Advanced Metallurgy - Information and guidelines for topic 3.5 High-Temperature Oxidation Behavior during heat treatment of Fe-Ni-Cr Alloys

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General Guidance for Oxidation Simulations

- When fixing the steel composition, refer it to a defined mass (e.g. 100 g) rather than using normalized mole or weight fractions. During oxidation, oxygen is added to the system, which increases the overall mass. Working with an absolute mass basis ensures that mass balances remain transparent and that the calculated amounts of oxide phases correspond to physically meaningful quantities.
- Begin with simple, binary or ternary alloy compositions to identify general oxidation behaviour and phase formation trends. Once the behaviour is understood, additional alloying elements can be introduced stepwise. Carbon should be excluded in initial simulations, as it can form CO/CO_2 gas species, complicating convergence and making interpretation more difficult.
- To study oxidation at fixed temperature, calculate stable phases as a function of the oxygen chemical potential. In Thermo-Calc, this is expressed as the natural logarithm of oxygen activity $\ln(a_{O_2})$. Varying $\ln(a_{O_2})$ corresponds to changing the oxidizing potential of the atmosphere.
- Alternatively, fix the oxygen activity (i.e. select a constant value for $\ln(a_{O_2})$) and calculate phase stability as a function of temperature. This allows you to determine oxidation onset temperatures, oxidation equilibrium states at service conditions, and the stability ranges of oxide phases.
- The **Phase Diagram** module enables the variation of two parameters simultaneously (e.g. oxygen activity and temperature, or composition and temperature). This is useful for visualizing oxidation phase boundaries and identifying conditions under which different oxide scales or internal oxidation occur.
- The **Diffusion Module** (DICTRA) can be used to compute oxygen concentration-depth profiles as a function of time and temperature. To obtain meaningful results, ensure that both the corresponding thermodynamic and mobility databases for steels are selected. This allows diffusion-controlled oxidation phenomena such as internal oxidation fronts to be approximated.
- Moving-interface simulations for the CORUNDUM phase on steel typically fail because mobility data for oxide phases are not included in the mobility databases. Without diffusion coefficients for the oxide region, the interface kinetics cannot be solved. Thus, results from such simulations should be interpreted with caution or avoided.
- If desired, custom mobility data for the oxide phase can be defined manually. The DICTRA example `exi3a` (Help - Manual Folder - Diffusion Module - Diffusion Module (DICTRA) Console Mode Example Macros.pdf - Go to 'Diffusion in complex phases - diffusion in iron oxide') demonstrates how to assign user-defined mobilities for FeO growth on Fe. This approach can be used if you want to explore the oxidation behaviour in more detail, but it goes beyond what we expect from the students.

Why do we use $\ln(a_{O_2})$ when calculating oxidation with Thermo-Calc?

- Oxidation behaviour is governed by the **chemical potential of oxygen**, which determines whether oxidation occurs and which oxide phases are stable.
- For gases, the chemical potential does not depend directly on concentration, but on the **activity** of the gas. For an ideal gas, activity is proportional to its partial pressure:

  $$a_{O_2} \approx \frac{p_{O_2}}{p^\circ}$$

- The chemical potential of oxygen is expressed as:

  $$\mu_{O_2} = \mu_{O_2}^\circ + RT\ln(a_{O_2})$$

  meaning that **oxygen activity directly controls the driving force for oxidation**.
- This enters the Gibbs free energy change for oxide formation:

  $$\Delta G_{\text{ox}} = \Delta G^\circ + RT\ln(a_{O_2})$$

  Therefore, varying $\ln(a_{O_2})$ changes whether oxidation is favourable and which oxide forms.
- **Oxide stability diagrams are therefore naturally expressed as a function of** $\ln(a_{O_2})$. This is the same principle used in Ellingham diagrams.
- In Thermo-Calc, specifying $\ln(a_{O_2})$ allows the software to correctly evaluate the oxygen chemical potential and determine the stable phases at a given temperature.
- Using the logarithmic form also makes the calculation numerically stable, since real oxidation conditions span **many orders of magnitude** in oxygen partial pressure (typically $\ln(a_{O_2})$ from about -60 to -20).

Thermo-Calc Oxidation Setup (Step-by-Step)

- Select the **Steels and Fe Alloys** (TCFE + MOBFE) database package. This ensures that the correct phases and phase stabilities relevant to steels and their oxides are available. Using a non-steel database may lead to missing oxide phases or incorrect stability fields.
- Open the **Equilibrium Calculator** and switch to **Advanced Mode**. The Advanced Mode allows direct control of the thermodynamic state variables and phase constraints, which is necessary for defining oxygen activity and for working with absolute amounts rather than normalized compositions.
- Set **system size** to **Gram** or **kg**, assign a fixed mass (e.g. 100), and disable normalization. Oxidation increases the total mass of the system because oxygen is introduced. Using a fixed mass basis keeps the composition physically meaningful and prevents automatic re-normalization from hiding mass changes due to oxide formation.
- Input the alloy composition as **amount of component** for each element rather than mole or weight fractions. This ensures that the initial metallic composition is defined in absolute terms. Thermo-Calc will then compute the distribution of elements among metal and oxide phases based on equilibrium thermodynamics, without enforcing normalization.
- Add oxygen as a boundary condition: choose **activity referred to phase** → **GAS** → $\mathbf{O_2}$, enable the **ln** option, and assign a value (e.g. -50). This step defines the oxygen chemical potential. The selected $\ln(a_{O_2})$ value represents the oxidizing strength of the atmosphere, analogous to controlling p_{O_2} in an experiment.
- Select a **One Axis** calculation to vary a single thermodynamic variable. This mode allows systematic evaluation of how equilibrium phases change as a function of one parameter, such as oxygen activity or temperature.

- Under **Axis Definition**, choose $\ln(a_{O_2})$ referred to the **GAS** phase and set an appropriate range, typically -60 to -20. This range spans realistic oxygen potentials encountered from highly reducing to strongly oxidizing environments. The output will show which oxide phases form at each oxygen chemical potential and provide insight into oxidation sequence and oxide scale stability.
- The topic is also addressed in the tutorial by N. Grundy, recorded at EPFL Mediaspace (start at approx. minute 09:00):
  `https://mediaspace.epfl.ch/media/24+11+21+-+Exercise+-+Thermo-Calc+Demo+Part+II/0_0roeykg3`