The influence of oxygen activity on the behaviour of UO2

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Motivations

Quantify the influence of oxygen activity on the behaviour of UO$_2$, starting from point defects …

- Interpret results from out-of-pile property measurements
- Try to control, enhance or mitigate its effects:

  develop materials whose properties are tailored, develop and control fuel cycle processes
I) Oxygen potential and deviation from stoichiometry

II) Point defect populations in U-O2+/−x and their dependence upon oxygen activity

III) Consequences on

• self-diffusion properties
• mechanical properties
• radiation environment? Some complicating factors

IV) Conclusions
I-1 Fluorine structure of UO$_2$ and deviation from stoichiometry

- Fluorine ionic-covalent compound

- UO$_{2+x}$ ➔
  - Insertion of interstitial atoms in octahedral sites (O$_i$’’)
  - Oxidation of cations +4 à +5 ou +6 depending on degree of non-stoichiometry…
Gibbs’ rule of $\phi$: N of intensive parameters necessary and sufficient to determine the system

Solid exchanging with gas phase

$\Delta G(O_2) = RT \ln (pO_2)$ (Molar free enthalpy of oxygen or oxygen potential)

Intensive parameter which has to be controlled in exactly the same way as say temperature (Gerdanian, Dodé)
II-1 Which majority defect at « exact » stoichiometry

- Defects controlled transition metal oxides by basic equilibria [1]:

\[ \emptyset \rightleftharpoons h^0 + e' \]
\[ \emptyset \rightleftharpoons O''_i + V^{o^n}_o \]
\[ \emptyset \rightleftharpoons U_i + V_U \]

- \( UO_2 \) oxygen deficient/excess transition metal oxide & intrinsic ionisation\(^1\):
  - \([e'] \sim [h^0] >> [O''_i] \sim [V^{o^n}_o] >> [V_U]-[U_i]\)
  - Basic reason: SC (small gap) \( \Rightarrow \) electronic conductor
  - DFT+U \(^2\) calculations: \( E_f(e'-h^0) \sim 1.7 \) eV \(< E_f(V^{o^n}_o-O_i) \sim 3.3 \) eV \(< E_f(V_U-U_i) \sim 11 \) eV

Model which accounts for impurities and equilibrium pO\(_2\)\(^{[1]}\)

- Reproduce as many experimental data as possible as a function of oxygen activity, T, doping: \(\sigma \ x^{[2]} \Rightarrow [h^0]\), \(x^{[3]} \Rightarrow [O \text{ defects}]\)

- Consistency with DFT\(^{[4,5,6]}\) calculation of formation energies

\[
\begin{align*}
\emptyset & \rightleftharpoons h^0 + e' \\
\frac{1}{2}O_2 & \rightleftharpoons O''_1 + 2h^0 \\
O_o & \rightleftharpoons W' + h^0
\end{align*}
\]

\[\sigma \text{ [S/m]}\]

\[\text{Deviation from stoiometry}\]

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\[\text{[1] To be published (2013)}\]

\[\text{[2] P. Ruello et al. JACS 88 (2005)}\]


Predominant electronic defects

Transition from a single defect regime to a di-interstitial W’ at roughly $10^{-4}$

$[\text{defects}] \sim \text{PO}_2^\alpha$
III-1 Effect of PO2 on oxygen self-diffusion

\[ D_O^* = f_{O'}[O_i']D_{O'} + f_{V'O}[V'O]D_{V'O} \]

\[ D_O^* = P_{O2}^\alpha \times e^{-\frac{Em\alpha}{kT}} + P_{O2}^\beta \times e^{-\frac{Em\beta}{kT}} \]

\( \alpha \) and \( \beta \), Em characteristic of the mediating defect
III-2 Application to oxygen self-diffusion at $x \sim 0^{[1,2]}$

Data comparable for «stoichiometric» UO$_2$ (But p(O$_2$) is neither controlled nor measured)

- X estimate impossible below $2 \times 10^{-3}$
- Markin & Bones: $\Delta x \sim 0.0025 \Rightarrow$ 4 orders of mag. on p(O$_2$) at 700°C

2 - 3 orders of magnitude in part due to:
- Small changes in oxygen content $\sim 2$ orders of magnitude$^{[1]}$
- Impurities $\sim 1$-2 orders of magnitude$^{[2]}$

Both p(O$_2$) & $y$ must be controlled, measured

III-3 Comparable (theoretical) approach to U self-diffusion[1]

Near-stoichiometric region, high T

LDA+U calculations
- Energies associated with equilibria \( \Rightarrow \) data for point defect model
- Migration energies (NEB) \( \Rightarrow \) (assumed diffusion mechanism) activation energies

\[
\begin{align*}
\emptyset \leftrightharpoons U_i + V_U \\
K_{FU} = [U_i] \cdot [V_U] \\
\emptyset \leftrightharpoons V_U + 2V_O \\
K_S = [V_U] \cdot V_O^2
\end{align*}
\]

If \( e' \sim h^\circ \), then

- Vacancy assisted mechanism: \( D_u \sim [V_u] \; e^{-E_m/kT}, \; D_u \sim e^{-E\text{-}E_m/kT} \; p_{O_2}(T) \)
- \( \text{Ar/H}_2 \) and residual \( \text{H}_2\text{O}_{\text{vap}} \) determine \( p_{O_2} \) \( \Rightarrow \) \( E_a \sim 4\text{eV} \)
- If interstitial mechanism: \( D_u \sim [U_i] \; e^{-E_{m_i}/kT}, \; D_u \sim p_{O_2}^{-1} \) (\( E_a \sim 15 \text{eV} \))

III-4 Comparison between experiment-theory

- $e' \sim h^o$
- $[\text{def. } U] < [\text{def. } O]$
- 3 order of magnitude dispersion
- $E_a \sim 3.6 - 5$ eV for single crystals
- $E_{\text{atheoretical}} \sim 4$ eV $\Rightarrow$ vacancy mechanism

Results are rationalised based on PO2 dependence of [defect]
Irrespective of temperature or composition

\[ [\text{Defect}_{\alpha}] \sim P_{O2}^{q_\alpha} \times \exp\left(-\frac{E_\alpha}{kT}\right) \]

q_\alpha, E_\alpha characteristic of defect (composition, charge, formation energy)

Electrical conductivity, O, neutron scattering, PAS for Vu (collaboration with CNRS CEMHTI)

D_{U/O} \sim P_{O2}^{q_\alpha} \times \exp\left(-\frac{E_\alpha + E_m}{kT}\right)

q_\alpha, E_\alpha + E_m, characteristic of diffusion mechanism (formation & migration)

Self-diffusion

In UO2+x [electronic]>>[oxygen]>>[uranium]
IV- Conclusions

Oxygen activity controls defect concentrations hence atomic transport properties

- Sintering, mechanical properties, microstructural changes, diffusion and release of volatile fission products

- Property measurements should whenever possible be carried out under controlled atmospheres, not composition

- Means of comparing property measurements to theory (first principles)
  - Measurement of U/O/FP = f(T, po2, ∇T), see announcement
  - Merge U-O defect models & use compound energy formalism?
  - Correlation between mechanical properties and self-diffusion
Hoping for a PhD position to fill at Cadarache starting October 2014

- Subject: measurement, interpretation and modelling of electrical & atomic transport properties of UO2+x (doped with Nb/rare earths). Mainly U.

- Recently acquired and developed equipment ADELAIDE