Ab initio Thermodynamics of Oxide Phase Stability

The stability of metals and metal oxides at elevated temperatures is a crucial problem in many industries such as aerospace, power generation, metallurgical processing, chemical engineering, automotive, petrochemicals, and catalysis. Will a catalyst remain stable at elevated temperature or revert to an inactive form? Might formation of a non-protecting oxide film cause loss of strength in a supersonic aircraft?

To address these questions, scientists at Accelrys employed a combination of tools (classical thermodynamics & ab initio quantum mechanics) to compute Ellingham[1] diagrams, plots of the standard free energy of reaction ($\Delta G°$) vs. temperature. The stability of materials at high temperatures has been traditionally investigated in metallurgy and materials engineering using such plots. Ellingham diagrams provide a simple and rapid means to determine the threshold temperature and oxygen pressure required for oxide formation. Formation of oxides is the most common reaction in high temperature corrosive environments, and therefore has a direct relevance to the industries mentioned above.

The study focussed on the oxidation of corundum-type oxides (M_2O_3) into rutile-type structures (MO_2), where M=Rh and Ru. These metals were considered because of their relevance in industrial catalytic processes. Both, Rh and Ru oxides occur naturally in the rutile structure. However, whereas rutile-type RuO2 has proved to be the preferred phase over a wide range of temperatures and pressures, its rhodium isomorph (RhO_2) transforms into the corundum form (alpha-Rh_2O_3) at 750 °C under ambient oxygen pressure. This is a known component in the poisoning of three-way emission catalysts. The corundum form of ruthenium oxide (Ru_2O_3), in contrast, has never been observed. Why the difference?

The present results combining CASTEP density functional calculations with classical thermodynamics techniques predict that a Ru_2O_3 phase cannot be observed due to the high stability of RuO$_2$ with respect to reactions due to both Ru and ambient oxygen.[2] In contrast, the ambient oxygen pressure at which alpha-Rh_2O_3 decomposes into RhO_2 was found to increase with temperature[3] consistently with experimental findings.[4]
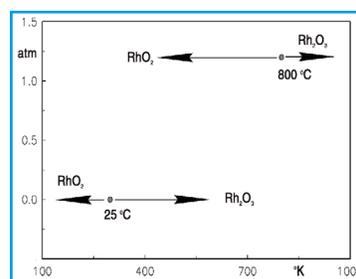
▲ *Figure 1. Calculated oxygen partial pressure in atm vs temperature (K) for a-Rh_2O_3 decomposition into RhO_2 at 298 K (25 °C) 1073 K (800 °C), respectively. Oxygen pressure and temperature regimes at which the alpha-Rh_2O_3, or alternatively, the RhO_2 phase is thermodynamically preferred are indicated by arrows pointing right or left, respectively.*

Techniques like the ones employed here provide rapid and cost-effective ways of predicting the behavior of metal oxides in high temperature environments. By employing modeling methods, a broad range of elements, crystal structures, and environmental conditions can be screened rapidly in silico, and the results provided in a commonly-used representation.

References

1. See http://www.corrosion-doctors.org/HotCorrosion/ellingham.htm

2. M. E. Grillo, *Phys. Rev. B* **70**, 184115 (2004).

3 . M. E. Grillo, *Comp. Mat. Sci.* **33**, 83 (2005).

4 . G. Bayer and H. G. Wiedemann, *Thermochim. Acta* **15**, 213 (1976).

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