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CHEMICAL ENGINEERING DIVISION
FUELS AND MATERIALS CHEMISTRY
SEMIANNUAL REPORT

January-June 1972

by

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ABSTRACT

To aid in evaluating the performance of fast-breeder reactor fuels, high-temperature studies are being made of the U-Pu-O-Na, U-Nd-O, U-Ce-O, and U-Mo-O systems, and modeling studies of oxygen potentials over oxide fuels are being performed. Studies of the oxygen/metal composition of uranium-plutonium mixed oxides in equilibrium with sodium and Na_2MoO_4 , where $M = \text{Pu}_y\text{U}_{1-y}$, were extended to a Pu/(Pu+U) ratio of 0.1 for temperatures of 600-900°C. Kinetic studies of the reaction of sodium with sintered mixed-oxide pellets are reported. Oxygen potentials over $\text{U}_{0.9}\text{Ce}_{0.1}\text{O}_x$, $\text{U}_{0.95}\text{Ce}_{0.05}\text{O}_x$, and $\text{U}_{0.9}\text{Nd}_{0.1}\text{O}_x$ are reported. Studies of the activities of MoO_2 over urania- MoO_2 mixtures are presented. A model for calculation of oxygen pressures over UO_{2+x} is presented and comparisons with experiments are given; the agreement between calculated and experimental values is excellent.

An ion microprobe mass analyzer is being applied to the analysis of irradiated fuel. Analysis of irradiated stainless steel cladding has shown a very steep gradient in the oxygen content. Analysis of fission products in mixed-oxide fuel has shown that the instrument has excellent detection sensitivity for all fission products of interest. Electron probe microanalysis has been used to determine the molybdenum content in noble-metal inclusions and in the fuel matrix of four irradiated mixed-oxide fuels. The Mo- MoO_2 "redox-indicator" method has been applied to the data to determine the oxygen potential gradient in the columnar- and equiaxed-grain regions of these fuels. Laboratory experiments are being performed to assess the effects of selected cesium and molybdenum compounds on the mechanism of attack of stainless steel cladding.

SUMMARY

Materials Chemistry and Thermodynamics

The information obtained in this program can be used to interpret and evaluate the performance of fast-breeder-reactor fuels. The reaction of (U,Pu) O_2 fuel with sodium coolant, in the event of a cladding failure, the effect of fuel burnup on oxygen potentials, interactions of fuel with

fission products, and determination of oxygen potentials over oxide fuel systems are being studied to provide information needed for long-term operation of LMFBR fuels.

U-Pu-Na-O Phase and Reaction Studies. The study of the O/M composition of uranium-plutonium mixed oxides which are in equilibrium with sodium and Na_2MO_4 , where $M = \text{Pu}_y\text{U}_{1-y}$, has been extended to mixed oxides with a Pu/(U+Pu) ratio of 0.10. The lattice parameter method was used. Data obtained at 600, 700, 800 and 900°C are reported and compared with values calculated from thermodynamic data.

Progress in the study of the reaction of sodium with sintered mixed-oxide pellets in sealed nickel capsules is reported. Improvements were made in the experimental procedure in order to minimize sources of oxygen for the reaction other than that in the mixed-oxide pellets. The course of the reactions is followed by metallographic examination of the product pellets. Four photomicrographs are shown which compare the effect of temperature and initial O/M composition of the pellets upon the extent of the reaction.

Effect of Fuel Burnup on Oxygen Potentials. Oxygen potentials for the U-Nd-O system, where $\text{Nd}/(\text{U}+\text{Nd}) = 0.1$, have been found to be slightly higher than those for unalloyed urania at 2250°K. Oxygen-to-metal ratios for the solid-solution compositions $\text{U}_{0.9}\text{Ce}_{0.1}\text{O}_x$ and $\text{U}_{0.95}\text{Ce}_{0.05}\text{O}_x$ remain nearly constant, near 2.00, and generally slightly deficient in oxygen over a wide variation of oxygen potentials at temperatures of ~1800°K or lower. Above 2000°K, significant deviations from stoichiometry occur in the direction of oxygen deficiency. Exploratory measurements of the total pressure of uranium-bearing species have been made at 1704 and 1807°K. The results indicate an enhanced volatility of uranium-bearing species compared with the volatility of unalloyed urania.

U-Pu-O Fuel-Fission Product Interaction. The activity of MoO_2 over urania- MoO_2 mixtures has been computed using experimental data obtained from ion currents of MoO_3 over mixtures of urania- MoO_2 and MoO_2 -Mo. The results indicate that at high temperatures MoO_2 forms a solid solution in urania. The activity coefficient of MoO_2 depends on the oxygen-to-cation ratio of the oxide phase in the hypostoichiometric range and appears to approach the value for an ideal solution as the ratio approaches two.

Partial Pressures of Vapor Species and Oxygen Potentials in the U-Pu-O System. A model has been developed for calculating oxygen pressures from the UO_{2-x} metal-rich boundary to $\text{UO}_{2.1}$. The model is based on the law of mass action, the free energy of formation of UO_2 and U_4O_9 , and phase-boundary data. Oxygen pressures calculated with the model are in excellent agreement with experimental observations.

Chemistry of Irradiated Fuels and Materials

The chemical behavior of irradiated fast-reactor fuels is being studied to aid in understanding the complex processes that occur in the fuel during irradiation. Data on the migration behavior of fission products as well as an understanding of the mechanisms of fuel-cladding interactions are needed to assess the effects of these factors on the useful lifetime of fuels.

Fuel Analysis Techniques. The ion microprobe mass analyzer has been applied to analysis of irradiated fuels and cladding. Analyses of the cladding of SOV-1 has shown a very steep oxygen gradient, with most of the oxygen present near the fuel-cladding interface. Analysis of an irradiated mixed-oxide fuel has shown it to contain impurities of low atomic number and to yield the expected fission-product spectrum.

Electron Probe Microanalysis of Irradiated Fuels. Electron probe microanalysis of General Electric fuels F2R and F2Z and NUMEC fuels C-11 and C-15, all of which are UO_2 -20 wt % PuO_2 fuels, has shown that fission-product molybdenum is present in the fuels in metallic form in noble-metal inclusions and in oxidized form in the fuel matrix. The application of the Mo/MoO_2 "redox indicator" method to these data has enabled calculations to be made of the radial oxygen potential gradient for each of the fuels. A comparison of the calculated oxygen pressure for the four fuels shows a relatively narrow pressure range for a given radial position.

Fission Product-Cladding Interactions. To assess the effects of fission products on cladding attack, laboratory experiments have been conducted, in which various oxygen-containing cesium and molybdenum compounds were encapsulated in stainless steel and heat-treated. The results indicated that the type and severity of corrosive attack of the stainless steel are related to the presence of cesium and to the oxygen potential.

I. MATERIALS CHEMISTRY AND THERMODYNAMICS (M. G. Chasanov)

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This program has as its major objective the production of phase-diagram, thermodynamic, kinetic, and other chemical data needed for interpretation and evaluation of fast-breeder-reactor fuel performance. Information is sought to aid in the understanding of sodium-fuel interactions, cladding attack, fission-product redistribution in the fuel, plutonium segregation, and fuel swelling. The information produced in this program should prove valuable in devising methods for control of these deleterious processes.

A. U-Pu-Na-O Phase and Reaction Studies (A. E. Martin and J. Schilb)

One of the potential problems in the liquid-metal fast-breeder power reactor is the chemical interaction of the sodium coolant with the U-Pu-oxide fuel in the event of a breach in the stainless steel cladding. Such a reaction could cause fuel swelling and cladding rupture. The severity of the problem may determine how long failed fuel elements can be left in the reactor core and also whether or not failed fuel elements can be stored in the reactor sodium.

We are studying, out of reactor, the reaction of sodium with uranium-plutonium mixed oxides in sealed nickel capsules. Both equilibrium and kinetic studies are in progress.

In ANL-7877 (p. 11), the steps in establishing the oxygen-to-metal (O/M) composition of the mixed-oxide phase in equilibrium with sodium and Na_2MO_4 at various temperatures were described. (Na_2MO_4 , where M represents $\text{Pu}_y\text{U}_{1-y}$, was previously established as the Na-U-Pu-O phase which forms in the reaction of sodium with mixed oxides.) A lattice-parameter method was used. The lattice parameter of the mixed-oxide phase in the equilibrium mixture was measured, and from the relationship of lattice parameter with O/M composition, the latter was established. (The relationship of O/M versus lattice parameter is based on literature data when available or on experimental data obtained on mixed-oxide pellets that have been reduced in hydrogen.) As reported in ANL-7877, this method was used successfully on mixed oxides with a Pu/(U+Pu) ratio of 0.20. The O/M data obtained were in essential agreement with calculated data.

The method has now been extended to mixed oxides with a Pu/(U+Pu) ratio of 0.10. Reactions were conducted at 700, 800, and 900°C for 14, 11, and 8 days, respectively. In addition, one reaction was conducted for 4 days at 900°C and then continued for 34 days at 600°C. Free sodium was removed from all products with ethyl alcohol. The lattice parameters of the mixed-oxide phase in the products of the reaction at 600, 700, 800, and 900°C were measured as 5.4660, 5.4655, 5.4660, and 5.4662, respectively.

For the oxides having Pu/(U+Pu) = 0.10, the conversion of the lattice-parameter values to corresponding O/M compositions has been somewhat difficult. When a plot of O/M versus lattice parameter, a_0 , based on data from Karlsruhe,¹ is used, the derived O/M compositions of the mixed-oxide phase reacted with sodium at 600, 700, 800, and 900°C are 1.989, 1.991, 1.989,

and 1.98g, respectively. The Karlsruhe calibration plot is based on only two data points, which were at O/M compositions of 1.95 and 2.00. Nevertheless, the validity of the data is indirectly supported by the similarity of its slope, namely, $0.0276 \Delta a_0 / (\Delta O/M)$, to those obtained in other literature studies²⁻⁴ for oxides with Pu/(U+Pu) compositions ranging from 0.15 to 0.42.

A calibration plot of O/M versus a_0 was also produced as a part of this study. It was based on X-ray measurements made on pellets which had been reduced in hydrogen. Six data points from an O/M ratio of 1.96 to 1.99 were obtained. However, the slope of the line, namely, 0.0127, was less than half of that of the lines from the literature data cited above. Our data are presumably faulty for unknown causes, but possibly may be faulty owing to some impurity in the mixed oxide. Based on these calibration data, the O/M compositions of the mixed oxide reacted with sodium at 600, 700, 800, and 900°C are 1.97₁, 1.97₅, 1.97₁, and 1.96₉, respectively.

It is interesting to compare the above O/M values based on the experimental study with those obtained from calculations using thermodynamic data (see Section I.D of this report). The calculated O/M values of the mixed-oxide phase in equilibrium with sodium and Na₂MO₄ at temperatures of 600, 700, 800, and 900°C are 1.98₃, 1.98₃, 1.98₄, and 1.98₄, respectively. It is apparent that these calculated values are in better agreement with the experimental values based on the Karlsruhe calibration data than with those based on the calibration data from this study.

A miscibility gap was reported⁵ in the hypostoichiometric region of the U-Pu-O phase diagram at a Pu/(U+Pu) section of 0.30 at temperatures below 500°C. Consequently, it appeared to be questionable whether the O/M composition of oxide of this Pu/(U+Pu) ratio in equilibrium with sodium and Na₂MO₄ could be established by the lattice-parameter method. A few tests were made to check this point. In one of these tests, a lattice-parameter measurement of the product mixed-oxide phase was found to be possible. The capsule had been heated for 6 days at 900°C and was then quenched to room temperature in mercury. The lattice parameter of the mixed-oxide phase was 5.4719 Å. The O/M composition corresponding to this lattice parameter, based upon literature data of lattice parameter versus O/M composition, is 1.90₃. This is considerably lower than the 1.95 O/M value calculated for a temperature of 900°C from thermodynamic data for mixed oxide of this Pu/(U+Pu) composition (see Section I.D of this report). Little reliance is placed upon the measured O/M value in this instance.

The experimental technique which is being used in the kinetic study of the reaction of sodium with mixed-oxide pellets with a Pu/(U+Pu) ratio of 0.20 was described in ANL-7877. In brief, the method consists of reacting sintered pellets with sodium in sealed nickel capsules at various temperatures and for various reaction times and then examining the product pellets metallographically for evidence of the extent and nature of the reaction. (Before the metallographic examination is made, the free sodium in the products is removed either by dissolution in ethyl alcohol or by evacuation at 450°C.)

The extent of the reaction has been found to depend mainly upon the O/M composition of the mixed oxide and upon the density of the pellets. With dense pellets, the reaction is often confined to the formation of a

reaction layer of Na_2MO_4 on the surface of the pellets and a minor amount of reaction at grain boundaries near the surface of the pellets and near cracks, if any, in the pellets. With less dense pellets, the reaction at grain boundaries extends to greater depths in the pellets. The attacked region has an as-etched appearance when in an as-polished condition. (Normally, grain boundaries in a sintered mixed-oxide pellet are not revealed in the as-polished condition.) In some instances, layers of Na_2MO_4 can be seen at these grain boundaries. With more severe attack, the pellets may partially or completely disintegrate into powders.

An initial series of tests was made with mixed-oxide pellets which had an O/M composition of 1.995 and a density of 90.5% of theoretical. The pellets were reacted with sodium which contained about 4 ppm oxygen. The thickness of the Na_2MO_4 reaction layer on the pellets was measured after two days of reaction at a series of temperatures. The thickness was 7, 17, 26, and 33 μm at temperatures of 600, 700, 800, and 900°C, respectively. At 600°C, the layer was found to form in the first few hours, but the thickness of the layer varied from 2 to 6 μm in different tests conducted under presumably duplicate conditions. This suggested that a substantial portion of the reaction at this temperature was caused by oxygen sources other than that of the mixed-oxide pellets. Improvements were then made in the preparation procedures. The nickel capsules were given a final anneal in hydrogen before being charged so as to remove oxides more effectively. Also, instead of adding sodium as chunks, it was added as a liquid. The sodium was melted in a small Erlenmeyer flask and a portion withdrawn by a pipette held beneath the surface of the liquid. A measured volume was then transferred to each capsule. In this way, the oxygen in the sodium, when it is charged to the capsule, is limited to about 1 ppm, which is the solubility of oxygen in sodium at its melting point. Also, the surface of the sodium in the capsule is kept to a minimum. The latter minimizes the trace amounts of oxygen picked up by the sodium in the capsule in the handling and final welding of the capsule in the helium-atmosphere glovebox. After these improvements were made in the preparation procedures, a reaction layer could not be detected on pellets which were reacted with sodium for 2 hr at 600°C.

Mixed-oxide pellets with O/M compositions of 1.960 and 1.970 were produced for kinetic studies by hydrogen reduction at 1590 and 1530°C, respectively. A comparison of the reaction of pellets of these compositions with sodium is of particular interest because the equilibration study had indicated that pellets with about the 1.960 O/M composition should not react with sodium at temperatures from 800 to 1100°C. Figures I-1 and I-2 compare the reaction of pellets of O/M compositions 1.970 and 1.960 with sodium at 900°C for two days. Figures I-3 and I-4 make a similar comparison for reaction for two days at 700°C. It is apparent that the pellets with O/M = 1.960 did not react at either temperature in the two-day reaction time. On the other hand, the pellets with O/M = 1.970 showed evidence of surface reaction, with a greater amount of reaction at 900 than at 700°C. A reaction layer is evident in the reaction at 900°C but only grain-boundary attack at 700°C. Thus, these tests confirm the findings of the equilibration study insofar as a two-day test at these temperatures is concerned.

Fig. I-1. Surface Region of Mixed-Oxide Pellet, $\text{Pu}/(\text{U}+\text{Pu}) = 0.20$, $\text{O}/\text{M} = 1.970$, After Exposure to Sodium for 2 Days at 900°C ; $330\times$, as Polished. ANL Neg. No. 308-2918

Fig. I-3. Surface Region of Mixed-Oxide Pellet, $\text{Pu}/(\text{U}+\text{Pu}) = 0.20$, $\text{O}/\text{M} = 1.970$, After Exposure to Sodium for 2 Days at 700°C ; $330\times$, as Polished. ANL Neg. No. 308-2919

Fig. I-2. Surface Region of Mixed-Oxide Pellet, $\text{Pu}/(\text{U}+\text{Pu}) = 0.20$, $\text{O}/\text{M} = 1.960$, After Exposure to Sodium for 2 Days at 900°C ; $330\times$, as Polished. ANL Neg. No. 308-2916

Fig. I-4. Surface Region of Mixed-Oxide Pellet, $\text{Pu}/(\text{U}+\text{Pu}) = 0.20$, $\text{O}/\text{M} = 1.960$, After Exposure to Sodium for 2 Days at 700°C ; $330\times$, as Polished. ANL Neg. No. 308-2917

B. The Effect of Fuel Burnup on Oxygen Potentials (M. Tetenbaum)

The compatibility of reactor fuel with the fuel cladding is influenced by the variation of oxygen potential in the outer zone of the fuel during burnup. A glovebox complex for transpiration studies is in the final stages of construction and testing for the measurement of oxygen potentials over the U-Pu-O system containing rare-earth (RE) fission products. Because cerium and neodymium are the major rare-earth fission products formed, they will be used in the studies.

While the glovebox is being completed, measurements of oxygen potentials over the U-Ce-O and U-Nd-O systems are in progress to aid in planning the U-Pu-O-RE measurements. The general techniques used for the preparation of U-RE-O solid solutions and for oxygen-potential measurements have been previously described.⁶

1. U-Nd-O System

The results of oxygen-potential measurements of the U-Nd-O system, where $\text{Nd}/(\text{U}+\text{Nd}) = 0.1$, at 2250°K are shown in Fig. I-5. For comparison, we have included $\Delta\bar{G}(\text{O}_2)$ values for the unalloyed urania system⁶⁻⁸ at 2250°K . It is apparent from Fig. I-5 that oxygen-potential values for the U-Nd-O system are somewhat--but not very much--higher than those for pure urania. On the other hand, the U-Nd-O values are ~ 20 kcal lower than extrapolated oxygen-potential values at 2250°K for the fuel system U-Pu-O.⁹ X-ray examination of the U-Nd-O solid solution having an O/M ratio of ~ 1.99 confirmed the presence of a face-centered-cubic fluorite structure with a lattice parameter of $a = 5.463_4 \text{ \AA}$. The decrease in lattice parameter with neodymium content, relative to stoichiometric urania ($\sim 5.470 \text{ \AA}$), is consistent with expectations.¹⁰

Fig. I-5

Oxygen Potential as Function of O/M Ratio for U-Nd-O, U-Ce-O, and Urania at 2250°K

It is interesting to note that if one assigns a valence of four for uranium in the oxygen-deficient compositions, then neodymium would appear to achieve a valence larger than its known value of three for compositions ranging from $O/M > 1.95$ to 2.00. On the other hand, if one accepts the known valence for neodymium, three, then in order to maintain charge balance, some of the uranium must be oxidized to U^{5+} or U^{6+} .

2. Extended Heating of U-Ce-O Solid Solutions

The results of extended heating of U-Ce-O solid solutions are summarized in Tables I-1 and I-2. These indicate that the O/M ratios for the solid-solution compositions $U_{0.9}Ce_{0.1}O_x$ and $U_{0.95}Ce_{0.05}O_x$ remain nearly constant, near 2.00, and generally slightly oxygen deficient over a wide variation of oxygen potentials at temperatures of $\sim 1800^\circ K$ or lower. Above $2000^\circ K$, the results show that significant deviations from stoichiometry occur in the direction of oxygen deficiency. This trend at the lower temperatures of small deviations from stoichiometry with a very large change of oxygen potential is consistent with the results¹¹ obtained with pure urania at relatively low temperatures, i.e., $< 2000^\circ K$. It is significant that at higher temperatures and with constant oxygen potential the U-Ce-O solid solutions show a greater oxygen deficiency than do U-Nd-O and pure urania systems. It is also significant that, with the U-Ce-O system and for constant oxygen potentials, the higher cerium composition appears to be more stable with regard to a stoichiometry shift in the direction of oxygen deficiency than is the low-cerium-content composition. This effect is illustrated in Fig. I-5 at $2250^\circ K$; the same effect was found at $2165^\circ K$. This trend is not in accord with expectations based on the measurements obtained at low temperatures.¹² We have to clarify these discrepancies by further experimentation.

Because the O/M ratios appeared to increase somewhat, even with decreasing oxygen potential, during the course of these extended heating experiments, we were concerned whether preferential vaporization of one of the metal species had occurred. A careful check of the transpiration apparatus ruled out the possibility of a leak. Chemical analysis of the residue after Run 9 (Table I-1) yielded the following results: 82.30 wt % uranium, 5.46 wt % cerium, and 12.26 wt % oxygen. These values add up to 100.02 wt %. From the analysis, one calculates that the Ce/(U+Ce) ratio remained unchanged at 0.1 after extended heating at temperatures ranging from 1700 to $1800^\circ K$. In addition, chemical analyses of the residues from runs carried out at the higher temperatures ($\sim 2250^\circ K$) showed negligible change in both Ce/(U+Ce) and Nd/(U+Nd) ratios.

3. Total Pressure of Uranium-Bearing Species

Exploratory measurements of the total pressure of uranium-bearing species over U-Ce-O compositions, where $Ce/(U+Ce) = 0.1$, have been made at 1704 and $1807^\circ K$. The results are summarized in Table I-3. For comparison, we have included in Table I-3 values for the total pressure of uranium-bearing species over stoichiometric urania derived from mass-effusion measurements of Ackermann, Gilles, and Thorn¹³ and from the transpiration measurements of Tetenbaum and Hunt.¹⁴ It is apparent that the total pressure of uranium-bearing species over near-stoichiometric U-Ce-O compositions are generally appreciably higher than those obtained, for comparison,

TABLE I-1. Extended Heating Experiments with
U-Ce-O Solid Solutions

$$\frac{\text{Ce}}{\text{U+Ce}} = 0.1$$

Run	T, °K	Heating Time, hr	$-\Delta\bar{G}(\text{O}_2)$, kcal/mol	O/M
1	1704	12.0	116	1.998
2	1646	4.5	122	2.004
3	1704	8.5	124	1.989
5	1704	12.5	123	1.996
6	1704	12.0	133	2.000
7	1704	5.8	133	2.004
9	1807	8.9	123	1.992
19	1807	2.9	127	1.991
20	2035	1.6	129	1.998
21	2026	4.0	153	1.983
22	2160	2.8	153	1.939
23	2250	1.9	156	1.921

TABLE I-2. Extended Heating Experiments with
U-Ce-O Solid Solutions

$$\frac{\text{Ce}}{\text{U+Ce}} = 0.05$$

Run	T, °K	Heating Time, hr	$-\Delta\bar{G}(\text{O}_2)$, kcal/mol	O/M
1	1807	5.0	119	1.980
11	1807	12.9	125	1.996
12	1807	2.6	142	1.998
13	1807	2.7	145	2.000
14	1807	3.1	He only	1.994
15	1807	3.0	130	1.996
16	1656	4.0	134	1.994
17	1538	6.8	128	1.996
18	1807	2.6	127	2.001
24	2250	2.8	154	1.887
25	2165	2.5	154	1.896

TABLE I-3. Total Pressure of Uranium-Bearing Species Over the U-Ce-O System

T, °K	Flow Rate, ml/min	$\frac{\text{Ce}}{\text{U} + \text{Ce}} = 0.1$			$-\log p(\text{U}), \text{ atm}$		$-\Delta\bar{G}(\text{O}_2), \text{ kcal/mol}$		Volatility Ratio
		$-\Delta\bar{G}(\text{O}_2), \text{ kcal/mol}$	O/M	$-\log p(\text{U}), \text{ atm}$	$\text{UO}_{2.00}$		$\text{UO}_{2.00} \quad \text{UO}_{1.99}$		
					TH ^a	AGT ^b			
1704	215	123	-	8.29	9.75	9.64	154	171	29
1704	320	123	1.99 ₆	8.33	9.75	9.64	154	171	26
1704	365	133	2.00 ₀	8.70	9.75	9.64	154	171	11
1704	425	133	2.00 ₄	8.64	9.75	9.64	154	171	14
1807	220	123	-	8.19	8.70	8.64	149	164	3
1807	380	123	1.99 ₂	8.22	8.70	8.64	149	164	3

^aTH = Reference 14.^bAGT = Reference 13.

over stoichiometric urania. The volatility ratio (relative to stoichiometric urania) is given in column 10. It should be realized, however, that the total pressure of uranium-bearing species over unalloyed urania decreases when the composition is reduced below stoichiometric toward the lower phase boundary until the congruent composition is reached, and, in general, the pressure increases rapidly when the composition exceeds stoichiometric. It is apparent from the limited data given in Table I-3 that the volatility ratio decreases during the sequence of runs. A trend with oxygen potential is suggested at 1704°K. As a further comparison, oxygen potential values over stoichiometric urania and $\text{UO}_{1.99}$ are given in Table I-3. Consistent with previous observations, the oxygen potential values over U-Ce-O compositions are higher than those obtained with unalloyed urania.

The decrease of volatility ratio at 1807°K appears to be in accord with expectations. It has been shown for the case of unalloyed urania that, past the congruent composition and with increasing oxygen content in the condensed phase, the increase in total pressure of uranium-bearing species is less pronounced with increasing temperature. A calculation of the total pressure of uranium-bearing species was made using the experimental oxygen-potential values shown in column 3 and free-energy-of-formation values for the gaseous species (UO , UO_2 , and UO_3) and the condensed phase. The calculated pressure did not account for the observed enhanced volatility. Considerably higher oxygen potentials, in the range -90 to -100 kcal/mol, are required in the calculation for agreement with the observed total pressure of uranium-bearing species.

The above results, although limited, may account for the cerium enhancement found by Chasanov and Fischer¹⁵ and Beisswenger, Bober, and Schumacher¹⁶ in their studies of the effects of thermal gradients on the ceria-uranium system. It is apparent that the increase in the total pressure of uranium-bearing species observed in these preliminary measurements warrants further investigation.

C. U-Pu-O Fuel-Fission Product Interaction

1. Studies of the U-Mo-O System (I. Johnson, P. M. Danielson)

The chemistry of the U-Mo-O system is being investigated to provide a basis for understanding the distribution of molybdenum between the metallic inclusions and the oxide matrix observed in the post-irradiation examination of oxide fuel pins. The ratio of the concentration of molybdenum in the oxide matrix to the concentration in the noble-metal-alloy inclusions may be used to estimate the oxygen potential as a function of position in fuel pins.¹⁷

Recently, a more complete analysis has been made of the results of studies of the vaporization behavior of mixtures of hypostoichiometric urania and molybdenum dioxide we reported previously.¹⁸ In the earlier studies, the vapor composition over mixtures of $\text{UO}_{1.96}$ and MoO_2 was determined at constant temperature using a Knudsen effusion-mass-spectrometric method. It was observed that the partial pressures of the four molybdenum oxide gaseous species (MoO_2 , MoO_3 , Mo_2O_6 , and Mo_3O_9) decreased with time as the vaporization took place. In all cases the partial pressures were

significantly smaller than the values observed over a mixture of MoO_2 and Mo. The experiment was done by successive additions of 2, 2, and 4 wt % MoO_2 to a sample of $\text{UO}_{1.96}$. X-ray examination of samples taken at the end of each vaporization period indicated urania and metallic molybdenum.

The activity of MoO_2 in a urania- MoO_2 mixture may be estimated from the ratio of the partial pressures of a given molybdenum oxide gaseous species over the mixture and over a MoO_2 -Mo mixture. Gaseous MoO_3 is formed by the disproportionation reaction

Hence the activity of MoO_2 in the urania- MoO_2 mixture is given by the equation

$$a_{\text{MoO}_2} = \left(\frac{p_{\text{MoO}_3}}{p_{\text{MoO}_3}^0} \right)^{2/3} = \left(\frac{I_{\text{MoO}_3}}{I_{\text{MoO}_3}^0} \right)^{2/3} \quad (2)$$

where p_{MoO_3} and $p_{\text{MoO}_3}^0$ are the partial pressures of MoO_3 over the urania- MoO_2 -Mo and the MoO_2 -Mo systems, respectively, while I_{MoO_3} and $I_{\text{MoO}_3}^0$ are the ion currents due to MoO_3 observed using the mass spectrometer. It is assumed that the relation between ion current and partial pressure for the mass spectrometer is the same for the two experiments. The observed ion-current ratio for MoO_2 ions cannot be used for deriving its activity owing to the lack of proportionality between the observed ion current for MoO_2 and the partial pressure of MoO_2 . The MoO_2 ions are formed by direct ionization of MoO_2 gaseous species and by electron-impact fragmentation of MoO_3 .

The MoO_3 ion ratio was used to derive the MoO_2 activity as a function of time. The results obtained after the first addition of MoO_2 are shown in Fig. 1-6. It is seen that the activity, which initially is near 0.4, decreases rapidly until a value of about 0.01 is reached. The break in the curve at about 250 min corresponds to the end of the first heating period. These activity data may be used to estimate the oxygen potential of the system, if it is assumed that the mixture is in equilibrium with pure metallic molybdenum. The equation used is

$$\Delta \bar{G}_{\text{O}_2} = \Delta G_{\text{MoO}_2}^0 + RT \ln \frac{a_{\text{MoO}_2}}{a_{\text{Mo}}} \quad (3)$$

where $\Delta G_{\text{MoO}_2}^0$ is the standard free energy of formation of MoO_2 at the temperature T (1693°K in these studies). It was found that $\Delta \bar{G}_{\text{O}_2}$ varied from about -74.6 to -84.7 kcal/mol between the beginning and end of the vaporization. The equivalent oxygen-to-metal ratios for pure urania corresponding to these oxygen potential values are 2.0007 and 2.0000, respectively.¹⁹

The processes which took place during these experiments appear to be as follows. When the hypostoichiometric urania and MoO_2 are heated

Fig. I-6. Activity of MoO_2 in $\text{UO}_{1.96} + 2$ wt % MoO_2 at 1693°K

together for the first time, the urania reduces some of the MoO_2 to form metallic molybdenum and slightly hyperstoichiometric urania, i.e.,

The excess MoO_2 then dissolves in the urania. The initial MoO_2 activity of the solid solution is about 0.4 for the experiment shown in Fig. I-6. As vaporization from the system takes place, gaseous molybdenum oxides are evolved. The average composition of these gaseous oxides is approximately three oxygen atoms to one molybdenum atom. Thus, the oxygen-to-cation (uranium plus molybdenum) ratio of the solid oxide phase is gradually decreased. The oxygen potential will then decrease rapidly. From the initial composition and the weight loss, the mole fraction of MoO_2 was calculated to have decreased from 0.025 to 0.010 during the experiment shown in Fig. I-6. Thus, the apparent activity coefficient for MoO_2 changed from about 14 initially to about 1.0 at the end of the experiment. This large change in activity coefficient is most likely associated with the change in the oxygen-to-cation ratio of the oxide rather than the small change in MoO_2 concentration. The equilibrium among four- and six-valent molybdenum and uranium cations in the oxide probably changes markedly with the oxygen-to-cation ratio of the oxide when the value of this ratio changes from values slightly greater than two to values slightly less than two.

The analysis presented indicates that at high temperatures MoO_2 forms a solid solution in urania. The activity coefficient depends markedly on the oxygen-to-cation ratio of the oxide phase in the hyperstoichiometric range and appears to approach ideal-solution behavior as the ratio approaches two. Therefore, even for hypostoichiometric fuels, a small concentration of MoO_2 in the oxide phase of a fuel is to be expected. The concentration will be dependent on the temperature and the oxygen potential and therefore will be a function of the power level and burnup in a fuel pin.

D. Partial Pressures of Vapor Species and Oxygen Potentials in the U-Pu-O System (P. E. Blackburn)

1. A Model for UO_{2+x}

Oxygen pressures or potentials in LMFBR U-Pu-oxide fuel are important for a number of reasons. The magnitude of the oxygen potential at the cladding-fuel interface will determine the extent of cladding attack by oxygen and by some of the fission products such as cesium and molybdenum. The oxygen potential of the fuel also determines whether sodium coolant will interact with the fuel in case of cladding failure. Since fuel and fission-product-oxide pressures depend on the oxygen potential, fuel and fission-product redistribution by vapor transport is related to the oxygen potential in the fuel. Some other physical properties such as creep and diffusion are related to oxygen potential as well. For these reasons it is important to have accurate oxygen pressures for the fuel.

A model is being developed by us for U-Pu-oxide fuel which may be used to calculate oxygen potentials from thermodynamic and phase data. The model can be used to interpolate or extrapolate measured potentials over wide oxygen content and temperature ranges. In addition, the model will be extended to include the effects of dissolved fission products (e.g., rare earths, zirconia, and molybdenum oxide) on the oxygen potentials.

The model is being developed in a stepwise fashion, starting with UO_{2+x} , then adding plutonium, and finally incorporating fission products. Since UO_2 constitutes the bulk of the fuel, a valid model must predict accurate oxygen pressures over metal-rich and oxygen-rich urania. This report is concerned with a model for UO_{2+x} .

The major concern in the treatment used here is to present a model which gives reasonably accurate pressures and which fits the experimental data. An attempt was made to make the model as simple as possible without losing accuracy. Our initial approach is somewhat similar to that taken by others, but the development of the model differs significantly. The treatment is based primarily on the law of mass action. Thus, we consider the equilibrium among the cations and anions in the solid with gaseous oxygen.

In the following development of the model, expressions are formulated for metal-rich and for oxygen-rich UO_2 , and then the two sets of equations are combined. The combined equations may be used to calculate oxygen pressures, at a given temperature, for any composition from the UO_{2-x} boundary to $\text{UO}_{2.1}$ or the equations may be used to calculate compositions from oxygen pressures.

a. UO_{2-x}

For UO_{2-x} , we assume the following equilibrium exists between cations and anions in the lattice and oxygen gas

For this equilibrium, one may write

$$\ln p_{\text{O}_2} = 2 \ln \frac{\text{U}_4}{\text{U}_2} + 2 \ln \text{OU} + \ln K_1 \quad (2)$$

where U_4 is the concentration of U^{4+} , U_2 is the concentration of U^{2+} , OU is the concentration of O^{2-} (or O/U ratio), and K_1 includes activity coefficients and the temperature-dependent equilibrium constant. The notation was chosen to be used with a computer program. The choice of U^{2+} rather than U^{3+} is based on Tetenbaum and Hunt's¹⁴ measurements. Their data fit $\ln p_{\text{O}_2} = -n \ln x + c$, where n is nearly equal to 2. Equation 2 may be written in terms of x , the oxygen deficiency in urania, where $\text{U}_4 = 1 - x$, $\text{U}_2 = x$, and $\text{OU} = 2 - x$, i.e.

$$\ln p_{\text{O}_2} = 2 \ln (1 - x) - 2 \ln x + 2 \ln (2 - x) + \ln K_1 \quad (3)$$

The activity of uranium, a_{U} , may be calculated by use of a Gibbs-Duhem equation. That is

$$d \ln a_{\text{U}} = - \frac{n_{\text{O}_2}}{n_{\text{U}}} d \ln p_{\text{O}_2} \quad (4)$$

Integrating, we find

$$\ln a_{\text{U}} = -\ln(1 - x) + 2 \ln x + x + C_1 \quad (5)$$

It has been shown that the activity of uranium for two-phase $\text{U} + \text{UO}_{2-x_s}$ (where x_s is the oxygen deficiency in metal-rich uranium at the boundary) is very close to one.²⁰⁻²⁴ Using an activity of 1 at $x = x_s$, we may evaluate the integration constant C_1 and substitute it in Eq. 5

$$\ln a_{\text{U}} = -\ln \left(\frac{1 - x}{1 - x_s} \right) + 2 \ln \left(\frac{x}{x_s} \right) + x - x_s \quad (6)$$

To evaluate $\ln K_1$ in Eq. 3, we note that at $x = 0$

$$\ln p_{\text{O}_2} \Big|_{x=0} + \ln a_{\text{U}} \Big|_{x=0} = \frac{\Delta G_f^{\text{UO}_2}}{RT} \quad (7)$$

When Eqs. 3 and 6 are substituted in Eq. 7 and x is set equal to zero, we find

$$\ln K_1 = \frac{\Delta G_f^{\text{UO}_2}}{RT} - 2 \ln 2 - \ln(1 - x_s) + 2 \ln x_s + x_s \quad (8)$$

For small values of x_s (i.e., <0.12), $\ln K_1$ may be represented by a linear equation

$$\ln K_1 = \frac{-156600}{T} + 27.2 \quad (9)$$

based on Martin's phase data for UO_{2-x_s} ²⁶ and literature data for $\Delta G_f^{\text{UO}_2}$.^{26,29} Thus, the logarithm of the oxygen pressure from Eqs. 3, 8, and 9 is given by

$$\ln p_{\text{O}_2} = 2 \ln(1 - x) - 2 \ln x + 2 \ln(2 - x) - \frac{156600}{T} + 27.2 \quad (10)$$

Equation 10 may be rewritten in terms of the concentrations of U4, U2, and OU as

$$\ln p_{\text{O}_2} = 2 \ln \frac{\text{U4}}{\text{U2}} + 2 \ln \text{OU} - \frac{156600}{T} + 27.2 \quad (11)$$

Instead of calculating oxygen pressure from the composition, we calculate the uranium valence concentrations as a function of temperature, oxygen pressure, and oxygen concentration. This procedure is necessary for calculating pressures near UO_2 . For this purpose, Eq. 11 may be used to determine the ratio of U^{4+} to U^{2+} , that is

$$\text{U4/U2} = \frac{p_{\text{O}_2}^{1/2}}{\text{OU}} \exp(78,300/T - 13.6) \quad (12)$$

b. UO_{2+y}

A similar procedure is used for UO_{2+y} to determine the relative concentration ratio dependence of U^{6+} to U^{4+} on temperature, oxygen pressure, and oxygen concentration. For this, the following equilibrium

yields an equation for oxygen pressure

$$\ln p_{\text{O}_2} = 2 \ln \text{U6/U4} + 2 \ln \text{OU} + \ln K_2 \quad (14)$$

where U6 is the concentration of U^{6+} , U4 is U^{4+} concentration, OU is oxygen concentration, and K_2 is a temperature-dependent equilibrium constant which includes activity coefficients. Here we have assumed that U^{4+} oxidizes to U^{6+} rather than U^{5+} , based on measurements of the change in oxygen pressure with oxygen content for $y < 0.1$.³⁰

Equation 14 may be written in terms of y , the excess oxygen concentration

$$\ln p_{O_2} = 2 \ln y - 2 \ln(1 - y) + 2 \ln(2 + y) + \ln K_2 \quad (15)$$

Applying Gibbs-Duhem

$$d \ln a_{UO_2} = - \frac{n_{O_2}}{n_{UO_2}} d \ln p_{O_2} \quad (16)$$

Integrating and noting that when $y = 0$, $a_{UO_2} = 1$, we find the activity of UO_2 to be

$$\ln a_{UO_2} = -y + \ln(1 - y) + 2 \ln\left(\frac{2 + y}{2}\right) \quad (17)$$

To evaluate $\ln K_2$, we note at the boundary UO_{2+y_s}

$$\begin{aligned} \ln p_{O_2} \Big|_{y_s} + 8 \ln a_{UO_2} \Big|_{y_s} &= \frac{2\Delta G_f U_4O_9 - 8\Delta G_f UO_2}{RT} \\ &= 2 \ln y_s - 2 \ln(1 - y_s) + 2 \ln(2 + y_s) + \ln K_2 \\ &\quad - 8 y_s + 8 \ln(1 - y_s) + 16 \ln\left(\frac{2 + y_s}{2}\right) \end{aligned} \quad (18)$$

With Gronvold's³¹ phase-boundary data and Rand and Kubachewski's³² equation for the free-energy difference

$$2\Delta G_f(U_4O_9) - 8\Delta G_f(UO_2) = -86700 + 105.3T - 23T \log T$$

Eq. 18 is simplified to a linear equation for $\ln K_2$

$$\ln K_2 = \frac{-33000}{T} + 10.4 \quad (19)$$

In fitting Eq. 19 to the data, values of y_s were limited to those less than 0.11 because the equations are only good for $0 < y \leq 0.11$. Substituting Eq. 19 in Eq. 15

$$\ln p_{O_2} = 2 \ln y - 2 \ln(1 - y) + 2 \ln(2 + y) - \frac{33000}{T} + 10.4 \quad (20)$$

or in terms of U_6 , U_4 , and OU

$$\ln p_{O_2} = 2 \ln \frac{U_6}{U_4} - 2 \ln OU - \frac{33000}{T} + 10.4 \quad (21)$$

Rearranging and solving for U_6/U_4

$$\frac{U_6}{U_4} = \frac{p_{O_2}^{1/2}}{OU} \exp(16500/T - 5.2) \quad (22)$$

c. Oxygen-Pressure Calculation

In addition to Eqs. 12 and 22, two other equations are needed for single-phase urania. For one mole of urania, the sum of the uranium ions equals one, i.e.

$$U_2 + U_4 + U_6 = 1 \quad (23)$$

Finally, the oxygen concentration can be found by assuming electric neutrality

$$OU = 3U_6 + 2U_4 + U_2 \quad (24)$$

With these four equations, it is necessary to choose two of the six variables (U_2 , U_4 , U_6 , OU , p_{O_2} , and T) to define the system. A computer program was written to calculate oxygen pressures for given oxygen concentrations and temperatures. An alternative program calculates oxygen concentrations from temperature and oxygen pressure. Each program also calculates the concentrations U_2 , U_4 , and U_6 . Since Eqs. 12 and 22 include a valence dependence on the oxygen concentration, it is necessary to iterate until the calculated oxygen concentration reaches a constant value.

The program developed has been used to calculate oxygen-pressure curves at 2705, 2390, and 2080°K for comparison with measured oxygen pressures. The curves for the atomic oxygen pressure at these three temperatures and the phase boundary are plotted in Fig. I-7 with Tetenbaum and Hunt's⁶ measurements over UO_{2-x} and Martin's phase-boundary data.^{7,25}

Fig. I-7. Calculated and Observed Atomic Oxygen Pressures Over UO_{2-x} . ANL Neg. No. 308-2826

Curves calculated for UO_{2+y} (for $0 < y < 0.1$) from 900 to 1400°C are in excellent agreement with pressures measured by Hagemark and Brolfi.³⁰

d. Relation of Uranium Cation Concentrations to Partial Pressures

The variation in U2, U4, and U6 concentrations in the solid can be shown to parallel the corresponding partial pressures of UO, UO_2 , and UO_3 gas. For the UO_{2-x} region, the activity of U and oxygen partial pressures can be computed by rearranging Eqs. 6 and 3. Thus the uranium activity is

$$a_U = \left(\frac{1 - x_g}{x_g^2} e^{-x_g} \right) \frac{x_g^2 e^x}{1-x} \quad (25)$$

and the oxygen pressure is

$$P_{\text{O}_2} = K_1 \left(\frac{(1-x)(2-x)}{x} \right)^2 \quad (26)$$

The pressure of UO is given by

$$P_{\text{UO}} = a_U \cdot P_{\text{O}_2}^{1/2} \exp [-\Delta G_f(\text{UO}, g)/RT] \quad (27)$$

Equations 25 and 26 may be substituted in Eq. 27. The terms $[(1-x_g)/x_g^2]e^{-x_g}$, K_1 , and $\exp [-\Delta G_f(\text{UO}, g)/RT]$ can be represented by $\exp(A/T + B)$ and the remaining terms can reasonably be approximated by $2x$. The resulting equation is

$$P_{\text{UO}} = x \exp \left(\frac{-47700}{T} + 11.7 \right) \quad (28)$$

or in terms of uranium valence

$$P_{\text{UO}} = \text{U2} \exp \left(\frac{-47700}{T} + 11.7 \right) \quad (29)$$

Pressures calculated from the simplified Eq. 29 are within 20% of those calculated using all terms in Eqs. 25, 26, and 27.

By a similar argument, it can be shown that the pressure of UO_2

$$P_{\text{UO}_2} = a_U \cdot P_{\text{O}_2} \exp [-\Delta G_f(\text{UO}_2, g)/RT] \quad (30)$$

where $\Delta G_f \text{UO}_2$ was taken from Ackermann et al.¹² can be represented by

$$P_{\text{UO}_2} = \text{U4} \exp (-69000/T + 18.9) \quad (31)$$

Equation 31 reproduces the variation in UO_2 pressure from $\text{UO}_{1.6}$ to $\text{UO}_{2.1}$ to within 5% of that using all terms in Eqs. 25, 26, and 30.

For $\text{UO}_3(g)$, the pressure is given by

*The free energy of formation of UO_3 of Ackermann et al.⁸ was corrected with Blackburn and Danielson's³³ relative ionization cross sections.

$$P_{\text{UO}_3} = a_{\text{UO}_2}^{1/2} P_{\text{O}_2} \exp \{ [(\Delta G_f(\text{UO}_2, \text{s}) - \Delta G_f(\text{UO}_3, \text{g}))/RT] \} \quad (32)$$

where literature values are used for $\Delta G_f(\text{UO}_2, \text{s})$ ²⁶⁻²⁹ and for $\Delta G_f(\text{UO}_3, \text{g})$.³⁴ The activity of UO_2 and oxygen pressure can be calculated from Eqs. 17 and 20. When appropriate substitutions are made, the pressure is

$$P_{\text{UO}_3} = U_6 \exp (-45000/T + 16.6) \quad (33)$$

Equation 33 gives pressures for UO_3 within 23% of those using all terms in Eqs. 17, 20, and 32.

e. Application of the U-Pu-O Oxygen Potential Model to the Sodium-Fuel Reaction

The treatment used here for the uranium dioxide phase has been used, with some modifications, to devise a model for calculating the oxygen pressures over PuO_{2-x} . The two models were combined, assuming that PuO_{2-x} forms an ideal solution with UO_{2-x} , to produce a model for U-Pu oxide. The details of these derivations will be given in the next semi-annual report.

The calculated oxygen pressures for the U-Pu oxide agree for some compositions and temperatures and disagree for other compositions and temperatures with those of Woodley³⁵ and of Rand and Markin.⁹ The latter two studies also disagree. The oxygen potentials calculated from the model appear to be close to an average for these two studies (particularly the oxygen-pressure dependence on temperature).

In the last semiannual report (ANL-7877, p. 10), we presented calculated O/M ratios for $\text{U}_0.8\text{Pu}_{0.2}\text{O}_{2-x}$ in equilibrium with sodium and Na_2MO_4 (the reaction product) as a function of temperature. These oxygen concentrations were based on extrapolations of Rand and Markin's⁹ oxygen pressures for U-Pu oxide. The calculated equilibrium oxygen content of the fuel decreased with decreasing temperature. A calculation with Woodley's oxygen pressure data shows the opposite effect, *i.e.*, increasing oxygen content of the fuel with decreasing temperature.

Table I-4 shows the calculated equilibrium oxygen content of U-Pu oxide as a function of plutonium content and temperature and of uranium oxide as a function of temperature. This table is based on oxygen potentials calculated with the U-Pu-oxide oxygen-pressure model.

Table I-4 also shows the equilibrium oxygen concentration of sodium based on Henry's law and the oxygen solubility data of Kassner and Smith.³⁶

Experimental oxygen concentrations in fuel determined by Martin and Schilb (see Section A of this report) are also listed in Table I-4. There is much better agreement between the measured and calculated values based on the oxygen-pressure model than those calculated with either Rand and Markin's or Woodley's oxygen pressures.

Table I-4. Calculated and Experimental Isothermal Oxygen Contents of Fuel and Sodium for Fuel-Sodium Reaction

Temperature		$U_{0.7}Pu_{0.3}O_2$	$U_{0.8}Pu_{0.2}O_2$	$U_{0.9}Pu_{0.1}O_2$	UO_2		ppm	
^{°F}	^{°C}	O/M	O/M	O/M	O/M		O ₂ in Na ^c	
		calca	calca measb	calca measb	calca meas			
621	327	1.93 ₁	1.95 ₇ -	1.98 ₀ -	2.00 -		0.01	
801	427	1.93 ₇	1.96 ₀ -	1.98 ₁ -	2.00 -		0.20	
981	527	1.94 ₂	1.96 ₃ (1.95 ₅) ^b	1.98 ₂ -	2.00 -		1.6	
1161	627	1.94 ₅	1.96 ₄ -	1.98 ₃ (1.98) ^b	2.00 2.00		8.0	
1341	727	1.94 ₇	1.96 ₆ -	1.98 ₃ (1.98) ^b	2.00 2.00		30	
1521	827	1.94 ₉	1.96 ₇ 1.95 ₈	1.98 ₄ 1.98	2.00 2.00		95	
1701	927	1.95 ₀	1.96 ₈ 1.95 ₉	1.98 ₄ 1.98	2.00 2.00		170	

^aCalculated with oxygen potential model for U-Pu oxide.

^bSee section A.

^cCalculated with Henry's law, oxygen solubility in sodium,³⁶ and equilibrium oxygen pressures.

^dMay be kinetically controlled. In an operating fuel pin, the oxygen activity (a_{O_2}) is a function of the pin radius because of the large temperature differential.

II. CHEMISTRY OF IRRADIATED FUELS AND MATERIALS (C. E. Johnson, C. E. Crouthamel)

The study of the chemical behavior of irradiated fast-reactor fuels has as its principal objectives the fundamental understanding of the behavior of fast-reactor fuel elements and the development of models to describe their performance under a variety of operating conditions. Special emphasis has been placed on understanding the relationship of oxygen potential gradient to fission-product distribution and to cladding attack.

A. Fuel-Analysis Techniques

1. Ion Microprobe Analysis of Irradiated Fuel (C. E. Johnson, D. V. Steidl)

An ion microprobe mass analyzer (IMMA) has been purchased by the Chemical Engineering Division for application to fuels and materials problems encountered in LMFBR programs. With this instrument, sample atoms are ionized by a finely focused ion beam that impinges on the sample surface. Ions of many different elements can be used for sample bombardment, the choice depending on the matrix and the element to be determined. The sample ions are collected and mass analyzed in a double-focusing mass spectrometer with high collection efficiency. The IMMA will supplement the capabilities of the electron probe microanalyzer (EPM) for analyzing fuels in several important ways. The IMMA provides uniform sensitivity of detection at the parts-per-million level for the full mass range of elements. This is especially important for the low mass range. With the EPM, the elements hydrogen to boron cannot be detected and the elements from carbon through oxygen can be detected only with low sensitivity. Furthermore, since the IMMA collects isotopic data, it provides a direct means for differentiating between fission products and structural materials.

The IMMA was received from Applied Research Laboratory of Sunland, California, early in January 1972, and the final check of instrument specifications was completed early in March.

To provide the capability for examining irradiated fuels, heavy-metal shielding has been strategically located around the sample chamber for operator protection. Because little space is available within the sample chamber, all heavy-metal shielding was fastened to the instrument unistrut frame external to the sample chamber. With the large pieces of iron used for magnets and other instrumental members, only minimal additional shielding was needed to provide capability for handling irradiated fuels.

Our initial experiments with the IMMA have focused on the distribution of oxygen in irradiated fuel cladding and on the identification of fission products in the oxide-fuel matrix.

The cladding from SOV-1, a vibratorily compacted fuel irradiated to 5.0 at. % burnup at 20 kW/ft, had previously been shown (ANL-7877, p. 38) by vacuum fusion analysis to contain large quantities of oxygen, namely, about 3000 ppm. A section of SOV-1 cladding was analyzed for oxygen with

the IMMA using a $^{28}\text{N}_2^+$ ion beam; the beam current was 4.6×10^{-9} A and the beam diameter was 10.5 μm . Each sample location was first thoroughly "cleaned" by etching with the nitrogen ion beam to ensure that the area being analyzed was free of surface contamination. After a consistent analysis had been obtained in a given location, digitized data were collected for the $^{32}\text{O}_2^+$ peak intensity. These data were then converted into parts per million of oxygen, using steels of known oxygen contents as standards. The data are shown in Fig. II-1, where oxygen concentration is plotted as a function of distance from the inner surface to the periphery of the cladding section. The oxygen concentration is very high near the inner surface, but decreases quickly to a level that is about twice that of archive cladding material. The steepness of the oxygen profile indicates that the oxygen is concentrated near the cladding-fuel interface.

In Fig. II-2 are shown ion microprobe scanning images of the distribution of ^{16}O , ^{87}Rb , ^{133}Cs and ^{98}Mo in SOV-1 cladding at the fuel-cladding interface. In each picture, the degree of whiteness increases with higher ion concentrations. Examination of the oxygen scanning image shows a very high concentration near the interface. This layer is probably composed of chromium and iron oxides. The center of the first large grain near the interface, shown in Fig. II-2a (top center), is the location of the first sample point in Fig. II-1 (50 μm from inner edge of cladding). It is readily seen that the major fraction of the oxygen found by vacuum fusion analysis (3000 ppm) is located in a thin layer on the inner surface

Fig. II-1.

Oxygen Profile for SOV-1
Cladding ($^{28}\text{N}_2^+$ beam:
 4.6×10^{-9} A, 10.5- μm dia).
ANL Neg. No. 308-2944.

a. Oxygen-16

b. Cesium-133

c. Rubidium-85

d. Molybdenum-98

Fig. II-2. Ion Microprobe Scanning Images of Cladding of Fuel Element SOV-1 at the Fuel-Cladding Interface (all images 180 by 150 μm). ANL Neg. No. 308-2948.

of the cladding. Calculations have shown that complete oxidation to chromic oxide of the chromium in a 1- μm -thick layer of cladding would contribute 7800 ppm oxygen to cladding analysis. Close inspection of the oxygen picture shows that the dot intensity decreases with increasing distance from the interface. Thus, this qualitative pictorial information confirms the distribution of oxygen shown in Fig. II-1.

Figure II-2c shows, for the first time, the presence of rubidium in the area of the fuel-cladding interface. Although the presence of rubidium in this area has been predicted, its low concentration has precluded detection by electron probe microanalysis. The presence of cesium and molybdenum was expected; previous electron probe examinations of irradiated fuels have established these elements as common constituents in the region of the fuel-cladding interface. Cesium is thought to be one of the major contributors to cladding attack, and its reaction with stainless

steel cladding materials under different oxidizing potentials is reported in Section II.C, below.

Mass spectra have also been collected on an irradiated fuel sample using $^{16}\text{O}^-$ as the bombarding ion beam. The fuel examined was SOVG-17, a sol-gel fuel which had been irradiated to 3.2 at. % burnup at 13 kW/ft. Typical spectra collected from examination of the fuel near the cladding are shown in Fig. II-3 and -4. Figure II-3 shows the low-mass region (mass 1 to 50) where the principal ions observed were of materials that are probably present in impurities in the mixed-oxide fuel. From prior experimental work, the concentrations of these impurities have been estimated to be in the parts-per-million range. Figure II-4 shows the spectra obtained for the mass region from 85 through 149. One can easily observe the typical double-humped, mass-abundance curve for fission; the low-mass region of this curve extends from mass 85 to about 112 and the high-mass region from 133 to 150. The assignments of mass numbers to fission products are given in Table II-1. It should be noted that the inert gases krypton and xenon do not appear in this list; their extremely high ionization potential probably precludes their being observed in the mass scan.

For the region of mass from 85 through 100, the identification of fission products is relatively easy because little interference from other isotopes is encountered, except at mass 90, where zirconium makes a small contribution to the strontium intensity. In the region from mass 101 to 120, monoxides (the oxygen source is the primary beam or the fuel) of the elements Rb, Sr, Y, Zr, and Mo are likely to be present. This is also the region where fission yields begin to decrease significantly. The major contribution to the peak intensity in this region is probably from

Fig. II-3.

Mass Spectra from Ion Microprobe Examination of SOVG-17: Mass Region 1 to 50. ANL Neg. No. 308-3106.

Fig. II-4.

Mass Spectra from Ion Microprobe
Examination of SOVG-17: Mass
Region 85 to 149. ANL Neg. No.
308-3099.

TABLE II-1. Mass Assignment for Fission-Product
Spectra from SOVG-17

Mass Number	Fission-Product Element
85,87	Rubidium
88,90	Strontium
89	Yttrium
90,91,92,93,94,96	Zirconium
95,97,98,100	Molybdenum
99	Technetium
101,102,104	Ruthenium
103	Rhodium
105,106,107,108,110	Palladium
133,135,137	Cesium
138	Barium
139	Lanthanum
140,142	Cerium
141	Praseodymium
143,144,145,146	Neodymium
147	Promethium
147,148,149	Samarium

monoxide species rather than the low-yield fission products. Again, for the region from mass 133 through 148, isotope identification is unencumbered by interferences, but above mass 148 monoxide species are expected to be major contributors to peak intensity.

Our preliminary studies on fission products in mixed-oxide fuel indicate that, during ion microprobe examination, the behavior of molybdenum is different from that of neighboring elements. For example, the signals for $^{90}\text{Sr}^+$ remain constant at a high peak intensity for long periods of time (50-80 min), whereas those for $^{100}\text{Mo}^+$ decrease in a short period of time (2-4 min) to a peak intensity that is near background level. At the present time, it is not clear whether the low signal is indicative of an inherent lack of sensitivity for molybdenum or is the result of vaporization of molybdenum from the sample. Mass spectra obtained for MoO_2 using an oxygen ion beam have shown the species Mo^+ , MoO^+ , MoO_2^+ , MoO_3^+ , Mo_2^+ , Mo_2O^+ and $(\text{MoO})_2^+$, with Mo^+ and MoO^+ species being the most intense. Spectra obtained with nitrogen as the ion beam indicate some improvement in sensitivity, but molybdenum still disappears quickly from the spectra. Because the $^{16}\text{O}^+$ signal (oxygen coming from the sample) is quite large, oxidation processes may be taking place. Another possibility is that the molybdenum may be stratified in the sample, and the bulk concentration may be considerably below that found on the surface of the sample.

B. Postirradiation Studies of Mixed-Oxide Fuels (C. E. Johnson, C. A. Seils, K. E. Anderson, G. Staahl, C. Wach)

1. Electron Probe Microanalysis of Irradiated Fuels

Studies of the spatial distribution of fission-product elements and fuel constituents in irradiated mixed-oxide fuels can provide insight into the chemical reactions that occur in a fuel during irradiation. Principal among these studies has been the electron probe microanalysis of irradiated fuels for the molybdenum content of both the oxide phase and the noble-metal alloy phase. The use of these data in estimating the oxygen potential gradient across the fuel radius is described in the following subsection.

Recent studies have focused on examination of the distribution of molybdenum in four UO_2 -20 wt % PuO_2 fuels: the General Electric fuel elements F2R and F2Z and the NUMEC fuel elements C-11 and C-15. Some of the data on these fuels have been presented previously (ANL-7877), but are included here for completeness. The physical characteristics and irradiation conditions for these fuels are summarized in Table II-1. The fuel materials are all coprecipitated $^{235}\text{UO}_2$ -20 wt % PuO_2 in pellet form. The smear densities ranged from 82 to 94.3% of theoretical. Irradiations were performed at maximum linear power rates of 12.9 to 16.0 kW/ft, with burnups ranging from 4.7 to 9.7%.

The most reliable method of determining low levels of fission-product molybdenum in the mixed-oxide matrix involves a closely spaced, point-by-point counting procedure across the MoL_α X-ray spectral peak to determine the maximum peak height and suitable background corrections. Automation of this procedure was described previously (ANL-7877, p. 28). The results of electron probe microanalysis for molybdenum in the mixed-oxide matrix of fuel elements F2R, F2Z, C-11, and C-15 are given in Table II-3 in terms of weight percent molybdenum as a function of distance from fuel center.

Two processes appear to be controlling the distribution of molybdenum in the oxide matrix during irradiation, with a change in mechanism

TABLE II-2. Physical Characteristics and Irradiation Conditions of Mixed-Oxide Fuel Elements

Fuel Element	Density, % of Theo.		O/M Ratio	Cladding Material	Burnup, at. %	Max. Linear Power Rating, kW/ft	Calculated Temp during Irradiation, °C		
	Pellet	Smear					Fuel Centerline	Fuel Surface	Cladding
C-11	90.6	88.6	2.000	316 SS	9.7	14.0	2238	882	532
C-15	85.0	82.4	1.998	316 SS	9.7	12.9	2095	893	541
F2R	95.5	94.3	2.000	347 SS	6.5	16.0	2500	865	549
F2Z	89.2	87.2	1.988	316 SS	4.7	13.3	2300	909	563

TABLE II-3. Molybdenum Concentration in UO_2 - PuO_2 Matrix of Fuel Elements F2R, F2Z, C-11, and C-15

F2R		F2Z		C-11		C-15	
Distance From Fuel Center, ^a mm	Molybdenum Concentration, wt %	Distance From Fuel Center, ^a mm	Molybdenum Concentration, wt %	Distance From Fuel Center, ^a mm	Molybdenum Concentration, wt %	Distance From Fuel Center, ^a mm	Molybdenum Concentration, wt %
0.349	0.0516	0.433	0.0585	0.810	0.0416	0.844	0.0489
0.408	0.0727	0.472	0.0609	0.850	0.0594	0.880	0.0496
0.738	0.0609	0.486	0.0776	0.866	0.0330	0.922	0.0506
0.754	0.0539	0.754	0.0531	1.341	0.0283	1.084	0.0593
0.995	0.0330	1.13	0.0442	1.425	0.0298	1.391	0.0359
1.467	0.0334	2.17	0.0439	1.676	0.0637	1.411	0.0441
1.481	0.0386	1.35	0.0581	1.830	0.0666	1.497	0.0390
1.917	0.0371	1.52	0.0395	1.998	0.0343	1.643	0.0376
2.179	0.0793	1.89	0.0437	2.123	0.0546	1.900	0.0421
2.431	0.364	1.96	0.0550	2.193	0.0470	1.972	0.0266
2.763	0.740	2.09	0.0784	2.347	0.0943	2.118	0.0241
2.738	0.414	2.32	0.152	2.350	0.0946	2.207	0.0517
2.738	0.387	2.36	0.238	2.730	0.398	2.277	0.0564
		2.46	0.296	2.735	0.316	2.403	0.0733
		2.75	0.329	2.738	0.408	2.528	0.123
		2.75	0.299	2.750	1.15	2.626	0.235
		2.77	0.211			2.738	0.265
		2.78	0.253			2.738	0.381
						2.738	0.447

^aFuel Radius = 2.794 mm.

occurring in the hotter regions of the columnar grains. In the highest temperature region near the central void, pore migration toward the hotter end of the thermal gradient is occurring. Gases are trapped in voids, with the result that near the central void the concentration of molybdenum is greater than that found midway through the columnar-grain region. Over the rest of the fuel, molybdenum transport appears to be controlled by the temperature and the local oxygen potential. The net result is vaporization with subsequent condensation of large quantities of molybdenum in the unrestructured region of the fuel.

Electron probe microanalysis was also carried out on the characteristic metal inclusions found in the columnar- and equiaxed-grain regions of the four fuels. The principal constituents of these inclusions are molybdenum, technetium, ruthenium, rhodium, and palladium. The inclusions were first examined to determine their elemental makeup and homogeneity. After the inclusions were found to be homogeneous throughout, count-rate data were obtained for each component, and these data were computer-processed by a technique described previously (ANL-7877, p. 30) to yield weight percent of each component. The data for molybdenum, which were of principal interest in this study, are presented in Table II-4 for all four fuels.

Within the group of fuels studied, one can observe the effects that fuel density and linear power rate have on the transport of fission products during irradiation. These two parameters are integrally coupled in setting the temperature gradient in a fuel. Higher power rates tend to lead directly to higher centerline temperatures. However this effect is tempered somewhat by the effect that fuel density has on thermal conductivity and ultimately on the development of the temperature gradient. For a given power level, the closer the fuel density approaches theoretical, the better the thermal conductivity and the smaller the thermal gradient. Lower density fuels have poorer thermal conductivity and will develop a larger thermal gradient. Furthermore, at lower density the fuel porosity is higher and the potential for vapor transport increases.

In the four fuels studied, the combined effect of power level, density, and porosity is indicated to a great extent by the concentrations of molybdenum in the noble-metal inclusions. In F2R, the molybdenum content in the inclusions approaches the value calculated on the basis of fission-yield ratios of the noble metal fission products, whereas for C-15 the molybdenum content is only about one-eighth of that expected. Here the density (and porosity) differences (94.3% smear density for F2R vs 82.4% for C-15) appear more important than the differences in power rating (16.0 vs 11.7 kW/ft). It is generally accepted that interconnected porosity is minimized for systems with densities greater than 92%.

The data for the distribution of molybdenum in these four fuels is discussed further in the following section.

2. Estimation of Oxygen Potential Gradient in Irradiated Mixed-Oxide Fuel from Distribution of Molybdenum

A method has been devised for estimating the oxygen potential gradient in irradiated mixed-oxide fuels based on the distribution of molybdenum between the alloy phase and the oxide phase. Details of the

TABLE II-4. Molybdenum Concentration in Noble-Metal Inclusions in Fuel Elements F2R, F22, C-11, and C-15

F2R		F22		C-11		C-15	
Distance From Fuel Center, ^a mm	Molybdenum Concentration, wt %	Distance From Fuel Center, ^a mm	Molybdenum Concentration, wt %	Distance From Fuel Center, ^a mm	Molybdenum Concentration, wt %	Distance From Fuel Center, ^a mm	Molybdenum Concentration, wt %
0.405	62.4	0.521	41.38	0.805	17.3	0.89	7.31
0.545	55.6	0.524	40.97	0.975	19.5	1.00	8.61
0.550	58.6	0.863	41.94	1.160	19.9	1.09	8.11
0.739	51.3	0.936	46.12	1.422	19.9	1.26	9.49
0.748	54.6	1.110	40.58	1.542	20.5	1.42	10.5
0.827	56.8	1.526	46.11	1.713	19.3	1.67	11.6
0.836	54.3	1.541	44.32			1.78	11.0
1.020	47.9	1.672	46.13				
1.06	49.2	1.896	42.20				
1.21	48.1	2.027	45.96				
1.25	50.4	2.316	40.03				
1.28	48.0						
1.45	38.0						
1.49	43.9						
1.49	43.2						
1.68	30.5						
1.77	30.1						
1.93	34.4						
1.94	45.5						

^aFuel radius = 2.794 mm.

method and the reasons for selecting the Mo/MoO₂ system as a "redox-indicator" system were presented previously (ANL-7877, pp. 34-37). The basic concept of the method involves the assumptions that (1) at each point in the fuel during irradiation a local equilibrium exists between oxidized molybdenum in the fuel matrix and reduced molybdenum in noble-metal inclusions, and (2) this equilibrium is frozen into place when the fuel pin is cooled.

The noble-metal inclusions are found only in the columnar- and equiaxed-grain regions of the fuel. Although great differences are observed in the molybdenum content of these inclusions from one fuel to another, the molybdenum content of inclusions in a given fuel is relatively constant. In the columnar- and equiaxed-grain regions, molybdenum is also found in the oxide matrix, presumably existing as molybdenum dioxide in solid solution with urania and plutonia. In the unrestructured, outer region of the fuel, molybdenum is frequently found in a relatively pure metallic state or alloyed with palladium or iron. In this region, it is also found in ternary compounds with cesium and oxygen, e.g., Cs₂MoO₄. Because present thermodynamic data are insufficient to describe the more complex system existing in the unrestructured region, we have restricted our interest to the more readily definable Mo(Alloy)-MoO₂(oxide) system in the columnar- and equiaxed-grain regions of the fuel.

With the assumption, stated previously, that during irradiation a local equilibrium exists between these oxidized and reduced forms of molybdenum, the following equation may be used to calculate the oxygen potential at each position in the fuel pin:

$$\Delta \bar{G}_{O_2} = \Delta G_{f, MoO_2}^\circ + RT \ln \frac{a_{MoO_2}}{a_{Mo}} \quad (1)$$

where $\Delta G_{f, MoO_2}^\circ$ is the standard free energy of formation of MoO₂, a_{Mo} is the activity of molybdenum in a noble-metal alloy inclusion, and a_{MoO_2} is the activity of molybdenum (as the dioxide) in the oxide matrix adjacent to the metallic inclusion. The temperature of the fuel in each area of interest is estimated and the molybdenum contents of the alloy inclusion and the oxide matrix (as determined by electron probe microanalysis) are converted into activities by the methods described previously (ANL-7877). The application of this method to estimation of the oxygen potential in the fuel element C-15 was also presented in that report. The method has now been applied to the fuel elements F2R, F2Z, and C-11, using the molybdenum data given in the preceding section.

The data for all four fuels have been plotted in Fig. 11-5 as $\Delta \bar{G}_{O_2}$ (partial molar free energy of oxygen) versus absolute temperature. The figure also includes calculated curves defining the change in oxygen potential with temperature for a number of initial O/M ratios in mixed-oxide fuels. The solid lines were computed from a model developed by Blackburn,³⁷ which is based on the urania-plutonia vapor pressure data of Battles *et al.*³⁸ and the ionization-cross-section data of Blackburn and Danielson.³⁹ The dashed line is a computation for mixed-oxide fuel using a model developed by Rand and Markin.⁴⁰ The Rand and Markin model for calculating oxygen potentials in a mixed urania-plutonia system was developed using the emf data of Markin and McIver⁴¹ and the assumption that the gradient in the oxygen composition across the fuel will be

Fig. II-5.

ΔG_{O_2} as a Function of Temperature. ANL Neg. No. 308-3000.

determined by a constant CO_2/CO or H_2O/H_2 ratio in the gas phase rather than by a constant oxygen potential. In extending this model to the higher temperatures of interest, Rand and Markin made certain assumptions about the change in partial molar enthalpy of oxygen with temperature. Present information seems to indicate that the mixed-oxide system is more oxidizing than predicted by Rand and Markin.

The Blackburn model makes use of the observations by Markin and McIver⁴¹ that the oxygen potential can be correlated with the average plutonium valence (assuming that uranium is tetravalent) for hypostoichiometric fuel and with the average uranium valence (assuming that plutonium is tetravalent) for hyperstoichiometric fuel. However, instead of using the empirical relations of Markin and McIver, Blackburn relates the cation concentrations to phase-boundary and integral thermodynamic values for the oxide phase. The model³⁷ compares favorably with available mass-spectrometric data over the temperature range from 1000 to 2400°K.

In the fuel region where the Mo/MoO_2 redox indicator was applied, the data obtained from the four irradiated fuels are consistent with the

model developed by Blackburn³, which predicts that the irradiated fuel will be hypostoichiometric. This is not predicted by the Rand and Markin model. The general trend of the irradiated-fuel data is toward $O/M = 2.00$ at cooler regions in the fuel.

The data of Fig. II-5 have been replotted in Fig. II-6 as oxygen-to-metal (O/M) ratio as a function of fuel radius. This plot illustrates more clearly the extent of hypostoichiometry developed in the central regions of the fuel as oxygen migrates out toward the cladding. During the entire irradiation, the cladding is acting as an oxygen getter, and it is predicted that, when experimental data are available, they will show that the O/M ratio drops below 2.00 near the cladding. It is seen from Fig. II-6 that, over the columnar- and equiaxed-grain regions of the fuels studied, the O/M ratio was less than 2, that is, the fuel was hypostoichiometric in the hotter regions. Since the fuels F2R, C-11 and C-15 were initially stoichiometric, these results conflict with the Rand and Roberts hypothesis,⁴² which predicts no changes in the O/M ratio for a stoichiometric fuel in a thermal gradient. It is seen that the greatest departures from stoichiometry were found for fuel pins F2R and F2Z, which operated at the highest linear power ratings and thus had the highest center temperatures.

A comparison of the radial oxygen pressure gradients for the four fuels, given in Fig. II-7, shows that within a narrow range, values for the oxygen pressure are similar at similar radial positions. This was the case even though the four fuels varied in burnup from 4.7 to 9.7 at. %.

Fig. II-6.

Variation of O/M Ratio with Fuel Radius. ANL Neg. No. 308-2999.

Fig. II-7.
Variation of Oxygen Pressure
with Fuel Radius. ANL Neg.
No. 308-3009.

All fuels exhibit trends which indicate a very low oxygen pressure near the cladding. This latter feature is not unexpected because the cladding acts as an oxygen sink throughout the irradiation life of the fuel. The oxygen pressure gradient is probably established early in the fuel life, perhaps at the same time as the fuel restructuring takes place, and, if the power level remains constant, the gradient remains nearly the same throughout the life of the fuel pin.

During the initial period of irradiation when fuel restructuring and redistribution of oxygen are occurring, oxygen is transported out of the hot central region to the cooler regions and the tendency for oxidation of the cladding is increased. Increase in linear power will bring an attendant increase in the radial temperature gradient and thereby a greater oxygen gradient in the fuel. Increased burnup of the fuel will also release oxygen which, if not buffered by the fuel or fission products, can lead to additional processes for the transport of oxygen to the cool end of the temperature gradient; again the tendency for oxygen to reach the cladding is increased. The probable formation of ternary oxide compounds (e.g., Cs_2MoO_3 , Cs_2UO_4) in the outer cooler regions of the fuel will tend to fix some of the oxygen which would otherwise reach the cladding.

The quantity of oxygen reaching the cladding is also very dependent on the initial O/M of the fuel. Present FFTF specifications require hypostoichiometric fuels (O/M = 1.94) to minimize the effects of oxygen attack on the cladding. The worst possible case is the use of hyperstoichiometric fuel and for this fuel the situation may be somewhat different in

that during the early restructuring period the fuel will release its excess oxygen. Without opportunity to react with or be buffered by fission products this oxygen will be quickly transported to the cladding, and in the case of stainless steels, begin reacting with the chromium component. This early release of oxygen presents an opportunity for oxidation of the cladding and substantially increases the probability of corrosive attack.

Studies such as these, in which the initial stoichiometry, burnup, linear power, etc., can be related to oxygen potential, should provide better information than is presently available for producing fuels in which cladding attack will not prevent the achievement of goal burnup.

C. Fission Product-Cladding Interactions (J. E. Battles, G. E. Staahl)

Postirradiation examination of fast-reactor fuel ($\text{UO}_2\text{-PuO}_2$) elements has frequently revealed that the stainless steel cladding has suffered corrosive attack at the fuel-cladding interface. Both uniform oxidation and intergranular penetration along grain boundaries have been observed. Since the lifetime of fuel pins might be diminished by this corrosive attack, it is important to understand the mechanism of attack so that procedures can be recommended for its control or prevention. In elucidating the mechanism of any type of corrosive attack, the reactants and reaction products must first be identified, and the conditions required for reaction must be established.

Maiya and co-workers⁴³ of the Materials Science Division (ANL) have conducted laboratory studies on the kinetics of the reaction of cesium oxide with stainless steels of Types 304, 304L, 304H, 316, and 318. In all cases, severe intergranular attack of the stainless steel was observed. There was no evidence of uniform oxidation or dissolution. These laboratory tests yielded reaction rates that are several orders of magnitude greater than those observed in irradiated fuel pins. Johnson *et al.*,⁴⁴ by means of electron probe microanalysis of irradiated fuel pins, have shown that cesium, molybdenum, and oxygen are present in the areas of intergranular attack on stainless steels. They have suggested that the oxygen potential and temperature at the fuel-cladding interface are the principal controlling parameters. Perry *et al.*⁴⁵ have observed mixed intergranular attack and uniform oxidation of the stainless steel cladding in postirradiation examinations of mixed-oxide fuel pins. They also have observed oxygen and fission-product cesium, molybdenum, tellurium, and iodine concentrated in the grain boundaries in areas of intergranular attack. Rubin and co-workers⁴⁶ have conducted laboratory experiments in which mixed uranium-plutonium oxides of various O/M ratios with additives of cesium oxide, cesium iodide, cesium molybdate, molybdenum trioxide, and tellurium* were encapsulated in Type 316 stainless steel and then heated in a thermal gradient (550-1150°C). The additives were placed initially at the high-temperature end of the capsule. Intergranular attack was observed when the O/M of the fuel was ≥ 2.00 or when cesium oxide compounds having high oxygen potentials were used. Fitts *et al.*⁴⁷ have observed simultaneous uniform oxidation and intergranular attack of Type 316 stainless steel upon oxidation in a low-oxygen atmosphere.

Laboratory studies have been conducted in our program to establish the reactants and reaction conditions that will simulate the type of corrosive attack observed in irradiated fuel elements. Differential thermal analysis

*The additives were cesium oxide alone or in combination with the other components.

(DTA) was used to examine several compositions in the $\text{Cs}_2\text{O}-\text{Cs}_2\text{MoO}_4-\text{MoO}_3$ system. These substances were selected because previous studies at this and other laboratories⁴³⁻⁴⁷ have shown that cesium, molybdenum, and oxygen are present in the area of intergranular attack on stainless steel.

The DTA crucibles were machined from Type 304 stainless steel rod and were 0.225 in. high by 0.187 in. dia with a 0.015-in.-thick wall. The crucible bottom contained a small stem for positioning the crucible on the DTA thermocouple. Because of the small size of the crucible, it was necessary to effect closure by pressing a fitted plug into the open end of the crucible to prevent possible damage to the sample material during welding. The experiments were conducted in an atmosphere of flowing ultra-high-purity helium.

The test conditions and results of the DTA experiments are summarized in Table II-5. In general, the DTA results indicated that reactions were occurring between the stainless steel and the sample materials. Each DTA crucible was subsequently sectioned and examined metallographically and by the electron microprobe. The specimens for metallographic examination were oil polished to retain the sample residue and reaction products. Metallographic examination of the sectioned crucibles confirmed that reaction with the stainless steel had occurred in each experiment. After metallographic and electron microprobe analysis, the specimens were etched with oxalic acid to reveal carbide precipitates. In all crucibles, carbide precipitates were present in the grain boundaries and intragranularly along slip planes or twins.

Figure II-8 shows a photomicrograph and electron microprobe X-ray scanning images of a representative segment of the cross section of the DTA crucible from Run CS-2 (Cs_2O^* in a Type 304 stainless steel crucible). The residual sample material (the darker area in Fig. II-8a) appears to consist of two phases. The stainless steel (the lighter area at the top of Fig. II-8a) exhibits a thin zone of shallow intergranular attack at the interface. X-ray diffraction analysis of the residual sample material indicated that the major phase had a fcc structure with a lattice parameter of 8.37 Å. The structure is typical of spinels, AB_2X_4 ; however, it does not correspond to any of the known compounds expected in this system. The results of the electron microprobe analysis are given in Figs. II-8b to II-8f, which show, respectively, the specimen current image and X-ray scans for iron, chromium, nickel, and cesium. Iron depletion in the stainless steel (darker areas in the upper portion of Fig. II-8c) occurred mainly in localized areas in the region of attack. Areas of iron enrichment of the residual material (lighter areas in the lower portion of the figure) may also be seen. Figure II-8d shows the distribution of chromium in the stainless steel and residual sample material. In the latter portion of the figure, chromium enrichment has occurred in an area in which little, if any, iron enrichment had occurred (see Fig. II-8c). In Fig. II-8f, the cesium is seen to be concentrated primarily in the residual sample material, but some cesium has penetrated the stainless steel, both intra- and intergranularly.

As shown in Fig. II-9a, the DTA crucible containing 50 mol % Cs_2O -50 mol % Cs_2MoO_4 (Run CM-1, Table II-5) experienced both uniform oxidation and

* This material was shown by X-ray diffraction analysis to be Cs_2O with perhaps Cs_2O_2 as a very minor phase.

TABLE II-5. DTA Experiments in Type 304 Stainless Steel Crucibles

Run No.	Material ^a	Experimental Conditions ^b	Results	Type of Attack
CS-2	Cs ₂ O	Five thermocycles; maximum temp. of each cycle: 730°C; holding temp. between cycles: 650°C; time: 120 hr	Breaks at 395 and 440°C in first cycle; size of breaks diminished with each cycle; X-ray diffraction showed AB ₂ X ₄ as major phase	Shallow intergranular attack
CM-1	50 mol % Cs ₂ O- 50 mol % Cs ₂ MoO ₄	Eleven thermocycles; maximum temp. of each cycle varied from 670 to 925°C; time: 100 hr	Breaks at 560-570°C; X-ray diffraction showed only Cs ₂ MoO ₄	Uniform oxidation and shallow intergranular attack
CM-7	Cs ₂ MoO ₄	Six thermocycles; maximum temp. of each cycle: 950°C; holding temp. between cycles: 650°C; time: 120 hr	Thermogram erratic at high temperatures; no reaction peaks at lower temperatures; X-ray diffraction showed only Cs ₂ MoO ₄	Uniform oxidation
CMM-1	70 mol % MoO ₃ - 30 mol % Cs ₂ MoO ₄	Eleven thermocycles; maximum temp. of each cycle varied from 670 to 925°C; time: 100 hr	Eutectic about 455°C; liquidus about 500°C	Uniform oxidation

^aCs₂O prepared by J. L. Settle, CEN (X-ray diffraction showed Cs₂O with perhaps Cs₂O₂ as a very minor phase); Cs₂MoO₄ purchased from Rocky Mountain Research Inc., MoO₃ purchased from Mallinckrodt Chemical Co.

^bLowest temperature of each cycle, ~100°C.

a. PHOTOMICROGRAPH 300X
AS-POLISHED

b. SPECIMEN CURRENT

c. IRON $K\alpha$

d. CHROMIUM $K\alpha$

e. NICKEL $K\alpha$

f. CESIUM $L\alpha$

Fig. II-8. Photomicrograph and Electron Microprobe Scanning Images of Corrosive Attack on Type 304 Stainless Steel by Cs_2O from DTA Run CS-2. (All X-ray images are 80 by 100 μm .) ANL Neg. No. 308-2910.

a. PHOTOMICROGRAPH 600X
AS-POLISHED

b. SPECIMEN CURRENT

c. IRON K_{α}

d. CHROMIUM K_{α}

e. NICKEL K_{α}

f. CESIUM L_{α}

Fig. II-9. Photomicrograph and Electron Microprobe Scanning Images of Corrosive Attack on Type 304 Stainless Steel by $\text{Cs}_2\text{O} + \text{Cs}_2\text{MoO}_4$ from DTA Run CM-1. (All X-ray images are 80 by 100 μm .)
ANL Neg. No. 308-2887, Rev.1.

shallow intergranular attack and its appearance is quite different from that of the crucible material shown in Fig. II-8a. X-ray diffraction analysis of material removed from the crucible indicated the presence of Cs_2MoO_4 only. From electron microprobe analysis, the specimen current image (Fig. II-9b) shows the outline of a grain boundary just beyond the area of corrosive attack. Figures II-9c through 9f show the X-ray scans for iron, chromium, nickel, and cesium, respectively. From the X-ray images, it is apparent that cesium (Fig. II-9f) has penetrated the stainless steel intergranularly and intragranularly; molybdenum penetration (not shown in the figure) was very slight. Also, Figs. II-9c and 9e indicate localized depletion of iron and nickel in the areas of attack and along grain boundaries. As shown in Fig. II-9d, the chromium distribution is unusual, with areas of enrichment and depletion occurring in the more severely attacked area and chromium enrichment in the grain boundary areas depleted of iron and nickel. The residue material was predominantly cesium and molybdenum with several isolated islands of iron, chromium, and nickel.

The type of corrosive attack observed in the DTA crucibles containing Cs_2MoO_4 (Run CM-7) and 70 mol % MoO_3 -30 mol % Cs_2MoO_4 (Run CMM-1) was unlike the types of attack observed in Runs CS-2 and CM-1. In Run CMM-1, a small amount of uniform oxidation of the stainless steel was observed, whereas the crucible from Run CM-7 exhibited some characteristics of internal oxidation.

A major difficulty associated with some of the DTA experiments was loss of sample material during the latter parts of the experiments. This was particularly true of Run CS-2, in which the sample loss was about 3 mg in the first 72 hr and about 40 mg in the final 48 hr (initial charge, ~80 mg). Examination revealed that corrosive attack had occurred at the plug-crucible junction, which then permitted the liquid material to creep from the crucible. Although the loss of sample material was less in the other DTA experiment, it appears probable that all materials were more or less open to the helium atmosphere (<10 ppm O_2) and that some reaction with atmosphere contaminants could have occurred.

The results of another experiment, which did not include thermal cycling, are of particular interest since they illustrate a classic example of intergranular attack. In this experiment (GS-12), "cesium oxide" from a commercial supplier was encapsulated by heliarc welding in an annealed Type 304 stainless steel tube and hence was not subject to loss of sample material or reaction with atmospheric contaminants in the helium atmosphere. X-ray diffraction analysis of the as-received material showed that it was predominantly Cs_2O_2 and Cs_2O_3 with a very minor amount of Cs_2O , in contrast with the relatively pure cesium oxide (Cs_2O) used in the DTA experiments. The capsule containing the $\text{Cs}_2\text{O}_2 + \text{Cs}_2\text{O}_3$ was heated at 690°C for 117 hr. X-ray diffraction analysis of material removed from the capsule after the heat treatment yielded a pattern identical to that obtained in Run CS-2 (i.e., single phase AB_2X_4 , $a_0 = 8.37 \text{ \AA}$). The photomicrograph shown in Fig. II-10 indicates that considerable intergranular attack has occurred. The electron microprobe X-ray scans showed that the grain boundaries had been depleted of iron and nickel and enriched with cesium. Some grain boundaries were depleted of chromium while others were enriched.

Fig. II-10. Photomicrograph of Intergranular Attack in Type 304 Stainless Steel Caused by Commercially Supplied Cesium Oxide ($\text{Cs}_2\text{O}_2 + \text{Cs}_2\text{O}_3$) in Run GS-12. As-polished (600X). ANL Neg. No. 308-2907.

A comparison of the results of experiments CS-2 and GS-12 indicates that the oxidizing potential has an important effect on the type of corrosive attack.

Because these preliminary experiments indicated the importance of the oxidizing potential of cesium compounds on the nature of the corrosive attack, additional laboratory experiments were conducted to investigate this behavior further. The use of welded capsules prevented loss of sample material during the experiments and also prevented any reaction with contaminants (e.g., H_2O and O_2 in the helium atmosphere) as experienced in the DTA experiments. In these experiments, Cs_2O , $\text{Cs}_2\text{O}_2 + \text{Cs}_2\text{O}_3$, CsOH , CsCl , Cs_2MoO_4 , MoO_3 , cesium metal and carbon in various combinations were encapsulated in 20% cold-worked Type 316 stainless steel tubing (1.2 in. long by 0.23-in. dia with a 0.015 in.-thick wall) and then heated at 650°C for 120 or 144 hr. After the heat treatment, each capsule was sectioned* and the sections were examined metallographically; selected capsules were also examined by the electron microprobe. Residual material was removed from each capsule and analyzed by X-ray diffraction. The sample materials used and the results of the X-ray diffraction and metallographic examinations are presented in Table II-6.

* The end portions with the welds (~ 0.2 in.) were removed and the remaining tubing was cut to form three sections. These sections were mounted vertically to allow metallographic examination of the bottom, middle and top portions of each capsule.

TABLE II-6. Summary of Isothermal Capsule Experiments Using Type 316 Stainless Steel (20% cold worked) at 650°C

Run No. ^a	Sample Material, ^b mol %	X-ray Diffraction Results	Metallographic Results
CO-1	50 Cs ₂ O + 50 Cs	Liquid cesium flowed from capsule when cut open. X-ray sample could not be obtained.	Shallow intergranular attack.
CO-2	Cs ₂ O	Same as Run CO-1.	Shallow intergranular attack.
CO-3	75 Cs ₂ O + 25 MoO ₃	Same as Run CO-1.	Shallow intergranular attack, more extensive than in Run CO-2.
CO-4	50 Cs ₂ O + 50 MoO ₃	Cs ₂ MoO ₄ .	Slight indication of uniform oxidation.
CO-5	25 Cs ₂ O + 75 MoO ₃	X-ray pattern could not be identified, probably a Cs-Mo-O compound.	Uniform oxidation.
CO-6	MoO ₃	MoO ₃ with one or more minor phases unidentified.	Uniform oxidation.
CO-7	50 "Cs ₂ O" + 50 Cs ₂ MoO ₄	Cs ₂ MoO ₄	Intergranular attack, about 2-3 mils.
CO-8	Cs ₂ O	Liquid cesium flowed from capsule when cut open. X-ray sample could not be obtained.	Shallow intergranular attack.
CO-9	50 Cs ₂ O + 50 Cs ₂ MoO ₄	Major phase not identified; Cs ₂ MoO ₄ was a minor phase.	Intergranular attack less severe than in Run CO-7.
CO-10	50 "Cs ₂ O" + 50 CsOH	AB ₂ X ₄ , fcc structure similar to spinels.	Severe intergranular attack, capsule ruptured; average penetration 5-6 mils, greater in some areas.
CO-11	50 Cs ₂ O + 50 CsOH	X-ray diffraction pattern could not be identified.	Shallow intergranular attack, more extensive than in Run CO-3.
CO-12	50 "Cs ₂ O" + 50 CsCl	X-ray pattern not obtained.	Intergranular attack, about 2-4 mils.
CO-13	50 Cs ₂ O + 50 CsCl	Liquid cesium flowed from capsule when cut open.	Shallow intergranular attack.
CO-14	50 "Cs ₂ O" + 50 C	X-ray pattern could not be identified.	Intergranular attack, about 3-4 mils.
CO-15	50 "Cs ₂ O" + 50 MoO ₃	Cs ₂ MoO ₄	Uniform oxidation; uniform layer of oxide, thicker where sample material contacted capsule wall.
CO-16	50 CsCl + 50 Cs ₂ MoO ₄	CsCl and Cs ₂ MoO ₄	Isolated areas of uniform oxidation observed.
CO-17	50 CsCl + 50 CsOH	Not enough material remained in capsule to obtain an X-ray sample.	Very severe intergranular attack, capsule ruptured; some other areas of nearly total penetration.
CO-18	"Cs ₂ O"	AB ₂ X ₄ , same as CO-10.	Intergranular attack, about 3-4 mils.
CO-19	70 Cs ₂ O + 30 MoO ₃	Same as Run CO-1	Shallow intergranular attack, same as Run CO-3.
CO-20	Cs ₂ MoO ₄	Cs ₂ MoO ₄	No apparent attack.

^aRuns CO-1 through CO-6 were heated for 120 hr. All other runs were for 144 hr.^b"Cs₂O" designates commercially supplied cesium oxide, which was shown by X-ray diffraction to be predominately Cs₂O₂ and Cs₂O₃.

The types of corrosive attack observed metallographically can be classified into three distinct categories: (1) shallow intergranular attack, (2) uniform oxidation attack, and (3) intergranular attack. The various forms of attack are described below.

Shallow intergranular attack was observed in Runs CO-1, -2, -3, -8, -11, -13, and -19 (Table II-6). In these capsules the appearance of the residual materials (after sectioning) indicated that the material had been partially or totally liquid during the heat treatment. Furthermore, liquid cesium was observed to flow from these capsules (except CO-11) when they were opened, thereby indicating that the sample material (Cs_2O) had been reduced by the stainless steel. Shallow intergranular attack was observed in each section, with the amount of attack being slightly greater in the bottom section of each capsule. Figure II-11 shows a photomicrograph and electron microprobe X-ray images of a section of Capsule CO-8 (the capsule material is shown in the top portion of the figure). The shallow intergranular attack shown in the photomicrograph (Fig. II-11a) is representative of that observed in the other capsules that underwent similar attack. The attack probably was initiated along grain boundaries, but as reduction of the cesium oxide occurred, attack by the liquid metal appears to have centered at the triple point of grain boundaries. In this capsule (CO-8), the attack does not appear to be connected to the interior surface. However, in Capsule CO-11 where the corrosion was more extensive, the attack was open to the interior surface in some areas. Comparison of the electron microprobe X-ray images (Figs. II-11c through 11f) for iron, chromium, nickel, and cesium show that the attacked areas are void of iron, chromium, and nickel and enriched in cesium. Also, the entire zone of attack shows considerable depletion of chromium, with nickel enrichment at the interface.

Shallow intergranular attack was confined to those capsules that contained Cs_2O alone, in combination with 50 mol % Cs, CsCl , or CsOH , and in combination with <50 mol % MoO_3 . As stated previously, in all but one experiment (CO-11; $\text{Cs}_2\text{O} + \text{CsOH}$), the Cs_2O was reduced to metal by the stainless steel, and liquid cesium was observed when the capsules were opened.

The extent of attack of the stainless steel was minimal for the capsules containing Cs_2O , $\text{Cs}_2\text{O} + \text{Cs}$, and $\text{Cs}_2\text{O} + \text{CsCl}$. More extensive attack occurred with the addition of MoO_3 , and the most severe attack was found when CsOH was the additive. The severity of attack appears to have increased with increased oxidizing potential; however, because CsOH may undergo reaction by several mechanisms, further study of this compound is needed to define its role more precisely. Nevertheless, it is certain that the oxidizing potential in the capsules containing MoO_3 or CsOH was considerably above that of Cs_2O , namely, $\sim 10^{-19}$ atm at 650°C .⁴⁸ Thus the results indicate that the shallow intergranular attack involves a complex chemical reaction and that this attack may be associated with a liquid-solid reaction.

Uniform oxidation was observed in the capsules from Runs CO-4, -5, -6, -15, and -16 (Table II-6). Capsule CO-15, which contained $\text{Cs}_2\text{O}_2 + \text{Cs}_2\text{O}_3$ and MoO_3 , exhibited the most severe attack. In this capsule, a uniform oxide layer was formed on the interior surface of the stainless steel in contact with the sample material (bottom section). The photomicrograph and electron microprobe X-ray images of a typical area are shown in Fig. II-12. In Fig. II-12a, the black area between the oxide layer on the stainless steel and

a. PHOTOMICROGRAPH 300X
AS-POLISHED

b. SPECIMEN CURRENT

c. IRON K_{α}

d. CHROMIUM K_{α}

e. NICKEL K_{α}

f. CESIUM L_{α}

Fig. II-11. Photomicrograph and Electron Microprobe Scanning Images of Shallow Intergranular Attack on Type 316 Stainless Steel by Cs_2O in Run CO-8. (All X-ray images are 80 by 100 μm .) ANL Neg. No. 308-2911.

a. PHOTOMICROGRAPH 300X
AS-POLISHED

b. SPECIMEN CURRENT

c. IRON K α

d. CHROMIUM K α

e. NICKEL K α

f. CESIUM L α

Fig. II-12. Photomicrograph and Electron Microprobe Scanning Images of Uniform Oxidation of Type 316 Stainless Steel by $\text{Cs}_2\text{O}_2 + \text{Cs}_2\text{O}_3$ and MoO_3 in Run CO-15. (All X-ray images are 80 by 100 μm .) ANL Neg. No. 308-2909.

the mounting material (bottom of figure) was probably caused by loss of sample during polishing. The electron microprobe X-ray images for iron, chromium, and nickel (Figs. II-12c through 12e) show that chromium and nickel enrichment and iron depletion have occurred in the oxidized area of the stainless steel. The X-ray scanning images of this sample show that the small piece of sample material adhering to the oxide layer (Fig. II-12a) is mostly cesium (Fig. II-12f) and molybdenum (not shown in figure) with a slight amount of iron (Fig. II-12c) from the stainless steel. X-ray diffraction analysis of the sample residue yielded Cs_2MoO_4 only. [Cs_2MoO_4 (mp, $\sim 950^\circ\text{C}$) is a solid at the test temperature.] In all capsules exhibiting uniform oxidation, examination of the sample residues indicated that the materials had remained solid* and that very little sintering had occurred. Also, very little attack occurred in the stainless steel except in the area of direct contact with the sample material (i.e., the bottom section of the capsule).

Although the uniform oxidation observed in Capsule CO-15 appears to be somewhat similar to the air oxidation of stainless steel, the depth of attack is much greater than the thickness of the scale formed on Type 316 stainless steel oxidized in air under similar conditions, i.e., 650°C for 144 hr. Also, the oxidation appears to have occurred by an inward reaction with islands of essentially unreacted alloy, whereas in the air oxidation of stainless steel, the protective oxide layer of mostly Cr_2O_3 is formed by the outward diffusion of chromium. From these observations, it is apparent that uniform oxidation (Fig. II-12a) is not a simple oxidation reaction but a more complex reaction involving cesium as well as oxygen. Also, the appearance of the residual material and the location of the attack suggest that the reaction involved solids rather than liquids.

Intergranular attack was observed in seven of the capsule experiments listed in Table II-6; these were Runs CO-7, -9, -10, -12, -14, -17, and -18. The most severe intergranular attack occurred in Runs CO-10 and -17, in which the capsules ruptured; these ruptures occurred because of the extent of intergranular attack and not from mechanical defects. A photomicrograph of the ruptured section of Capsule CO-17, showing severe intergranular attack, is presented in Fig. II-13. Also evident in the figure is the propagation of uniform oxidation from the grain boundaries. A photomicrograph and electron microprobe X-ray images for Capsule CO-10 are shown in Fig. II-14. The photomicrograph (Fig. II-14a) shows extensive intergranular attack along the interior surface (top of Fig. II-14a), with the crack extending through the capsule wall. Also, the exterior surface shows extensive intergranular attack radiating from the crack. Uniform oxidation propagating from grain boundaries also occurred to a slight degree at the interior surface (bottom of Fig. II-14a). Comparison of the X-ray images for iron, chromium, nickel, and cesium (Figs. II-14c through 14f) shows that the grain boundaries have been largely depleted of iron and nickel and enriched with cesium. Chromium depletion is evident along some grain boundaries, whereas other grain boundaries show chromium enrichment. The chromium depletion appears to occur in those grain boundaries with the greatest cesium concentration. Also, the X-ray images indicate that some

* It is possible that a small amount of liquid could have been present early in the experiment and was later consumed by reaction with the stainless steel or interaction in the sample material [e.g., $\text{Cs}_2\text{O}(l) + \text{MoO}_3(s) \rightarrow \text{Cs}_2\text{MoO}_4(s)$].

Fig. II-13. Photomicrograph of Ruptured Section of Capsule CO-17, which Contained CsOH and CsCl. As-polished (600X). ANL Neg. No. 308-2908.

iron, chromium, and nickel have been transported to the reaction-product zone on the interior surface of the capsule (lower left corner of Figs. II-14c through 14e). The intergranular attack was less severe in the other capsules than that shown in Figs. II-13 and II-14a.

Intergranular attack was observed in all capsules containing the commercially supplied cesium oxide (Cs_2O_2 and Cs_2O_3); in these capsules the oxygen potential was established by the oxygen pressure in equilibrium with Cs_2O_2 and Cs_2O_3 . The available data⁴⁹ indicate that the oxygen pressure over $\text{Cs}_2\text{O}_2 + \text{Cs}_2\text{O}_3$ is about 10^{-2} atm or greater at the test temperature (650°C). An exception to the observed experimental trend for intergranular attack was Capsule CO-15, which contained MoO_3 in addition to $\text{Cs}_2\text{O}_2 + \text{Cs}_2\text{O}_3$. X-ray diffraction showed that the sample residue was cesium molybdate, and a significant oxide layer had formed on the interior of the capsule wall. The formation of cesium molybdate would reduce the oxygen potential.

In the capsules that experienced intergranular attack, the sample residues appear to have been at least partially liquid during the heat treatment, whereas in Capsule CO-15, the sample residue had remained powdery. Also, intergranular attack occurred over the entire length of the inner surface of each capsule. In Capsule CO-15, uniform oxidation was largely confined to the bottom section in contact with the sample material; very little attack was observed elsewhere. This behavior suggests that intergranular attack involves a liquid-solid reaction.

The results obtained in these experiments indicate that, in the presence of various cesium compounds, the type of corrosive attack experienced by the

a. PHOTOMICROGRAPH 192X

b. SPECIMEN CURRENT

c. IRON K_{α} d. CHROMIUM K_{α} e. NICKEL K_{α} f. CESIUM L_{α}

Fig. II-14. Photomicrograph and Electron Microprobe Scanning Images of Intergranular Attack on Type 316 Stainless Steel by Cs_2O_2 + Cs_2O_3 and CsOH in Run C-10. (All X-ray images are 80 by 100 μm .) ANL Neg. No. 308-2912.

stainless steel is dependent on the oxygen potential and the physical state of the reactant. At low oxygen potentials (10^{-19} atm with Cs_2O), it appears that upon increasing the temperature the oxide melts and initiation of intergranular attack begins. However reaction of the oxide with the stainless steel changes the nature of the reacting species and attack becomes localized at triple points in grain boundaries. At higher oxygen potentials (10^{-10} to 10^{-3} atm) the physical state of the reactant is most important. If it remains solid during the experiment, as in the case of MoO_3 , only uniform oxidation occurs. However if the reactant is molten, then severe intergranular attack results.

Recently Götzman and Hofmann⁵⁰ have reported on a cesium-accelerated oxidation of stainless steel cladding. They subjected a piece of stainless steel at 800°C for 1000 hr to (1) $\text{UO}_{2.08}$, (2) $\text{UO}_{2.08} + \text{Cs}$ and (3) $\text{UO}_{2.00} + \text{Cs}$. No attack was noted in Experiments 1 and 3 but severe attack was noted in Experiment 2. This is a very clear indication of the influence of cesium in a high-oxygen environment.

Thus, it is apparent that the corrosive attack observed in these capsules can involve rather complex chemical reactions in which cesium and oxygen, individually or in combination, are the controlling reactants.

The addition of Cs_2MoO_4 , CsCl , and carbon to the cesium oxides (Cs_2O and $\text{Cs}_2\text{O}_2 + \text{Cs}_2\text{O}_3$) did not appreciably affect the type or extent of corrosive attack. However, the addition of CsOH to the $\text{Cs}_2\text{O}_2 + \text{Cs}_2\text{O}_3$ (Capsule CO-10) greatly increased the extent of intergranular attack. Also, the shallow intergranular attack observed in Capsule CO-11, which contained CsOH and Cs_2O was more severe than in Capsule CO-8, which contained Cs_2O only. These results and the extreme intergranular attack observed in Capsule CO-17, which contained CsCl and CsOH , indicate that CsOH is capable of greatly accelerating the corrosive attack of stainless steel.

The influence of carbide precipitates in the grain boundaries or chromium depletion adjacent to the carbides on the intergranular attack of stainless steel is unknown at this time. The formation of carbide precipitates (sensitization) occurs when stainless steel is heated at about 400 – 800°C . The photomicrograph in Fig. II-15 shows a typical section of Capsule CO-16, which has been etched to reveal the carbide precipitates. As shown in Fig. II-15, the carbides have precipitated along slip planes within the grains, as well as along the grain boundaries. The presence of cesium, oxygen, and molybdenum in the grain boundaries of stainless steel showing intergranular attack seems to indicate that the carbide precipitates or the chromium-depleted zone is involved in intergranular attack. The importance of carbide precipitation will be further investigated.

In summary, reactions between Type 316 stainless steel and some cesium-bearing compounds have been observed in laboratory experiments; these have been classified as shallow intergranular attack, uniform oxidation, and intergranular attack. Some general observations made during these capsule experiments are as follows:

- (1) Cesium oxide (Cs_2O) is reduced to the metal by reaction with stainless steel; shallow intergranular attack is the observed form of corrosion.

Fig. II-15. Photomicrograph of a Typical Section of Capsule CO-16 Etched to Reveal Carbide Precipitates.
ANL Neg. No. 308-2906.

- (2) The higher cesium oxides ($\text{Cs}_2\text{O}_2 + \text{Cs}_2\text{O}_3$) cause intergranular attack of the stainless steel. The formation of an electrolyte phase appears to be a necessary part of intergranular attack.
- (3) Cesium hydroxide (CsOH), the most reactive of the additives studied, significantly enhances intergranular attack when added to either Cs_2O or $\text{Cs}_2\text{O}_2 + \text{Cs}_2\text{O}_3$.
- (4) The most severe intergranular attack was caused by the combination of CsOH and CsCl .
- (5) The type and severity of corrosive attack appear to be related to the presence of cesium and to the oxygen potential.
- (6) Shallow intergranular attack and intergranular attack appear to be liquid-solid reactions.
- (7) Uniform oxidation appears to occur with solid systems having high oxygen potentials. At a temperature above the melting point of such a system, intergranular attack would be expected.

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