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Title
THE REDISTRIBUTION OF RUTHENIUM IN UO2 IN A TEMPERATURE GRADIENT

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Research Division

THE REDISTRIBUTION OF RUTHENIUM IN UO_2 IN A
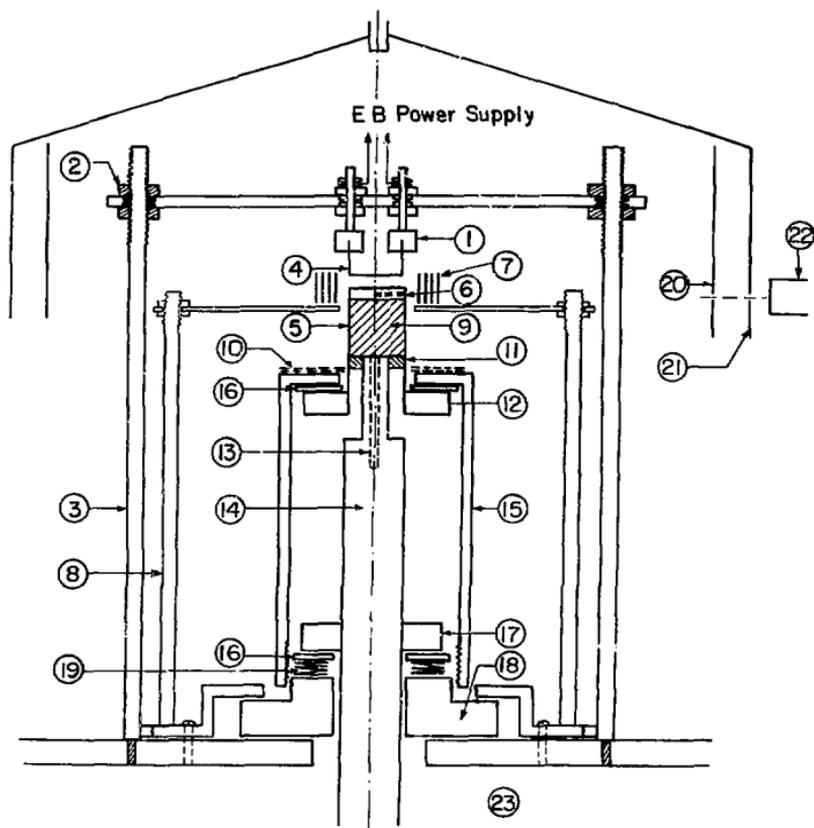TEMPERATURE GRADIENT

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1. INTRODUCTION

It is well know that at high temperature and in a high temperature gradient the fission products in oxide fuel elements redistribute. The redistribution of these species has a significant influence on the performance of the fuel element. It is believed that thermal diffusion might play an important role in the redistribution of fission products dissolved in the fuel matrix. By using estimated parameters, Nichols et. al. [1] theoretically analyzed the kinetics of redistribution of barium in irradiated UO_2 fuel based on thermal diffusion. Beisswenger et. al. [2] studied the thermodiffusion in system UO_2-CeO_2.

Ruthenium is one of the fission products and together with Rh,Tc,Pd and Mo, forms metallic inclusions distributed along grain boundaries or in the central void of the fuel element. Originally these fission products are uniformly produced throughout the element; why they move to the high temperature region and by what mechanism are not known. It was believed that the metallic inclusions migrate bodily in UO_2 at high temperatures and in steep temperature gradients [3-5]. However a recent experiment[6] has shown that metallic inclusions such as W,Mo,Ru do not migrate as entities. The present study is concerned with the temperature gradient-driven mobility of ruthenium in UO_2 as a means of better understanding the redistribution of metallic fission products in oxide fuel elements.

2. EXPERIMENTAL

The experiments were carried out in the high temperature - temperature gradient furnace described in Ref. 6 and shown in Fig. 1. The temperature

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Fig. 1   Temperature gradient furnace

4. tungsten filament	5. tungsten crucible
6. black body hole	9. specimen
11. cooling contact ring	14. molybdenum cooling rod

measurement was made by pyrometer, with an accuracy of about $\pm$ 20°C. The pryrometer was calibrated with W - Re thermocouple up to 2200°C. By heating the top of the tungsten crucible and cooling the bottom end of the sample with a molybdenum rod, the furnace can produce 1500 - 2000° K/cm temperature gradient.

The samples were made by General Electric Company. Before sintering, nuclear grade UO_2 powders were mixed uniformly with 99% pure Ru powders having particle sizes ranging between 1μm - 10μm. The samples were sintered in hydrogen atmosphere at 1700°C for 4 hours. A recheck of the stoichiometry showed the samples to be $UO_{2.000}$. Two 0.001" thick rhenium foil disks were placed on the top and the bottom of the sample in order to prevent possible reaction between tungsten crucible and UO_2. Thanks to the rhenium foils, the sample could be extracted after the experiment without breaking the tungsten crucible, which is very expensive.

In order to simulate the temperature distribution in a UO_2 fuel element under irradiation and to maximize the thermal diffusion effect, the highest possible temperature of the hot end of the sample was chosen. The maximum temperature achieved was $\sim$2800 K, which is about the temperature near the central void of a fast reactor fuel element. The temperature of the cold end of the sample was $\sim$1700 K, which corresponds to that of the equiaxed grain zone of the fuel element.

One way to measure the heat of transport (the characteristic parameter of thermal diffusion) is to let the system reach equilibrium in a temperature gradient; the heat of transport can be then obtained from the

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slope of the plot of $\ln C$ vs $\frac{1}{T}$ [7,8]. In the UO_2 - Ru system, rough estimates indicate that even at the highest possible experimental temperature (say 2800 K) and the shortest sample (say 0.25 cm), the time to reach equilibrium would be at least 20 days. However, such an experiment is not feasible. Even if the furnace could sustain such a long time at high temperature, the sample would certainly shrink considerably by evaporation. The other method chosen in this study is to measure the heat of transport in a non-equilibrium condition, which can much shorten the duration of experiment. Suppose the experiment is run with specified temperature, temperature gradient, length of sample and time, and the distribution of Ru after the anneal is measured. The calculated distribution of Ru can be obtained by solving the thermal diffusion equation numerically. The heat of transport appearing in the theory is adjusted to give the best fit of the experimental and theoretical profiles.

Each experiment lasted about 28 to 34 hours in order to produce detectable redistribution. After the experiments, the samples were either cut with a diamond saw into slices $30\mu m$ - $50\mu m$ thick or else layers of about the same thickness were ground off one by one for X-ray fluorescence analysis, which had previously been calibrated with standard Ru/UO_2 samples. The detection limit is a Ru/U atom ratio of 2×10^{-4}, and the accuracy of the analysis is around 10 - 15 % depending on the quality of Ru contained in the sample. Optical microscopy and SEM were used for visual examination of the samples before and after the experiments.

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3. RESULTS

A. Temperature Gradient Experiments

Three experiments were conducted at different temperatures, temperature gradients, sample thicknesses, and times. Initially the concentration of Ru in the samples was uniform. After the experiments, the Ru particles partially dissolved into the UO_2 grain boundaries, and Ru redistributed along the thermal gradient. Microscopic observation of the sample (Fig. 2) showed that the radii of the Ru particles did not change; instead, voids were created in the centers of the particles. There were no gaps between Ru particles and the matrix. After the experiments, a second phase identified as URu_3 was observed along the UO_2 grain boundaries. These had the same appearance as those reported in Ref. 6.

The Ru concentration profiles are shown in Figs. 3-5. The results show that large amounts of Ru diffused up the temperature gradient and accumulated at the hot ends. Because the temperature at the cold end is much lower, the Ru concentration here is essentially unchanged. Ru is depleted in the middle parts of the samples, leaving a concave-shaped Ru concentration profile. Ru in the low temperature regions could not diffuse sufficiently rapidly to compensate for the loss of Ru in the middle region. It is very obvious from Figs. 3-5 that the higher the temperature, and the steeper the temperature gradient, the more ruthenium diffuses towards the hot zone.

After the experiment the Ru concentration should satisfy mass conservation, but it is seen from Figs. 3-5 that there has been some loss of Ru. This loss might have resulted from severe evaporation at the hot end, where the temperature reached 2800 K, well above the melting points
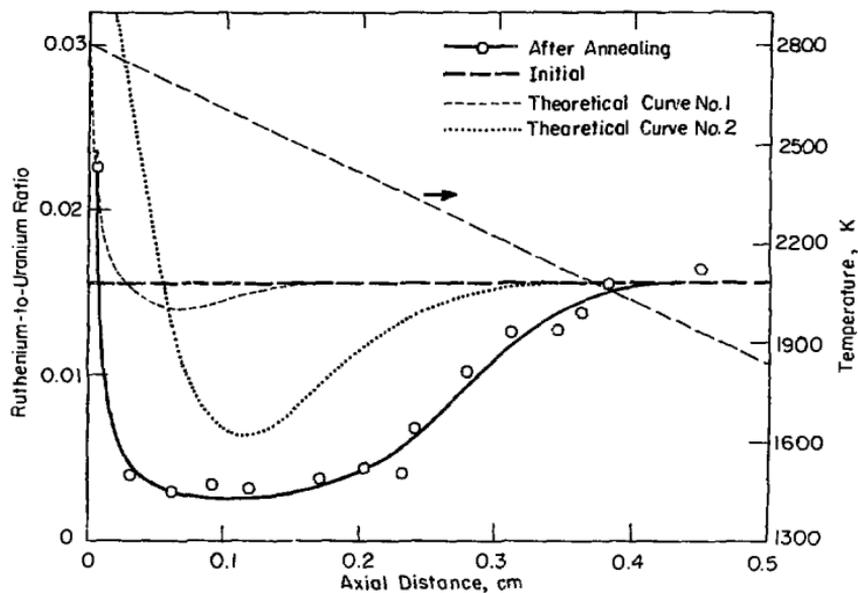
(A)

(B)
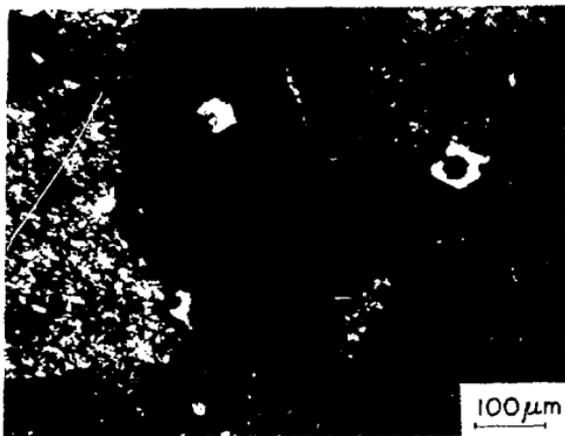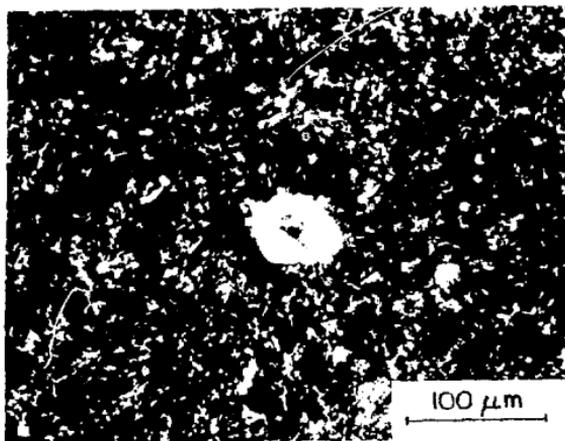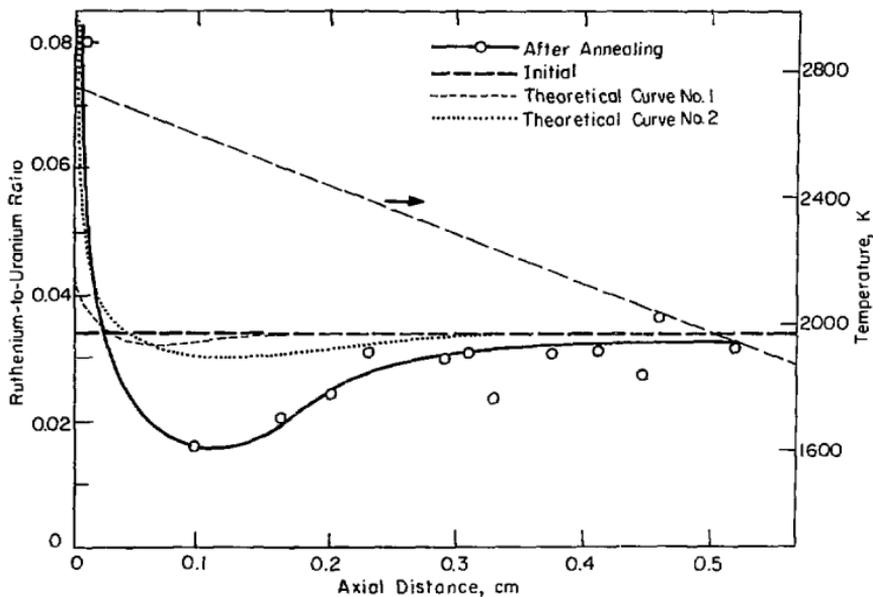
Fig. 2   Ruthenium Particles Showing Voids in the Centers

T_h = 2800 K;   G = 1931 K/cm; L = 0.51 cm; t = 33 hrs

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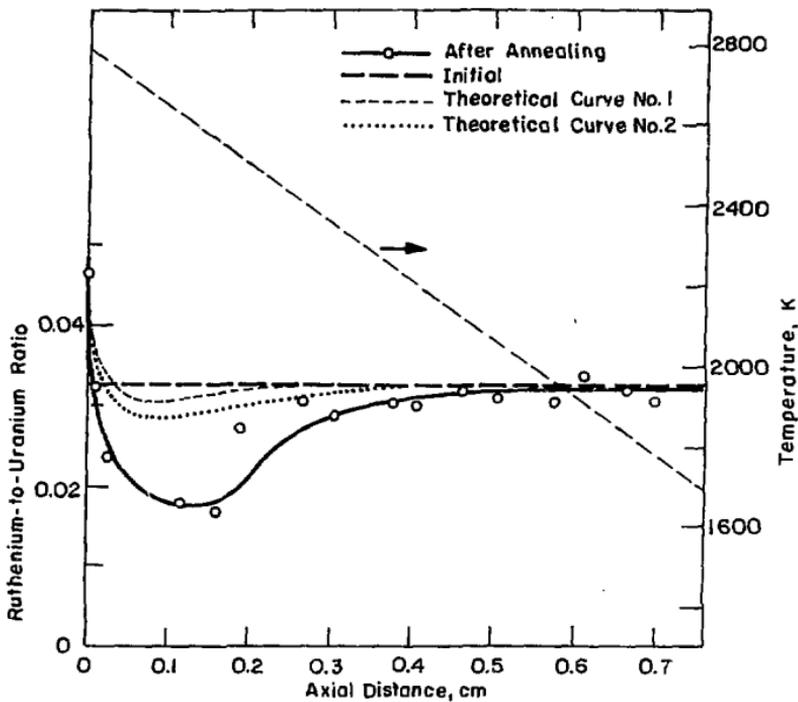Fig. 3 Redistribution of Ruthenium Along Sample No. 1;
T_h = 2800 K; G = 1930 K/cm, L = 0.51 cm, t = 33 hrs

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Fig. 4   Redistribution of Ruthenium Along Sample No. 2

T_h = 2770 K; G = 1660 K/cm; L = 0.57 cm, t = 33.6 hrs.

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Fig.5   Redistribution of Ruthenium Along Sample No. 3

T_h = 2780 K; G = 1440 K/cm; L = 0.76 cm, t = 27 hrs

of Ru and URu_3 (T_{Ru} = 2523 K, T_{URu_3} = 2170 K). The UO_2 sample and some Ru might have evaporated, resulting the differences between theoretical and experimental curves. Actually each sample had a concave top, the depth of the depression being about 0.3 - 0.4 mm.

B. Isothermal Annealing Experiment

In order to make sure that the redistribution described above was due to the thermal gradient rather than to reaction of ruthenium with the crucible metal, an isothermal anneal was performed (fig 6). The Ru concentration in the main part of the sample did not change. The low Ru concentrations on the top and the bottom surfaces are believed to be due to loss by evaporation. The vapor pressure of Ru at 2470 K is 2×10^{-3} atm [9], while that of UO_2 at the same temperature is 1×10^{-4} atm [10]. Also, from microscopic observation, the original Ru particles on the end surfaces had disappeared, leaving holes of the same size. These results show that neither the tungsten crucible nor the rhenium foils influence the distribution of ruthenium in UO_2 during the high temperature experiments. The second phase, which has been identified as URu_3, was observed in the grain boundaries of the UO_2.

C. Stoichiometry

The original stoichiometry of the samples was $UO_{2.000}$. During the high temperature gradient experiments, the tungsten crucible reduces the oxide, and oxygen in the resulting UO_{2-x} redistributes. A sample was sliced into wafers after temperature gradient experiment to determine the stoichiometry change along its length. The stoichiometry of each slice was determined by thermogravimetric method [11]. Fig. 7 gives

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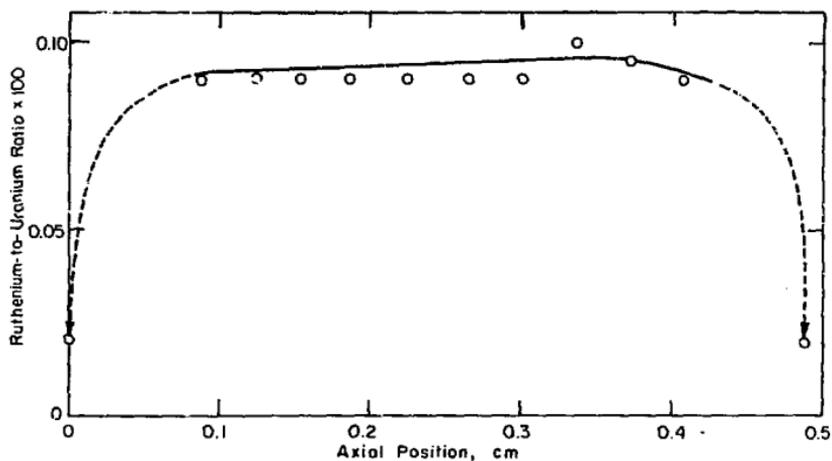
Fig. 6   Ruthenium Concentration Profile Along a Sample After
          Isothermal Annealing at T = 2370 K for 3 hrs and
          T = 2470 K for 1 hr; Both Ends Covered with Ruthenium
   Foil.

stoichiometry profile along the sample. Oxygen migrated down the
temperature gradient and accumulated at cold region, thus depleting
the hot region. After the experiment, the average stoichiometry is
O/U = 1.998, which indicated that the tungsten crucible reduced
stoichiometric urania. Assuming that the profile represents the
equilibrium distribution of oxygen in the sample in the temperature
gradient at temperature, the heat of transport of oxygen vacancies
in UO_2, by the plot shown in Fig.8, is -138 ± 53 KJ/mole, which is
comparable with that found by other investigators, - 125 ± 60 KJ/mole[12].

4. DISCUSSION

   A. Model

       Before the experiment, the Ru particles were uniformly distributed
in the samples. Under the temperature gradient, the Ru particles
dissolve in the grain boundaries, in which the Ru also diffuses. The
rate-controlling step of the dissolution of Ru into the grain boundaries
is the diffusion from surfaces of particles into grain boundaries.
Transport from the inside to the surfaces of Ru particles seems faster
compared to dissolution from the surfaces to the grain boundaries so
that there are no gaps between the UO_2 and the particles. We assume that
the Ru particles are spherical with constant radius R_0, the temperature
gradient along the sample is constant and on every cross section perpen-
dicular to the thermal gradient the temperature is constant. The problem
is thus one dimension, and the thermal diffusion equation can be expressed
as:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial X}\left[D \left(\frac{\partial C}{\partial X} + \frac{QC}{KT^2} \frac{dT}{dX}\right)\right] + 4\pi R_0 D(C_s - C)N \tag{1}$$

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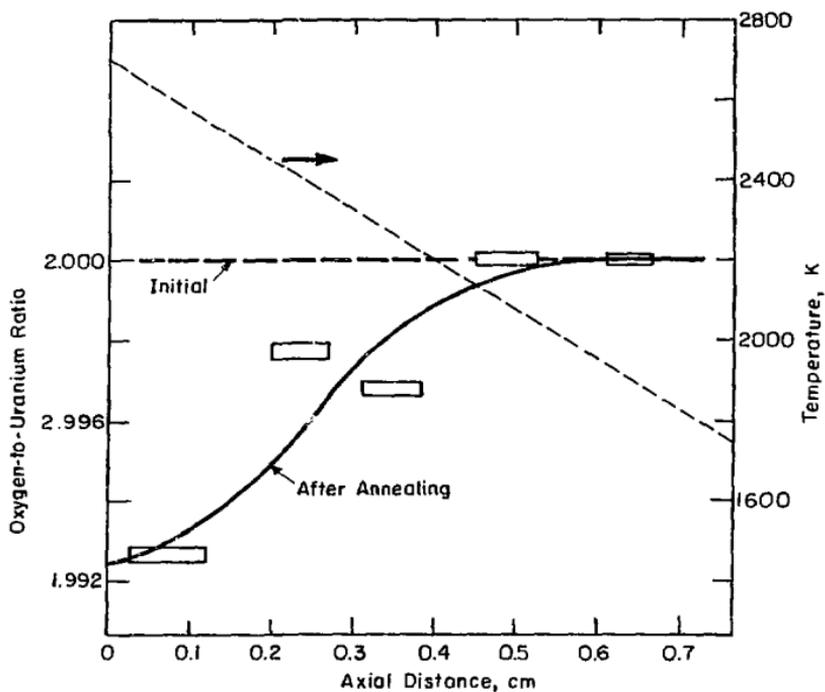
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Fig. 7 Stoichiometry Change Along Sample Following
Thermal Gradient Annealing

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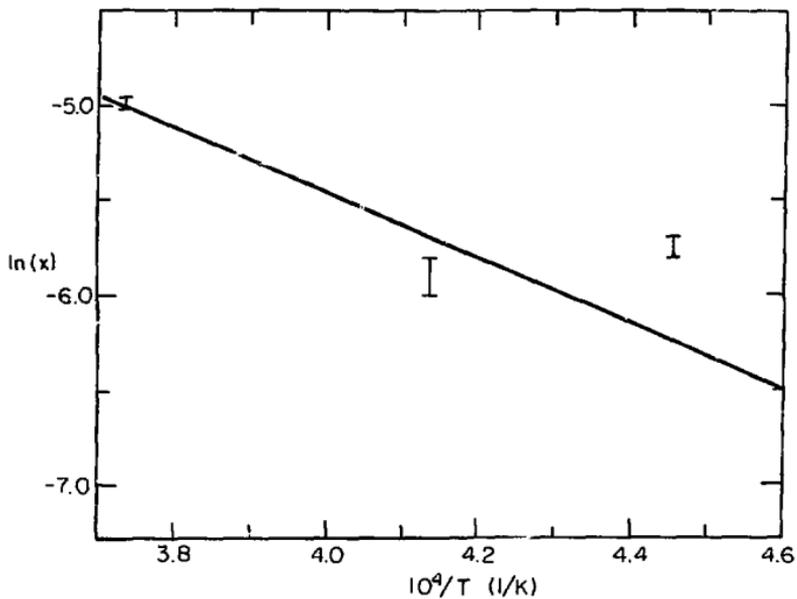
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Fig. 8 Determination of the Heat of Transport of Oxygen in
UO_{2-x} from the Distribution of Fig. 7

where

C = concentration of dissolved Ru in UO_2, g-atoms Ru/g-atom U

N = number of Ru particles per unit volume of UO_2

Q = heat of transport of Ru in UO_2, Kcal/mole

T = temperature K

K = gas constant

D = diffusivity of Ru in UO_2, cm^2/s

X = distance, measured from hot face cm

C_s = terminal solubility of Ru in UO_2

$C_s = C_{so} e^{-H/KT}$

t = time

The first term in the brackets is the ordinary diffusion term, the second is the thermal diffusion term and the third represents the dissolution, which is related to the size of the central hole in the Ru particles by:

$$\frac{d}{dt} \left(\frac{4}{3} \pi R^3 N \rho_{Ru} \right) = 4\pi R_o D (C_s - C) N \rho_U$$

or

$$\frac{dR^3}{dt} = \frac{3R_o (C_s - C) D \rho_U}{\rho_{Ru}} \tag{2}$$

where

R = radius of the central void in the Ru particle

ρ_{Ru} = density of solid ruthenium, g-atoms/cm^3

ρ_U = density of solid uranium, g-atoms/cm^3

the total concentration of Ru in UO_2 is:

$$C_t = C + \frac{4}{3}\pi \ (R_0^3 - R^3) \ N\rho_{Ru} + C_p \tag{3}$$

C_p = concentration of precipitated Ruthenium as URu_3

Assuming

$$\frac{dT}{dX} = G,$$

$$D = D_0 exp(-\frac{E}{KT})$$

T_h = the temperature on the hot end of the sample

$$T = T_0 + GX$$

equation (1) becomes

$$\frac{\partial C}{\partial t} = D \ \frac{\partial^2 C}{\partial X^2} + V \ \frac{\partial C}{\partial X} + WC + S \tag{4}$$

where

$$V = D \left(\frac{G(Q+E)}{K(T_0+GX)^2} \right)$$

$$W = \frac{DG^2Q}{K(T_0+GX)^3} \left(\frac{E}{(T_0+GX)} - 2 \right) + 4\pi R_0 DN$$

$$S = 4\pi R_0 DNC_s$$

I.C.

$$C(X,0) = 0$$

$$C_t(X,0) = C_0$$

$$R(X,0) = 0$$

B.C.

$$J = 0 \quad \text{at } X=0, \ X=L$$

where   J = flux of dissolved Ru in UO_2

L = Length of the sample

An attempt at an analytical solution of the thermal diffusion equation shows that the solution cannot be expressed in terms of analytical functions [13]. Furthermore the equation here now has another term $\left[4\ R_c D(C_s - C)N\right]$ which is related to a nonlinear ordinary differential equation of dissolution, Eq. (2), when R equals to R_0, this term disappears in Eq. (1). Thus the equations have to be solved by numerical methods [14].

The numerical analysis shown in the Appendix is used in solving the thermal diffusion and dissolution equations. The method is similar to Marino's method [14] but there are some differences:

(1) Marino's method only applies to equilibrium conditions, (i.e., the concentration of solute maintained at the terminal solubility limit) whereas the method used here can handle the non-equilibrium concentration case.

(2) Marino's method does not consider the appearance of a second solid phase, which can be handled by the method used here.

In order to compare the calculated redistribution profiles of Ru with the data, the theoretical curves are presented in Fig. 3-5. The apparent diffusivity and effective solubility of Ru in UO_2 for the theoretical curves labelled #1 were taken from Ref. 6:

$D = 155\ \exp\ (-127.7\ KCal/KT)$

$C_s = .64 \times 10"\ \exp\ (-147.2\ KCal/KT)$

For comparison, another pair of D and S were also used in the calculations which are:

$D = 0.03\ \exp\ (-70\ \ KCal/KT)$

$C_s = .13 \times 10^9\ \exp\ (-112\ \ KCal/KT)$

In both cases, the heat of transport of Ru was chosen as

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$Q = -180$ KCal/mole

B. Comparison of Experiment and Theory

Comparing the experimental redistribution profiles (Figs. 3-5) and
the curves from theory, shows that in the cold regions the Ru concen-
tration essentially remains unchanged due to low diffusivity; in the
middle part of the sample, Ru is depleted due to thermal diffusion and
lack of Ru replenishment from the low temperature region; in the high
temperature region, Ru accumulates except at the top of the sample
where severe evaporation occurs. The similarity of experimental and
theoretical curves means that a certain extent, thermal diffusion
describes the process which occurs in the sample under a temperature
gradient.

From quantitative point of view, the redistribution of Ru in the
experiments is relatively more extensive than predicted by the theory.
The difference between experiments and theory may have resulted from use of
incorrect parameters. For example, the terminal solubility of Ru in UO_2
used in the theoretical computation is an "apparent solubility", which
may be much larger than the real solubility of Ru in UO_2 [6]. The over-
estimated terminal solubility of Ru in UO_2 causes a large back concentration-
gradient diffusion to counterbalance the thermal diffusion. Actually it
may be that most of Ru treated theoretically as "dissolved" Ru here may
actually exist as the URu_3 compound which does not contribute to the back
diffusion. The fact that Ru accumulates in hot zone implies that the heat
of transport of Ru in UO_2 is larger than the activation energy of the real
terminal solubility of Ru in UO_2. Second, the differences are partly due
to the evaporation of Ru on the top of the samples which makes the

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redistribution of Ru in UO_2 larger.

5. CONCLUSIONS

1) The redistribution of Ru in UO_2 in a thermal gradient is substantial, with Ru moving up the temperature gradient. The apparent heat of transport of Ru in UO_2 is negative. This is believed to be the same mechanism which causes fission product Ru to redistribute in oxide fuels.

2) The tungsten crucible reduces stoichiometric urania and the oxygen in UO_2 under steep temperature gradient moves down the temperature. The heat of transport of oxygen vacancy in UO_2 is - 138 ± 53 KJ/mole.

APPENDIX:

The numerical analysis method used in computing the theoretical redistribution profile of Ru in UO_2 is briefly described as below.

(1) The specimen is divided into M elements and M+1 nodal planes.

(2) R_o,D,C_s,G are known, initial conditions are $R(X,0) = 0$; $C(X,0) = 0$; $C_t(X,0) = C_o$; DX and DT are the space step and the time step, respectively.

(3) Compute C by using finite difference method. Eq.(1) of the text becomes:

$$A1(j)C_{j+1,K+1}+A2(j)C_{j,K+1}+A3(j)C_{j-1,K+1} = A4(j)$$

where

$$A1(j)=-\tfrac{1}{2}(D1+V1)$$

$$A2(j)= 1-\tfrac{1}{2}(W1-2D1)$$

$$A3(j)= -\tfrac{1}{2}(D1-V1)$$

$$A4(j) = \tfrac{1}{2}(D1+V1)C_{j+1,K}+(1+\tfrac{1}{2}(W1-2D1))C_{j,K}+\tfrac{1}{2}(D1-V1)C_{j-1,K}+S1(j)$$

$$D1 = \frac{D\ DT}{DX^2} \quad ; \quad V1 = \frac{V\ DT}{2\ DX} \; ;$$

$$W1 = W\ DT \quad ; \quad S1 = S\ DT \; .$$

(4) The boundary conditions are:

$$\frac{\partial C}{\partial X} + \frac{QC}{KT^2} = 0 \qquad \text{at } X = 0, \text{ and } X = L$$

where L is the length of the sample.

(5) Compute R by using the finite difference form of Eq.(2).

(6) Check if $R \geqslant R_o$ when $R \geqslant R_o$, set $R = R_o$,

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(7) Check C and R if they are consistent with mass conservation by using the following formula

$$\int_0^L C\ dX = \int_0^L \frac{4}{3}\pi R^3 N\ \rho_{Ru}\ dX$$

(8) Check if C exceeds the terminal solubility, there will be precipitation, when $C \geqslant C_s$, then $C_p = C - C_s$, and set $C = C_s$

(9) Compute C_t

$$C_t = C + \frac{4}{3}\pi N\ \rho_{Ru}\ (R_0^{\ 3} - R^3) + C_p$$

(10) Check if the total mass conservates by using the following formula:

$$\int_0^L Ct\ dX = C_0 L$$

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ACKNOWLEDGMENT