Totally eliminate or reduce the operating tensile stress in the material → proper component design, heat treatment of the material etc.
- Proper selection of material-environment combination (from available knowledge) to avoid stress corrosion.

# Real world stress corrosion cracking

