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*Compatibility in
Space Reactor Fuel Systems*

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COMPATIBILITY IN SPACE REACTOR FUEL SYSTEMS

by

R. E. Mason and R. B. Matthews

ABSTRACT

Isothermal out-of-pile tests for compatibility between Nb-1Zr, tungsten or rhenium, and UN identified high-temperature interactions. These tests demonstrated uranium transport to the inner surface of the cladding and zirconium transport from the cladding to the pellet surface. A URe_2 layer was found on the rhenium barrier of tests performed at 1800 K. No other reactions between UN and rhenium were observed. Interdiffusion of rhenium and tungsten with Nb-1Zr was consistent with rates reported in the literature. Significant cladding grain growth was observed in specimens tested at or above 1600 K.

One compatibility pin was heated until the cladding melted and the pin was breached. The pin components began melting below the melting point of Nb-1Zr. The cladding and end caps were first to melt; then the liquid partially dissolved the tungsten in barrier and disks and the UN from the surface of the pellet.

I. INTRODUCTION

A reactor system in orbit can reject heat only by radiant heat transfer. Thus, the reactor must operate at temperatures greater than 1100 K forcing the cladding and the fuel of the reactor to operate between 1400 K and 1600 K. At these temperatures, Nb-1Zr reacts with UN, so fuel pins are fabricated with an inert refractory material (rhenium or tungsten) between the fuel and cladding to eliminate contact between Nb-1Zr and UN. Compatibility tests were designed to investigate reactions and reaction rates between UN and rhenium or tungsten and between Nb-1Zr and rhenium or tungsten. Isothermal out-of-pile compatibility tests on the Nb-1Zr/(W,Re)/UN system were performed specifically to (a) identify chemical reactions between fuel pin components, (b) determine if any material combinations and operating temperatures could cause catastrophic failures, (c) evaluate the effect of reaction structures on fuel pin components, and (d) evaluate the effectiveness of diffusion barriers in preventing or slowing reactions between the fuel and cladding.

II. BACKGROUND

Chemical interactions between Nb-1Zr and UN were demonstrated in the Pratt and Whitney Aircraft Corporation (PWAC) program (DeCrescente et al. 1965). Reaction products were an Nb-U alloy and Nb₂N particles dispersed throughout the cladding.

Uranium diffusion into the Nb-1Zr was observed in compatibility samples that used tungsten disks and were isothermally tested. Uranium penetration after 5000 h and 5863 h was 70 and 120 μm , respectively. Cladding tested for less than 3500 h (Fig. 1) showed no uranium penetration.

The compatibility test apparatus was a pellet in a Nb-1Zr tube, a refractory alloy disk (tungsten, molybdenum, etc.) on the pellet ends, and Nb-1Zr end caps. The diffusion couple was the pellet ends, the disk, and the end caps. The compatibility samples were tested at temperatures up to 1800 K in a dynamic vacuum of between 10^{-5} and 10^{-6} torr. No barrier was placed between the pellet cylindrical surface and the Nb-1Zr tubing.

Fig. 1. Uranium penetration depth in PWAC compatibility test samples.

Compatibility tests were performed at 1700 K for 100 h using 25- μm - and 1016- μm -thick tungsten disks. Reaction precipitates of Nb_2N were found in the Nb-1Zr regardless of the tungsten thickness.

A diffusion couple was also tested at 1811 K using a 25- μm -thick tungsten disk between the UN pellet and the Nb-1Zr end caps. The UN decomposed in this test. No information on the posttest condition of other components was provided. A combination of high temperature and vacuum resulted in decomposition of the UN pellet.

The cladding of fuel pins irradiated for 11 000 h at approximately 1477 K showed no uranium penetration. PWAC postulated that the vacuum environment of the diffusion couples contributed to the increased reaction rate.

Intact and defective simulated fuel pins were tested in a common lithium bath for times between 1 000 h and 11 000 h at 1477 K (DeCrescente et al. 1965). No change was found in the fuel microstructure of the sound pins. Fine precipitates of Nb_2N were dispersed throughout the Nb-1Zr cladding wall in both sound and defective pins. Niobium penetration into the tungsten barrier was found to be a linear function of time, with penetration of niobium into the tungsten barrier faster in the defective pins than the intact pins (Fig. 2). The reaction product in the intact pins was a NbW alloy. The reaction layer in the defective pins was a Nb/W/U alloy.

Uranium metal was found in the grain boundaries of fuel in the defective pins and not in the fuel of the intact pins. The external surface of both intact and defective pins of the long-duration tests contained diffused uranium. Defective pins tested for 3000 h or longer showed lithium attack on the UN pellet. Researchers at PWAC speculated that interstitial UO_2 at the grain boundaries was attacked by the lithium and uranium was transported through the lithium to the external pin surfaces. However, attack only on pins tested for long times is evidence that an incubation period exists before uranium can migrate in the system. During the incubation period, the UN is reduced by nitrogen removal until the UN stoichiometry is low enough that uranium can be removed from the fuel and transported through the system.

Fig. 2. Penetration depth of niobium into the tungsten barrier of PWAC simulated pins.

III. EXPERIMENT DESIGN AND CONDUCT

The test matrix in Table I was developed to scope the compatibility of UN/W/Nb-1Zr and UN/Re/Nb-1Zr fuel-pin systems using UN pellets fabricated at Los Alamos and cladding typical of that used in irradiation tests. The test variables were time-at-temperature, metal components, and fuel composition. Twenty-eight couples were fabricated. Testing was completed on 26, and posttest examinations were completed on 24.

TABLE I. Compatibility Test Matrix

Test	Disk		Fuel Pellet Characteristics				Test Time (h)	Temp (K)
	Top	Bottom	Oxygen (ppm)	Carbon (ppm)	Density (%TD)	X/U		
5116-R8	Re	Re	160	280	93	1.030	1083	1400
5116-R9	Re	Re	160	3200	95	0.991	1083	1400
5116-W11	W	W	80	3200	95	0.991	1083	1400
5116-W5	W	W	160	280	93	1.030	1083	1400
0483#5 ^a	W	W	80	3200	95	0.991	2501	1500
0483#7 ^a	Re	Re	80	3200	95	0.991	2501	1500
5116-R1	Re	Re	160	280	93	1.030	2501	1500
5116-W1	W	W	160	280	93	1.030	2501	1500
5116-R5	Re	Re	160	280	93	1.030	4000	1500
5116-W12	W	W	160	280	93	1.030	4000	1500
5116-R2	Re	Re	80	3200	95	0.991	5000	1500
5116-R10	Re	Re	160	280	93	1.030	5000	1500
5116-W2	W	W	80	3200	95	0.991	5000	1500
5116-W13	W	W	160	280	93	1.030	5000	1500
0483#4 ^a	W	W	80	3200	95	0.991	1001	1600
0483#6 ^a	Re	Re	80	3200	95	0.991	1001	1600
S2	W	W	100	3200	95	1.017	101	1700
S1	None	Re	100	3200	95	1.017	101	1700
5116-SW1	W	W	80	3200	95	0.991	302	1800
5116-SW2	W	W	160	280	91	1.070	302	1800
5116-SW3	W	W	160	280	91	1.070	302	1800
5116-SR1	Re	Re	160	280	91	1.070	302	1800
5116-SR2	Re	Re	80	3200	95	0.991	302	1800
5116-SR3	Re	Re	160	280	91	1.070	302	1800
5125-2	W	W	863	1520	95	1.003	~1/2	>2350
0483#8	None	None	80	3200	95	0.991	control	^b
5125-C	W	W	863	1520	95	1.003	control	^b

^aA zirconium foil was wrapped around the pin. The foil reacted with the cladding during the test.

^bNot applicable.

A. Component Design and Assembly

The compatibility pin design is shown in Fig. 3. The pin consisted of a UN pellet, a disk (rhenium or tungsten) on each end of the pellet and between the Nb-1Zr end caps, a tungsten tube (barrier) surrounding the UN pellet, and a Nb-1Zr cladding tube. The fill gas was helium at 0.75 atm at 295 K. The pin was sealed in the tantalum tube, which was also filled with helium. Tungsten or rhenium disks separated the UN pellet ends from the Nb-1Zr end caps and formed the Nb-1Zr/(W or Re)/UN diffusion couple. Interface surfaces (end-cap ends, both sides of the disks, and both ends of the pellets) were polished for the 1400 K, 1500 K, and 1800 K tests (see Appendix A for details).

Figure 4 shows the top end-cap weld. This weld microstructure was typical of that found in the tested samples. The welding procedure did not affect the test region of the pin.

Two compatibility pins tested at 1600 K and two tested at 1800 K included a zirconium foil between the tantalum capsule wall and the compatibility pin. The foil was added as a nitrogen and oxygen getter.

Table II gives the pretest chemistry of materials used in the diffusion couple tests. Analyses methods are described in Appendix B. Except for the Nb-1Zr rod used to make the end caps, the nitrogen, oxygen, and carbon concentrations were low. The Nb-1Zr tubes (cladding) were end pieces of tubing used to fabricate the SP-1 and SP-2 irradiation test pins.

The UN was synthesized from UO_2 using the carbothermic reduction/nitriding process (Matthews et al. 1986). The UN powder was pressed into green pellets of $\sim 70\%$ of T.D. and then sintered to $>93\%$ T.D. with a 24-h hold at 2473 K in 1 atm of nitrogen. The pellets were heated in argon to 1773 K and cooled in argon below 1773 K.

Fig. 3. Compatibility pin design.

Fig. 4. Microstructure of a top end-cap weld.

TABLE II. Pretest Chemistry of Pin Components

Test	Component	Lot number	Impurities (ppm)				Grain Size (μm)	Pellet	
			0	C	N	H		(wt%)	(X/U)
S	End caps		ND ^a	ND	ND	ND	ND		
	Tubing	SP1,SP2	170	90	20	20	ND		
	W disks	shelf(SP1)	65	290	<10	ND	ND		
	Re disks	shelf	40	45	5	1	32		
	Barrier	SP-1,SP-2	141	<10	13	ND	ND		
	Pellets	0497A2	100	3200	ND	ND	ND	5.273	1.013
0483	End caps	47035	380	35	5	2	ND		
	Tubing	SP1,SP2	170	90	20	20	ND		
	W disks	shelf(SP1)	93	<10	100	ND	ND		
	Re disks	shelf	40	45	5	1	32		
	Barrier	SP-1,SP-2	141	<10	13	ND	ND		
	Pellets	0482	80	3200	ND	ND	ND	5.134	0.99
5116	End caps	530126	ND	ND	ND	ND	ND		
	Tubing	U1-3878G	60	10	5	ND	ND		
	W disks	shelf(SP1)	93	<10	100	ND	ND		
	Re disks	shelf	40	45	5	1	32		
	Barrier	shelf	141	<10	13	ND	ND		
	Pellets								
	High Carbon	0482	80	3200	ND	ND	ND	5.134	0.99
	High Nitrogen	04905A	160	480	ND	ND	ND	5.861	1.07
	Standard	04902A	160	480	ND	ND	ND	5.650	1.03
5125	End caps	530126	ND	ND	ND	ND	ND		
	Tubing	U1-3878G	60	10	5	ND	ND		
	W disks	shelf(SP1)	93	<10	100	ND	ND		
	Re disks	shelf	40	45	5	1	32		
	Barrier	shelf	141	<10	13	ND	ND		
	Pellets	5123AS1	863	1520	ND	ND	49.7	5.355	1.001

^aND = not determined. Shelf = Excess material with an undocumented pedigree.

B. Experimental Conduct

Each capsule was loaded into a tantalum tube with a tantalum spacer in the tube to position the pin at the thermocouple (TC) elevation. The test samples were heated to temperature in 4 h in a 10^{-4} torr vacuum. Once the test temperature was achieved, the furnace was filled with argon and sealed.

The only exception was the 1700 K test. In this test, argon flowed very slowly through the furnace. Oxygen and nitrogen concentrations in the argon were below 10 ppm.

Occasionally a power outage shut the furnace off. When this occurred, the temperature dropped to room temperature in ~ 15 min. The furnace was then restarted with a 4-h ramp to temperature.

The argon gas in the furnace was not changed unless the furnace was opened to check or remove samples. At the end of the 1800 K test, the furnace was cooled in 4 h. All other tests were terminated with a rapid cool to room temperature (less than 15 min to 300 K).

Table III gives the temperatures measured with two thermocouples and an optical pyrometer. The difference between thermocouple measurements was due to thermocouples placed at slightly different positions in the furnace.

Posttest analysis consisted of metallurgical and chemical examinations plus microprobe analysis. Each section was mounted and longitudinal sections were cut. One longitudinal section was used for metallographic examinations and the other was used for chemical analyses. Five samples were examined using the electron microprobe.

The epoxy was removed from the section not examined on the metallograph using the process described in Appendix A. Cladding, UN pellets, disks, and liner pieces were analyzed for oxygen, nitrogen, and carbon on a LECO analyzer.

TABLE III. Temperature Condition of the Diffusion Couple Tests

Test Objective (K)	Optical Pyrometer Temp (K)	Thermocouple 1 Temperature (K)	Thermocouple 2 Temperature (K)	Apparent Temp (K)
1700	NA ^a	1700	NA ^a	1700
1600	1660	1601	1587	1600
1400	1420	1398	NA	1400
1500	1555	1500	1460	1500
1800	1760	1798	1779	1790

^aNA = not available.

IV. EXPERIMENTAL RESULTS

The reacting system contained two elements (Re and W), one compound (UN), and one alloy (Nb-1Zr). In addition, carbon, nitrogen, and oxygen impurities in the components and from the furnace environment contributed to the interactions observed in the test samples.

The posttest oxygen (Table IV), nitrogen (Table V), and carbon (Table VI) contents were tabulated. Cladding sections were taken opposite the pellet ends and from the mid-length region so that impurity gradients could be detected. As shown in Tables IV through VI, no impurity gradient along the cladding length was detected. In general, there was an increase in oxygen, carbon, and nitrogen in the Nb-1Zr components and no significant change in the bulk UN pellet chemistry.

Posttest nitrogen in the cladding was higher than pretest levels. An Auger scan was performed on the 2500-h test sample (1500 K) to locate nitrogen concentration gradients in the cladding and the end caps. No gradients were found. Nitrogen from the UN pellet apparently diffused uniformly throughout the Nb-1Zr.

TABLE IV. Posttest Oxygen Content of Test Components

Test	Time (h)	Temp (K)	Cladding				Barrier (ppm)	Disk (ppm)	Pellet (ppm)
			Top (ppm)	Mid (ppm)	Bottom (ppm)	Av (ppm)			
Re disks in compatibility pins									
R9	1083	1400	ND ^a	4200	ND	4200	ND	ND	ND
0483#5	2500	1500	ND	ND	ND	ND	ND	ND	ND
R1	2500	1500	ND	ND	ND	ND	ND	ND	ND
R5	4000	1500	488	499	500	496	172	ND	750
R2	5000	1500	607	533	456	532	330	ND	445
R10	5000	1500	541	478	482	500	140	ND	800
0483#6	1001	1600	ND	42	ND	42	ND	ND	ND
S1	101	1700	ND	33	ND	33	ND	ND	ND
SR1	302	1800	ND	ND	ND	ND	ND	ND	ND
SR2	302	1800	306	222	395	308	ND	ND	ND
SR3	302	1800	ND	40	ND	28	85	600	ND
W disks in compatibility pins									
W11	1083	1400	ND	4400	ND	4400	ND	ND	ND
0483#7	2500	1500	ND	ND	ND	ND	ND	ND	ND
W1	2500	1500	830	730	585	715	ND	ND	ND
W12	4000	1500	1001	945	580	842	380	ND	775
W2	5000	1500	550	517	586	551	260	ND	495
W13	5000	1500	499	480	513	497	20	ND	920
0483#4	1001	1600	ND	ND	ND	ND	ND	ND	ND
S2	101	1700	779	67	413	420	ND	ND	ND
SW1	302	1800	717	341	330	335	ND	ND	ND
SW2	302	1800	70	69	65	68	ND	ND	ND
SW3	302	1800	ND	178	ND	178	1005	ND	ND
Control			270	180	260	2387	54	ND	ND

^aND = not determined.

Pretest nitrogen in the pellets is given in Table II, and posttest levels are provided in Table V. The nitrogen in the high-carbon pellets was essentially the same (~5.13 wt% nitrogen). Pellets fabricated with a sesquinitride surface layer (5.861 wt% nitrogen) were reduced during the tests to nitrogen concentrations between 5.3 and 5.4 wt%. The Nb-1Zr cladding and end caps adsorbed the nitrogen lost from the pellet.

Deposits found on the tungsten liner and the cladding were UO_2 (see Fig. 5). The relative number of UO_2 particles found in each pin is shown in Fig. 6. Each number and/or bar gives the relative quantity of UO_2 deposits found in a pin. The deposits had little porosity and apparently grew by vapor transport. For UO_2 to form, zirconium in the cladding (0.7 to 1 wt% zirconium in the niobium) must be completely reacted with oxygen and nitrogen. Totally reacted zirconium required oxygen concentrations of 2500–3500 ppm. The oxygen concentrations were much below the saturation level (except the samples tested at 1400 K) and the combined carbon, nitrogen, and oxygen concentrations were below the required level. Since UO_2 particles were observed and complete reaction of zirconium is required before they can form, zirconium was completely reacted only in local areas.

TABLE V. Posttest Nitrogen Analysis of Test Components

Test	Time (h)	Temp. (K)	Cladding				Barrier (ppm)	Disk (ppm)	Pellet (wt.%)
			Top (ppm)	Mid (ppm)	Bottom (ppm)	Av (ppm)			
Re disks in compatibility pins									
R9	1083	1400	ND ^a	4820	ND	4820	ND	ND	ND
0483#5	2500	1500	ND	ND	ND	ND	ND	ND	ND
R1	2500	1500	ND	ND	ND	ND	ND	ND	ND
R5	4000	1500	75	39	91	69	ND	ND	5.36
R2	5000	1500	16	8	9	11	10	ND	5.13
R10	5000	1500	15	24	7	15	<10	ND	5.37
0483#6	1001	1600	ND	5	ND	5	ND	ND	ND
S1	101	1700	ND	64	ND	64	ND	ND	ND
SR1	302	1800	ND	ND	ND	ND	ND	ND	ND
SR2	302	1800	157	79	94	110	ND	ND	ND
SR3	302	1800	ND	50	ND	50	223	165	5.41
W disks in compatibility pins									
W11	1083	1400	ND	5220	ND	5220	ND	ND	ND
0483#7	2500	1500	ND	ND	ND	ND	ND	ND	ND
W1	2500	1500	930	330	94	451	ND	ND	ND
W12	4000	1500	88	108	35	238	ND	ND	ND
W2	5000	1500	7	27	79	38	40	ND	5.15
W13	5000	1500	8	14	30	17	40	ND	5.31
0483#4	1001	1600	ND	ND	ND	ND	ND	ND	ND
S2	101	1700	339	ND	665	500	ND	ND	ND
SW1	302	1800	560	68	86	238	ND	ND	ND
SW2	302	1800	592	387	44	341	ND	ND	ND
SW3	302	1800	ND	356	ND	356	576	ND	ND
Control			43	10	30	28	ND	ND	ND

^aND = not determined.

Grain boundaries in the cladding from pins tested for 4000 h and 5000 h at 1500 K were decorated with ZrO_2 precipitates and occasionally with ZrU precipitates (element ratio was not determined). Grain boundary precipitates were only observed in the 1500 K test samples tested for 4000 h and 5000 h.

Zirconium chips were placed in the tantalum sample can as oxygen getters and as a control material to determine if oxygen was in the furnace. At the end of the 5000-h test (1500 K), the oxygen concentration was 1800 ppm and the nitrogen concentration was 1600 ppm, where pretest oxygen and nitrogen concentrations were 23 ppm and 38 ppm, respectively.

Even though each compatibility pin was sealed in a tantalum capsule and placed in a tantalum tube and sample can, the cladding and the reaction system were contaminated by air from a very slow air leak in the furnace.

All pins tested at or above 1600 K showed significant grain growth in the Nb-1Zr end caps and cladding tube. Equiaxed grains in the cladding were found only in the compatibility pins tested at or below 1500 K. The end caps had large grains; some were nearly $1/2$ the diameter of the end cap. The grain size along the length of the cladding was greater than 500 μm in cladding tested at or above 1600 K.

TABLE VI. Posttest Carbon Analysis of Test Components

Test	Time (h)	Temp (K)	Cladding				Barrier (ppm)	Disk (ppm)	Pellet (ppm)
			Top (ppm)	Mid (ppm)	Bottom (ppm)	Av (ppm)			
Re disks in compatibility pins									
R9	1083	1400	ND ^a	ND	ND	ND	ND	ND	ND
0483#5	2500	1500	ND	ND	ND	ND	ND	ND	ND
R5	4000	1500	240	360	180	260	170	ND	635
R2	5000	1500	134	72	147	118	ND	ND	3120
R10	5000	1500	74	114	449	212	ND	ND	815
0483#6	1001	1600	ND	ND	ND	ND	ND	ND	ND
S1	101	1700	ND	ND	ND	ND	ND	ND	ND
SR1	302	1800	ND	91	ND	ND	ND	ND	ND
SR2	302	1800	ND	ND	ND	ND	ND	ND	ND
SR3	302	1800	ND	ND	ND	ND	ND	ND	570
W disks in compatibility pins									
W11	1083	1400	ND	ND	ND	ND	ND	ND	ND
0483#7	2500	1500	ND	ND	ND	ND	ND	ND	ND
W1	2500	1500	ND	ND	ND	ND	ND	ND	ND
W12	4000	1500	780	470	570	607	40	ND	75
W2	5000	1500	97	133	209	146	ND	ND	2960
W13	5000	1500	<10	70	152	74	ND	ND	695
0483#4	1001	1600	ND	ND	ND	ND	ND	ND	ND
S2	101	1700	ND	ND	ND	ND	ND	ND	ND
SW1	302	1800	61	107	75	81	ND	ND	ND
SW2	302	1800	ND	ND	ND	ND	ND	ND	ND
SW3	302	1800	ND	ND	ND	ND	ND	ND	1550
Control			210	110	95	75	ND	ND	ND

^aND = not determined.

Fig. 5. Microstructure and microprobe elemental scans across a deposit on the corner of the tungsten barrier tested at 1800 K for 302 h.
 (a) Microstructure and scan location.
 (b) Microprobe x-ray scan for elements.

Fig. 6. Relative UO_2 deposit distribution in compatibility samples. Each number and bar gives the relative quantity of deposit found in a pin. The relative oxygen particle concentrations are defined as
 0 : no oxygen particles.
 1 : a number of oxygen phase particles.
 2 : a small number of oxygen phase particles at a barrier gap or across from pellet corners.
 3 : a large number of oxygen phase particles at a barrier gap or across from pellet corners.
 4 : a large concentration of oxygen phase particles between the cladding and the tungsten barrier.

A. Rhenium Interactions

The pellet end, disks, and end caps were designed to provide diffusion interaction rates. A diffusion bond between the Nb-1Zr end caps and the rhenium disks usually formed along the Nb-1Zr/Re interface. A diffusion bond between the UN pellet and the rhenium disks did not form in any of the test samples. A reaction layer from vapor deposition formed on the pellet side of the disk in the samples tested at 1800 K.

The interdiffusion layer thicknesses in the rhenium at the Re/Nb-1Zr interface are provided in Table VII. Interaction depths were measured from photomicrographs and by the electron microprobe. Both measurements are in reasonable agreement. An interaction correlation was developed by Westinghouse (Arcella 1974) for Re-Nb interdiffusion and has the form

$$X = [3600 t \exp -(0.4899 + 42880/T)]^{1/2}, \quad (1)$$

where X is the net interdiffusion zone width in micrometers, T is the temperature (K), and t is the aging time (hours). Interaction thickness using Eq.(1) at 1500 K, 1600 K, and 1800 K and corresponding test data are shown in Fig. 7. Interdiffusion layer thicknesses are generally lower than the Westinghouse equation predictions. The Westinghouse equation is a conservative estimate of the reaction rate between these materials because free-standing tubes will not be in intimate contact with the cladding during the early stages of reactor operation.

The thicknesses of the reaction layer, URe_2 , on the surface of the rhenium disk on the pellet side are given in Table VII. All three pins with rhenium disks, which were tested at 1800 K, had a surface layer similar to that shown in Fig. 8. The layer was usually uniform at the disk periphery and was irregular farther into the interior of the disk surface. The gray phase (see Fig. 8) on the outside was UO_2 and the layer sandwiched between was URe_2 . The URe_2 was expected (see Fig. C-1). The interface on the rhenium disk was very sharp, indicating growth controlled by uranium vapor transport to the reaction layer and uranium diffusion through the reaction layer to form the URe_2 interface.

The microprobe examination of samples tested at 1800 K for 302 h identified elemental components at a Re/Nb-1Zr interface near the cladding wall (see Fig. 9 for scan location). Oxygen, uranium, and zirconium as well as rhenium and niobium were identified. Oxygen, uranium, and zirconium were not found in the interior interaction zones, only at the edges.

Fig. 7. Westinghouse niobium diffusion rate into rhenium and Los Alamos compatibility test results.

TABLE VII. Interaction Zone at the Re/Nb-1Zr Interface

Test Temp (K)	Test time (h)	Diffusion Depth		Surface layer (μm)
		Metallograph (μm)	Microprobe (μm)	
1400	1083	0	ND ^a	0
1500	2500	~10	ND	0
1500	4000	7	ND	0
1500	5000	6	ND	0
1600	1001	~9	5	0
1700	101	10	10	0
1800	302	4 to 18	25 to 35	8 to 13

^aND = not determined.

Fig. 8. Microstructure and elemental scans across a surface layer on the rhenium disk of a pin tested at 1800 K for 302 h.

- (a) Microstructure and scan location.
 (b) Microprobe x-ray scan for elements.

Fig. 9. Microstructure and elemental scans across an interaction layer between a rhenium disk and the end cap of a pin tested at 1800 K for 302 h.
 (a) Microstructure and scan location.
 (b) Microprobe x-ray scan for rhenium, uranium, niobium, oxygen, and zirconium.

B. Tungsten Interactions

No interaction between the UN pellets and the tungsten disks was observed in any of the test samples. Interaction occurred at some locations along the contact plane of the tungsten disks and Nb-1Zr end caps. The interaction depths are provided in Table VIII. Microprobe analysis was performed on only one specimen, and the interaction depth of the microprobe agreed with measurements from the photomicrograph. Shunk (1969) reported the possibility of a two-phase structure. On the other hand, Elliott (1965) reported a completely miscible niobium and tungsten system. The microstructures of these compatibility tests indicated complete miscibility. The interaction correlation developed by Westinghouse for tungsten and niobium or Nb-1Zr was (Arcella 1974)

$$X = [3600 t \exp -(3.8689 + 37390/T)]^{1/2}. \quad (2)$$

Figure 10 shows predicted interaction depths using Eq.(2) at 1500 K, 1600 K, and 1800 K and corresponding test data. The experimental interdiffusion layer depth is the same or lower than that from the study reported by Westinghouse. Again, the Westinghouse data are a conservative estimate of the reaction rate between these materials because free-standing tubes will not be in intimate contact with the cladding during the early stages of reactor operation.

Two reaction structures, grain restructuring and a surface layer, were found on the tungsten disks in the test at 1400 K. Both are shown in Fig. 11. The grain restructuring was probably a result of uranium in the grain boundaries, but no analysis was performed to identify the elements in the restructured layer. A surface layer on the tungsten disk along the W/Nb-1Zr interface was found in the test samples at 1400 K. Table VIII provides the thickness of this layer. Constituents of the layer were not identified.

TABLE VIII. Interaction Zone at the W/Nb Interface

Test Temp (K)	Test time (h)	Diffusion Depth		Surface layer (μm)
		Metallograph (μm)	Microprobe (μm)	
1400	1083	0	ND ^a	13
1500	2500	9	5 to 10	0
1500	4000	24	ND	0
1500	5000	11	ND	0
1600	1001	2	ND	0
1700	101	0	ND	0
1800	302	12 to 23 6 to 80 ^b	ND	0

^aND = not determined.

^bMost of this structure was in the Nb-1Zr with only $\sim 20 \mu\text{m}$ in the tungsten.

Fig. 10. Westinghouse niobium diffusion rate into tungsten and SP-100 compatibility data.

Fig. 11. Interaction structures on the tungsten disks tested at 1400 K for 1083 h.

C. Uranium Migration and Interactions

Interaction of Nb-1Zr and uranium from the UN pellet is expected when the two components are in contact or when a good diffusion couple between the UN, tungsten, and cladding exists (DeCrescente et al. 1965). The Los Alamos compatibility tests showed that significant uranium migration also occurs by vapor transport when there is a gap in the barrier. As shown in Fig. 12, the diameter of the pellet was smaller where the tungsten liner was not between the UN and the Nb-1Zr cladding. Pellets tested at 1500 K, 1700 K, and 1800 K had decreased diameters when there were gaps in the barrier. The pellet surface was coated with a (Zr,U,N) reaction layer in those areas where UN evaporation was obvious.

Uranium from the pellet surface diffused into the cladding. Table IX gives the interaction depths of uranium in the cladding, the uranium concentration on the surface, and the surface layer thickness on the fuel pellet.

Figure 13 shows a reaction layer on the cladding of the 101-h test sample at 1700 K. The reaction layer was found where gaps in the tungsten barrier existed. The layer also extended down the length of the tube until it disappeared near the mid-length of the diffusion couple. The reaction layer in the cladding had the same thickness ($\sim 10\ \mu\text{m}$) as uranium penetration found by microprobe analysis. The reaction layer was depleted of zirconium and rich in uranium. No distinct surface reaction layer was found in the cladding of the test samples at 1400 K, 1500 K, or 1800 K, but microprobe scans on the cladding of these tests found uranium diffused into the cladding (see Table IX).

Figure 14 shows the uranium penetration profile in the cladding opposite a gap in the tungsten barrier. The gap between the barrier and the disk (between a and b of Fig. 14) was $\sim 27\ \mu\text{m}$. The uranium concentration on the surface of the cladding was 7.2 wt% and the penetration depth was $50\ \mu\text{m}$. At the pellet mid-length, where the tungsten barrier appeared to be intact, the uranium concentration on the surface of the Nb-1Zr cladding was about 0.2 wt% and the penetration depth was $\sim 20\ \mu\text{m}$. The penetration depth and surface concentration in the mid-length area was not uniform. No uranium penetration was found along the mid-length section of the sample tested at 1500 K for 2300 h.

Fig. 12. Microstructure of a pellet end showing UN evaporation from surfaces where the barrier was missing during the test.

Fig. 13. Cladding microstructure showing reaction layer on interior and exterior surfaces of the Nb-1Zr cladding tested at 1700 K for 101 h.

TABLE IX. Interactions in Cladding and Fuel

Test	Uranium Interaction Depth in the Nb-1Zr (μm)				Interaction Depth on UN Pellet (μm)		Concentration in Nb-1Zr (wt%)	
	Microprobe ID				Large ^a Gap	Small ^b Gap	Large ^a Gap	Small ^b Gap
	Metallurgical		Mid- Length	Across from Gap				
	OD	ID						
R disks in compatibility pins								
R9	0	0	ND ^c	ND	0	-	-	-
#5	0	0	ND	ND	13 to 17	3	-	-
R1	0	0	ND	ND	0	-	-	-
R5	0	0	20 ^d	50 ^d	0	-	1.7	-
R2	0	0	ND	ND	0	-	-	-
R5	0	0	ND	ND	0	-	-	-
#6	0	0	ND	ND	0	-	0	0
S1	38	41	ND	41	11	12	3	-
SR1	ND	0	ND	ND	200	-	7.2	0.2
SR2	0	0	ND	ND	23	-	-	-
SR3	0	0	ND	ND	24 to 30	-	-	-
W disks in compatibility pins								
W11	0	0	ND	ND	11	-	-	-
#7	0	0	ND	ND	8	10	-	-
W1	0	0	0 ^d	40 ^d	0	-	-	1.2
W2	0	0	ND	ND	0	-	-	-
W12	0	0	ND	ND	0	-	-	-
W1	0	0	ND	ND	0	-	-	-
#4	0	0	ND	ND	0	-	-	-
S2	39	36	ND	36	7 to 11	-	-	-
SW1	0	0	ND	ND	0	-	-	-
SW2	0	0	ND	ND	0	-	-	-
SW3	0	0	ND	ND	0	-	-	-

^aLarge gap across from the bottom of the pellet.

^bSmall gap across from the bottom of the pellet where the barrier was set on the disk.

^cND = not determined.

^dNo layer was evident in the photomicrographs. The uranium penetration depth was found on the microprobe analysis.

No uranium was found in the tungsten barrier at any location examined. A few UN particles were found in barrier cracks. Since uranium was not found in the bulk of the tungsten barrier, migration of the uranium at the mid-length region was probably through small cracks or along the grain boundaries of the large columnar grains.

The nearly linear uranium concentration profile (Fig. 14) indicated that diffusion of uranium into the cladding was not the rate-limiting process. Transport of uranium from the fuel to the cladding is the controlling mechanism.

(a)

(b)

Fig. 14. Microstructure and microprobe scan on the inside edge of the cladding at the bottom end of a pin tested at 1800 K for 302 h.

- (a) Microstructure and scan location.
- (b) Microprobe x-ray scan for elements.

D. Zirconium Migration and Interactions

A (Zr,U,N) reaction layer (brownish-gold in color) was observed on pellets tested at 1500 K, 1600 K, 1700 K, and 1800 K. The layer on pellets tested at 1500 K was denser than that found on the pellets tested at 1700 K and 1800 K. The (Zr,U,N) interaction layer was found on pellet corners or along the sides of pellets at locations that did not have the tungsten barrier between the UN pellet and the Nb-1Zr cladding. The zirconium concentration of the reaction layer shown in Fig. 15a was 8 wt%, with uranium and nitrogen as the other constituents. No oxygen was detected. Microprobe analysis of the surface layer on a pellet tested for 4000 h at 1500 K found the zirconium concentration between 15 and 25 wt%. The reaction layer shown in Fig. 15b was found on all four corners of the pellet. Low concentrations of oxygen and rhenium were detected in the first 10 μm on one of the corners examined. These impurities were not found in the reaction layers at the other three corners.

(a)

(b)

Fig. 15. Interaction layers on the surface of UN pellets.

- (a) (Zr,U,N) layer on the surface of a pellet tested at 1700 K for 100 h.
- (b) (Zr,U,N) layer on the surface of pellet tested at 1500 K for 2500 h.

The zirconium migrated from the cladding. Zirconium depletion on the inside surface of the cladding generally corresponds to the depth of uranium penetration (Fig. 14). These tests have demonstrated that, under the right conditions, zirconium is mobile and diffuses out of the cladding.

The cladding microstructure in Fig. 13 shows a reaction zone on the outside surface of the cladding tested at 1700 K. Oxygen contamination was suspected, but the microprobe analysis detected only zirconium depletion and no oxygen or uranium. Zirconium depletion on the outside of the cladding was found only on compatibility samples tested at 1700 K. No mechanism for zirconium depletion on the outside surface has been found. The tests should be repeated to determine the operating mechanisms.

E. Nitrogen Gas Migration

The primary objective of the test at 1800 K was to determine the effect of sesquinitride on the compatibility behavior of the pins. Three of six pins had an $\sim 18\text{-}\mu\text{m}$ layer of U_2N_3 deposited on the pellet surfaces. One had a standard pellet and two had high-carbon pellets. No unusual reactions with the cladding or end disks were observed. The only anomalous structure was the UO_2 on some of the pellet corners (Fig. 16). No sesquinitride was found on the surface of any of the pellets after testing. Sesquinitride on pellets decomposed and was deposited in the cladding.

Hardness of the cladding did not change with different test temperatures or pellet carbon content. The hardness of cladding and end caps of the samples loaded with high-nitrogen pellets was harder than the cladding and end caps of samples loaded with the other pellets (Fig. 17).

(a)

(b)

Fig. 16. Microstructure and microprobe elemental scans across a deposit on the corner of a pellet tested at 1800 K for 302 h.

(a) Microstructure and scan location.

(b) Microprobe x-ray scan for elements.

Fig. 17. Microhardness results on compatibility samples tested at 1800 K.

F. Transient Behavior

Transient behavior of the fuel pins is a reactor safety issue that must be addressed before the reactor is operated. Preliminary transient calculations for the SP-100 reactor demonstrated that if all of the coolant were lost, the pins could reach the melting point of niobium in less than 30 min. To identify gross transient behavior, we heated a compatibility pin from 1000 K to ~ 2500 K in 24 min. The pin condition after a fast ramp to the melt temperature is shown in Fig. 18. The pin breached between 2300 K and 2400 K. The Nb-1Zr cladding melted and the pin released the fill gas in a sudden burst. An internal pin pressure of about 6 atm and a furnace pressure at about 1×10^{-7} torr were not a sufficient pressure difference to cause the pin to deform or balloon. Failure was a gas burst through the site of the initial melting. The liquid completely masked the location where the gas escaped.

The melt was apparently a eutectic mixture of niobium and impurities from the reacting system. Failure was between 350 K and 450 K below the melting point of Nb-1Zr (2740 K). The void above the top disk formed when the Nb-1Zr end cap melted and flowed into pin gaps and the exterior surface of the pin. The liquid filled all of the gaps in the pin and pooled on the outside of the bottom-end cap. The liquid partially dissolved the tungsten barrier, tungsten disk, and UN pellet in the last few seconds of the test.

The pin was longitudinally sectioned and a typical microstructure is shown in Fig. 18. The two-phase structure of the solidified liquid indicated a liquid- and solid-precipitate solution at the time of pin failure. All components of the system were wetted by the liquid. Next to the fuel, the structure is mostly single phase. The transient samples were not analyzed on the microprobe so the constituents in the solidified material are not known.

The pellet used in the transient test was fabricated with a molybdenum second phase in the top 0.2 mm of the pellet. The molybdenum was only in the top end and not on any other surface. The reaction liquid apparently started at the top of the pin. There is, however, no microstructural evidence that the molybdenum enhanced liquid formation. The second-phase structure is not significantly different from the pretest structure and the liquid was formed at many other locations where the molybdenum phase was not observed. The Mo-Nb phase diagram (see Appendix C) indicates that at ~ 22 at.% molybdenum, the melting temperature of niobium is decreased from 2741 K to 2630 K or decreased by about 100 K. We believe that the molybdenum had little effect on the transient behavior of the test. However, the test should be repeated to verify that conclusion.

The microstructure indicated a liquid-solid precipitate mixture. The single-phase microstructure next to the UN pellet is probably very rich in uranium. Niobium, as it flowed next to the UN, probably reacted to form NbN, thus freeing uranium, which then assisted in the dissolving process. The melt temperature of NbN is about 100 K higher than niobium, so it was probably a solid precipitate. The niobium flowed to the UN pellet and reacted with the UN to form uranium liquid and NbN precipitates, thus forming the structure shown in Fig. 19.

The tungsten disk next to the void in the top-end cap was dissolved by the liquid (Fig. 18). Tungsten and niobium form a completely miscible system. The reaction liquid dissolved the tungsten and flowed out of the pin.

Fig. 18. Transient tested simulated fuel pin. Scale is in mm increments.

- (a) Posttest pin condition.
- (b) Cross section.

Fig. 19. Melt microstructure of a transient tested pin showing dissolution of the UN pellet and the tungsten barrier.

V. DISCUSSION

Uranium dioxide particles were found in many of the compatibility samples. The UO_2 particles were generally found on the cladding where the barrier was cracked or missing. The majority of reactions occurred at or near gaps in the barrier. Apparently excess oxygen in the system accelerated the reaction process found in the compatibility tests.

Material loss from the pellet surface was most evident where the barrier was cracked or missing. Both nitrogen and uranium loss from the surface of the pellet was evident by the reduced pellet diameter.

Nitrogen dissociation from the UN is essential for any reaction in the system to begin. Once the nitrogen is lost, free uranium is available to react or migrate to other components in the pin. Chemical analysis of the cladding indicated slightly increased concentrations of nitrogen and oxygen. Nitrogen evaporation was most prominent at the corners of the pellets where there was a break in the barrier and a direct transport path through the gap to the Nb-1Zr cladding existed. As the nitrogen evaporated, the level of oxygen increased until UO could act as a transport molecule. As soon as the oxygen reached the cladding, it was taken up by the zirconium until the zirconium was entirely reacted. Thereafter, UO_2 precipitated on the barrier or the cladding inner surface.

Two processes probably controlled the reaction rates during the tests. Early in the test, uranium migration and other interaction rates were controlled by the rate of nitrogen dissociation from the pellet and the evaporation of the uranium and/or UO from the surface of the pellet. The nitrogen dissociation rate was the controlling process until the zirconium in the cladding reacted totally with oxygen and nitrogen. Saturation of the zirconium probably occurred in local regions of the pin, especially near breaks in the tungsten barrier. Once the zirconium in the cladding was completely reacted, the oxygen no longer diffused into the cladding but was available to combine with uranium or zirconium to form a transport molecule or to deposit on the surface of the cladding as UO_2 . The second process was faster with the uranium migration rate controlled by UO vapor transport.

Figure 7 shows interdiffusion rates of the metal components for the Re/Nb-1Zr system, and Fig. 10 for the W/Nb-1Zr system. As demonstrated in those figures, the interdiffusion layer depth is the same or lower than that predicted with the Westinghouse equations. The Westinghouse data are a conservative estimate of the reaction rate between these materials.

Uranium penetration into the Nb-1Zr end caps of the PWAC test began after 3500 h. This probably indicates an incubation time is required to reduce UN pellet surface. Once the surface was hypostoichiometric, uranium migrated through gaps, cracks, or grain boundaries in the tungsten barrier to the Nb-1Zr end cap. In the current compatibility tests, the tungsten disk was too thick to penetrate (290 to 370 μm for the tungsten disks and 218 to 390 μm for the rhenium disks) in the test periods used, so uranium penetration into the end caps through the tungsten disks was not observed.

In the compatibility tests, vapor transport across open gaps begins at least by 2500 h and possibly as early as 1500 h if the reaction is linear (see Fig. 20). The uranium penetration rate into the cladding was faster in the Los Alamos tests than the PWAC uranium penetration rate through the tungsten to the end cap because the barrier was helium gas rather than solid tungsten or rhenium. There was no mention of an interaction layer on the Nb-1Zr cladding surface of the PWAC compatibility test pins.

The incubation time required for uranium to begin migrating through the barrier in the gas phase at gaps in the cladding is test specific. It depends on the beginning pellet stoichiometry, the impurities in the cladding and the pellet, the gap-gas composition, and the test temperature. Therefore, it is difficult to extrapolate the incubation time to in-reactor pins or another test having different initial conditions and different test conditions.

Migration of the zirconium from the cladding was unanticipated. The cladding is the only source of zirconium, so a "metal" vapor or compound vapor (ZrO , etc.) transported zirconium from the surface of the cladding to the surface of the fuel. Oxygen in the system contributed heavily to the migration rate. Also, the free energy of ZrN is more negative than UN so the zirconium will form a nitride and release uranium to enhance the reactions.

Fig. 20. Uranium penetration depth into Nb-1Zr cladding from the Los Alamos and PWAC compatibility tests.

VI. CONCLUSIONS

These compatibility tests demonstrated that, under the conditions of the tests, the tungsten and rhenium barriers reduce reactions that could limit the expected lifetime of reactor fuel pins. However, the observed reactions and elemental migrations probably limit the useful lifetime of the pins to less than 7 years.

The tests demonstrated that uranium and zirconium can be transported by vapor as well as by diffusion, that vapor transport of elements from pin components may limit the life expectancy of the fuel pins, and that the mechanical structure and microstructure of the cladding are altered at operating temperatures of 1600 K and above.

The general findings of the phase 1 compatibility test are as follows:

- Oxygen as an impurity enhanced the migration of uranium and zirconium. Oxygen in the form of UO_2 particles was found in about 50% of the test pins.
- Uranium migrated from the surface of the UN pellets and diffused into the Nb-1Zr cladding.
- Zirconium migrated from the surface of the cladding and deposited on the surface of the UN pellets.
- The barrier limits or slows the evaporation rate of UN from the surface of the pellets.
- A second-phase layer of URe_2 on the surface of the rhenium disk was found on pins tested at 1800 K.
- A second-phase layer deposited on the surface of the tungsten disk on pins tested at 1400 K. The composition was not determined.

Unfortunately, the presence of oxygen in the test furnaces probably enhanced the migration of uranium and zirconium. Thus, the results are compromised. Plans for continued ex-pile compatibility testing are discussed in Appendix D.

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APPENDIX A

METAL FORMING AND TREATMENT PROCEDURES

The disks were machined by electron discharge machining (EDM) in oil to the tolerances given in Table A-I. The EDM process was performed using an oil coolant.

Interface surfaces (end-cap ends, both sides of the disks, and both ends of the pellets) were polished for the 1400 K, 1500 K, and 1800 K tests. The end caps were put in a stainless steel collet and polished with diamond paste on a metallographic polishing wheel. The disks were glued to the surface of a stainless steel mount and polished as smooth as possible. After one surface was polished, the disk was turned over and the opposite side was polished.

The tantalum capsule tubes and end caps were cleaned using the following procedure:

- (1) Soak in Oxylene (M-6) in an ultrasonic bath for 5 min.
- (2) Wash for 5 min in hot distilled water in an ultrasonic bath.
- (3) Rinse for 5 min in ethanol in an ultrasonic bath.
- (4) Dry in argon gas.

After machining, the disks (rhenium and tungsten) were cleaned by the following procedure:

- (1) Vapor degrease for 2 min at 80°C using trichloroethylene.
- (2) Alkaline clean for 5 min at 80 to 90°C with agitation. Mi-Clean 20 at 50 grams per liter was used.
- (3) Rinse in warm distilled water.
- (4) Dip in 20% HCl at room temperature.
- (5) Rinse in warm distilled water.
- (6) Rinse in flowing RO/DI water.
- (7) Dry in air.

HCl was chosen as the cleaning acid for both materials because it removed any residue left from the alkaline cleaner.

Posttest cleaning of the pin components was performed to remove the epoxy used to seal the pin components in place. All pins were longitudinally sectioned. One longitudinal section was used for metallographic examination and the other for chemical analysis. Epoxy in the half used for chemical analysis was dissolved in EPSO LOVE #299 (Hardman Inc.). The dissolving solutions contained

7.4% Ethanol
57.6% Methyl Chloride
32.8% Trichloroethylene
2.2% Methyl Acetate

The pin was then cut into segments for chemical analysis. The cladding was sectioned into three pieces: one from the region around the top of the pellet; one from the region near the mid-length of the pellet; and one from the bottom end of the pellet. Fuel, cladding, and barrier sections were again placed in the epoxy solvent to dissolve any remaining epoxy. The pieces were dissolved in the solvent then put in an ultrasonic cleaner filled with trichloroethylene and rinsed for 5 min, and then air-dried.

TABLE A-I. Liner and Disk Dimension Requirements

Material	Length or thickness (in.)	Diameter (in.)	Wall Thickness (in.)
CVD Liners ^a	0.500 ± 0.010	0.245 ± 0.246	0.005 ± 0.001
Top disk	0.005 ± 0.001	0.246 ± 0.001	^b
Bottom disk	0.005 ± 0.001	0.233 ± 0.001	^b

^aCVD = chemical-vapor-deposit.

^bNot applicable.

APPENDIX B

ANALYSIS METHODS

The pretest rhenium sheet and Nb-1Zr rod were analyzed for nitrogen and oxygen using the Leybold-Heraeus NOA 2003 instrument. In this instrument, the sample was heated in a graphite crucible to 2775–3275 K by a pulse of low-voltage electrical current. Oxygen in the sample reacted with carbon in the crucible to form carbon monoxide and nitrogen was simultaneously released as free nitrogen. These gases were fluxed by the helium carrier gas from the crucible through hot copper oxide where the carbon monoxide was oxidized to carbon dioxide. The carbon dioxide was measured using infrared detection and adsorbed on ascarite. The percentages of oxygen and nitrogen in the sample were calculated with an integral microcomputer using response factors derived from the analysis of standards before the unknowns.

The standard used to calibrate the instrument before the analysis was traceable to National Bureau of Standards reference materials. Generally, two portions of each sample were analyzed and the average reported.

Oxygen and carbon concentrations in the pellets were determined using the procedure described above.

Uranium in the pellets was determined by burning the UN pellet to U_3O_8 and deriving the uranium concentration from the weight change.

Nitrogen in the pellet was determined by subtracting the uranium, oxygen, and carbon weights from the sample weight.

APPENDIX C

THERMODYNAMIC PROPERTIES

Refractory compounds generally decompose to the element and then evaporate. Carbon, nitrogen, and oxygen are essentially invisible elements. The physical properties of elements and compound combinations possible in these compatibility tests are provided in Table C-I.

Five binary phase diagrams of elements active in the reactions observed in the compatibility tests are included. They are the phase relations between uranium and rhenium (Fig. C-1), niobium and rhenium (Fig. C-2), niobium and uranium (Fig. C-3), niobium and nitrogen (Fig. C-4), and niobium and molybdenum (Fig. C-5).

TABLE C-I. Physical Properties of Material
in the Compatibility Pins

Compound	Density (g/cm ³)	Melting Point (K)
Nb-1Zr	8.57	2741
NbN	8.4	2846
U	19.05	1405
UN	14.32	2903
Zr	6.49	2128
W	19.35	3688
Re	20.53	3453
ZrN	7.09	3235

Fig. C-1. Uranium-rhenium binary phase diagram (Elliott 1965).

Fig. C-2. Niobium-rhenium binary phase diagram (Elliott 1965).

Fig. C-3. Niobium-uranium phase diagram (Elliott 1965).

Fig. C-4. Niobium-nitrogen phase diagram (Elliott 1965).

Fig. C-5. Niobium-molybdenum phase diagram (Elliott 1965).

APPENDIX D

COMPATIBILITY TEST PLANS

Phase 1 test results demonstrated that the primary material transport mechanism is vapor transport. The tests demonstrated that vapor transport elements from pin components may limit the life expectancy of the fuel pins and that the mechanical and microstructural make-up of the cladding is altered at operating temperatures of 1500 K and above.

The results also demonstrated that, under the conditions of the tests, the tungsten and rhenium barriers reduce reactions that could limit the expected lifetime of fuel pins. The second test phase will attempt to obtain better rate data to answer the question of how long the pins are expected to last.

PROPOSED WORK

The primary objective of the second phase of the compatibility testing is to determine fuel pin design changes that will permit operation of SP-100 fuel pins for up to 60 000 h at high temperatures. The specific objectives are listed below.

- a. Determine any material combinations and operating temperatures that would cause catastrophic failures.
- b. Evaluate how the reaction structures affect component integrity, ductility, strength, and useful pin lifetime.
- c. Evaluate the effectiveness of diffusion barriers in preventing or slowing the reactions.
- d. Evaluate the effect of fuel impurities on fuel/liner/cladding compatibilities.
- e. Develop preliminary prediction methods to estimate the lifetime of nuclear fuel pins.
- f. Evaluate the effect of simulated fission products on the system compatibility.

Based on the results of these tests, design changes and equilibrium conditions can be identified so that the goal lifetime of the reactor can be realized.

Diffusion Couples and Simulated Pins

The test matrix of Table D-I was designed to evaluate the compatibility of the UN/W/Nb-1Zr and the UN/Re/Nb-1Zr fuel-pin systems. The tests will demonstrate out-of-pile compatibility of fuel used in the FSP-1 irradiation tests and demonstrate the behavior of rhenium barriers in the pin geometry. High-temperature tests will accelerate the reaction rates.

The parameters being investigated are time-at-temperature, interdiffusion rates, and chemical reaction rates of UN/W/Nb and UN/Re/Nb.

Posttest analyses will be

- a. Metallography to determine interaction zone depths, changes in hardness, and changes in microstructure.
- b. Microprobe examination to determine the elements in interaction zones and determine interaction zone depths.

- c. Gas analysis of the residual gas composition in the simulated fuel pin after the test is completed.
- d. Tensile test of the diffusion couple to determine changes in cladding ductility as a result of interactions.
- e. LECO analysis for nitrogen, oxygen, and carbon impurities.
- f. LECO analysis to follow the change in X/U of the fuel pellets.
- g. Auger analysis when appropriate.

TABLE D-I. Test Matrix

Temp	Time	X/U	Barrier	Comments
1500	100	1.0	CVD Re	FSP-1 fuel (measure X/U)
1500	1000	1.0	CVD Re	
1500	3000	1.0	CVD Re	
1650	100	1.0	CVD Re	FSP-1 fuel (measure X/U)
1650	1000	1.0	CVD Re	
1650	3000	1.0	CVD Re	
1650	100	1.0	CVD W	
1800	100	1.0	CVD Re	FSP-1 fuel
1800	100	1.x	CVD Re	FSP-1 fuel (measure X/U)
1800	100	TBD	CVD Re	Pellets from 1st 1800 K; 100 h
1800	1000	1.x	CVD Re	

Vapor Transport

The proposed test rig is shown in Fig. D-1. The purpose of the rig is to put material components in a test configuration so that vapor transport and vapor-solid reaction rates can be measured without the test device being a factor. These parameters can then be incorporated in models that, if combined with the simulated pin data and the irradiated pin data, can be used to predict fuel behavior during high-temperature exposure during irradiation. The primary components (Nb-1Zr, UN pellets, and rhenium) are an integral part of the test rig so that synergistic evaporation, vapor transport, and reaction mechanisms occurring in a fuel pin will be observed.

As shown in Fig. D-1, plates of Nb-1Zr or tungsten will be placed on the top and bottom ends of a large-diameter pellet of UN. The plates will be separated a known distance from the pellet with a tungsten wire. This configuration is ideal for fundamental vapor transport studies since the vapor transport will be a straight path from pellet surface to the refractory alloy surface. The disk would include a section in the center that can be mechanically tested for the tensile strength. This will provide information on how the tensile properties of the cladding or barrier changes.

During the test, the nitrogen partial pressure will be controlled by flowing gas mixtures or, before starting the test, nitrogen partial pressure will be set with flowing gases and then the furnace sealed, which will leave a predetermined gas mixture as a static gas during the test.

The advantage of this design is that a tensile specimen can be tested and ductility changes determined. In addition, the other parts of the plate can be chemically analyzed, metallographically examined, their hardness determined, and a microprobe analysis performed. Posttest analyses will be

- a. Metallography to determine interaction zone depths, changes in hardness, and changes in microstructure.
- b. Microprobe examination to determine the elements in interaction zones and determine interaction zone depths.
- c. Gas analysis of the residual gas composition in the simulated fuel pin after the test is completed.
- d. Tensile test of the diffusion couple to determine changes in cladding ductility as a result of interactions.

Fig. D-1. Vapor transport test cup.

High-Temperature Failure

Four diffusion couple-type test specimens will be tested. The first will be heated until the cladding bursts from internal pressure at 1 atm (as fabricated). The other three will be taken to temperatures 50 K, 100 K, and 150 K below the temperature at which the first specimen failed and held at that temperature for up to 72 h to determine if failure is time dependent at lower temperatures. The results of these tests will be evaluated and additional tests will be designed and performed, if required.

Fabrication and Examination Costs

The fabrication and testing costs will be the same for all samples. There are three types of analyses that should be used on the compatibility samples. The three types and the cost to fabricate, test, and analyze each are given below.

1. Complete test with microprobe and Auger analyses.

<u>Task</u>	<u>Man-hours</u>	<u>Dollars</u>
Fabrication	5	400
Testing	10	700
Chemical analysis	5	400
Metallography	45	3 500
Microprobe	40	8 000
Auger	20	2 000
Total		16 000

2. Test with analyses not including Auger analyses.

<u>Task</u>	<u>Man-hours</u>	<u>Dollars</u>
Fabrication	5	400
Testing	10	700
Chemical analysis	5	400
Metallography	45	3 500
Microprobe	40	8 000
Total		13 000

3. Test with analyses not including microprobe or Auger analyses.

<u>Task</u>	<u>Man-hours</u>	<u>Dollars</u>
Fabrication	5	400
Testing	10	700
Chemical analysis	5	400
Metallography	45	3 500
Total		5 000

If 4 samples receive the most extensive sample plan (1), 8 receive sample plan (2), and 10 receive the minimum plan (3), then the total cost to perform the compatibility tests would be \$170 000.

4 by sample plan 1	\$40 000
8 by sample plan 2	\$80 000
10 by sample plan 3	\$50 000
Total	\$170 000

The results must be not only tested, but analyzed and documented, which will require the full time work of a staff member for about six months. The total cost is then about \$220 000.