Lecture 31

Thermodynamics of Interfaces
Surface Free Energy and Surface Tension

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Topics to Discuss

● Interface: Definition and classification

● Surface Free Energy and Surface Tension
  - ☐ Gas - liquid interfaces
  - ☐ Interfaces other than gas - liquid interface
 - ☐ Three-phase interface and wettability

Introduction

Importance of interface

- Atomic and microscopic structure of grain boundaries (physical metallurgy)
- Electrical effects at interfaces and adsorption from solution (extractive metallurgy)
- Colloidal stability (polymer chemistry)
- The rheology of surface films (lubrication engineering)
- Wetting and detergency (extractive metallurgy, physical metallurgy, …)
- Adsorption of gases on solids (extractive metallurgy, physical metallurgy, …)

- **Thin film and nanotechnology**

Definition and Classes of Interface

- **Interface is a general term, referring to the boundary between any two phases and also grain boundaries within a single crystalline phase.**

- **Surface refers specifically to boundary between a condensed phase and its own vapour phase (or, frequently, vacuum, an inert gas, or air)**
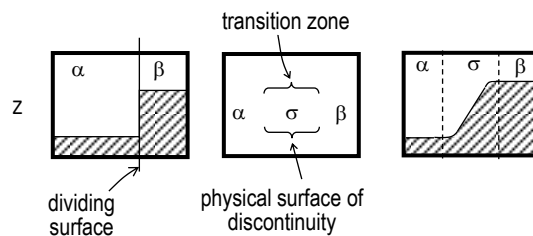
FIGURE 9.1: (a) The hypothetical boundary of zero thickness between two phases; (b) Visualisation of a zone of transition, σ, between the two phases defining a physical surface of discontinuity; (c) Sketch of the variation of the density of any property Z through the zone of transition.

Interfaces in Metallic Systems

1. Free surfaces of crystal (solid/vapour interface)

☐ it is the boundary between the condensed phase (solid/liquid) and it is vapour phase (generally air)

☐ **vaporisation** and **condensation** transformation, **reactions** between gaseous and condensed phase, **nucleation** of gas bubbles inside a liquid metal.

2. Grain boundaries (α/α interface)

☐ separates crystals with the same composition and crystal structure, but a different orientation in space

☐ important in **recrystallisation**, (i.e. transformation of a highly deformed grain structure into new undeformed grains)

3. Interphase interfaces (α/β interfaces)

☐ separate two different phases with different crystal structures and/or compositions

☐ plays an important role in determining the **kinetics of phase transformations**, reduction of solid oxide by gas mixture during **extraction of metal** (such as, iron making), the transfer of substances between liquid slag phase and liquid metal in **refining process** (such as steel making), and **corrosion of metals**.

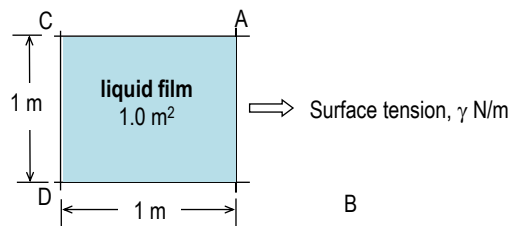# Surface Free Energy and Surface Tension
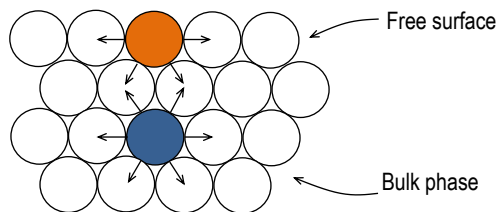
FIGURE 9.2
Section normal to free surface of a solid phase. A particle in the free surface is bonded with lesser number of neighbours than a particle in the bulk phase.

● **The properties of phases near the surface differ substantially from those in the bulk.**

☐ different co-ordination numbers
☐ different patterns of thermal motion
☐ different energy of molecules

- **Energy of a particle in a free surface is higher than that of a particle in the bulk phase .**
  - ☐ If the area of a surface is increased, the energy of surface, also know as the **surface free energy**, is also increased.
  - ☐ The free energy (measured in Joules) required to create 1.0 m² of new interfacial area per square metre is known as the **Gibbs surface free energy**, γ.

- **Because a reduction in surface area of the liquid results in a reduction in free energy of the system, the surface of the liquid will tend to contract as far as possible.**
  - ☐ This tendency of liquid surfaces to contract causes a tangential force in the free surface. This is known as the **surface tension** and defined as the force acting at right angles in the surface.

- **The work of reversible isothermal formation of 1 m² of new surface is mathematically equal to the work done in stretching the surface by 1 m along a 1 m line against surface tension.**

C _____ A

1 m | liquid film 1.0 m² | ⟹ Surface tension, γ N/m

D |←— 1 m —→| B

FIGURE 9.3
AB is a line 1 m long in the surface of a liquid film. The energy required to stretch the liquid surface from AB to CD is γ Joules if BD is 1 m long and the surface tension is γ N/m.

- **Thus the surface tension γ N/m is numerically equal to the surface free energy γ J/m² and has the same dimension of unit (MLT⁻²).**

TABLE 9.1

Average surface free energies of selected metals.

Crystal	Temperature (C)	Surface tension (N/m)
Water	100	0.059
Water	20	0.073
Sodium chloride	910	0.106
Steelmaking slag	1600	0.400
Mercury	20	0.480
Gold	1130	1.100
Copper	1150	1.100
Steel (0.4 % C)	1600	1.560

Example: Gas/Liquid Interfaces

atmosphere (P_A)

liquid metal

h

r
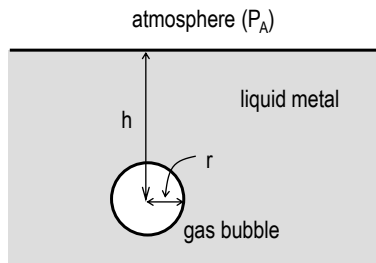
gas bubble

FIGURE 9.4
Nucleation of a spherical gas bubble inside a liquid metal.

Pressures acting on the gas bubble :

1. The atmospheric pressure, P_A

2. The metal head pressure, P_M, and

3. The pressure required to create and to maintain the gas/metal surface of the bubble against the surface tension, P_γ.

At equilibrium, the gas pressure inside the bubble must be equal to the total pressure

$$P_B = P_A + P_M + P_\gamma \qquad (9.1)$$

$$P_B = P_A + h\rho g + 2\gamma/r \qquad (9.2)$$

● P_B **increases as the depth of bubble beneath the metal h increases, and the radius of bubble r decreases**

● **If a gas bubble to nucleate homogeneously, the radius of the bubble must be very small, perhaps of the order of the size of a single molecule. So the P_γ term of Eq.(9.2) is expected to be very high.**

Consider the possibility of a gas bubble nucleating homogeneously with a radius 10^{-9} m at a depth 0.3 m below the surface of liquid steel.

$$g = 9.81 \text{ m/s}^2 \qquad \rho = 7400 \text{ kg/m}^3 \qquad \gamma = 1.56 \text{ N/m}$$

Using Eq.(9.2) and 1 atm $= 1.01 \times 10^5$ N/m^2, we get

$$P_B = P_A + h\rho g + 2\gamma/r$$
$$P_B = 1 \text{ atm} + 0.22 \text{ atm} + 30900 \text{ atm} \cong 30900 \text{ atm}$$

● **The amount of gas pressure inside the gas bubble required for its homogeneous nucleation is roughly equal to the pressure solely required to create and maintain the gas/metal surface of the bubble against the surface tension.**

● **The atmospheric pressure and the metal head pressure have a very negligible effect against nucleation of the gas bubble.**

Does vacuum degassing has any effect on degassing?

- **The amount of gas dissolved in the liquid metal is usually small and development of such an enormous value of gas pressure (P_B or, P_γ) is difficult to attain.**

- **Hence, the possibility of homogeneous nucleation of gas bubble in liquid metal is always impossible.**

- **For a gas bubble to nucleate, therefore, an existing gas-metal interface must be available – that is the bubble must nucleate heterogeneously.**

- **In that case, the value of P_γ would not be required and nucleation of gas bubble would not be a problem anymore.**

  The following can act as the pre-existing gas-metal interface and the bubble can nucleate on it:

  ☐ surface of the liquid
  ☐ an inclusion
  ☐ the container of the liquid

Practical Example:

Degassing of liquid metal during casting/metal refining

☐ vigorous stirring

☐ flushing the melt by inert gases (nitrogen, argon, etc.)

☐ creating fresh crevices by scratching the smooth-walled crucible

Example: Liquid/Liquid Interfaces

Interaction between liquid slag and liquid metal in steel making process

● **Separation of liquid slag from liquid steel is generally difficult due to the attraction of particles of one liquid for those of the other.**

  ☐ This reduces the tendency of the particles to be pulled away from the interface due to the surface tension at the liquid/liquid interface.

Stock's law

● **Large particles should sink or rise (depending on their specific gravity) through a liquid metal faster than smaller particles.**

  ☐ For example, oxide slags of SiO_2 and MnO floated out of liquid steel at a velocity proportional to their diameter.

Rosegger's Law

● **The rate of removal of slag component depends upon their composition as well as their size.**

  ☐ Small alumina rich particles separate more rapidly than the larger silica particles.
  ☐ The small difference in density could not account for this anomaly
  ☐ It is the interfacial tension between the particles and the liquid steel that controls this abnormal behaviour.
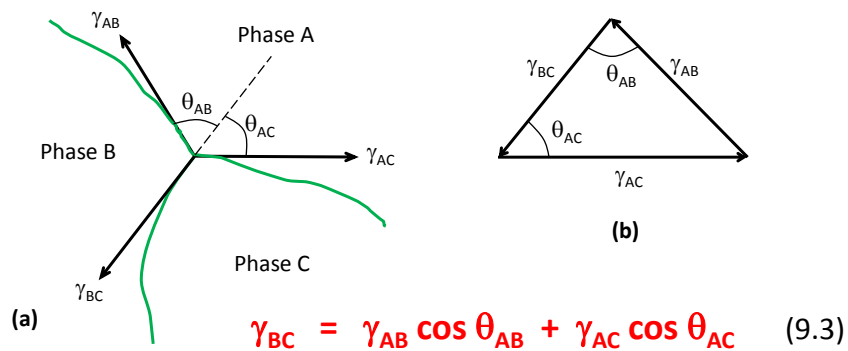
● **A high interfacial tension between the particles and the liquid metal would create a small attractive force between the liquid steel and the oxide particles and, consequently, a small dragging force opposing the motion of the particle. So separation of oxide particles would be easy.**

● **On the other hand, a low interfacial tension would cause a large attractive force and, consequently, a high dragging force opposing the motion of the particle causing a slower rate of separation.**

- **The addition of Al_2O_3 increases the interfacial tension of FeO, whilst the addition of SiO_2 and MnO decrease it.**

  ☐ liquid steel is not attracted to Al_2O_3
  ☐ the rate of removal of Al_2O_3 is high.

- **This is one particular reason why aluminium, besides producing a more stable oxide than silicon or manganese, has an advantage over other deoxidants as far as the rare of removal of deoxidation products is concerned.**

Example: Three-Phase Interface

(a)

(b)

$$\gamma_{BC} = \gamma_{AB} \cos \theta_{AB} + \gamma_{AC} \cos \theta_{AC} \qquad (9.3)$$

FIGURE 9.5

(a) Interfacial tensions at the junction between three phases. γ_{AB} represents the interfacial tension between the phases A and B and is drawn along the tangent of the AB phase boundary at the junction. γ_{AC} and γ_{BC} are drawn similarly.

(b) At equilibrium, the summation of these forces is zero.

Example:

The heterogeneous nucleation of a gas bubble on top of a solid phase (inclusion, etc.) floating around inside a liquid metal, creating a common boundary between a liquid, a solid and a gas.
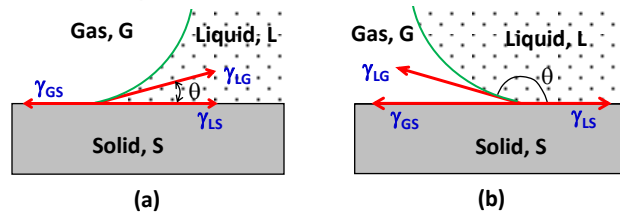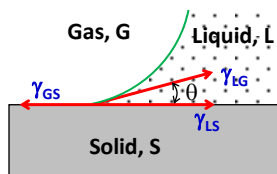

FIGURE 9.6

Contact between gas (G), liquid (L) and solid (S) phases where the solid phase has a flat surface and θ is the contact angle.   (a) $\theta < 90°$, (b) $\theta > 90°$

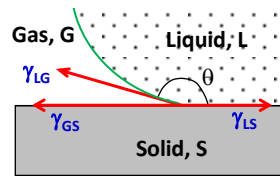$$\gamma_{GS} \; = \; \gamma_{LG} \cos \theta_{LG} \; + \; \gamma_{LS} \qquad (9.4)$$

$$k \; = \; \cos \theta_{LG} \; = \; \frac{\gamma_{GS} - \gamma_{LS}}{\gamma_{LG}} \qquad k \; = \; \text{wetting coefficient}$$

$$k \; = \; \cos \theta_{LG} \; = \; \frac{\gamma_{GS} - \gamma_{LS}}{\gamma_{LG}}$$

● **If $\theta < 90°$, $\cos \theta$ is positive and $\gamma_{LS} < \gamma_{GS}$.**

☐ $k \geq 0$, and **the solid is wetted by the liquid**.

☐ This means that the liquid particles have stronger attraction for solid particles than the attraction between the gas and the liquid particles (Fig. 9.6a).

☐ For complete wettability, $\theta = 0°$.

$$k = \cos\theta_{LG} = \frac{\gamma_{GS} - \gamma_{LS}}{\gamma_{LG}}$$

Gas, G Liquid, L

γ_{LG}

θ

γ_{GS} γ_{LS}

Solid, S

- **If θ >90°, cos θ is negative and $\gamma_{LS} > \gamma_{GS}$.**

  - ☐ k≤0, and **the solid is not wetted by the liquid**.

  - ☐ Hence the attraction of liquid particle for solid particles is not as strong as the attraction between the liquid and the gas particles (Fig. 9.6b).

  - ☐ For complete non-wettability, θ = 180°.

TABLE 9.2
Contact angles of different interfaces. (measured in air unless otherwise stated)

Liquid phase / solid phase	Contact angle, θ
Water / glass	0
Tin / copper	25
Water / sphalerite (ZnS)	30
Lead / steel (in vacuum)	70
Water / steel	70-90
Water / paraffin wax	110
Mercury / glass	130-150
Mercury / steel	150

Determining the Shape of Grain Boundary
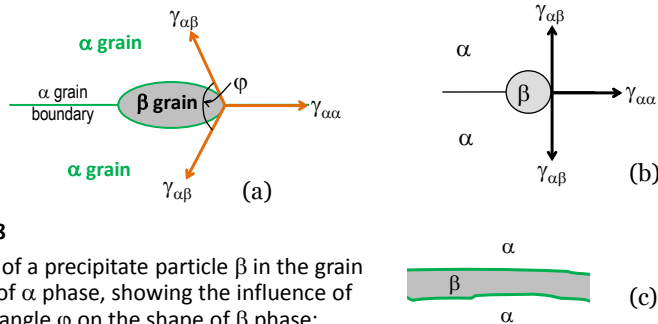
FIGURE 9.8

The shape of a precipitate particle β in the grain boundary of α phase, showing the influence of interfacial angle φ on the shape of β phase:

(a) $0 < \varphi < 180°$, (b) $\varphi = 180°$, (c) $\varphi = 0°$.

● **Depending on the relative magnitude of $\gamma_{\alpha\alpha}$ and $\gamma_{\alpha\beta}$, the angle φ can take any value from 0 to 180°.**

    ☐   If $\varphi = 180°$, the β particles become spherical.

    ☐   If $\varphi = 0°$, the β particle run along the grain boundary, forming a film.

Steel refining process

☐ FeO and FeS have a φ value close to zero degree and thus FeS forms along the grain boundary. Being brittle, it weakens the structure, which is known as **cold shortness**.

☐ To remove the harmful effect of sulphur, manganese is added to steel. MnS, having $\varphi > 180°$, does not wet steel at the grain boundary and precipitates throughout the steel matrix.
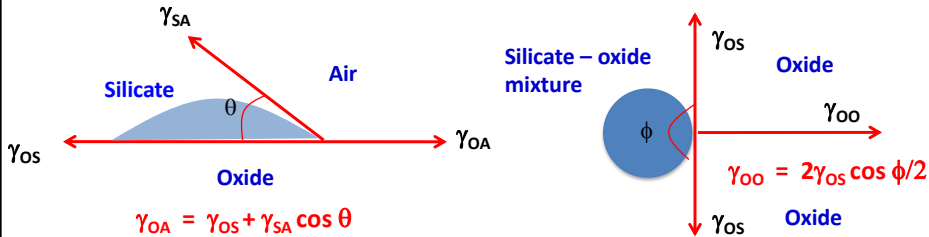
Grain growth/coarsening process

☐ During heating, the metallic structure will rearrange itself to reduce its grain boundary energy by increasing its average grain size reducing the grain boundary to volume ratio.

Sintering process

☐ Pores between the powder particles tend to become spherical and contract until a substantially sound solid part is produced.

Example

A liquid silicate with surface tension of 500 ergs/cm² makes contact with a polycrystalline oxide with an angle $\theta = 45°$ on the surface of the oxide. If mixed with the oxide, it forms liquid globules at three grain intersections. The average dihedral angle ϕ is 90°. If we assume the interfacial tension of the oxide-oxide interface, without the silicate liquid is 100 dynes/cm, compute the surface tension of the oxide.

γ_{SA}

Silicate — Air

θ

γ_{OS}

Oxide

$\gamma_{OA} = \gamma_{OS} + \gamma_{SA}\cos\theta$

Silicate – oxide mixture

γ_{OS} Oxide

ϕ

γ_{OO}

$\gamma_{OO} = 2\gamma_{OS}\cos\phi/2$

γ_{OS} Oxide

Given data:
$\gamma_{SA} = 500$ ergs/cm²
$\gamma_{OO} = 100$ dyne/cm
$\theta = 45°$, $\phi = 90°$

$\gamma_{OO} = 2\gamma_{OS}\cos\phi/2$

$100 = 2\gamma_{OS}\cos45$

$\gamma_{OS} = 707$ erg/cm²

$\gamma_{OA} = \gamma_{OS} + \gamma_{SA}\cos\theta$

$= 707 + 500\cos45$

$= 1060.7$ erg/cm²

Next Class

Lecture 32

Thermodynamics of Interfaces
Adsorption