

# High Temperature Materials Corrosion Challenges for Energy Conversion Technologies

by Elizabeth Opila

Energy conversion processes are often employed at high temperatures to increase thermodynamic efficiencies or to provide enhanced kinetics for electrochemical processes. While high temperature operation offers these benefits, the thermodynamic driving force and kinetics of any accompanying high temperature corrosion processes are also increased. In this paper, corrosion issues relevant to energy conversion by Rankine cycle, Brayton cycle turbines, nuclear power, solid oxide fuel cells, high temperature thermoelectric systems, and solar concentrator systems are discussed. Corrosion mechanisms, component life prediction, and strategies for mitigating high temperature corrosion specific to each energy technology are addressed.

## What Is High Temperature Corrosion?

High temperature corrosion is the chemical attack of solid functional or structural materials resulting in degradation of the desired properties. Typically the material reacts with a gaseous environment consuming the material of interest, often forming undesirable reaction products. Carl Wagner developed the theory elucidating the electrochemical nature of high temperature corrosion whereby continued formation of reaction products occurs by transport of electronic and ionic species in the solid state product phase.<sup>1</sup> The definition of “high temperature” can begin at temperatures as low as 300 to 500°C, where water is present as a vapor rather than liquid (cf. aqueous corrosion), but can vary with material systems. For example zirconium nuclear fuel cladding oxidation is a catastrophic problem at 1200°C whereas oxidation of SiC is minimal at this temperature.

High temperature corrosion scientists attempt to understand the driving forces for the corrosion processes as well as the rate at which corrosion occurs. Thus corrosion mechanisms are described in terms of the thermodynamics and kinetics of reactions. Which products will form and at what rate? Thermodynamic stability of corrosion products are typically calculated using free energy minimization techniques now easily conducted with commercially available software (FactSage,<sup>2</sup> Thermocalc,<sup>3</sup> Pandat<sup>4</sup>). Accuracy of these results relies on complete thermochemical databases, which are not available for all material systems. *Ab initio* Density Functional Theory is a valuable method to calculate thermodynamic

data where none are available; however, experimental validation may still be required, especially for transition metal oxides where theory is still maturing.<sup>5</sup> The relative stability of oxide corrosion products are shown on an Ellingham-Richardson diagram as shown in Fig. 1. Oxides shown lower on the plot have a larger negative free energy of formation and are thus more stable.

Understanding kinetics of high temperature reactions requires characterization of changes in the complex phase assemblages of both reactants and products found in most energy applications. The rate of the corrosion reaction can be limited by surface chemical reactions, solid state diffusion through corrosion products in which condensed phase defect chemistry dominates, liquid phase diffusion, or gas phase transport processes. Figure 2 shows the relative solid state diffusion rate of dominant diffusing species<sup>6</sup> for a number of technologically relevant oxides.

The formation of liquid or gaseous corrosion products must also be considered since these reactions can be dominated by diffusion processes that are much faster than solid state transport considered above.

The formation of liquid corrosion products from salts and slags can result in dissolution of protective solid oxides. The continued dissolution and precipitation of reaction products in liquid films existing in chemical potential gradients results in a continuous fluxing process that rapidly consumes the underlying structural material.<sup>7</sup> Many energy conversion technologies including combustion processes (Brayton, Rankine cycles) or electrochemical conversion of hydrogen (SOFC) produce high temperature water vapor products. Water vapor is especially reactive and can degrade both metals and oxides by the formation of gaseous metal hydroxides. Knowledge of stable gaseous metal hydroxides as well as the rate at which they form is essential to predicting material degradation in many energy conversion applications, as recently summarized.<sup>8</sup>

The challenge of predicting and increasing thermochemical lifetimes of complex material systems in complex environments is to understand the interplay between the formation of equilibrium phases predicted by thermodynamics (Fig. 1) versus the reaction kinetics (Fig. 2). Materials systems for high

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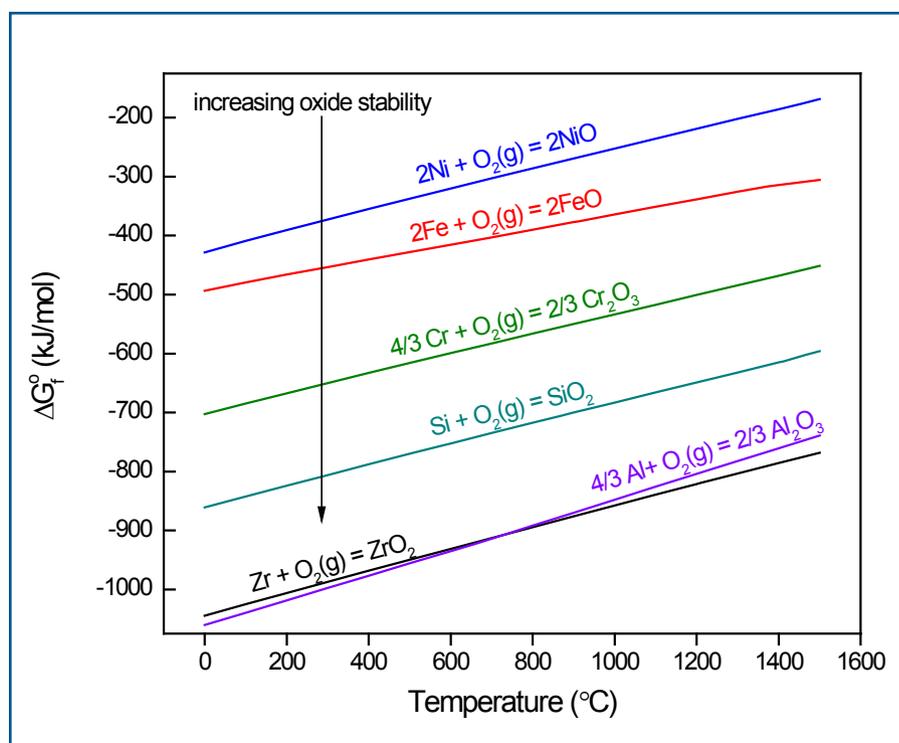


FIG. 1. Ellingham diagram portraying relative stability of oxides relevant to high temperature corrosion. Data from FactSage Pure Substance data base.<sup>2</sup>

temperature applications should be designed so that slow growing reaction products are thermodynamically stable and allowed to establish protective diffusion barriers. For example in aluminum-containing Ni-base superalloys the thermodynamically stable oxidation product is  $\text{Al}_2\text{O}_3$ , whereas NiO, being a more defective oxide, grows more rapidly. Alloy designers have identified the critical levels of aluminum in Ni-base superalloys required to establish slow growing  $\text{Al}_2\text{O}_3$  scales rather than faster forming NiO scales. In some cases, highly stable corrosion products can form with rapid reaction kinetics, e.g.,  $\text{ZrO}_2$  formation from Zr oxidation, or liquid and gaseous products can form making mitigation of high temperature corrosion challenging.

The following sections explore high temperature corrosion issues important for a series of energy conversion technologies. This discussion is not exhaustive but highlights critical degradation issues in high temperature energy technologies. When available, strategies for mitigating the high temperature corrosion reactions are also described.

### Power Generation by Rankine or Brayton Cycles

Conventional coal-fired power plants generate power via the Rankine cycle in which the combustion process is used to heat water to produce steam that powers a turbine, generating electricity. The fireside and steam side of chromia-forming ferritic steels typically used for the heater tubes present different corrosion problems.<sup>9</sup> Coal has a wide variety of chemistries<sup>10</sup> that result in varying amounts of sulfur and chlorine in the combustion environment as well as widely varying oxide ash compositions containing Al, Si, Ca, Fe, K, Na, and Mg oxides. Challenges for predicting the corrosion reactions on the fireside of the boiler include the formation of nonequilibrium phases as combustion products and as condensates (such as sulfides and sulfates) in cooler portions of the boiler tubes. Corrosion by  $\text{HCl}(\text{g})$  and rapid corrosion when low melting temperature sulfates form are major concerns. Degradation on the steam side of the heater tubes is related to the high water vapor contents and its effect on oxide morphology, oxide adherence, and oxide volatility.<sup>11</sup> Coal can also be gasified to form syngas ( $\text{CO}(\text{g}) + \text{H}_2(\text{g})$ ) in an integrated combined cycle, using heat to power a conventional steam turbine and employing the syngas in a Brayton cycle gas-fired turbine. Water vapor attack is again the prime concern in the gas-turbine environment where the higher temperatures can necessitate the use of Ni-base alloys rather than steel.

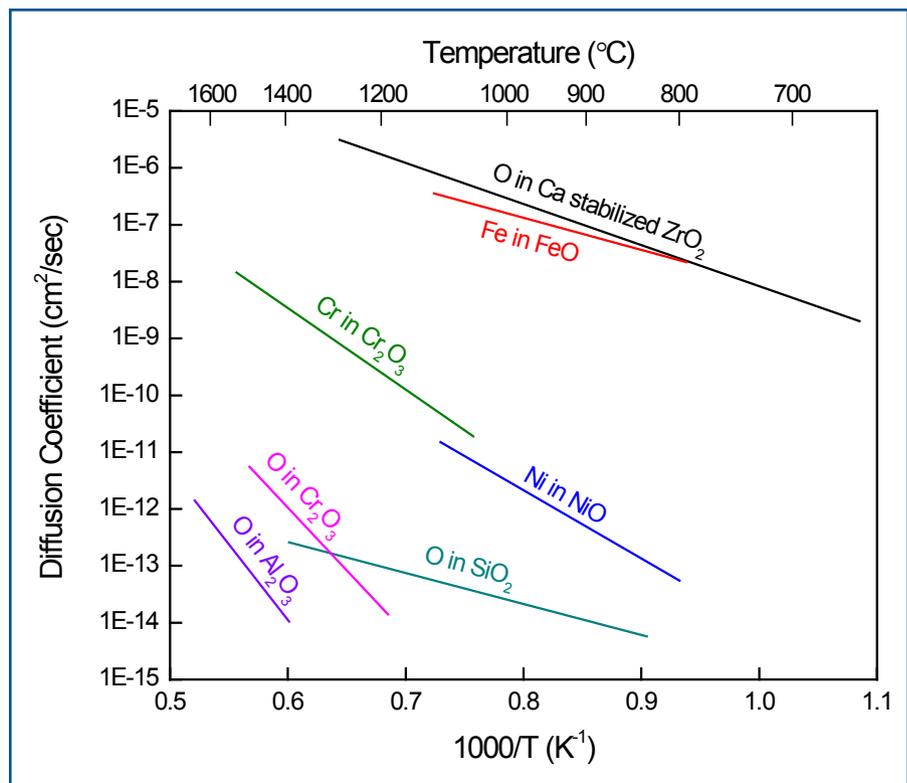


FIG. 2. Diffusion coefficients in oxides relevant to high temperature corrosion. Data from *Introduction to Ceramics*.<sup>6</sup>

Efforts to increase efficiency and/or more effectively capture carbon include using oxygen instead of air (oxyfiring) or increasing the steam temperature from about 600°C to 760°C (Advanced Ultra-Supercritical).<sup>9</sup> The increased temperatures and high steam contents will result in more rapid material degradation and the need for higher-temperature Ni-base alloys.

Natural gas is an alternative fuel to coal which is used in a combined cycle (Rankine plus Brayton). The gas-fired turbines operate at higher temperatures, thus alloy/coating system life is limited due to more rapid diffusion and oxidation rates. Just as for coal-fired power generation, the desire to increase efficiencies and lower emissions drives the search for higher temperature materials.

Significant efforts to replace fossil fuels with biomass are being made, especially in Europe. Biomass (e.g., straw and grass) typically contains higher alkali and chlorine contents than coal, but lower sulfur.<sup>12</sup> Chlorine can result in the formation of stable gaseous metal chlorides such as  $\text{FeCl}_3(\text{g})$ , non-adherent oxide layers, and low-melting phases, all of which accelerate the consumption of the underlying alloy.

Improved material performance is sought for all conditions by developing higher temperature alloys or more corrosion resistance coatings, typically containing more Cr or Al. These solutions are expensive, so significant increases in efficiencies, longer lifetimes, or reduced emissions are required.

### Nuclear Power

Nuclear power plants typically use fissile  $^{235}\text{UO}_2$  as fuel. Fission results in the release of thermal energy that is used to heat pressurized water. The pressurized water flows through heat exchanger tubes, heating secondary water to produce steam which drives a turbine using the Rankine cycle. Under normal operating conditions, aqueous corrosion of reactor components is the degradation mode of concern. Aqueous corrosion is outside the scope of this review. However, under Loss of Coolant Accident (LOCA) conditions, temperatures rapidly increase and high temperature corrosion reactions control the reactor failure and radioactive product release. These mechanisms recently achieved notice in light of the reactor failures at the Fukushima Daiichi power plant after the magnitude 9.0 earthquake and resulting tsunami.<sup>13</sup> Three high temperature reaction mechanisms during LOCA are of particular note. First, the zirconium alloy (Zircaloy) fuel cladding reacts with steam. Due to the exothermic nature of Reaction 1



oxidation proceeds at a runaway rate at temperatures above about 1200°C generating large amounts of hydrogen.<sup>14</sup> The high levels of hydrogen can result in explosions which damage the reactor containment systems. Second, volatile fission products are released from the fuel

matrix, react with the steam/hydrogen gas mixture flowing through the reactor core and can be released into the environment through the damaged containment.<sup>15</sup> Finally, the high temperature fuel reacts with reactor vessel and structural materials forming a molten mixture. Subsequent injection of water can result in dissolution of the reacted fuel mixture which can be released to the environment with subsequent cooling water leaks.<sup>16</sup>

Of these three, issues, the oxidation of zirconium alloys is most well understood.<sup>14,17</sup> Current research focuses on developing alternative fuel cladding materials to replace zirconium alloys with more slowly oxidizing materials. Figure 1 shows that SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Cr<sub>2</sub>O<sub>3</sub> are all stable oxides, and more importantly, Fig. 2 shows that oxygen transport through these oxides is significantly slower than that through ZrO<sub>2</sub>. Thus Si-, Al-, and Cr- containing materials are all candidates for fuel cladding with better oxidation performance in LOCA. Cheng *et al.* examined the oxidation rates of alternative cladding materials and concluded that SiC, high Cr (>20 wt%) alloys or Al-forming alloys all show significantly improved oxidation resistance at high temperature LOCA conditions. The oxide scale thickness generated in 8 h at 1200°C in 1 MPA steam for candidate cladding materials are compared to Zircaloy-2 in Fig. 3. The oxide scale thickness is a relative measure of the oxidation rate, and thus the amount of hydrogen generated in reactions similar to reaction 1. Further evaluation of these candidate fuel cladding materials, including their response to radiation exposure, is needed.

A second area of concern during LOCA, is the release of fission products during vaporization reactions. Short lived fission products including <sup>131</sup>I and <sup>137</sup>Cs are of interest due to their radioactive danger. Vapor species such as Cs(OH) and CsI are expected to form in amounts greater than the metal vapor partial pressures, increasing transport rates out of the hot

core. Cubicciotti<sup>15</sup> has calculated the equilibrium partial pressures of these and many other fission vapor products as a function of temperature, H<sub>2</sub>O/H<sub>2</sub> ratio and pressure under LOCA-relevant conditions. Equilibrium calculations are expected to be relevant due to the high temperatures of interest. In addition, Cubicciotti<sup>18</sup> also calculated vapor transport rates based on his equilibrium thermodynamic calculations. Many of the calculations use estimated thermochemical data, demonstrating the need for more accurate thermochemical measurements and calculations.

Finally, consideration of reactions occurring during reactor core melting are of importance. Melted fuel will react with concrete,<sup>18</sup> stainless steel reactor vessel components and zirconium alloy fuel cladding as well as other structural components of the reactor.<sup>16</sup> The resulting phase assemblage is expected to be very complex<sup>16</sup> with long-term environmental hazards due to potential radioactive material release if complete isolation of contaminated water is not maintained.

Development of more oxidation resistant fuel cladding and improved thermochemical data for gas, liquid, and solid phases formed during LOCA events are needed.

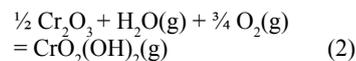
### Solid Oxide Fuel Cells

Solid Oxide Fuel Cells (SOFC) offer increased efficiencies relative to combustion by the direct electrochemical conversion of hydrogen and other more complex fuels to electricity. Because SOFCs operate at intermediate (500-700°C) or high (700-900°C) temperatures relative to PEM fuel cells, they offer the advantages of fuel flexibility and lower cost catalysts. The advantages of operation at elevated temperatures, however, also results in high temperature materials degradation issues.

SOFCs are complex systems typically consisting of (La,Sr)MnO<sub>3</sub> (LSM) cathodes, Y<sub>2</sub>O<sub>3</sub>-stabilized ZrO<sub>2</sub> (YSZ)

electrolytes, Ni-YSZ anodes, ferritic Fe-Cr interconnects as well as glass sealants. Thermochemical degradation mechanisms include (1) poisoning of active surfaces by species resulting from fuel impurities or volatilization of SOFC components, and (2) solid state interdiffusion and reaction between various cell components. Yokokawa has recently assessed material degradation mechanisms that affect durability and reliability of SOFCs.<sup>19</sup> Research needs for increased thermochemical durability of SOFCs are also cited in a companion article in this issue.<sup>20</sup>

One important degradation reaction is the paralinear oxidation of Fe-Cr interconnect materials to form Cr<sub>2</sub>O<sub>3</sub> with simultaneous volatilization of the oxide by the following reaction:



The formation of the CrO<sub>2</sub>(OH)<sub>2</sub> gaseous species results in Cr-poisoning of the cathode. Thermodynamics for Reaction 2 have recently been established allowing for more accurate prediction of poisoning rates.<sup>21,22</sup> This problem has been somewhat mitigated by the development of interconnect alloys that oxidize to form less volatile oxides, or oxides that do not result in cathode poisoning.<sup>23</sup>

An example of solid state interdiffusion and reaction is the formation of La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> from reaction of the LSM cathode and YSZ electrolyte.<sup>19</sup> Alternative cathode and electrolyte compositions are being investigated with the goal of sufficient electrochemical activity at lower temperatures where diffusion is less of a problem. Materials under investigation include lanthanum strontium cobaltite cathodes and lanthanum strontium gallium magnesium oxide electrolytes. Movement to intermediate temperature oxide fuel cells can reduce both the thermodynamic driving force and the kinetics for degradation reactions.

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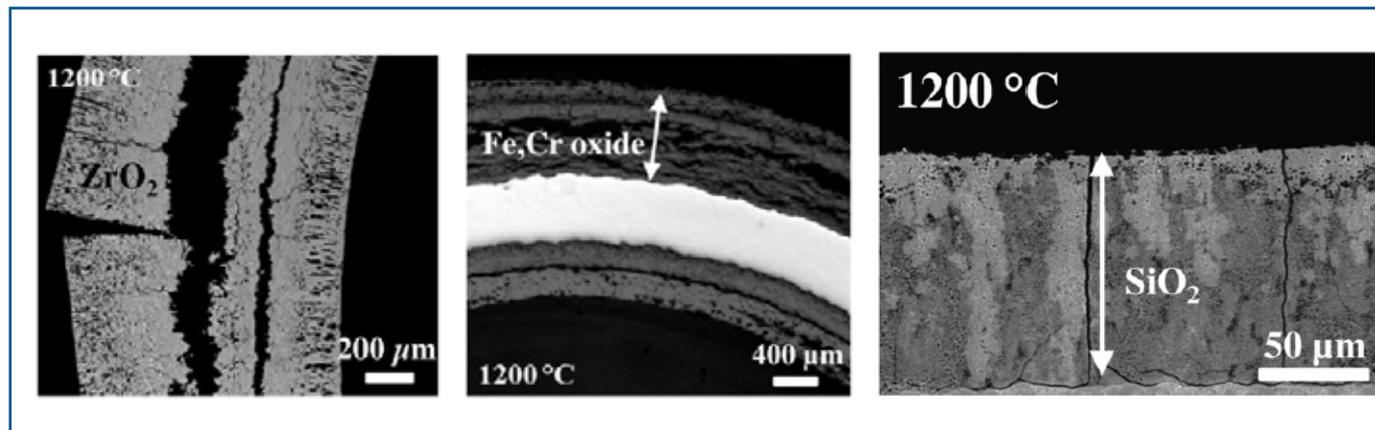


Fig. 3. Oxides formed on Zircaloy 2, 317 stainless steel and SiC (left to right) after exposure at 1200°C in 1 MPA steam for 8 hours.<sup>17</sup>

## Thermoelectric Energy Conversion

Thermoelectric devices convert heat directly to electrical energy based on the Seebeck effect. Charge carriers, electrons, and holes, diffuse in a temperature gradient from the hot side to the cold side leading to measurable current flow. Thermoelectric materials have been used for deep space probes and are now proposed for waste heat recovery from conventional Rankine and Stirling power generation technologies as well as other industrial processes and transportation systems.<sup>24</sup> The efficiency of thermoelectric materials depends on a high electrical conductivity decoupled from a low thermal conductivity as measured by a figure of merit ZT. Most thermoelectric research focuses on increasing this figure of merit.<sup>24-26</sup> The best thermoelectric materials are narrow band gap semiconductors, limiting property optimization strategies. Thermal conductivity is reduced through the choice of complex crystal lattices or introduction of nanoscale grain or phase boundaries that scatter phonons. Electrical conductivity is increased via doping. The theoretical efficiency of thermoelectric devices can also be improved by increasing the temperature difference between the hot-side and cold-side of the thermoelectric thus driving the move to higher temperature materials.

Many of the highest ZT materials are antimonides and tellurides, which suffer from high sublimation rates and poor oxidation resistance.<sup>27</sup> For example, antimony vaporizes to form Sb, Sb<sub>2</sub>, Sb<sub>3</sub>, Sb<sub>4</sub> species that can reach very high partial pressures and result in rapid consumption of the solid thermoelectric device.<sup>27</sup> In addition, antimony is very reactive with typical metallic contact materials, so that diffusion barrier layers are likely needed to prevent degradation of interconnects. The high temperature durability of thermoelectrics is a research area that is somewhat neglected, though vital for application of thermoelectrics to waste heat recovery.

Some research is being conducted on half Heusler intermetallic compounds<sup>25</sup> or even oxide thermoelectric materials<sup>28</sup> that would be significantly more stable in high temperature oxidizing conditions. The identification, characterization, and development of earth-abundant, nontoxic, moderately efficient thermoelectric materials for waste heat recovery is an area of interest that warrants additional research effort.

## Concentrated Solar Power

Concentrated Solar Power (CSP) conversion to heat is an energy technology currently receiving substantial interest, as in the U.S. Department of Energy Sun

Shot Initiative announced in 2011 (<http://www1.eere.energy.gov/solar/sunshot/csp.html>). CSP offers advantages over photovoltaic electricity generation in the use of broad-spectrum sunlight and potential for hybridization with other technologies to store and convert heat to shift power generation from peak sunlight times. CSP collector concepts include parabolic troughs, heliostat fields, linear Fresnel reflectors, and parabolic dish concepts.<sup>29</sup> Each concept offers potential advantages in interfacing with heat storage, as well as installation and operational cost. In addition, operating temperatures vary from 300 to 2000°C, which affects materials degradation mechanisms and rates. Thermochemical degradation of solar receiver tubes, cavity receivers, or particle receiver materials is an area of concern, especially for heliostat fields and associated tower receivers that operate at the highest temperatures. Heliostat field collectors have a low level of technology maturity, and thus research in the area is just beginning.

Solar collectors must be matched to appropriate heat storage concepts. Heat storage can be accomplished via sensible heat (heating a material), latent heat (phase change), or chemical heat (reversible chemical reaction).<sup>30</sup> Molten salts such as NaNO<sub>3</sub> and KNO<sub>3</sub> can be used as Heat Transfer Fluids (HTF) or phase change materials due to their high sensible and latent heats in the temperature range of 100 to 600°C. LiF and alkali carbonates have potential as phase change materials at temperatures up to about 900°C. Reversible metal-metal oxide reactions are another method to store heat. In many cases molten salt or molten metals are envisioned as components of the heat storage concept. Corrosion of storage tanks in contact with molten salts or metals is a concern for long term application of solar concentrators. Molten salts are already used in the chemical and metals industries providing an experience base for corrosion issues.<sup>30</sup> Some concepts would employ particles as heat transfer materials, thus eliminating liquid phase corrosion problems. Concentrated solar power can also be directly employed to produce hydrogen by high temperature water splitting as described in a companion paper in this issue.<sup>31</sup> High temperature water vapor interactions with the active materials then become a concern as previously described for combustion and SOFC environments.

## Summary

Many energy conversion technologies operate at high temperatures where oxidation/corrosion driving forces can be large and degradation reaction kinetics are fast. Thermodynamics and kinetics of reactions between components and environments within the energy conversion system must be considered to predict system lifetimes. Common aspects of materials

development and materials choices exist across conventional Rankine cycle, Brayton cycle, nuclear power, solid oxide fuel cell, thermoelectrics, and concentrated solar power. High temperature materials with slow growing stable oxide phases are most desirable. Molten corrosion products or heat transfer fluids can increase degradation rates. Sublimation and volatilization reactions can form gaseous products at very rapid rates and must be accounted for. Thermochemical data are needed to predict material lifetimes in the extreme environments of high temperature energy conversion technologies. ■

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## References

1. G. Y. Yurek, "Mechanisms of Diffusion-Controlled High-Temperature Oxidation of Metals," pp. 397-446 in *Corrosion Mechanisms*, Edited by F. Mansfeld. Marcel Dekker, Inc., New York, 1987.
2. C. W. Bale, P. Chartrand, S. A. Degterov, G. Eriksson, K. Hack, R. Ben Mahfoud, J. Melançon, A. D. Pelton, and S. Petersen, *Calphad*, **26**, 189 (2002).
3. J. Andersson, T. Helander, L. Höglund, P. Shi, and B. Sundman, *Calphad*, **26**, 273 (2002).
4. S. Chen, S. Daniel, F. Zhang, Y. A. Chang, X.-Y. Yan, F.-Y. Xie, R. Schmid-Fetzer, and W. A. Oates, *J. Chem. Phys.*, **136**, 150901 (2012).
6. W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, *Introduction to Ceramics*; p. 240, John Wiley & Sons, New York, 1976.
7. R. A. Rapp, *Metallurgical and Materials Transactions A*, **31A**, 2105 (2000).
8. P. J. Meschter, E. J. Opila, and N. S. Jacobson, *Ann. Rev. Mater. Res.*, **43**, 559 (2013).
9. B. Pint, *JOM*, **65**, 1024 (2013).
10. S. C. Kung, *Oxidation Metals*, **77**, 289 (2012).

11. S. R. J. Saunders, M. Monteiro, and F. Rizzo, *Progress in Materials Science*, **53**, 775 (2008).
12. H. P. Nielsen, F. J. Frandsen, K. Dam-Johansen, and L. Baxter, *Progress in Energy and Combustion Science*, **26**, 283 (2000).
13. R. Pool, *Engineering & Technology*, **6**, 32 (2011).
14. F. Tanabe, *J. Nucl. Sci. Technol.*, **49**, 18 (2012).
15. D. Cubicciotti and B. R. Sehgal. *Nucl. Technol.*, **65**, 266 (1984).
16. P. C. Burns, R. C. Ewing, and A. Navrotsky, *Science*, **335**, 1184 (2012).
17. T. Cheng, J. R. Keiser, M. P. Brady, K. A. Terrani, and B. A. Pint, *J. Nucl. Mater.*, **427**, 396 (2012).
18. D. Cubicciotti, *Pure Appl. Chem.*, **57**, 1 (1985).
19. H. Yokokawa, T. Horita, K. Yamaji, H. Kishimoto, and M. Brito, *J. Kor. Cer. Soc.*, **49**, 11 (2012).
20. J. Nicholas, *Interface*, **22(4)**, 49 (2013).
21. E. J. Opila, D. L. Myers, N. S. Jacobson, I. M. B. Nielsen, D. F. Johnson, J. K. Olminky, and M. D. Allendorf, *J. Phys. Chem. A*, **111**, 1971 (2007).
22. M. Stanislawski, E. Wessel, K. Hilpert, T. Markus, and L. Singheiser, *J. Electrochem. Soc.*, **154**, A295 (2007).
23. J. W. Fergus, *Materials Science and Engineering: A*, **397**, 271 (2005).
24. J. Fleurial, *JOM*, **61**, 79 (2009).
25. J. R. Sootsman, D. Y. Chung, and M. G. Kanatzidis, *Agnew. Chem. Int. Ed.*, **48**, 8616 (2009).
26. T. M. Tritt, *Ann. Rev. Mater. Res.*, **41**, 433 (2011).
27. J. A. Nesbitt, E. J. Opila, and M. V. Nathal, *J. Electron. Mater.*, **41**, 1267 (2012).
28. J. W. Fergus, *J. Eur. Cer. Soc.*, **32**, 525 (2012).
29. D. Barlev, R. Vidu, and P. Stroeve, *Solar Energy Mater. Solar Cells*, **95**, 2703 (2011).
30. A. Gil, M. Medrano, I. Martorell, et al., *Renewable and Sustainable Energy Reviews*, **14**, 31 (2010).
31. M. D. Allendorf, *Interface*, **22(4)**, 63 (2013).



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