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NUCLEAR MATERIALS RESEARCH PROGRESS REPORTS FOR 1979

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Publication Date
1979-12-01

Peer reviewed
Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA
Materials & Molecular Research Division

NUCLEAR MATERIALS RESEARCH PROGRESS REPORTS FOR 1979

D. R. Olander

December 1979

Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48
NUCLEAR MATERIALS RESEARCH PROGRESS REPORTS
FOR 1979

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This work was supported by the U. S. Department of Energy under Contract W-7405-ENG-48
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ALUMINUM IODIDE STRESS CORROSION CRACKING OF ZIRCALOY

by Shih - Hsiung Shann

I. Introduction

Through the study of iodine stress corrosion cracking of zircaloy, we found that this phenomenon can occur at very low iodine partial pressures (~10^{-3} torr) (1). Inside a reactor fuel pin, iodine will be present mainly as cesium iodide according to thermodynamics. There is some possibility that other kinds of iodides can attain a partial pressure in the mtorr range. This shows the need for the study of stress corrosion cracking by metal iodides. Further study may also help us in understanding the fracture mechanism of zircaloy.

II. Experimental

The apparatus is the same as that used in the iodine experiments (1), except that a Knudsen cell replaces the iodine doser. Aluminum iodide crystals are placed in the Knudsen cell and heated to create a molecular beam to impinge on the zircaloy specimen. Thermodynamic analysis suggest that only one major species, AlI_3(g) is present in the vapor phase. The vapor pressures of all other components are several orders of magnitude lower.

III. Results

For the same length of time to failure, AlI_3 can cause stress corrosion cracking at lower partial pressures than that of I_2. For failed specimens, a plot of ln t_f vs ln P_{AlI_3} shows a slope of
-2/3 ± 0.1 (Fig. 1) compared to a slope of -1/2 ± 0.02 for molecular iodine. Some specimens failed by pinhole failure, some by tearing. In both types of failures, fracture surfaces showed cleavage type brittle fracture (Fig. 2 and Fig. 3).

Through EDAX examination of the fracture surface, we can detect both aluminum and iodine signals. There is a tendency for both signals to decrease on moving in from the tube outside surface into the crack (Fig. 4 and Fig. 5).

IV. Planned Experiments
A. Iron iodide stress corrosion cracking of zircaloy will be studied.
B. Cesium iodide stress corrosion cracking of zircaloy will be investigated.

Reference
Fig. 1 EFFECT OF ALUMINUM IODIDE EXPOSURE ON ZIRCALOY SCC: THE TIME TO FAILURE DECREASES AS THE 2/3 POWER OF THE AI$_3$ PRESSURE
Fig. 2 SEM FRACTOGRAPHY OF PINHOLE TYPE FAILURE (Zr-2 (9Ax32) FAILED AFTER 36.7 HR. 53 PSI (365 MPa), 300 °C, 1.38x10^-3 TORR All) (5,000x).
Fig. 3  SEM FRACTOGRAPHY OF BURST TYPE FAILURE (Zr-2, 9AX32) FAILED AFTER 9.4 HR, 53 PSI (365 MPa), 300° C, 2.0x10⁻³ TORR AlI₃) (10,000x).
Fig. 4  ALUMINUM EDAX SIGNAL DECREASES ON MOVING IN FROM OUTSIDE SURFACE OF THE TUBE INTO THE CRACK (FOR DIFFERENT POSITIONS AND DIFFERENT SPECIMENS).
Fig. 5  IODINE EDAX SIGNAL DECREASES ON MOVING IN FROM OUTSIDE SURFACE OF THE TUBE INTO THE CRACK (FOR DIFFERENT POSITIONS AND DIFFERENT SPECIMENS).
SELF-DIFFUSION OF OXYGEN IN HYPOSTOICHIOMETRIC URANIA

by Kee Kim

1. Introduction

Oxygen self-diffusion in hypostoichiometric uranium oxides is of importance in predicting the rate of oxygen redistribution and other physicochemical processes occurring in an irradiated fuel pin. Although there have been many measurements of oxygen diffusion in ordinary oxides and in hyperstoichiometric urania (1), similar measurements in hypostoichiometric urania have been proven very difficult mainly because it is a defect structure stable only at high temperature, and its oxygen diffusivity is likely to be large enough to render conventional methods unworkable (i.e., gas phase mass transfer of isotopic exchange are rate limiting). The method proposed involves a diffusion couple consisting of U\(^{18}\)O\(_{2-x}\) wafer sandwiched to a U\(^{16}\)O\(_{2-x}\) wafer by a bond of liquid uranium. When heated, the \(^{18}\)O and \(^{16}\)O will interdiffuse. The liquid uranium at the interface is intended to eliminate a gap resistance to oxygen transfer.

II. Experimental

A. Sample preparation

Two identical UO\(_2\) wafers were prepared, which were 1.3 cm in diameter and 1mm thick. They were polished by diamond abrasive to promote a better contact.

\(^{16}\)O in one of those UO\(_2\) wafers was exchanged by \(^{18}\)O using an H\(_2^{18}\)O - H\(_2\) mixture at 1500\(^\circ\)C:

\[
U^{16}O_2 + H_2^{18}O \rightarrow U^{18}O_2 + H_2^{16}O
\]  

(1)

The ratio H\(_2^{18}\)O/H\(_2\) was approximately 10\(^{-2}\), which would yield the oxygen potential for UO\(_{2.0}\) at the temperature. Since the oxygen potential changes sharply in the vicinity of stoichiometric UO\(_{2.0}\), the ratio is
not very critical to maintain the stoichiometry at UO. (See fig. 1). The desired H₂O/H₂ ratio was obtained by flowing hydrogen through H₂ ¹⁸O of which temperature was controlled. After 43 hours, by measuring the weight before and after, it was determined that approximately 70% of the ¹⁶O was replaced by ¹⁸O.

In order to have the same history, exactly the same procedure was applied to the other UO₂ wafer using normal water. The ¹⁸O enriched wafer and the normal wafer were reduced in hydrogen at 1950°C at the same time in order to match the stoichiometries:

\[ \text{UO}_2 + x \text{H}_2 + \text{UO}_2-x + x \text{H}_2\text{O} \]  

(2)

Using the thermogravimetric method, the stoichiometrics of the reduced samples were determined to be O/U = 1.96 after a four hour reduction.

B. Diffusion Experiment

Fig. 2 shows the setup of the diffusion experiment. The diffusion couple was enclosed by molybdenum. Rhenium foils were used in order to prevent any possible reaction between molybdenum and urania. Two wafers were pressed by a tantalum rod in order to promote good contact. After the experiment the diffusion couple was cut in half and the profile of ¹⁸O concentration was obtained by using an ion microprobe. (2,3). Fig. 3 shows the photomicrograph of the cut surface and the line of microprobe of the first sample.

III. Results

Shown in fig. 4 is the normalized profile of ¹⁸O concentration in UO₁.⁹₈₅ after 20 min. at 1330°C. Fig. 5 is for UO₁.⁹₉₃ after 5 hours at 1190°C. Using the computer code MINUIT, data were fitted to the analytic solution:
\[
\frac{18_0}{18_{0+16_0}} = \sum_{n=1}^{\infty} e^{-\alpha_n^2 t} \frac{\left( \frac{B}{L} \right)^2 + \alpha_n^2}{\left( \frac{B}{L} \right)^2 + \alpha_n^2 + \left( \frac{B}{L} \right)} \cos \alpha_n z \sin \alpha_n l \alpha_n \]

\(D = \) Oxygen self diffusion coefficient in UO\(_{2-x}\) (unknown)

\(\alpha_n = \) Constants \((\alpha_n \tan(\alpha_n) - B = 0)\)

\(t = \) time

\(z = \) distance from the interface

\(l = \) thickness of the wafer

\(B = \left( \frac{D}{D^*} \right) \left( \frac{C^*}{C} \right) \left( \frac{\delta}{\delta^*} \right)\)

This is an unknown dimensionless parameter which characterizes liquid uranium resistance to oxygen transport.

(If there were no resistance, B = \(\infty\))

\(D^* = \) diffusivity of oxygen in liquid uranium

\(C^* = \) concentration of oxygen in liquid uranium

\(C = \) concentration of oxygen in UO\(_{2-x}\)

\(\delta = \) thickness of liquid uranium bond

Fig. 4 is very symmetric and the fitting yielded

\(D = 8.9 \times 10^{-8} \text{ cm}^2/\text{sec} \) and \(B = 71\) and

for Fig. 5, \(D = 3.5 \times 10^{-8} \text{ cm}^2/\text{sec} \) and \(B = 4\).

**Discussion**

1. Assuming that the pre-exponential \(D_0\) in \(D = D_0 \exp \left(-\frac{E}{RT}\right)\) is proportional \(\propto x\) in UO\(_{2-x}\), those two values were combined to yield an activation energy \(E = 5.5\) kcal/mole.

The activation energy of UO\(_{2-x}\) has never been reported since no oxygen diffusion has been measured on the substantially hypostoichiometric side where vacancy mechanism dominates and activation energy would not include the defect formation energy. However, measurements have been made on the isostructural fluorite related anion deficient
oxides CeO$_{2-x}$ (4.5) and PuO$_{2-x}$ (6.7). In these cases it was given as $3.6 \sim 11.9$ Kcal/mole and $4.6 - 10.5$ Kcal/mole, respectively. The obtained value $5.5$ Kcal/mole is well within these values. In addition, quite interestingly, Catlow and Lidiard (8) theoretically calculated vacancy activation energy of $5.77$ Kcal/mole, which is in good agreement with this work.

2. Comparing the $D$ at $1190^\circ$C with the value of stoichiometric $UO_2$ of Marin and Contamin (1), it is about two orders of magnitude larger. This is believed to be the contribution from the nonstoichiometry.

3. Theoretical works by Murch and Thorn (9) predict values more than two order of magnitude higher. However, as the authors acknowledge, the simplified model may not be accurate and there may be some other process which dominates the oxygen diffusion process.

4. The thickness $\delta$ of liquid uranium bond was about 16 times thicker for the second experiment than the first one. According to

$$B = \left( \frac{D^L}{D} \right) \left( \frac{C^L}{C} \right) \left( \frac{\delta}{\delta} \right)$$

assuming other factors remain relatively constant, $B$ should be 16 times smaller for the second experiment than the first one. The result $\frac{B_1}{B_2} = \frac{71}{4} \approx 18$ is relatively in good agreement with the prediction.

References:


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(7) A. S. Bayoglu and R. Lorenzelli, J. Nucl. Mater. 82, 403 (1979)


(10) P. E. Blackburn, J. Nucl. Mater. 46, 244 (1973)


Fig. 1 Variation of oxygen potential with temperature and O/U ratio (ref. 10) with two-phase boundary based on ref. 12.
Fig. 2 Diffusion experiment setup
Fig. 3 Cut surface of the diffusion couple and the line of probe of #1 experiment (T = 1330° C, 20 min.)
Fig. 4 Normalized profile of $^{18}O$ concentration of experiment #1.

$T = 1330^\circ C$

$O/U = 1.985$

$t = 20$ min
Best fit to Eq. 3

$T = 1190 \, ^\circ \text{C}$

$O/U = 1.993$

t = 5 hr 40 min

$\triangle$ No. 1 Traverse

$\square$ No. 2

Fig. 5  Normalized profile of $^{18}O$ concentration of experiment #2
THE SURFACE CHEMISTRY OF EPITAXIAL SILICON

DEPOSITION BY THERMAL CRACKING OF SILANE

by M. Farnaam

I. Introduction

Semiconductor and solar energy industries make extensive use of thermal cracking reactions such as $\text{SiH}_4(g) \rightarrow \text{Si} + 2\text{H}_2(g)$ for deposition of epitaxial layers of silicon in fabrication of integrated circuits and solar photovoltaic devices. Investigations towards lower costs, higher productivity, and better uniformity have resulted in the conclusion that higher vacuum levels and lower gas pressures allow a better control of the deposition process. The crucial need for still better control of the epitaxial growth process can be realized via certain findings such as the fact that free solar cells with efficiencies less than 10% are not economical. Further development and miniaturization of the epitaxially grown circuits will probably rely on application of molecular beam technique in the deposition process. This encourages modulated molecular beam experiments in contrast to conventional techniques which do not have advantages such as phase lag measurement.

II. Experimental

A. Apparatus modification and specimen preparation:

The experiments of 1978 ended with the problem of production of a bumpy growth morphology on the surface of the silicon crystal in the region exposed to silane, and appearance of triangular etch pits in the region not exposed to silane. In order to reduce the effect of contamination from the environment, the system was disassembled and the main stainless steel body
of the system was cleaned and degreased. The diffusion pump in the target chamber was replaced by an Electro-Ion Pump made by Granville Phillips which is composed of a titanium sublimation pump and an ion pump. This step resulted in the base pressure of $2 \times 10^{-9}$ torr in the target chamber which is considered as a good level of vacuum for this type of experiment.

In order to minimize the effects of surface defects, a new type of crystal produced by Epitaxy Incorporated was used. These crystals were prepared by deposition of a 6 μm undoped Si epitaxial layer on a single crystal silicon wafer with resistivity of $0.47 \ \Omega \cdot \text{cm}$, 375 μm thick and 5 cm in diameter, cut along (111) face. A triangular sample with sides about 17 mm perpendicular to (112) directions was broken from the crystal using a sharp object without touching the surface of the sample, which required several careful attempts. A slight blow of N₂(gas) was sometimes required to clean the surface from the few very small crystal particles inadvertently thrown on the surface during the breaking.

B. Specimen Heating:

Because of the triangular shape of the specimen, resistive heating could no longer be used. Therefore a round sample holder made of tantalum was designed for electron bombardment heating. Some preliminary experiments showed that the best design consisted of a disk $\approx 25$ mm in diameter with a hole $\approx 10$ mm in diameter in the middle which allows direct heating of the sample by electron bombardment.

A sample was heated in this apparatus under the conditions shown in Table 1.

<table>
<thead>
<tr>
<th>Time</th>
<th>Temperature</th>
<th>Background Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 minutes</td>
<td>$\approx 1150^\circ C$</td>
<td>$7 \times 10^{-9}$ torr</td>
</tr>
<tr>
<td>30 minutes</td>
<td>$\approx 1300^\circ C$</td>
<td>$2 \times 10^{-8}$ torr</td>
</tr>
<tr>
<td>and 30 minutes</td>
<td>$\approx 1100^\circ C$</td>
<td>$4 \times 10^{-9}$ torr</td>
</tr>
</tbody>
</table>
After the heating, the sample appeared as bright as before heating, and scanning electron microscope was not able to show any features on the surface. However, the surface of the sample around the corners, where it contacted the tantalum target holder was dull and showed some morphology under SEM. These heating experiments were repeated and always resulted in featureless surfaces.

A similar heating experiment was carried out for about 30 minutes at \( \approx 100^\circ C \) but with exposure to a SiH₄ flux of \( \approx 1 \times 10^{15} \) molecules/cm²⋅sec at the surface. Again, SEM did not show any features. Repetition of this experiment at higher fluxes of SiH₄ (\( \approx 3 \times 10^{15} \) molecules/cm²⋅sec) for longer periods of time (\( \approx 2 \) hrs.) still resulted in featureless surfaces when examined by SEM.

C. Data Acquisition:

In a series of experiments, the temperature of the crystal, the intensity of the silane beam, and the frequency of modulation were changed while the mass spectrometer was tuned to H₂⁺, Si⁺, SiH⁺, SiH₂⁺, SiH₃⁺, and SiH₄⁺ signals. The output of the mass spectrometer was fed into a lock-in amplifier and a two phase accessory which provided in-phase and out of phase components of each signal for the chart recorder. A computer program was used for processing the data in order to calculate the reaction probability and the phase lag. Figures 1, 2, 3 and 4 show the output of the program.

III. Planned Experiments

Construction of a reliable model for the reaction still requires answers to the following questions:

1. Are hydrogen atoms produced during the cracking of silane?

An isotope exchange experiment is planned which will involve simultaneous exposure of the crystal to modulated SiH₄ and steady state SiD₄ beams.
Detection of a comparable HD signal by mass spectrometer would mean that hydrogen atoms are produced on the surface.

2. How much time do the reflected SiH$_4$ molecules spend on the silicon surface?

A transit phase lag measurement experiment utilizing a mixed SiH$_4$/Ar beam is planned. By measuring phase lag of the SiH$_4$ + signal with respect to an Ar$^+$ signal, the residence time of reflected SiH$_4$ molecules can be deduced.

3. The contamination of the surface and possible surface phase transitions?

A simultaneous Auger & LEED analysis of the crystal surface would determine the effect of temperature and contamination on surface phase transitions, if there are any.

References:

6) Private Communications with B. A. Joyce.
$\text{SiH}_4/\text{Si} \text{ REACTION}$

$f = 20 \text{ Hz.}$

$I = 4.6 \times 10^5 \text{ Molecules/} \text{cm}^2 \cdot \text{Sec.}$
APPARENT REACTION PROBABILITY, $\epsilon$
APPARENT REACTION PROBABILITY, \( \varepsilon \)

PHASE LAG (Degrees), \( \phi \)

Frequency (Hz)

\( I = 4.6 \times 10^5 \) Molecules/cm\(^2\)-sec

\( T = 1443 \) K

SiH\(_4\)/Si REACTION
I. Introduction

Safety analysis of nuclear reactors requires knowledge of the equation of state (i.e., the vapor pressures of all species as a function of temperature) and the evaporation kinetics of the fuel material at temperatures well above the melting point. Because of the material limitation at high temperature of conventional techniques, entirely new experimental techniques had to be developed. A number of different heating techniques, mainly by utilizing transient pulse heating have been proposed.\textsuperscript{1-4} A survey on the various techniques is given in a specialists' meeting in 1978.\textsuperscript{5}

The laser pulse heating technique, together with the mass spectrometry and automatic optical pyrometry measuring techniques, is being utilized and developed in this lab.\textsuperscript{6}

In addition to the confirmation of last year's measurements on vapor cloud angular distribution, liquid-droplet formation, and surface temperature measurement by optical pyrometer, a special attention has been paid to the laser performance and pulse-to-pulse consistency. Also, a surface analyzer has been used for crater profile measurement after laser irradiation. A great deal of effort has been devoted to the development of the gasdynamic modeling of super-sonic jets from laser evaporated material and the understanding of the kinetic effects due to fast transient. In considering the fact that with the equation of state measured in highly nonequilibrium condition, the quasi-equilibrium
assumption still has to be made in the reactor disassembly calculation, and the fact that the decrease in fuel stoichiometry during transient temperature evolution, can only be quantified on the assumption of thermodynamic equilibrium during laser heating, the computer code developed to solve one-dimensional heat conduction and diffusion equations have been revised for more general calculational purposes.

II. Experiments

A sketch of the experimental set up is shown in Fig. 1. There were no major changes compared to the last year report, except: (1) a second beam correcting lens is used to reduce the laser beam divergence, and instead of using plane total reflector for the laser cavity, a 2-meter radius of curvature reflector is used, and (2) a biomation 4-channel waveform digitizer is used for data recording and processing.

III. Results

A. Angular Distribution and Temperature Measurement

The angular distribution of the vapor molecules ejected from \( \text{UO}_2 \) by laser impingement was reproduced this year. The apparatus shown in Fig. 2 is similar to the one shown in last year's report, except, instead of mounted vertically (in y-z plane), the collector assembly was mounted horizontally (in x-y plane). The \( \text{UO}_2 \) target was subject to two laser shots. The incident laser energy of the run was 25.75 Joules. The angular distribution result is shown in Fig. 3 (expressed in triangles) along with the result last year (in circles). The two measurements are very consistent and correspond quite well with \( \cos^2 \theta \) distribution.

The calculated maximum surface temperature corresponding to
this laser energy and measured power trace with time and transverse
distribution was 4380 K according to the code developed here. The
maximum surface temperature measured by the automatic optical pyro-
meter was 4405 K after correction for 0.92 spectral emissivity,
which again shows consistent temperature measurement.

B. Liquid-droplet Investigation

The evidence in last year's report showed that some UO₂ liquid-
droplets were condensed on the aluminum collectors. However, because
of the comparative x-ray counts of aluminum and uranium peaks from
EDAX (Energy Dispersive Analysis of X-rays) while focused on and off
the spheres, there was still a suspicion that some of the spheres
seen on scanning electron microscope might have been aluminum coated with
uranium instead of whole uranium droplets. Hence, some of the
aluminum disks were replaced by molybdenum and the polishing and
cleaning processes were carefully handled. The scanning electron
micrographs of aluminum and molybdenum collectors are shown in
Fig. 4(a) and 5(a) respectively. The EDAX results in Fig. 4(b),
(c) and 5(b), (c) show that the aluminum or molybdenum peak is much
higher when electron beam is focused on the plane surface than that
on the spheres, while the uranium peak shows the opposite behavior.
It can, therefore, be concluded that the spheres seen by micros-
cope are principally uranium, which means that some uranium compound
did condense on the collectors; uranium oxide liquid droplets did
form due to laser irradiation. The mass fraction of the liquid
droplets is at most 0.01% of the total UO₂ collected on each disk.
Therefore, the formation of liquid droplets does not affect the vapor pressure measurement.

It is felt that cluster phenomena in the super-saturated vapor cloud would provide useful information on the accuracy of the vapor pressure measurement techniques. The dimer (U₂O₄) is to be investigated from high-mass-coil quadrupole mass filter.

C. Surface Morphology

The molten area estimated from the measured power density distribution on the focal spot and the computer code assuming one dimensional heat conduction is about three times (in terms of area) bigger than the molten area observed by microscope. The maximum surface temperature at the boundary observed in the microscope is expected to be higher than the melting temperature. The automatic optical pyrometer will be focused on this boundary to measure the surface temperature and compared with the computer code calculation. The power distribution technique by razor-blade is also being re-examined in terms of the data analysis procedure, the experimental technique and the consistency of the laser performance.

D. Crater Profile Measurement

Figs. 6 and 7 show the crater depth profiles measured by a surface analyser along the major and minor axis of the elliptical laser spot on the UO₂ target. The estimation of the total amount of UO₂ evaporated for the run last year (Fig. 6 and 7) was about 55 mg for 5 shots, an order of magnitude higher than the figures from the theoretical calculation (7.9 mg) and the neutron activation measurement (2.2 mg).
The liquid movement which is seen from the microscope and the depth profile curve is probably one of the reasons for this discrepancy. Sputtering due to the high power laser bombardment or the microexplosion beneath the surface due to low density (high porosity) sample, as the microcraters on the microscope picture show, may also be the explanation.

E. Surface Stoichiometry Depletion

The surface composition was calculated by solving the heat conduction and the oxygen diffusion equation for laser irradiation on UO$_2$ for the run of last year. Due to low cooling rate, the composition can never cross the lower solidus (or phase boundary), which means that precipitation of uranium metal should be impossible. It has been suggested that the uranium metal aggregates along the grain boundary was due to the reduction reaction of UO$_2$ with the tantalum holder.

Tantalum holder will be replaced by tungsten and slightly reduced UO$_2$ sample under H$_2$/H$_2$O atmosphere will be used to eliminate reaction between UO$_2$ and holder material. Surface will be examined before and after the laser irradiation.

F. Mass Spectrometer Calibration

Instead of using a Knudsen cell source for the mass spectrometer calibration, which requires terminating and opening up the system for change of target, an electron bombardment heater is used to heat the UO$_2$ pellet to ~2500 K as an open evaporation source for the calibration. The advantage is that the same target is used for calibration and for the laser evaporation experiment so that the vacuum system and electronics do not have to be disturbed between
calibration and laser run. The calibration results will be compared with the Knudsen cell calibration done earlier.

G. Vapor Pressure Interpretation

The attempt has been made to work out the gasdynamic modeling of the blasting free-jet of the evaporated material.

References:

1. Electrical Resistive Heating:
   A New Apparatus for Thermodynamical Measurements above 2500K, High Temp- High Pressure 8, 425 (1976)

2. Electron Beam Heating:
   D. A. Benson, Application of Pulsed Electron Beam Vaporization to Studies of UO₂, Report SAND-77-0429 (1977)

3. Neutron Pulse Heating:

4. Laser Beam Heating:
   M. Bober, J. U. Karow and K. Salvatzmann, IAEA Symp. on Thermodynamics of Nuclear Mat.
   IAEA-SM-190/34 Vienna October 1974


CH₂ Bromation

VAPORIZATION MEASUREMENT

Quadrupole Mass Spectrometer

Beam Correcting Lens

Nd-glass Laser

MgO Block

Photodiode

LASER POWER MEASUREMENT

CH₄ Target

UO₂ Target

Ion Collector

Fast Optical Pyrometer

Temperature Measurement

Vapor Flume

Beam Splitter

Beam Correcting Lens
Fig. 3 Angular distribution of mass flux in vapor plume from UO₂
Fig. 4  (a) Scanning Electron Micrograph of aluminum disk collector surface.
(b) EDAX analysis of the white spot on picture (a).
(c) EDAX analysis of other place than the white spot.
Fig. 5  (a) Scanning Electron Micrograph of molybdenum disk collector surface.
(b) EDAX analysis of the white sphere on picture (a).
(c) EDAX analysis of other place than the sphere.
Fig. 6  (a) Crater depth profile along the major axis.
(b) Surface roughness reference.
Fig. 7  (a) Crater depth profile along the minor axis.
(b) Surface roughness reference.
GAS DYNAMIC MODEL FOR LASER INDUCED EVAPORATION

by F. Tehranian

INTRODUCTION:

In laser evaporation studies of UO$_2$ at high temperatures (>4000K) in this lab, mass spectrometry has been used to detect the different vapor species and also the concentration of each of them in the downstream flow. But the main quantity of interest is the vapor pressure of UO$_2$ at different surface temperatures. To find this quantity a gas dynamic model is needed to relate the downstream measured quantities to those at the surface of the target.

At low target temperatures the density of molecules is so low that free molecular flow can be assumed in the whole region. This case is very easy to deal with and not of interest. At high temperatures, however, (e.g. strong evaporation by a laser) the molecules which are vaporized collide with each other in front of the target due to the high vapor density. In this case three different regions are believed to exist and the properties in different regions are related by matching conditions at their boundaries.

THE MODEL:

In the model considered here the flow of gas vaporized is divided into three regions in each of which the variations of properties are governed by equations which are characteristic of the kind of flow in that region. Fig. 1 shows schematically the regions considered for the flow.

Region I, which is called the Knudsen layer, has a thickness of the order of a few mean free path. The molecules moving from the surface have a Maxwellian velocity distribution at a temperature equal to surface temperature. But
the distribution of molecules immediately near the surface differs from the maxwellian due to non-equilibrium collisions which take place between them and finally bring them to equilibrium at a distance of a few mean free path from the surface where the molecules have a new maxwellian distribution. Because of the non-equilibrium nature of this region, the Boltzmann equation is the governing equation which has to be solved to give the actual distribution of the molecules. Ytrehus (1) and others have shown that the limiting velocity of molecules in Knudsen layer is the sonic velocity which occurs at high energy density and high vacuum. The properties go through large changes in this region and the net evaporation rate is reduced because of back scattering of the molecules due to collisions.

The second region shown in Fig. 1 is the hydrodynamic region which starts at the sonic point. The flow of the vapor in Region II resembles the supersonic free expansion of a gas from a sonic nozzle in vacuum.

As the vapor gets farther from the surface its density decreases because of expansion and finally a point is reached beyond which there are no more collisions between molecules (Region III in Fig. 1).

SAMPLE CALCULATIONS AND DISCUSSION:

Table 1 gives the freezing points calculated by using the sudden freeze model as given by Anderson (2). This calculation shows that the flow remains continuum regime (Region II) for the entire distance between the target and the ionizer, which is about 40 cm in our system.

* The freezing point is the plane of transition between Regions II and III.
TABLE 1: Freezing Point (Cm)

<table>
<thead>
<tr>
<th>$\gamma$</th>
<th>Sudden freeze model</th>
</tr>
</thead>
<tbody>
<tr>
<td>5/3</td>
<td>35</td>
</tr>
<tr>
<td>7/5</td>
<td>80</td>
</tr>
<tr>
<td>9/7</td>
<td>120</td>
</tr>
</tbody>
</table>

The conservation equations (Mass, Energy, Momentum) in Regions I and II have been solved simultaneously by matching the conditions at the boundary between them. It has been assumed that the flow of the vapor from the target is steady state.

These calculations show the results for a surface temperature of 4500k. The vapor pressure of UO$_2$ corresponding to this temperature from Bober (3) is about 25atm. The diameter of the vaporizing area is taken to be 0.6 m and hard sphere model is used for the collision cross section.

Temperature and number density variations as a function of distance are shown in Fig. 2 and Fig. 3 for three different values of specific heat ratio. In table 2, the number density of molecules calculated by the Langmuir equation for free molecular flow has been compared with the number density obtained in our model.

TABLE 2: Number density at X = 40 Cm

<table>
<thead>
<tr>
<th>$\gamma$</th>
<th>$\frac{N}{N_1}$ (from gas dynamic model)</th>
<th>$\frac{N}{N_1}$ (from angular distribution)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9/7</td>
<td>0.21</td>
<td>.31</td>
</tr>
<tr>
<td>7/5</td>
<td>0.33</td>
<td>.38</td>
</tr>
<tr>
<td>5/3</td>
<td>0.61</td>
<td>.52</td>
</tr>
</tbody>
</table>

$N = $ number density calculated by our model
$N_1 = $ number density calculated by Langmuir equation
The angular distribution in free jets has been given by Sherman (4) to be
\[ \frac{\rho(R, \theta)}{\rho(R_0, 0)} = \cos^2 \left( \frac{\pi \theta}{2 \phi} \right), \]
in which \( \phi \) is a function of the specific heat ratio. This distribution along with the \( \cos \theta \) distribution in free molecular flow have been used to get quick estimates of the ratios of centerline number densities in the two types of flows. The total flux of molecules at the surface of each of them has been obtained in terms of the centerline flux by integrating the angular distribution over the hemisphere. Then the ratio of the fluxes at the surface has been set equal to 0.82 given by YTREHUS (1). By using the velocity ratios obtained in our previous calculations, we were able to calculate centerline number density ratios. The results of this calculation are shown in the third column of table 2. Considering that the molecular density distribution in free jets and the velocity ratio which have been used in the computation are only approximately true, the results of the two calculations are in good agreement.

The angular distribution in free jets discussed above suggests that the flow is more forward directed in this type of flow than in free molecular flow for which the distribution is \( \cos \theta \). As a result we would expect a higher number density on the centerline in our model than that in the Langmuir model. But table 2 shows that the number density of molecules calculated by this model is always less than that using Langmuir free molecular model. There are two possible reasons. First in this model due to back scattering which occurs in the non-equilibrium region, the effective saturation number density will be about one third of its value at the surface of the target, although the evaporating flux is \( \sim 82\% \) of the free molecule value. Second, in our model
the velocity of the molecules reaches supersonic which is greater than the
average thermal velocity by a factor three. So the net result is a reduction
in centerline number density.

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Sonic Knudsen Point Layers

Freezing Point Target Hydrodynamic Region, Free Molecular Flow

Fig. 1: Flow Regions

\[ \text{Vapor Temperature, } T \quad \text{(°K)} \]

\[ \gamma \]

9/7

7/5

5/3

\[ X \quad \text{(cm)} \]

Fig. 2: Vapor Temperature vs Distance
Fig. 3.: Number Density vs Distance
I. Introduction

When heated to high temperature, UO₂ fuel rods have been found to release hydrogen-bearing gases which may attack the zircaloy cladding. One possible source of hydrogen (other than adsorbed H₂O) is hydrogen dissolved in the lattice of the solid. At present no reliable information on hydrogen solubility in UO₂ is available. Previous results by Wheeler (1) with single crystal UO₂ produced solubilities ranging from 0.03 to 0.4 micrograms of H₂/g UO₂ with no reproducibility and no apparent pressure dependence.

The objectives and experimental method used in this project were discussed in a previous report. (2) In this report the work on achieving and measuring high temperatures in the pressure furnace will be discussed.

II. Experiments With the Pressure Furnace

In order to study the solubility of hydrogen in hypostoichiometric UO₂, it is necessary to achieve a high temperature to reduce the stoichiometric UO₂. A temperature of at least 1300°C is needed in order to achieve any appreciable reduction.

The pressure furnace used is shown in Fig. 1. The samples are to be heated by induction inside a tungsten susceptor. The induction heater coil shown is connected to a 30 KW induction heater. The temperature is measured by a W/Re Thermocouple whose output signal is sent to a saturable core reactor which controls the power supply of the induction heater.

The furnace was first operated in an automatic mode with the thermocouple signal controlling the power. This is the preferred mode of operation as it establishes a stable temperature for a long period of time which may be
necessary in this experiment. In this mode it was only possible to achieve about 1200°C at about 60% power. After this the thermocouple output became erratic due to some electronic problem. On successive trials the same behavior was observed.

The furnace was then operated in a manual mode where the thermocouple signal is not used to control the power level. In this mode it is not as easy to keep the temperature at a constant value as the furnace tends to oscillate in power. With this method a temperature of 1730°C was obtained at 90% power. Higher power levels weren't possible due to shorting of the feedthroughs. In order to test the accuracy of the thermocouple reading the experiment was repeated using an optical pyrometer which by use of a pyrex plate on top of the furnace and a prism was able to sight into the susceptor during operation and thus measure the temperature. On heating the furnace, a similar power-temperature relation was observed as before with the maximum temperature observed to be 1750°C.

The ceramic feedthroughs of the coil have been replaced and the pressure furnace will soon undergo further testing. It is hoped that the furnace will be able to be run in the automatic mode as stated previously. The pressure furnace should be ready for operation in the coming year.

III. Experiments on Pore Structure of Uranium Dioxide

In order to study the retention and release of $\text{H}_2\text{O}$ vapor in $\text{UO}_2$ as described in a previous report (3), it is necessary to study the pore structure of the samples used. These experimental techniques that were used are $\text{H}_2\text{O}$ infusion (4), gas permeation (5,6), and gas effusion. (6,7). The first method has been described previously. (3) Briefly, gas permeation involves placing a $\text{UO}_2$ wafer between vacuum and a gas and measuring the amount of gas that
permeates through the wafer. The gas effusion method involves filling a pellet with Helium and then after pumping off the excess gas, measuring the outflowing helium as a function of time.

As stated previously, three methods were used to investigate internal pore structure. The sample investigated was prepared by Exxon Nuclear Co. It has an open porosity of 5% and total porosity of 13% as reported previously (3), these samples released a total of 17 micrograms D₂O/g UO₂. In order to understand this release, it is necessary to know not only the internal porosity but the surface area as well as the mean pore size.

The open and closed porosity were determined by the infusion method described previously. (3) The apparatus is shown in figure 2. Using this method an open porosity of 5.08 ± 0.08%, and a closed porosity of 15 ± 2% were determined. The pore morphology is shown in Fig. 5.

With the gas permeation method it is possible by use of a pressure dependence to determine constants that are related to the surface area as well as the mean pore size. The apparatus used is shown in figure 3. The permeating gas used is helium. It is used because of its ease in permeation as well as ease in detection by a helium leak detector. A 0.7 mm wafer of UO₂ which had been roughly polished was used in this apparatus. The wafer was placed in a sample holder which was sealed from above by tightening down on an O-ring and sealed below with vacuum grease. After evacuation of the system by a mechanical pump, valve B was closed and the system pressurized by opening valve A. A helium pressure of 20 torr was used. Valve A was closed and the signal of helium that had permeated through the UO₂ wafer was observed by the helium leak detector; a mass spectrometer system which is tuned to mass 4. A blank was run and no signal was observed. The UO₂ wafer, however, could not be tightly fitted into the holder, and the helium flow
rate varied from trial to trial. On tightening, the wafer broke, and a new sample exhibited the same behavior.

The other method used is the gas effusion method whose apparatus is shown in figure 4. By this method it is also possible to obtain an indication of open pore structure. In this method it is necessary to isolate the sample in a chamber filled with helium, subsequently pump out the chamber and then observe the helium effusion out of the sample. The sample is infused with helium by opening valve A. This is done at pressures up to 1 atm for about 1 hour. Valve A is then closed and valve B, which is a large valve with little flow restriction, is opened to a large mechanical pump. It is used to rough out the sample chamber quickly in order that most of the helium is removed from the chamber with little loss from the sample. This is done for one minute and is followed by opening valve C which is similar to B. The helium signal is then monitored as a function of time by the helium leak detector.

First, a blank was run in order to differentiate the signal from any background. The blank run produced a large background signal. This signal had a very large time constant, and was so large that it was not differentiable from the signal produced with a UO$_2$ pellet in place. This signal seems to be due to helium diffusing into minute cracks and interstices in the sample chamber. All metal valves whose seal faces the chamber have been installed but with similar results. In operation, it almost appears that there is a virtual leak present out of which the helium effuses.

In order to avoid any possibility of helium being trapped in interstices, a totally glass system is being constructed. It has three glass vacuum valves in which there should be a little trapping of helium. Preliminary tests on this
new apparatus have not been conclusive.

If the same incidence of helium absorption is observed, it is planned to alter the experiment somewhat. The sample will first be infused with helium in one sample chamber and then transferred to another chamber. This other chamber will be attached to both a vacuum pump and a leak detector. This chamber shall be rough pumped with the mechanical pump and then any helium that is still absorbed in the pores of the sample will be pumped out with the leak detector. Although not as sensitive as the previous method, its advantage is that the final single chamber will have no opportunity to absorb large amounts of helium.

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Fig. 1 HIGH PRESSURE FURNACE FOR INFUSING DEUTERIUM INTO SOLIDS.
Fig. 2 H₂O Infusion Method Apparatus for Measuring Internal Porosity.
Fig. 3 Permeation Method Apparatus
For Measuring Internal Pore Structure.
Fig. 4 Effusion Method Apparatus
For Measuring Internal Pore Structure
A. Elimination of the Gap

In the thermal gradient experiment, a concave gap is formed between the UO$_2$ specimen and the tungsten lid. The gap arises from: 1. thermal evaporation (the center of uranium oxide is always hotter than the oxide at the periphery); 2. the porosity in UO$_2$ sample (which is not completely eliminated by the isothermal sintering step), and the residual cracks between the UO$_2$ wafer and the pellet. Both of these void sources migrate to the hot lid under the influence of temperature gradient. Since the center of the tungsten lid is hotter than the periphery, the gap is concave in shape. The disadvantages of the gap are:

a. It destroys the physical integrity of the wafer, making it difficult to measure the migration distance.

b. It lowers the temperature of the UO$_2$ surface, thereby slowing down the migration rate of the inclusions. Several efforts were made to eliminate the concave gap:

1. Premelt UO$_2$ to get rid of porosity

Polycrystalline UO$_2$ was placed in a tungsten crucible, then heated up in vacuum to 1000°C for two hours to eliminate any adsorbed moisture. Then a tantalum lid was E.B. welded onto the crucible in vacuum. The whole crucible was then hung in a resistance heating tungsten furnace and heated up to 2900°C. After burning out a tungsten mesh heating element, (which was designed to operate at 2600°C), we did manage to melt UO$_2$ and get very high density UO$_2$. However, it was not porosity-free and was too brittle to be used.
in temperature gradient experiment. We could remove melted UO₂ out of tungsten crucible by dissolving the crucible in a mixture of \( \text{H}_2\text{SO}_4 \) + HF, but the specimens were not suitable for service.

2. **Reduce porosity by applying a temperature gradient to the samples.** Since porosity and voids migrate under the influence of a temperature gradient, by heating UO₂ in a temperature gradient furnace several times we hoped to eliminate the voids. We found that porosity could not be completely eliminated by repeated thermal gradient treatment. After several heat treatments, the UO₂ was still full of pores and was too fragile to be used in the thermal gradient experiment.

3. **Put a piece of iridium between UO₂ and the tungsten lid.** The concept is that even if a gap was formed, iridium would melt and fill the gap. Therefore, the temperature in UO₂ would not be lowered significantly. However, iridium reacts with both tantalum and tungsten crucibles and forms a low melting eutectic which destroys the crucible.

4. **Preferentially heating on the periphery.** We tried to achieve more uniform radial temperature distribution by heating more on the periphery of tungsten lid than on the center. The approaches are:
   a. Put the heating filament only along the edge of the lid.
   b. Make a shoulder on the tungsten crucible as shown in Fig. 1a. The edge is closer to the filament than the center, therefore, attracts more electrons and gets more heating. In addition, a cooling fin was placed in the top center of the crucible to dissipate heat. This approach was not successful because the fin melted.
c. Place a big tungsten block on top of the crucible as shown in Fig. 1b. The radial gradient is steeper near the periphery due to radiation heat loss. By using a tungsten block much bigger than the crucible, we hoped to get more uniform temperatures in the crucible. However, the tungsten block is too massive. We do not have enough power to heat the UO₂ to high enough temperature to check if this approach would work or not.

d. Thick-walled tungsten crucible. Change the wall thickness of the crucible from 0.015" to 0.045", so that more heat was conducted down the wall. This would bring up the temperature of UO₂ along the periphery.

e. Use thermal shield. Thermal shield was used around the tungsten lid to cut down the heat loss from side of crucible.

Although the modifications shown in Fig. 1 did not help, the combination of thick wall crucible, heating filament on the periphery and a thermal shield reduced the concave gap to about 10% of its original size (i.e. from ~2mm at the center to ~0.1mm).

B. Results of Migration Experiments with Tungsten and Molybdenum Spheres

After the problem of the concave gap was solved, several thermal gradient migration experiments were performed. Molybdenum and tungsten powders (spherical, ~ 1-5 micron in diameter) were used as inclusions. The top temperature at black body hole was between 2400°C and 2650°C. The bottom temperature of UO₂ was about 1200°C. Each sample was held at temperature for about 12 hrs. After each experiment, the sample was cut longitudinally, polished and examined with microscope for the extent of migration of the inclusions. There was no sign of migration of these inclusions, except on the periphery near the tungsten lid where some spherical tungsten
inclusions were observed. In the beginning, we thought those inclusions (which are spherical in shape and are about 5 micron in size) had migrated from the original powders placed at the pellet-wafer interface. But by using molybdenum as the inclusions, we still found spherical tungsten inclusions near the periphery of UO$_2$ at hot end. We concluded that they came from tungsten crucible by the following mechanism: the tungsten from the crucible dissolved and diffused in the UO$_2$ and precipitated out as inclusions during cooling down.

C. Ruthenium Inclusions - Isothermal Annealing

After trying numerous tungsten or molybdenum experiments in vain, we speculated that it may require a liquid inclusion for migration to occur. The fact that the metallic inclusions in reactor fuel were probably liquid during operation seems to support this hypothesis. We decided to try ruthenium as inclusions because it would be molten at our experimental condition and because it is one of the fission product found in metallic inclusion in the fuel.

Before each thermal gradient experiment, we sinter the inclusions in between the two pieces of UO$_2$ in a reducing atmosphere to control the stoichiometry and eliminate the porosity. In the case of the ruthenium powders (all less than 10μm), after isothermal sintering at 2100°C, we found unexpectedly that ruthenium had diffused into the UO$_2$ matrix and appeared on grain boundaries of the UO$_2$ (see Fig. 2).

To study this phenomena in more detail, we performed the isothermal anneals of ruthenium powders in UO$_2$ at different temperatures in an apparatus as shown in Fig. 3. After each experiment, we ground off (parallel to the original ruthenium plane) consecutive layers of UO$_2$ and counted the ruthenium concentration on the exposed surface by x-ray fluorescence. A typical diffusion profile is shown in Fig. 4. The data were fitted, using
MINUIT program, to the equation:

\[ C = C_0 \text{erfc} \left( \frac{X - X_0}{2 \sqrt{D t}} \right) \]  \hspace{1cm} (1)

where \( D \) = diffusion coefficient of ruthenium in UO\(_2\).

\( C_0 \) = solubility of ruthenium in UO\(_2\).

\( X_0 \) = position of initial interface.

\( X \) = diffusion distance.

We determined \( D \), \( C_0 \), and \( X_0 \) from the profile such as the one shown in Fig. 4. Experiments performed at different temperatures enable us to get \( D \) and \( C_0 \) as a function of temperature.

In order to prove that the observed migration of ruthenium into UO\(_2\) is really an atomic solution and diffusion process, we used a ruthenium disk (~75% T.D. and 0.7 mm thick) instead of powders in between the UO\(_2\) disks. We still found ruthenium in UO\(_2\). This proves that it is an atomic diffusion process; the powder particles do not move as an entity. In order to study the diffusion mechanism, ruthenium powders were sintered in between two single crystal UO\(_2\) disks at 2200°C for 12 hrs. No (or very few) ruthenium inclusions were found in the bulk of single crystal UO\(_2\), proving that the ruthenium migrates as atoms via grain boundaries. Using the detection microprobe to study the inclusions on the grain boundaries of UO\(_2\) in the isothermal sintering experiments, we found that the precipitates all have large amounts of uranium metal besides ruthenium metal. This suggests that the precipitates are the U-Ru intermetallic phases occasionally found in irradiated LMFBR fuels.

From the results of isothermal ruthenium experiments, we speculate that the metallic inclusions in reactor fuel do not migrate bodily, as is
commonly believed. Instead, they diffuse in the fuel as atoms. During cooling down, they precipitate out as inclusions.

D. Ruthenium Inclusions - Temperature Gradient Annealing

With the data obtained in the isothermal annealing experiment, we could predict the diffusion profile of ruthenium in UO₂ under the influence of temperature gradient by solving the diffusion equation:

\[ \frac{\partial c}{\partial t} = - \frac{\partial}{\partial z} \left( D(T) \left( \frac{\partial c}{\partial z} + \frac{c Q^*}{k T} \frac{\partial T}{\partial z} \right) \right) \]

(2)

\[ D(T) = D_0 e^{-Q/kT} \]

(3)

where

- \( C \) = concentration of ruthenium in UO₂
- \( z \) = diffusion distance
- \( D \) = diffusivity of ruthenium in UO₂
- \( Q^* \) = heat of transport for thermal diffusion
- \( T \) = temperature
- \( D_0 \) = pre-exponential factor for \( D \)
- \( Q \) = activation energy for ruthenium diffusion in UO₂

Or, we could try to fit the data to equation (2) and get the value of \( Q^* \). However, because the molecular diffusion term in equation (2) is much larger than the thermal diffusion term, it is probable that \( Q^* \) cannot be obtained this way. However, the gradient experiment can be used to obtain \( D_0 \) and \( Q \) in a single experiment and this can be used to check the results from the isothermal experiments.
Fig. 1. Various Shapes of Crucibles Designed for Peripheral Heating
Fig. 2. Ru on grain boundaries in a UO₂ matrix
Tantalum tightening nut

Molybdenum push rod

Molybdenum yoke

Tungsten alignment tube

UO₂ contact surfaces polished by 600 grit SiC paper

0.001" rhenium foil

Tungsten separator

Thick layer of ruthenium powder

Fig. 3. Isothermal Sintering Apparatus
Interface position by data fitting

Concentration profile by data fitting

Visual interface

Ratio of ruthenium to uranium count rate × 100

Distance from interface (μm)
I. Introduction

Oxide insulator materials exposed to the hot hydrogen fuel of a CTR plasma will be subject to chemical as well as physical corrosion (1, 2). To better understand the nature of the chemical attack, the reduction reactions of thermal atomic hydrogen with refractory oxides, UO_2 and Al_2O_3, are being studied by the modulated molecular beam method (3, 4).

Although previous studies have made qualitative observations of atomic hydrogen/oxide reactions (5, 6) and others have predicted corrosion rates based on thermodynamic equilibrium models (7), there is little information about the elementary reaction steps which comprise the overall reduction reaction and the values of the associated rate constants. This information can be obtained by modulated molecular beam mass spectrometry, which has been described in detail in previous publications (8, 9).

II. Experimental Modifications

Evaporation of solder from the connections in the high current leads to the tungsten dissociation oven resulted in contamination of the target and source chambers and necessitated cleaning of the source chambers and associated diffusion pump. All high current connections are now brazed to prevent recurrence of this problem.

III. Results

Results of the UO_2/H investigation indicate that reduction of UO_2 (slightly hyperstoichiometric) by atomic hydrogen proceeds by the production of water vapor and hypostoichiometric urania:

\[
\frac{1}{x} \text{UO}_2 + 2\text{H} \rightarrow \frac{1}{x} \text{UO}_{2-x} + \text{H}_2\text{O}
\]  

\[\text{(1)}\]
The reaction probability for water production as a function of UO$_2$ temperature was measured at a fixed H atom beam intensity and modulation frequency. The reaction probability increased from the noise level at low temperatures to a high temperature plateau at 1300°C. At the plateau, approximately one H atom out of seven striking the surface undergoes reaction and returns to the gas phase as water.

To investigate the effect of stoichiometry on the UO$_2$/H reaction, a second set of experiments is under way employing a UO$_{2-x}$ target which has been reduced below the lower phase boundary. The reduction of UO$_{2-x}$ below the lower phase boundary is theorized to proceed by the production of U:

$$\frac{1}{2-x} \text{UO}_{2-x} + 2\text{H} \rightarrow \text{H}_2\text{O} + \frac{1}{2-x} \text{U} \quad (2)$$

Initial results indicate no significant difference from those obtained using a hyperstoichiometric sample, however, these experiments are not yet complete. Possible product species such as U(g), UO(g), UH(g) have been sought, but not found.

Data on the reduction of Al$_2$O$_3$ have been taken at temperatures from 300°C to 2040°C (the melting point) at a fixed equivalent hydrogen atom pressure ($\approx$ 5 x 10$^{-4}$ torr). Water production by reduction of Al$_2$O$_3$ remains too low to be detected (i.e., reaction probability $\leq$ 10$^{-4}$) until the temperature is greater than 1300°C. The low reactivity of Al$_2$O$_3$ to H below 1300°C is consistent with the findings of others (10, 11). At higher temperatures, both H$_2$O and Al are detected by the mass spectrometer as gaseous reaction products. Other products, such as AlO, AlH, AlOH, Al$_2$O, and Al$_2$OH were sought, but not found. The reaction probability increases with temperature, but remains two orders of magnitude below the maximum value for the UO$_2$/H reaction. These data
indicate that the reaction proceeds according to:

\[
\frac{1}{3} \text{Al}_2\text{O}_3 + 2\text{H}_2(\text{g}) + \frac{2}{3} \text{Al}(\text{g}) + \text{H}_2\text{O}(\text{g})
\]  

(3)

Contrary to UO$_2$, the range of deviation from stoichiometry of Al$_2$O$_{3-x}$ is probably so small that even slight reduction of Al$_2$O$_3$ requires production of the metal. Because alumina cannot be rendered hypostoichiometric, its reduction by atomic hydrogen results in production of aluminum metal.

IV. Discussion

A) UO$_2$ and Al$_2$O$_3$ reactivity

The relative ease with which UO$_2$ is reduced by atomic hydrogen compared with Al$_2$O$_3$ has been discussed in a previous publication (12). One additional feature which may favor reduction of UO$_2$ over Al$_2$O$_3$ is scale morphology. If reduction of UO$_2$ produces an oxygen deficient scale which has "holes" through which the reaction may continue while reduction of Al$_2$O$_3$ produces a continuous Al scale with no "holes", then the reduction of UO$_2$ would be expected to proceed more rapidly than that of Al$_2$O$_3$.

B) UO$_{2-x}$ reactivity above and below lower phase boundary.

In the case of UO$_{2-x}$ with an overall composition below the lower phase boundary (i.e. in the 2-phase region) the oxygen potential is a constant throughout the bulk even as the reaction proceeds. Thus, there is no driving force (gradient) for oxygen bulk diffusion. Therefore, UO$_{2-x}$ below the lower phase boundary could be expected to behave qualitatively like Al$_2$O$_3$ with formation of a metallic scale. For the UO$_2$ reaction to proceed in this regime, either the U scale morphology must allow access of H to the bulk or the U produced must vaporize. In the case of single-phase UO$_{2-x}$ above the lower phase boundary, a
concentration gradient of oxygen can exist in the bulk. Thus, a chemical (oxygen) potential gradient could be produced across the sample, yielding a driving force for oxygen diffusion to supply the surface reduction reaction.

If bulk diffusion of oxygen is important in the UO$_2$ reduction reaction, then the UO$_{2-x}$ reduced target should exhibit less reactivity than the slightly hyperstoichiometric target. If no difference in reactivity is observed between the reduced and non-reduced UO$_2$ samples, then there must be no change in apparent reactivity with $x$, and bulk diffusion of oxygen would probably not be important to the reaction.

V. Future Experiments

1) Fresh Al$_2$O$_3$ samples have been prepared for study at the high temperatures where the reaction probability is large. Although the mass spectrometer noise background at these elevated temperatures makes measurements difficult, attempts will be made to obtain precise phase lag as well as reaction probability data since both these quantities are necessary to properly interpret the reaction mechanism.

2) Some observers have reported enhanced reduction reactions of Al$_2$O$_3$ in the presence of H$_2$O vapor (13, 14). The effect of H$_2$O vapor on the reduction reaction will be investigated by the use of a doser to provide a D.C. source of H$_2$O vapor to the Al$_2$O$_3$ surface.

3) The investigation of the reduction reaction using hypostoichiometric UO$_{2-x}$ polycrystalline wafers will continue. Because of the importance of the UO$_{2-x}$ experiment to interpretation of possible reaction mechanisms, possible stoichiometry changes (oxidation) due to "bakeout" preparation of the UO$_{2-x}$ samples in-situ prior to experimentation is also being investigated. Finally, a single-crystal UO$_2$ target
will be studied to determine the effect of grain boundaries and crystal orientation upon reactivity.

References


10. S. Veprek, Private Communication (June 16, 1978)


Natural salt deposits contain small cubical inclusions of brine distributed through the salt. Temperature gradients, resulting from storing heat-generating nuclear wastes in the salt, can cause the inclusions to move through the salt. Prediction of rate and amount of brine-inclusion migration is necessary for the evaluation of bedded or domed salts as possible media for nuclear waste repositories.

The objective of this investigation is to develop a rigorous model of thermal gradient migration of brine-inclusions. Tests of predicted migration velocities are accomplished by mounting NaCl or KCl single crystals on an optical microscope equipped with a hot stage attachment. Inclusions are fabricated by drilling a hole in the crystal, partially filling it with water and closing the hole with a rubber sealant.

All-liquid Inclusions

When a thermal gradient is applied along a <100> direction, the initially cubical inclusion changes shape, finally acquiring the shape of a square platelet (Fig. 1). The inclusion faces are {100} planes as these planes have a minimum surface energy. The steady state shape of an inclusion when the thermal gradient is in a different crystallographic orientation is more complex; the inclusion takes on a chevron shape with elementary {100} facets forming the interface.

The increase in salt solubility with temperature provides the driving force for salt diffusion from hot to cold faces of the inclusion. According to the theory proposed by Anthony and Cline [J. Appl. Phy. 42, 3380 (1977)] the inclusion velocity depends on the shape of inclusion and the thermal
gradient in the salt at the location of the inclusion. It is possible to obtain analytical expressions of migration velocity when the temperature gradient is along a <100> direction. When the latter is not realized, the process of migration and dependence of velocities on the shape of the inclusion is complex.

Kinetics of dissolution and deposition of salt at the hot and cold faces of the inclusion appear to be important and depend on dislocation density and crystal state of stress. Fig. 2 shows the inclusion velocity plotted against the inclusion temperature for NaCl and KCl single crystals where the thermal gradient is in a <100> orientation. The large scatter in the data is not well understood. It may be due to non-uniform distributions of dislocations in the crystal; there are regions of high dislocation density as well as regions with practically no dislocations in a typical crystal. Besides being important in the kinetics of dissolution and crystallization, dislocations could also hinder migration of the inclusions. To further investigate this, inclusion velocities will be measured in crystals of varying dislocation density. Etch-pit methods will be used to determine dislocation densities in crystals. This method involves treating chemically polished crystal surface with an etchant which forms pyramid-shaped pits on the surface indicating the presence of dislocations.

The effect of grain boundaries on migration of inclusions in an actual salt repository will be very important. These effects will be experimentally investigated in specially fabricated bi-crystals.

Gas-Liquid Inclusions

A gas-liquid inclusion has a roughly spherical gas phase within a cubic liquid inclusion when the thermal gradient is applied along a <100>
direction. The mechanism of thermal gradient migration of these inclusions is shown in Fig. 3. Water vapor evaporates from the hot side of the gas bubble in the brine and is transported to the cold side where it condenses. The condensed water is recycled to the hot side by backflow of the brine, which provides the mechanism for moving salt from the cold face of the inclusion to the hot face. The inclusion thus moves in the opposite direction from the salt flow.

Anthony and Cline [Acta Met. 20, 247 (1972)] proposed a simplified analytical model for the two phase inclusions by considering a cubic gas phase at the centre of a cubic liquid phase with laminar backflow of the brine. A more detailed theory of the two-phase inclusion migration process than that offered by Anthony and Cline has been developed. However, thermocapillarity and interfacial kinetic resistances to salt dissolution and precipitation effects have not been included. Kinetics at the cavity interfaces plays a major role in the migration of all-liquid inclusions and therefore should be incorporated. Also, a vapor bubble in a temperature gradient is subjected to a variation of surface tension which tends to move the interfacial film. This, in turn, drags with it adjacent warm liquid so as to produce a net flow around the bubble. This mechanism, known as thermocapillarity, is probably responsible for the strong convection currents in the liquid phase.

A theoretical model including kinetic and thermocapillarity processes will also be worked out.
Fig. 1 Photomicrograph of a liquid inclusion in single crystal of NaCl. The applied thermal gradient is along a <100> direction which is normal to the smaller side of square platelet shaped inclusion.
Fig. 3 Cross section of a cubical gas-liquid inclusion in an infinite medium of solid salt supporting a temperature gradient. The fluxes of water and salt which produce the reverse-gradient migration (down the thermal gradient) are indicated by arrows.