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Materials & Molecular Research Division

NUCLEAR MATERIALS RESEARCH PROGRESS REPORTS FOR 1979

D. R. Olander

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FOR 1979

Materials and Molecular Research Division
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CONTENTS

1. Aluminum Iodide Stress Corrosion Cracking of Zircaloy by S. Shann	1-7
2. Self-Diffusion of Oxygen in Hypostoichiometric Urania by K. Kim	8-17
3. The Surface Chemistry of Epitaxial Silicon Deposition by Thermal Cracking of Silane by M. Farnaam	18-25
4. The Kinetics of Laser Pulse Vaporization of UO_2 by C. H. Tsai	26-38
5. Gas Laser Model for Laser Induced Evaporation by F. Tehranian	39-45
6. Solubility of Hydrogen in Uranium Dioxide by D. Sherman	46-55
7. Thermal Gradient Migration of Metallic Inclusions in UO_2 by R. Yang	56-65
8. Molecular Beam Studies of Atomic Hydrogen Reduction of Oxides by D. Dooley	66-70
9. Thermal Gradient Brine-Inclusion Migration in Salt by A. J. Machiels and S. K. Yagnik.	71-76

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 ($\sim 10^{-3}$ 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, $\text{AlI}_3(\text{g})$ 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 $\ln P_{\text{AlI}_3}$ shows a slope of

$-2/3 \pm 0.1$ (Fig. 1) compared to a slope of $-1/2 \pm 0.02$ for molecular iodine. Some specimens failed by pinhole failure, some by tearing. In both types of failures, the 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

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XBL 801-4595

Fig. 1 EFFECT OF ALUMINUM IODIDE EXPOSURE ON ZIRCALOY SCC: THE TIME TO FAILURE DECREASES AS THE $2/3$ POWER OF THE AlI_3 PRESSURE

XBE 801-365

Fig. 2 SEM FRACTOGRAPHY OF PINHOLE TYPE FAILURE (Zr-2 (9Ax32)
FAILED AFTER 36.7 HR. 53 PSI (365 MPa), 300 °C, 1.38×10^{-3}
TORR AlI_3) (5,000x).

XBB 801-368

Fig. 3 SEM FRACTOGRAPHY OF BURST TYPE FAILURE (Zr-2 (9Ax32)
FAILED AFTER 9.4 HR. 53 PSI (365 MPa), 300^O C,
2.0x10⁻³ TORR AlI₃) (10,000x).

XBL 7911-7292

Fig. 4 ALUMINUM EDAX SIGNAL DECREASES ON MOVING IN FROM OUTSIDE SURFACE OF THE TUBE INTO THE CRACK (FOR DIFFERENT POSITIONS AND DIFFERENT SPECIMENS).

XBL7911-7293

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. ExperimentalA. 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 $1500^\circ C$:

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_2 . (See fig. 1). The desired H_2O/H_2 ratio was obtained by flowing hydrogen through $H_2^{18}O$ of which temperature was controlled. After 43 hours, by measuring the weight before and after, it was determined that approximately 70% of the ^{16}O was replaced by ^{18}O .

In order to have the same history, exactly the same procedure was applied to the other UO_2 wafer using normal water. The ^{18}O enriched wafer and the normal wafer were reduced in hydrogen at $1950^{\circ}C$ at the same time in order to match the stoichiometries:

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 ^{18}O 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 ^{18}O concentration in $UO_{1.985}$ after 20 min. at $1330^{\circ}C$. Fig. 5 is for $UO_{1.993}$ after 5 hours at $1190^{\circ}C$. Using the computer code MINUIT, data were fitted to the analytic solution:

$$\frac{18_0}{18_0 + 16_0} = \sum_{n=0}^{\infty} e^{-D \alpha_n^2 t} \frac{\left\{ \left(\frac{B}{\ell} \right)^2 + \alpha_n^2 \right\} \cos \alpha_n z}{\left\{ \left(\frac{B}{\ell} \right)^2 + \alpha_n^2 \right\} \ell + \left(\frac{B}{\ell} \right)} \cdot \frac{\sin \alpha_n \ell}{\alpha_n} \quad (3)$$

D = Oxygen self diffusion coefficient in UO_{2-x} (unknown)

α_n = Constants ($\alpha \ell \tan(\alpha \ell) - B = 0$)

t = time

z = distance from the interface

ℓ = thickness of the wafer

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

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

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

D^{ℓ} = diffusivity of oxygen in liquid uranium

C^{ℓ} = concentration of oxygen in liquid uranium

C = concentration of oxygen in UO_{2-x}

δ = 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 $D = D_0 \exp(-E/RT)$ is proportional to x in UO_{2-x} , those two values were combined to yield an activation energy $E = 5.5 \text{ kcal/mole}$.

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 ~ 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°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 δ of liquid uranium bond was about 16 times thicker for the second experiment than the first one. According to

$B = \left(\frac{D^k}{D}\right) \left(\frac{C^k}{C_O}\right) \left(\frac{\ell}{\ell_0}\right)$, 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.

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XBL792-5670

Fig. 1 Variation of oxygen potential with temperature and O/U ratio (ref. 10) with two-phase boundary based on ref. 12.

XBL801-4615

Fig. 2 Diffusion experiment setup

Fig. 3 Cut surface of the diffusion couple and the line of probe of #1 experiment ($T = 1330^{\circ}\text{C}$, 20 min.)

XBL 801-4616

Fig. 4 Normalized profile of ^{18}O concentration of experiment #1.

XBL 801-4617

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 $\text{SiH}_4(\text{g}) \rightarrow \text{Si} + 2\text{H}_2(\text{g})$ 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.⁽¹⁾ 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^(2,3,4) which do not have advantages such as phase lag measurement.⁽⁵⁾

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 2×10^{-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 ⁽⁶⁾. 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 $\Omega\text{-cm}$, 375 μm thick and 5 cm in diameter, cut along (111) face. A triangular sample with sides about 17 mm perpendicular to $(\bar{1}\bar{1}2)$ 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 N_2 (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 ~ 25 mm in diameter with a hole ~ 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 1

20 minutes at $\sim 1150^\circ\text{C}$ in the background pressure of 7×10^{-9} torr
30 minutes at $\sim 1300^\circ\text{C}$ in the background pressure of 2×10^{-8} torr
and 30 minutes at $\sim 1100^\circ\text{C}$ in the background pressure of 4×10^{-9} torr

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 $\sim 1100^{\circ}\text{C}$ but with exposure to a SiH_4 flux of $\sim 1 \times 10^{15}$ molecules/ $\text{cm}^2\text{-sec}$ at the surface. Again, SEM did not show any features. Repetition of this experiment at higher fluxes of SiH_4 ($\sim 3 \times 10^{15}$ molecules/ $\text{cm}^2\text{-sec}$) for longer periods of time (~ 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 H_2^+ , Si^+ , SiH^+ , SiH_2^+ , SiH_3^+ , and SiH_4^+ 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 SiH_4 and steady state SiD_4 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.

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XBL 7912-5220

XBL 7912-5219

THE KINETICS OF LASER PULSE VAPORIZATION OF UO_2

by C. H. Tsai

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.¹⁻⁴ A survey on the various techniques is given in a specialists' meeting in 1978.⁵

The laser pulse heating technique, together with the mass spectrometry and automatic optical pyrometry measuring techniques, is being utilized and developed in this lab.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 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 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 pyrometer 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 UO_2 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 microscope 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 UO_2 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 (U_2O_4) 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 UO_2 target. The estimation of the total amount of UO_2 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 $\text{H}_2/\text{H}_2\text{O}$ 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.

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XBL 7712-6609

XBL 791-5658

ANGULAR DISTRIBUTION MEASUREMENT

Fig. 3 Angular distribution of mass flux in vapor plume from UO_2

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.

XBL 801-7842

Fig. 6 (a) Crater depth profile along the major axis.
(b) Surface roughness reference.

XBL 801-7843

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 ($>4000\text{K}$) 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)

γ	Sudden freeze model
5/3	35
7/5	80
9/7	120

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 $X = 40 \text{ Cm}$

γ	N/N_1 (from gas dynamic model)	N/N_1 (from angular distribution)
9/7	0.21	.31
7/5	0.33	.38
5/3	0.61	.52

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

$$\frac{\rho(R,\theta)}{\rho(R,0)} = \cos^2 \left(\frac{\pi\theta}{2\phi} \right), \text{ in which } \phi \text{ is a function of the specific heat}$$

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 ~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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Fig. 1: Flow Regions

XBL 803-4823

Fig. 2.: Vapor Temperature vs Distance

Fig. 5.1: Number Density vs. Distance

SOLUBILITY OF HYDROGEN IN URANIUM DIOXIDE

by Douglas Sherman

I. Introduction

When heated to high temperature, UO_2 fuel rods have been found to release hydrogen-bearing gases which may attack the zircaloy cladding. One possible source of hydrogen (other than adsorbed H_2O) is hydrogen dissolved in the lattice of the solid. At present no reliable information on hydrogen solubility in UO_2 is available. Previous results by Wheeler (1) with single crystal UO_2 produced solubilities ranging from 0.03 to 0.4 micrograms of $\text{H}_2/\text{g UO}_2$ 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 UO_2 it is necessary to achieve a high temperature to reduce the stoichiometric UO_2 . 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 H₂O vapor in UO₂ 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 H₂O 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 UO₂ 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 $D_2O/g\ UO_2$. 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 $5.08 \pm 0.08\%$, and a closed porosity of $15 \pm 2\%$ 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 UO_2 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 UO_2 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 UO_2 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, it's 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.

XBL 7712-6611

XBL 791-5624A

Fig. 2 H_2O Infusion Method Apparatus for Measuring Internal Porosity.

XBL 803-4836

Fig. 3 Permeation Method Apparatus
For Measuring Internal Pore Structure.

XBL803-4837

Fig. 4 Effusion Method Apparatus
For Measuring Internal Pore Structure

XBB 804-4146

THERMAL GRADIENT MIGRATION OF METALLIC INCLUSIONS IN UO_2

by R. L. Yang

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 UO_2 out of tungsten crucible by dissolving the crucible in a mixture of $\text{H}_2\text{SO}_4 + \text{HF}$, 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 UO_2 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 UO_2 was still full of pores and was too fragile to be used in the thermal gradient experiment.

3. Put a piece of iridium between UO_2 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 UO_2 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 UO_2 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 UO_2 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 UO_2 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 $10\mu\text{m}$), 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:

$$C = C_0 \operatorname{erfc} \left(\frac{X - X_0}{2 \sqrt{Dt}} \right) \quad (1)$$

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 ($\sim 75\%$ 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 UO_2 under the influence of temperature gradient by solving the diffusion equation:

$$\frac{\partial c}{\partial t} = - \frac{\partial}{\partial z} \left\{ - D(T) \left(\frac{\partial c}{\partial z} + \frac{C}{kT} \frac{Q^*}{T} \right) \right\} \quad (2)$$

$$D(T) = D_0 e^{-Q/kT} \quad (3)$$

where C = concentration of ruthenium in UO_2

z = diffusion distance

D = diffusivity of ruthenium in UO_2

Q^* = heat of transport for thermal diffusion

T = temperature

D_0 = pre-exponential factor for D

Q = activation energy for ruthenium diffusion in UO_2

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.

(a)

(b)

XBL 302-46 43A

Fig. 1. Various Shapes of Crucibles Designed for Peripheral Heating

XBB 802-2016

Fig. 2. Ru on grain boundaries in a UO_2 matrix

XBL802-4642A

Fig. 3. Isothermal Sintering Apparatus

XBL 802-268

MOLECULAR BEAM STUDIES OF ATOMIC HYDROGEN REDUCTION OF OXIDES

by Douglas F. Dooley

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:

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:

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 $\text{U}_{(g)}$, $\text{UO}_{(g)}$, $\text{UH}_{(g)}$ have been sought, but not found.

Data on the reduction of Al_2O_3 have been taken at temperatures from 300°C to 2040°C (the melting point) at a fixed equivalent hydrogen atom pressure ($\sim 5 \times 10^{-4}$ torr). Water production by reduction of Al_2O_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_2O_3 to H below 1300°C is consistent with the findings of others (10, 11). At higher temperatures, both H_2O and Al are detected by the mass spectrometer as gaseous reaction products. Other products, such as AlO , AlH , AlOH , Al_2O , and Al_2OH 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:

Contrary to UO_2 , the range of deviation from stoichiometry of $\text{Al}_2\text{O}_{3-x}$ is probably so small that even slight reduction of Al_2O_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_2O_3 reactivity

The relative ease with which UO_2 is reduced by atomic hydrogen compared with Al_2O_3 has been discussed in a previous publication (12). One additional feature which may favor reduction of UO_2 over Al_2O_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_2O_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_2O_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_2O_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_2O_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_2O_3 in the presence of H_2O vapor (13, 14). The effect of H_2O vapor on the reduction reaction will be investigated by the use of a doser to provide a D.C. source of H_2O vapor to the Al_2O_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.

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THERMAL GRADIENT BRINE-INCLUSION MIGRATION IN SALT

by A. J. Machiels and S. K. Yagnik

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 $\langle 100 \rangle$ 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 $\langle 100 \rangle$ 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 $\langle 100 \rangle$ 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 cubical liquid inclusion when the thermal gradient is applied along a $\langle 100 \rangle$

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.

XBB 802-2017

Fig. 1 Photomicrograph of a liquid inclusion in single crystal of NaCl. The applied thermal gradient is along a $\langle 100 \rangle$ direction which is normal to the smaller side of square platelet shaped inclusion.

XBL 802-261

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.