MSE-422 – Advanced Metallurgy 2025/26

Exercise 6 – 03.12.2025

Thermodynamic Modeling & Metals Processing

1. Thermodynamic Modeling

1.1 Regular Solution Model

A binary alloy system is modeled using the regular solution approximation. The Gibbs free energy of mixing is:

$$\Delta G_{\text{mix}} = RT\left(x_A \ln x_A + x_B \ln x_B\right) + \Omega x_A x_B.$$

1. **Spinodal condition** Derive the condition for spinodal decomposition by evaluating the second derivative of ΔG_{mix} with respect to x_A. Express the spinodal curve as a relationship between Ω and T.
2. **Critical temperature** For $\Omega = 20\,000$ J/mol and $R = 8.314$ J/mol·K, calculate the critical temperature for $x_A = x_B = 0.5$:
$$T_c = \frac{\Omega}{2R}.$$
3. **Free energy at T_c** Compute ΔG_{mix} at $T = T_c$ for $x_A = x_B = 0.5$ and compare:
   - ideal-solution contribution,
   - regular-solution interaction term.

1.2 Sub-Regular Solution Model (Cu–Ni System)

The Gibbs free energy of mixing for a binary Cu–Ni system is modeled using the sub-regular solution model:

$$\Delta G_{\text{mix}} = RT\left(x_{\text{Cu}} \ln x_{\text{Cu}} + x_{\text{Ni}} \ln x_{\text{Ni}}\right) + x_{\text{Cu}} x_{\text{Ni}}\left(L_0 + L_1(x_{\text{Cu}} - x_{\text{Ni}})\right),$$

where:

$$R = 8.314 \text{ J/mol·K}, \quad T = 1000 \text{ K}, \quad L_0 = -5000 \text{ J/mol}, \quad L_1 = 2000 \text{ J/mol}, \quad x_{\text{Ni}} = 1 - x_{\text{Cu}}.$$

1. For compositions $x_{\text{Cu}} = 0.2, 0.5, 0.8$, compute the Gibbs free energy of mixing:
$$\Delta G_{\text{mix}} = RT(x_{\text{Cu}} \ln x_{\text{Cu}} + x_{\text{Ni}} \ln x_{\text{Ni}}) + x_{\text{Cu}} x_{\text{Ni}}(L_0 + L_1(x_{\text{Cu}} - x_{\text{Ni}})).$$
   Compare the contributions of the ideal solution term
$$RT(x_{\text{Cu}} \ln x_{\text{Cu}} + x_{\text{Ni}} \ln x_{\text{Ni}})$$
   and the interaction parameter term
$$x_{\text{Cu}} x_{\text{Ni}}(L_0 + L_1(x_{\text{Cu}} - x_{\text{Ni}}))$$
   to ΔG_{mix}.

2. Phase Stability Analysis: A phase is stable if small fluctuations in composition do not cause a decrease in the total Gibbs free energy. Mathematically, stability requires:

$$\frac{\partial^2(\Delta G_{\text{mix}})}{\partial x_{\text{Cu}}^2} > 0$$

If $\frac{\partial^2(\Delta G_{\text{mix}})}{\partial x_{\text{Cu}}^2} < 0$, the system is unstable, and phase separation occurs. Based on the provided values of $L_0 = -5000$ J/mol and $L_1 = 2000$ J/mol, identify regions of phase stability and instability for the given compositions ($x_{\text{Cu}} = 0.2, 0.5, 0.8$).

3. Discuss how the signs and magnitudes of L_0 and L_1 affect the phase diagram and the miscibility gap.

2. Ti Making Process

Considering the low productivity and high cost of the Kroll process for Ti production, many researchers around the world are attempting to develop a new Ti melting process in which metallic Ti of the requested specification can be produced with high productivity and low cost. One representative process under development is the preform reduction process (PRP). High-purity metallic Ti powder (up to 99% pure) is produced by reduction with metal vapor.

1. Based on the Ellingham diagram, define possible metals that can be used for the reduction of $TiCl_4$.
2. Select the most appropriate reductant and explain why.
3. Define the overall reaction of the reduction process.

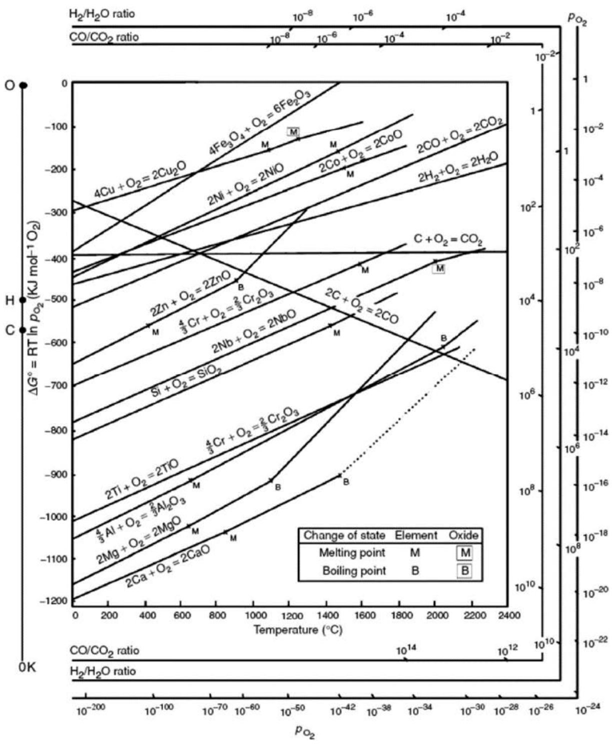

Figure 1: Ellingham diagram

3. Iron Making: The Blast Furnace

In a furnace, iron ore is reduced according to the following reaction:

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$

Coke with a composition of 94% C is used to produce CO by combustion with air at the bottom of the furnace. Of the coke charged, 90.5% burns to CO only.

1. Define the input and the output of the process.
2. Define the function of coke charged in the furnace.
3. Define the combustion reaction to produce CO.
4. Calculate the volume of CO required to produce 1000 kg of iron.
5. Calculate the weight of coke required to produce 1000 kg of iron.

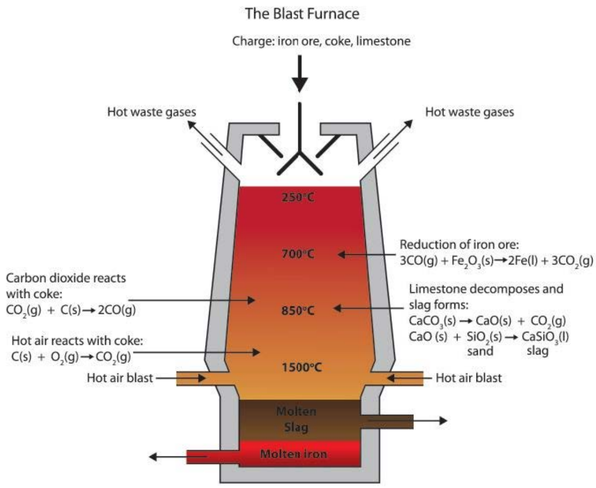

Figure 2: Blast furnace

4. Oxygen Converter Process

For a BOF heat, the following data are given:

	Hot Metal	Slag
Si	1%	–
P	0.15%	–
Mn	0.25%	2.5% MnO
C	3.5%	–
CaO	–	54%
FeO	–	18%
MgO	–	2.5%

Table 1: Composition of the pig iron and slag

The weight of the scrap is 10% of the hot metal, and the steel at the tap contains 0.2% C.

1. Name the reaction equations and oxidation products of the process.
2. Explain why lime is normally added during the converter process.
3. Calculate, per ton of steel, the weight of the hot metal charge (assume scrap as pure Fe).
4. Calculate, per ton of steel, the weight of slag produced.
5. Calculate, per ton of steel, the quantity of lime required.

5. Environmental Aspects of Steel Production

In the last years, wind power has been considered a regenerative, CO_2-emission-free energy source.
Wind power plants:

- Direct emissions: 0
- Indirect emissions from the manufacturing and installation (use of steel):
  - Amount of CO_2 per ton of steel produced: 1500 kg/ton
  - Amount of steel per wind capacity: 400 ton / 1 MW

Coal power plants:

- Direct emissions: 0.8 kg CO_2/1 kWh of electricity generated

(a) Calculate the minimum operating time that the installed wind power capacity has to run to offset the CO_2 emitted during steel production compared to conventional electricity production via hard coal power plants.

(b) How much energy can be produced by a coal power plant emitting the same amount of CO_2?

Note: The solutions to this exercise will be available on Moodle from the next exercise session.

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