

Oxidation

Which Materials Oxidize?

We wish engineering materials to be stable and not react with their environment, whether that environment be gas or liquid. Because we live in an oxygen-rich atmosphere, oxidation is often a concern. If a material is forming an oxide at its surface, then the underlying material is being consumed, and the engineering part is becoming weaker. Most oxide films are brittle and have poorer mechanical properties than the underlying materials.

Many ceramics are already compounds with oxygen, or they are chemically stable nitrides or carbides. This makes them inert to further combination with oxygen. Polymers generally do not react with oxygen at room temperature, though many burn at elevated temperatures. This leaves metals as the principal concern for oxidation attack.

Oxide Stability

Chemists rank the stability of oxides in terms of an “energy of formation,” often with a thermodynamic variable with the somewhat curious name of *free energy*. With the most common definition, a negative energy of formation indicates a stable oxide film that will form spontaneously on the underlying material. Conversely, a positive energy of formation indicates a stable underlying material that does not oxidize. This is somewhat irrelevant, however, as among the metals only gold is completely resistant to oxidation at all temperatures. For all other metals, the relevant question is not whether or not an oxide film will form. It will. More important is the nature of the resultant film.

Oxidation Rates

To measure the rate of oxidation, a metal sample is suspended by a platinum wire into a furnace held at a constant temperature. The wire is attached to a balance to continuously measure the mass of the wire and sample. Platinum is used for two reasons: it has a melting temperature of 1800 °C, which is higher than most other metals, and platinum itself oxidizes very slowly. To oxidize platinum to a depth of 0.1 mm at a temperature 70% of its melting point would reportedly require approximately 20 years. Thus, mass change measured during a test can be attributed entirely to the suspended metal sample.

When we examine oxidation behavior, we find that the results can be grouped into two broad categories. While one group of oxides does consume the underlying metal, the other group of oxides forms protective skins that are beneficial.

Oxidation Rates – Non-Protective Oxides

These oxide films are also described as exhibiting linear oxidation behavior from the experimental fit

$$\Delta m = k_L t,$$

where Δm is the change in mass, t is time, and k_L is a *kinetic constant* that obeys the Arrhenius law temperature dependence introduced in sub-subunit 1.5.2. Thus, k_L increases exponentially as the temperature is increased. k_L is usually positive. The sample gains weight as the oxide layer grows. However, microscopically we observe that the film either cracks or lifts off the underlying metal (called *spalling*). Fresh metal is continuously being exposed to continue oxidation. In a few cases, such as with tungsten and molybdenum, the oxides evaporate off as they form. This, too, continuously exposes fresh underlying metal, with k_L now being negative.

Oxidation Rates – Protective Oxide Films

Protective films are described as exhibiting parabolic oxidation from the experimental fit

$$(\Delta m)^2 = k_P t$$

where k_P is another kinetic constant, again obeying the Arrhenius law temperature dependence. As time increases, the rate of mass gain decreases. From calculus, we can calculate $d(\Delta m)/dt$ to find that:

$$(\text{rate of mass gain}) \sim \frac{1}{\sqrt{t}}.$$

Microscopically, we observe a tightly bonded, continuous skin. As the film increases in thickness, ions and/or electrons have to diffuse greater distances to continue oxide formation. This slows down the process. Aluminum is a familiar example. It is not that aluminum does not oxidize. Rather, the oxide skin that quickly forms is resistant to further growth. Titanium behaves similarly. Other examples are electronic chips based on silicon wafers. By purposely heating to form SiO_2 , the components are protected by a thin layer of glass.