Phase Diagrams—Understanding the Basics F.C. Campbell, editor

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CHAPTER **11**

Gas-Metal Systems

GAS-METAL SYSTEMS are important both during metallic processing and during exposure when placed in service, particularly in the evaluation of high-temperature oxidation and hot-gas corrosion. Engineering alloys react chemically when exposed to air or other more aggressive gases. Whether they survive or not depends on how fast they react. For a few metals, the reaction is so slow that they are virtually unattacked, but for others, the reaction can be disastrous. High-temperature service is especially damaging to most metals because of the exponential increase in reaction rate with temperature. The driving force for reaction of a metal with a gas is the Gibbs energy change, ΔG .

The driving force, ΔG , for a reaction such as aA + bB = cC + dD can be expressed in terms of the standard Gibbs energy change, ΔG^0 , by:

$$\Delta G = \Delta G^0 + RT \ln \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

where the chemical activity, a, of each reactant or product is raised to the power of its stoichiometric coefficient, and R is the gas constant. For example, the oxidation of a metal can be expressed by the reaction:

$$x\mathbf{M} + \frac{y}{2}\mathbf{O}_2 = \mathbf{M}_x\mathbf{O}_y$$

where M is the reacting metal, $M_x O_y$ is its oxide, and x and y are the moles of metal and oxygen, respectively, in 1 mol of the oxide.

The Gibbs energy change for the reaction is:

$$\Delta G = \Delta G^{0} + RT \ln \left[\frac{a \mathbf{M}_{x} \mathbf{O}_{y}}{(a \mathbf{M})^{x} (a \mathbf{O}_{2})^{y/2}} \right]$$

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In most cases, the activities of the solids (metal and oxide) are invarient; that is, their activities = 1 for pure solids, and for the relatively high temperatures and moderate pressures encountered in oxidation reactions, *a* can be approximated by its pressure. Therefore, at equilibrium where $\Delta G = 0$:

$$\Delta G^{0} = -RT \left[\frac{a_{\text{prod}}}{a_{\text{react}}} \right] = +\frac{y}{2} RT \ln pO_{2}$$

where pO_2 is the partial pressure of oxygen.

In solid solutions, such as an alloy, the partial molar Gibbs energy of a substance is usually called its chemical potential. If 1 mol of pure A is dissolved in an amount of solution so large that the solution concentration remains virtually unchanged, the Gibbs energy change for the mole of A $(\Delta \bar{G}_A)$ is:

$$\Delta \overline{G}_A = \mu_A - \mu_A^0 = RT \ln a_A$$

where μ_A^0 is the chemical potential of 1 mol of pure A, μ_A is the chemical potential of A in the solution, and a_A is the activity of A in the solution.

Thermodynamically unstable oxides are often formed in corrosion by gases. The Gibbs energy of formation of the oxide, ΔG , is less negative than for a stable oxide, but in fact an unstable oxide can often exist indefinitely with no measurable transformation. A common example is wustite (FeO), which is formed during the hot rolling of steel. Thermodynamically, it is unstable below 570 °C (1060 °F), but it remains the major component of mill scale at room temperature because the decomposition kinetics are extremely slow.

Rapid kinetics can also favor the formation of less stable oxide on an alloy. An alloy, *AB*, could oxidize to form oxides *AO* and *BO*, but if *BO* is more stable than *AO*, then any *AO* formed in contact with *B* should in theory convert to *BO* by the reaction:

$$B + AO \rightarrow BO + A$$

Nevertheless, if AO grows rapidly compared with BO and the conversion reaction is slow, then AO can be the main oxide found on the alloy.

Thermodynamically unstable crystal structures of oxides are also sometimes found. A growing oxide film tends to try to align its crystal structure in some way with that of the substrate from which it is growing. This epitaxy can cause the formation of an unstable structure that fits the substrate best. For example, cubic aluminum oxide (Al_2O_3) may form on aluminum alloys instead of the stable rhombohedral Al_2O_3 .

11.1 Free Energy-Temperature Diagrams

Metal oxides become less stable as the temperature increases. The relative stabilities of oxides are usually shown on a Gibbs energy-temperature diagram, sometimes called an Ellingham diagram (Fig. 11.1), for common metals in equilibrium with their oxides. Similar diagrams are available for sulfides, nitrides, and other gas-metal reactions. In Fig. 11.1, the reaction plotted in every case is:

$$\frac{2x}{y}\mathbf{M} + \mathbf{O}_2 = \frac{2}{y}\mathbf{M}_x\mathbf{O}_y$$



Fig. 11.1 Standard Gibbs energies of formation of selected oxides as a function of temperature. Source: Ref 11.1 as published in Ref 11.2

That is, 1 mol of O_2 gas is always the reactant, so that:

$$\Delta G^0 = RT \ln pO_2$$

For example, the Gibbs energy of formation of Al_2O_3 at 1000 °C (1830 °F), as read from Fig. 11.1, is approximately –840 kJ (–200 kcal) for 2/3 mol of Al_2O_3 .

The equilibrium partial pressure of O_2 is:

$$pO_2 = \exp\left(\frac{\Delta G^0}{RT}\right)$$

and can also be read directly from Fig. 11.1 without calculation by use of the *p* scale along the bottom and right side of the diagram. A straight line drawn from the index point labeled "0" at the upper left of the diagram, through the 1000 °C (1830 °F) point on the Al/Al₂O₃ line intersects the *p* scale at approximately 10^{-35} atm, which is the O₂ partial pressure in equilibrium with aluminum and Al₂O₃ at 1000 °C (1830 °F). This means that any O₂ pressure greater than 10^{-35} atm tends to oxidize more aluminum, while Al₂O₃ would tend to decompose to Al + O₂ only if the pressure could be reduced to below 10^{-35} atm. Obviously, Al₂O₃ is an extremely stable oxide.

The oxidation of a metal by water vapor can be determined in the same way. The reaction is:

$$xM + yH_2O = M_xO_y + yH_2$$

The equilibrium $pH_2:pH_2O$ ratio for any oxide at any temperature can be found by constructing a line from the H index point on the left side of Fig. 11.1. For example, for the reaction:

$$2AI(1) + 3H_2O(g) = A_2O_3(s) + 3H_2(g)$$

at 1000 °C (1830 °F), the equilibrium H_2 : H_2O ratio is 10¹⁰. A ratio greater than this will tend to drive the reaction to the left, reducing Al_2O_3 to the metal. A ratio less than 10¹⁰ produces more oxide.

Similarly, the oxidation of metals by carbon dioxide (CO_2) is also shown on Fig. 11.1. For the reaction:

$$xM + yCO_2 = M_xO_y + yCO$$

the equilibrium carbon monoxide (CO): CO_2 ratio is found from the index point marked "C" on the left side of the diagram. Oxidation of aluminum

by CO₂ has an equilibrium CO:CO₂ ratio approximately 10^{10} at 1000 °C (1830 °F).

11.2 Isothermal Stability Diagrams

For situations that are more complicated than a single metal in a single oxidizing gas, it is common to fix the temperature at some practical value and plot the other variables of gas pressures or alloy composition against each other. This produces isothermal stability diagrams, or predominance area diagrams, which show the species that will be most stable in any set of circumstances.

One Metal and Two Gases. These diagrams, often called Kellogg diagrams, are constructed from the standard Gibbs energies of formation, ΔG^0 , of all elements and compounds likely to be present in the system. For example, for the Ni-OS system, the ΔG^0 values of nickel monoxide (NiO) (s), nickel monosulfide (NiS) (l), nickel sulfate (NiSO4) (s), sulfur dioxide (SO₂) (g), sulfur trioxide (SO₃) (g), and S (l) are needed.

In Fig. 11.2, the boundary between the Ni (s) and NiO (s) regions represents the equilibrium Ni (s) + O_2 (g) = NiO (s); therefore, the diagram shows that at 977 °C (1790 °F), any O_2 pressure above approximately 10^{-11} atm will tend to form NiO from metallic nickel if pS_2 is low. Similarly, S_2 gas pressure greater than approximately 10^{-7} atm will form NiS from nickel at low pS_2 . Also, a mixed gas of 10^{-5} atm each of S_2 and O_2 should form nearly the equilibrium ratio of NiO (s) and NiSO₄ (s).



Fig. 11.2 The Ni-O-S system at 977 °C (1790 °F). Source: Ref 11.3 as published in Ref 11.2

If the principal gases of interest were SO₂ and O₂, the same ΔG^0 data could be used to construct a diagram of log *p* versus *p*SO₂, or as in Fig. 11.2, *p*SO₂ isobars can be added to the figure (the dotted lines). Thus, a mixed gas of 10⁻⁵ atm each of SO₂ and O₂ will form only NiO at 977 °C (1790 °F), with neither the sulfide nor sulfate being as stable.

When nickel metal is heated to 977 °C (1790 °F) in the open air with sulfur-containing gases, $pSO_2 + pS_2 + pO_2 \approx 0.2$ atm. The situation is shown by the dashed line in Fig. 11.2 labeled p = 0.2 atm.

An Alloy System and a Gas. Isothermal stability diagrams for oxidation of many important alloy systems have been worked out, such as that for the Fe-Cr-O system shown in Fig. 11.3. In this diagram, the mole fraction of chromium in the alloy is plotted against log pO_2 so that for any alloy composition the most stable oxide or mixture of oxides is shown at any gas pressure.

For an alloy system in gases containing more than one reactive component, the pressures of all but one of the gases must be fixed at reasonable values to be able to draw an isothermal stability diagram in two dimensions. Figure 11.4 shows an example of such a situation: the Fe-Zn system in equilibrium with sulfur and oxygen-containing gases, with SO₂ pressure set at 1 atm and temperature set at 890 °C (1635 °F).



Fig. 11.3 Stability diagram for the Fe-Cr-O system at 1300 °C (2370 °F). Source: Ref 11.2



Fig. 11.4 The Fe-Zn-S-O system for p = 1 atm at 890 °C (1635 °F). Source: Ref 11.4 as published in Ref 11.2

11.3 Limitations of Predominance Area Diagrams

Isothermal stability diagrams, like all predominance area diagrams, must be read with an understanding of their rules:

- Each area on the diagram is labeled with the predominant phase that is stable under the specified conditions of pressure or temperature. Other phases may also be stable in that area, but in smaller amounts.
- The boundary line separating two predominance areas shows the conditions of equilibrium between the two phases.

Also, the limitations of the diagrams must be understood to be able to use them intelligently:

- The diagrams are for the equilibrium situation. Equilibrium may be reached quickly in high-temperature oxidation, but if the metal is then cooled, equilibrium is often not reestablished.
- Microenvironments, such as gases in voids or cracks, can create situations that differ from the situations expected for the bulk reactant phases.
- The diagrams often show only the major components, omitting impurities that are usually present in industrial situations and may be important.

• The diagrams are based on thermodynamic data and do not show rates of reaction.

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REFERENCES

- 11.1 N. Birks and G.H. Meier, *Introduction to High Temperature Oxidation of Metals*, Edward Arnold, 1983
- 11.2 S.A. Bradford, Fundamentals of Corrosion in Gases, *Corrosion*, Vol 13, *ASM Metals Handbook*, ASM International, 1987
- 11.3 C.S. Giggins and F.S. Pettit, Corrosion of Metals and Alloys in Mixed Gas Environments at Elevated Temperatures, *Oxid. Met.*, Vol 14 (No. 5), 1980, p 363–413
- 11.4 T. Rosenqvist, Phase Equilibria in the Pyrometallurgy of Sulfide Ores, *Metall. Trans. B*, Vol 9B, 1978, p 337–351