High Temperature Vaporization into Different Environments

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MS&T 2019
Thermodynamics of Materials in Extreme Environments
October 2, 2019
Portland, OR
Vaporization

• At the appropriate temperature, all materials exhibit some degree of vaporization

• May be the limiting factor at high temperatures

• How does the amount of vaporization (net vapor flux) depend on the environment above the sample?
  – Vacuum (e.g. heat treatment)
  – Static Gas (e.g. heat treatment, processing)
  – Flowing Gas (e.g. gas turbine)
    • Laminar Flow
    • Turbulent Flow

• Model SiO₂ vaporization → SiO(g) + ½ O₂(g) (primary route)
  → SiO₂(g)

• Model each with equations from kinetic theory, fluid flow
  Flowing gases can also be modeled with Computational Fluid Dynamics (CFD)
Quantify Vaporization

• Thermochemical: Use partial pressure

• Focus on Vapor: Use $J_i$, vapor flux (mole/unit area-unit time) or (weight/unit area-unit time)

\[ J_i = \frac{h_i}{RT} (P_{i,S} - P_{i,\infty}) \]

\[ h_i = \text{Mass transfer coefficient} \]

• Focus on oxidation/corrosion issues of structural materials, use $R_i$, recession rate (unit length/unit time)

\[ R_i = \frac{\Sigma_i J_i}{\rho} \]

\[ \rho = \text{Density of oxide} \]
Vaporization into a Vacuum, Static Gas, Flowing Gas

Vacuum

Static over pressure

Laminar flow

Turbulent flow

Increasing free stream gas velocity, $v_\infty$

HKL equation

$$J_v = \frac{\alpha_v [P_{eq}(MO)]}{\sqrt{2\pi MRT}}$$

Fick’s first law

$$J = -\frac{D}{RT} \frac{P_{surf}}{d}$$

Laminar flow

$$J_l = 0.665 (Re)^{0.5} (Sc)^{0.33} \frac{D_i(p_{i,s})}{L}$$

Turbulent flow

$$J_t = 0.0365 (Re)^{0.8} (Sc)^{0.33} \frac{D_i p_t}{RTL}$$

Also model with CFD
Vaporization of Clean Surface into a Vacuum

- Derive flux from kinetic theory of gases
  - \( J = \frac{\alpha P}{(2\pi MRT)^{0.5}} \)
  - \( \alpha \) = vaporization coefficient (kinetic factor)

- Fundamental models* of vaporization developed from these conditions
  - Terrace-Ledge-Kink model
  - Vaporizing species moves to smaller coordination number site
  - \( A(s) \rightarrow A(l) \rightarrow A(a) \rightarrow A(g) \)

Vaporization from a SiO$_2$ coupon in a Vacuum

\[ J = \frac{\alpha P_{eq}(MO)}{\sqrt{2\pi MR T}} \]

\( \alpha = \text{vaporization coefficient (kinetic factor)} \)

- \( \alpha(\text{Pure metals}) \sim 1 \)
- \( \alpha(\text{Oxides}) \) 1 to \( 10^{-6} \)!
- \( \alpha(\text{SiO}_2) = (5 - 22) \times 10^{-3} \)
Vaporization into a Static Gas

- Inert Gas: Kinetic effect only
  - Fick’s first law
    \[ J_i = -D_i \frac{dc_i}{dx} = -D_i \frac{dP_i}{RT} \frac{dx}{dP_i} \approx -D_i \frac{P_o}{RT} \frac{1}{x} \]
  - Flux \( \propto \frac{1}{x} \)

- Reactive Gas
  - Kinetic effect
  - Thermodynamic Effect
    - Suppress vaporization
      \(-\text{SiO}_2(\text{s}) = \text{SiO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})\)
    - Enhance vaporization
      \(-\text{Cr}_2\text{O}_3(\text{s}) + \frac{3}{2} \text{O}_2(\text{g}) = 2\text{CrO}_3(\text{g})\)
Reactive Gas Over Pressure

Best shown with volatility diagrams (Kellogg 1966)

- Plot of $\log P(M_xO_y(g))$ vs $\log P(O_2)$
- Negative slope means: $\uparrow P(O_2)$, $\downarrow P(M_xO_y)$
  - $SiO_2$, $Al_2O_3$
- Positive slope means: $\uparrow P(O_2)$, $\uparrow P(M_xO_y)$
  - $Cr_2O_3$

Kohl et al., NASA TM-X-73682
Flowing Gas: Developing Boundary Layer

- Laminar $\rightarrow$ Turbulent by increasing Reynolds number
- $Re_x = \frac{\rho VL}{\mu}$ Increases with increasing $\rho$, $v$, $L$

- Velocity boundary layer: Edge at 99% of free stream velocity
- Turbulent region has steep gradient in velocity near surface: viscous sublayer
- Viscous sub-layer limits vapor flux; Flux in rapidly flowing inert gas = Flux in vacuum
Comparison of Fluxes for each Condition

\[ J(\text{vacuum with } \alpha = 1) > J(\text{vacuum with } \alpha = 0.02, \text{turbulent}) > J(\text{Laminar, static}) \]
Computational Fluid Dynamics (CFD): Maria Kuczmarski

- Set up small cells around samples
- Conservation of mass, momentum, energy within each cell.
- Define the problem
  - Coupon in a furnace: Model half the system to utilize symmetry

  - Steady state, incompressible fluid, include thermal diffusion
Laminar Flow CFD Results with Temperature Fixed: Velocities and $x(\text{SiO})$, $x(\text{O}_2)$

- Coupon disturbs flow: Boundary layer
- Distribution of SiO, O$_2$ after coupon
Recession for Laminar Flow

Solid line: Analytic
Dashed line: CFD
Turbulent Flow: CFD Results with Temperature Fixed Velocities and \( x(\text{SiO}), x(\text{O}_2) \)

- Coupon disturbs flow: Boundary layer
- Distribution of SiO, O\(_2\) after coupon more localized

Note boundary layer, flow changes on trailing edge
Recession for Turbulent Flow

Solid line: Analytic
Dashed line: CFD
Summary and Conclusions: Effect of Gas Atmosphere on Vaporization

- **Vacuum**: HKL equation from kinetic theory; modified by vaporization coefficient

- **Static over pressure**
  - Inert gas: Kinetic effect limits diffusion of vapor species, Fick’s first law
  - Reactive gas: May suppress or enhance reaction products
Summary and Conclusions: Effect of Gas Atmosphere on Vaporization

• Use analytic and CFD approach for laminar and turbulent flow

  – Both show more recession at leading edge; rates through turbulent flow approach rates through a vacuum
  – Laminar flow CFD about ¼ of recession predicted with analytic methods
  – Turbulent flow close near leading edge, but about an order of magnitude lower than that predicted with analytic methods
  – Differences likely due to heat transfer issues
    • We had to fix coupon temperature to avoid dramatic coupon cooling

• The analytical expressions provide good results which are easily obtained

• CFD offers a more comprehensive model of the process