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THE NITRIDATION RATES OF URANIUM-FISSIUM ALLOYS

by

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ABSTRACT

The nitridation rates of uranium-five percent fission alloys were investigated at temperatures from about 200 to 650 C and at nitrogen concentrations in argon from about 0.5 percent up to 100 percent. The effects of sodium coatings and irradiation of the alloy were examined. The nitridation rates of the alloys followed a parabolic law, with activation energies between 14 and 16 kcal/mole. The ignition behavior of irradiated alloy in nitrogen-argon mixtures was investigated briefly.

I. INTRODUCTION

The Experimental Breeder Reactor No. 2 (EBR-II), located at the National Reactor Testing Station in Idaho, is a fast power breeder reactor designed to establish the feasibility of fast reactors for central-station power plants. It is an integrated nuclear power plant, incorporating the reactor, a sodium boiler, and a fuel recycle processing facility. The spent fuel will be processed by pyrometallurgical methods, and new fuel elements will be fabricated remotely.

The first core loading of EBR-II consists of approximately 50 percent enriched uranium alloyed with five percent noble metal fission product elements. After discharge from the reactor, this material will be processed by melt refining, a procedure which consists of melting the chopped, clad pins in a zirconia crucible and liquating the molten metal at 1400 C for about 3 hr. Considerable fission product removal occurs during this treatment through the mechanisms of volatilization and selective oxidation by the crucible. The purified metal ingot resulting from the melt refining process is then formed into new fuel pins by injection casting. In order to avoid oxidation of unclad fuel alloy during processing, the fuel-processing cell is filled with an argon atmosphere.

The Argon Cell in the EBR-II Fuel Cycle Facility includes provisions for removal of oxygen and water, which will limit the concentrations of these impurities in the argon atmosphere to 5 ppm water and 20 ppm oxygen. Since no specific provision has been made for the removal of

nitrogen at the present time, the nitrogen concentration in the argon atmosphere will be determined by the rate of air inleakage to the cell and the rate of addition of pure argon. The volume of the cell is approximately 60,000 cu ft. The atmosphere will be recirculated at a rate of about 28,500 cu ft/min. Although the cell has been designed for minimum inleakage of air, the rate will not be known until the facility is in actual operation. If the inleakage rate is 20 cu ft of air per day, and 300 cu ft of cell gas is replaced with high-purity argon each day, the nitrogen concentration at equilibrium would be about five volume percent. It is not expected that this figure will be exceeded when the cell is placed in operation. A detailed discussion of the design and operation of the EBR-II Fuel Cycle Facility is provided elsewhere.⁽¹⁾

There are several stages in the fuel cycle at which nitrogen may cause difficulties if its concentration in the Argon Cell atmosphere remains relatively high (about five percent). These are listed in Table 1. Exposure of the clad pins to this atmosphere prior to the melt refining process might result in two problems: (1) the formation of uranium nitride "pin-shells" may prevent complete coalescence of the fuel pins during melt refining, thereby lowering the pouring yield of refined metal, (2) at temperatures above about 600 C, the nitridation reaction is likely to become self-propagating, with a resulting release of volatile fission products and conversion of the fuel to a form unsuitable for melt refining. Problems

Table 1 —

STAGES IN THE EBR-II FUEL CYCLE WHICH
MAY LEAD TO EXCESSIVE NITRIDATION⁽¹⁾

Stage	Estimated Temperature ^a (C)
1. Decanned pins in crucible charger	350
2. Pins loaded in melt refining crucible (based on a one-hour storage period in the crucible)	650
3. Product ingot from melt refining	525
4. Cast pins in Vycor molds	393
5. Cast pins in tray (single layer)	170
6. Stored skulls, heels, short cast pins, rejected pins, shards, small pieces and other scrap	350-700

^aEstimated temperatures are based on bare fuel, two total atom percent burnup, 15 days cooling, and no heat removal by forced convection.

in the injection casting procedure used for the fabrication of new fuel pins may also arise from the formation of excess nitride on the surface of the alloy. Since the exact nature of such problems is not known at this time, an effort has been made to determine the extent of nitridation of the fuel in argon-nitrogen atmospheres under a variety of conditions. The variables examined in this study include nitrogen concentration, temperature, irradiation, addition of cerium to the alloy, and the presence of sodium coatings (used for thermal bonding of the fuel alloy and cladding).

Extensive information has appeared in the literature on the preparation,(2-29) physical properties,(3 8-14, 30-48) and applications(13, 18-29, 49-72) of the uranium nitrides. The reaction of nitrogen or ammonia with uranium or uranium hydride is reported(5, 8-10) to produce a nitride of the approximate composition $UN_{1.7}$ at elevated temperatures and ordinary pressures. The sesquinitride, U_2N_3 , is formed by reduction of $UN_{1.7}$ with hydrogen.(5 8-10) To prepare the dinitride, UN_2 , nitrogen pressures of about 1800 psi are required.(8-10) Uranium mononitride, UN , is prepared by thermal decomposition of the higher nitrides at temperatures greater than 1300 C (8-10). The activation energies for the nitrogen-uranium reaction have been reported as follows:

Temp Range (C)	ΔE (kcal/mole)	Reference
350 to 660	18	15, 16
660 to 770	34	15, 16
550 to 750	25.5 ± 1.8	14
775 to 900	15.1 ± 2.0	14

The crystal structures(43-48) of UN , U_2N_3 , and UN_2 are (NaCl type), $a_0 = 4.880 \text{ \AA}$ (Mn_2O_7 type), $a_0 = 10.678 \text{ \AA}$, and (CaF₂ type), $a_0 = 5.31 \text{ \AA}$, respectively.

II. EXPERIMENTAL PROCEDURE

Two types of uranium-five weight percent fissium alloy, designated as Fissium I and Fissium II, were used in the experiments with unirradiated fuel pins. Fissium I has the following composition (weight percent): natural uranium (95.0), molybdenum (2.5), ruthenium (1.9), rhodium (0.3), palladium (0.2), and zirconium (0.1). This composition corresponds to the alloy being used as the first core loading in EBR-II. Fissium II was of the same composition as Fissium I except that 0.6 weight percent cerium was added. The composition of the Fissium II alloy is considered to be more nearly typical of the fuel that will be melt refined after irradiation. The alloys were analyzed spectrographically for impurities. The total impurity content of the metal was about 400 ppm; the concentration of each of the individual impurities was less than 100 ppm.

High-purity nitrogen, 99.99 percent, and argon containing 15 ppm oxygen and 200 ppm nitrogen were used for the gas mixtures. Commercial-grade sodium was used to prepare the sodium coatings on the pins.

To remove the oxide coatings on the surfaces of the Fissium I and Fissium II pins (0.144-in. in diameter), the samples were polished with 180 and 240 grit paper on a polishing wheel.

The nitridation rates were obtained from manometric measurements of the nitrogen consumed in a constant-volume system at room temperature. The apparatus, shown schematically in Figure 1, consisted of a quartz furnace tube placed vertically through two 6-in. resistance furnaces. The fissium samples were suspended by a platinum wire from a closed Vycor thermocouple tube in the center of the furnace tube. By means of the upper furnace, the samples were held at temperature in vacuum for periods ranging from 30 to 60 min before the gas was introduced. Six pieces of fissium alloy about one centimeter long were used in each experiment.

Figure 1
FURNACE ASSEMBLY FOR
NITRIDATION STUDIES

The same apparatus was used to determine the effect of sodium coatings on the pins on the rates of reaction. The procedure was similar to that used for the uncoated pins except that sodium which was contained in a small beaker, was placed in the bottom of the furnace tube and heated under vacuum by the lower furnace so as to form a sodium coating on the pins by sublimation.

The nitridation rate studies of irradiated uranium-fissium alloys were conducted remotely in the Senior Cave Facility of the Chemical Engineering Division with apparatus similar to that shown in Figure 1. The injection cast rods, designated Fissium III, were also 0.144 in. in diameter and had the following composition (weight percent): uranium-238 (85),

uranium-235 (10), molybdenum (2.5), ruthenium (1.9), rhodium (0.3) palladium (0.2), and zirconium (0.1). The alloy was irradiated in the Materials Testing Reactor⁽⁷³⁾ (MTR). During the irradiation in MTR the specimens were unclad and unrestrained, and were exposed to the NaK used as a heat transfer medium. When the pins were removed from the irradiation capsule, the adhering NaK was destroyed either by washing with butyl alcohol or by a carefully controlled exposure to dilute oxygen. The residual oxides of sodium, potassium, and uranium were then removed with 180 grit emery paper or with 30 and 60 mesh silicon carbide in a jar mill. The difference in cleaning procedures had no observable effect on the experimental results. In the experiments with irradiated samples, only one piece of alloy was used in each experiment.

III. RESULTS

A. Unirradiated Uranium-Fissium Alloy

The nitridation reactions followed a parabolic rate law over the observed temperature range from 197 to 504 C. The rates were measured over times up to 24 hr. Initial induction periods ranging up to 15 min were observed during the runs. The results of the experiments at 197, 308, and 504 C for Fissium I and Fissium II, both with and without sodium coatings, are presented in Figures 2 and 3.

Figure 2

NITRIDATION RATES OF FISSIUM I ALLOY

Atmosphere: N₂ (5 percent);
Ar (95 percent)
Composition of Fissium I
(see page 5)

Figure 3

NITRIDATION RATES OF FISSIUM II ALLOY

Atmosphere: N₂ (5 percent);
Ar (95 percent)
Composition of Fissium II
(see page 5)

If the logarithm of the amount of nitrogen consumed is plotted against the logarithm of time, a straight line with a slope of 0.5 is obtained for a parabolic rate law. Experimental values for these slopes and the rate constants, calculated for each reaction by determining the slopes of lines resulting from plotting the square of the amount of nitrogen consumed per unit surface area against time, are given in Table 2. From the Arrhenius plots (Figures 4 and 5), it is apparent that the reaction exhibits a normal temperature dependence.

Table 2

RATE CONSTANTS FOR THE NITRIDATION OF URANIUM-FISSIUM ALLOYS

Atmosphere: N₂ (5 percent); Ar (95 percent)

Alloy	Coating	Slope of Log-Log Plot	Rate Constant, $K \times 10^{11}$ [(g/sq cm) ² /min]		
			Temperature		
			197 C	308 C	504 C
Fissium I ^a	none	0.51	0.230	-	-
Fissium I	none	0.55	-	5.00	-
Fissium I	none	0.49	-	-	199
Fissium I	sodium	0.53	0.713	-	-
Fissium I	sodium	0.56	-	12.1	-
Fissium I	sodium	0.49	-	-	295
Fissium II ^b	none	0.52	0.236	-	-
Fissium II	none	0.54	-	5.60	-
Fissium II	none	0.50	-	-	186
Fissium II	sodium	0.53	0.938	-	-
Fissium II	sodium	0.56	-	15.2	-
Fissium II	sodium	0.54	-	-	325

^aFissium I composition (weight percent): natural uranium (95.0), molybdenum (2.5), ruthenium (1.9), rhodium (0.3), palladium (0.2), and zirconium (0.1).

^bFissium II composition identical with that of Fissium I except that 0.6 weight percent cerium was added.

Figure 4

TEMPERATURE DEPENDENCE OF PARABOLIC RATE CONSTANTS FOR NITRIDATION OF FISSIUM I

Atmosphere: N₂ (5 percent);
Ar (95 percent)

Composition of Fissium I (see page 5).

Figure 5

TEMPERATURE DEPENDENCE OF PARABOLIC RATE CONSTANTS FOR NITRIDATION OF FISSIUM II

Atmosphere: N₂ (5 percent);
Ar (95 percent)

Composition of Fissium II (see page 5).

The constants of the equation

$$K = Ae^{-\Delta E/RT} \quad (1)$$

were determined for each line in Figures 4 and 5. The parabolic rate constants are as follows:

$$\text{Fissium I, uncoated: } K = 6.29 \times 10^{-5} e^{-16,000/RT} (\text{g/sq cm})^2/\text{min} \quad (2)$$

$$\text{Fissium I, sodium-coated: } K = 3.09 \times 10^{-5} e^{-14,300/RT} (\text{g/sq cm})^2/\text{min} \quad (3)$$

$$\text{Fissium II, uncoated: } K = 5.12 \times 10^{-5} e^{-15,800/RT} (\text{g/sq cm})^2/\text{min} \quad (4)$$

$$\text{Fissium II, sodium-coated: } K = 2.58 \times 10^{-5} e^{-13,800/RT} (\text{g/sq cm})^2/\text{min} \quad (5)$$

The corresponding activation energies are 16.0 ± 2.0 , 14.3 ± 2.0 , 15.8 ± 2.0 , and 13.8 ± 2.0 kcal/mole. The probable error for values of K is ± 12 percent.

In Figure 6, the amounts of nitrogen consumed per square centimeter of metal surface at 308 C in 24 hr are shown as a function of the nitrogen concentration in argon. The nitridation rate proved to be independent of nitrogen concentration at levels above two percent for uncoated and above five percent for sodium-coated Fissium II samples.

Figure 6
NITRIDATION OF FISSIUM II AT 308 C
FOR 24 HOURS

Composition of Fissium II (see page 5).

B. Irradiated Uranium-Fissium Alloy

The nitridation rates for irradiated uranium-fissium alloys at various temperatures were found to depend on the extent to which the alloy

had been exposed to the air. The effect of prior air exposure on the observed nitridation rates is illustrated by the data in Table 3. Apparently, the polishing technique described earlier for cleaning the surface of the irradiated samples was not effective. Because of handling restrictions, it was not possible to reduce the time of air exposure prior to nitridation to less than about one-half hour. However, the nitridation rates of the irradiated fissium alloys which had received those short exposures to air did not differ greatly from the rates obtained with unirradiated material. In Figure 7, the quantity of nitrogen consumed per unit area at

Table 3

EFFECT OF PRIOR AIR EXPOSURE ON THE NITRIDATION RATES OF
IRRADIATED FISSIUM III ALLOY

Alloy: Fissium III,^a irradiated as indicated in MTR; NaK
removed by oxidation; uncoated single pin
Atmosphere: 100 percent nitrogen at one atm pressure

Burnup (atom percent)	Cooling Time (days)	Specific Activity ^b (c/g)	Prior Air Exposure ^c (days)	Temper- ature (C)	Relative Nitridation Rate ^d (percent)
0.87	100	4.3	~0	300	100
			12	300	84
			14	300	73
			18	300	50
1.20	90	4.8	~0	300	100
			7	450	20
1.18	20	14.3	~0	300	100
			8	300	0
			8	500	0
			13	300	0
			14	300	0
			15	650	0
			20	650	0
1.75	100	5.1	3	500	0

^aFissium III composition (weight percent): uranium-238 (85), uranium-235 (10), molybdenum (2.5), ruthenium (1.9), rhodium (0.3), palladium (0.2), zirconium (0.1).

^bSee Appendix, Equation 8, for basis of calculations of specific activity.

^cAt ambient temperature of the cave facility (~30 C).

^dThis rate refers to the percentage of the rate observed for material which had received the minimum prior exposure to air (about $\frac{1}{2}$ hour).

Figure 7
NITRIDATION RATES OF IRRADIATED
FISSION III ALLOY

Atmosphere: nitrogen, 1 atm
Temperature: 300 C
Alloy: Fission III, irradiated in MTR as indicated
(see page 11 for Fission III composition)

300 C is shown as a function of time for fission alloys of varying specific activity. The exposure to air was kept as small as possible. A curve for unirradiated Fission II alloy is shown for comparison. In additional experiments with unirradiated Fission II alloy in atmospheres of 2 percent nitrogen-98 percent argon and 5 percent nitrogen-95 percent argon, results coinciding with Curve 2, Figure 7, were obtained.

A single experiment was performed to determine the effect of a sodium coating on the nitridation rate of irradiated

fission alloy. A sodium-coated Fission III sample irradiated to 1.18 total atom percent burnup and cooled 80 days was examined at 500 C in 100 percent nitrogen. The result is shown in Figure 8. Exposure of the alloy to air prior to the experiment was limited to less than one hour. The NaK had been removed by controlled oxidation. In Figure 8 the results of this experiment are compared with those from an unirradiated, sodium-coated Fission II sample.

Figure 8
NITRIDATION RATES OF IRRADIATED AND UNIRRADIATED
SODIUM-COATED FISSION ALLOYS

Atmosphere: 100 percent nitrogen
Temperature: 500 C
Alloy Composition: Fission I (see page 5)
Fission III (see page 11)

Fission III Irradiation Conditions

Burnup: 1.18 atom percent
Cooling: 80 days
Specific Activity: 5.37 c/g
Prior Air Exposure: 1 hr

An attempt was made to determine the nitridation rate of an irradiated uncoated Fission III sample for comparison with the data in Figure 8. The NaK was removed from the irradiated alloy by controlled

oxidation, and the exposure to air prior to the experiment was about 30 min. The observed nitridation rate at 650 C in 100 percent nitrogen is shown in Figure 9. The temperature of the sample was not monitored during the experiment, but it appeared that sufficient heat was generated to cause the reaction to become self-propagating. During the course of the reaction the sample expanded radially and longitudinally, and became distorted. It was evident from visual examination that extensive uranium nitride formation had occurred.

Figure 9

NITRIDATION RATE OF IRRADIATED FISSIUM III ALLOY

Atmosphere:	100 percent nitrogen
Temperature (nominal):	650 C (see text above)
NaK Removal:	by controlled oxidation
Burnup:	1.18 total atom percent
Cooling Time:	100 days
Specific Activity:	4.26 c/g
Prior Air Exposure:	0.5 hr
Alloy Composition:	Fissium III (see page 11)

C. Ignition Experiments

As a result of the experiment at 650 C described above, four additional experiments were performed to investigate specifically the ignition behavior of irradiated fissium alloys in nitrogen-argon atmospheres. Flowing atmospheres were used in order to avoid nitrogen depletion in the vicinity of the samples. (All previous experiments had utilized a static system.) The same apparatus was used (Figure 1), but it was modified by opening the end of the Vycor thermocouple tube that supports the sample to provide an exit for the gas. The thermocouple was extended and placed at the bottom of the sample. The atmospheres used in the experiments consisted of 100, 5, 1, and 0.5 percent nitrogen in argon, with a flow rate of 100 cc/min. The furnace and sample temperatures were monitored continuously, and in each experiment the furnace temperature was increased at a rate of approximately 10 C/min.

The results of the ignition experiments are summarized in Table 4 and the temperature-time curves are shown in Figure 10. The results are not entirely unequivocal, since experimental limitations necessitated

Table 4

SUMMARY OF IGNITION EXPERIMENTS WITH IRRADIATED
FISSIUM III IN NITROGEN-ARGON ATMOSPHERES

Number of Pins:	1			
Burnup (total atom percent):	1.18			
NaK Removal:	oxidation			
Cooling Time (days):	100			
Flow Rate (cc/min):	100			
Heating Rate (C/min):	~10			
	Experiment No.			
	1	2	3	4
Weight (g)	6.42	5.86	7.66	7.18
Total Activity (c)	27.4	25.0	32.6	30.6
Activity of Volatile Isotopes (c)				
Xe ¹³³	6.48×10^{-5}	5.92×10^{-5}	7.74×10^{-5}	7.25×10^{-5}
Kr ⁸⁵	2.78×10^{-2}	2.54×10^{-2}	3.32×10^{-2}	3.11×10^{-2}
I ¹³¹	2.57×10^{-3}	2.34×10^{-3}	3.06×10^{-3}	2.87×10^{-3}
Atmosphere (percent)				
Nitrogen	100	5.0	1.0	0.5
Argon	0	95.0	99.0	99.5
Prior Exposure to Air (hr)	0.5	5.0	24.5	29.0
Initial Self-heating Temp (C)	660	660	730	none
Maximum Temp (C)	860	880	880	920
Fission Gas Release Temp (C)	660	660	660	660
Duration of Fission Gas Release (min)	6	16	21	30
Appearance of Fuel Pin				
Vertical Growth	yes	yes	yes	yes
Radial Expansion	yes	yes	yes	slight
Distortion	yes	yes	slight	no
Cracks	yes	yes	yes	yes

Figure 10
TIME-TEMPERATURE CURVES
FOR IRRADIATED FISSIUM III
IN NITROGEN-ARGON
MIXTURES

Alloy Composition: Fissium III
(see page 11)
Conditions: See Table 4

exposure of the samples to air for periods up to 29 hr prior to ignition experiments. However, no evidence has been found that exposures of this duration affect the ignition characteristics significantly. There appears to be little difference in the ignition behavior of the samples in atmospheres of 5 and 100 percent nitrogen. The reaction was moderated somewhat by reducing the nitrogen concentration to 1.0 percent; at 0.5 percent no self-heating was evident.

IV. DISCUSSION

A comparison of the nitridation rates of unirradiated, uncoated uranium-fissium alloy with the literature data for uranium can be made by extrapolating the lines in Figures 4 and 5 to give the parabolic rate constants at 600 C. This comparison gives the following results:

Fissium I:	$5.2 \times 10^{-9} \text{ (g/sq cm)}^2/\text{min}$
Fissium II:	$5.0 \times 10^{-9} \text{ (g/sq cm)}^2/\text{min}$
Uranium: ⁽¹⁶⁾	$4.0 \times 10^{-9} \text{ (g/sq cm)}^2/\text{min}$
Uranium: ⁽¹⁴⁾	$8.0 \times 10^{-9} \text{ (g/sq cm)}^2/\text{min}$

It appears that the presence of fissium elements in these concentrations does not affect the nitridation rate of uranium significantly. The rate constants shown above also agree well with previously determined values of about $3 \text{ to } 5 \times 10^{-9} \text{ (g/sq cm)}^2/\text{min}$ ⁽¹⁷⁾ for uranium-fissium alloy. Adda⁽¹⁶⁾ reported an activation energy of 18.0 kcal/mole for the nitridation of uranium at temperatures between 350 and 660 C, which is in reasonable agreement with the values of 15.8 and 16.0 kcal/mole that were obtained with the uranium-fissium alloys.

The sodium coatings on the fissium alloys increased the nitridation rates somewhat and decreased the activation energies by 1.7 to 2.0 kcal/mole. The differences were not considered large enough to justify an investigation of the mechanism causing this effect. Gill and Bokros⁽⁷⁴⁾ also found that sodium increased the nitridation rates of stainless steel.

The temperature dependence of the parabolic rate constants for the nitridation of Fissium I and II was indicated in Figures 4 and 5 and in Equations 2 through 5.

The effect of nitrogen concentration on nitridation rate was shown in Figure 6. The data indicate that the nitrogen-uranium reaction rate is independent of the nitrogen concentration above two percent for uncoated Fissium II and above five percent for sodium-coated Fissium II. Schnizlein et al.⁽¹⁷⁾ have reported similar results for the nitridation rates of uranium-fissium alloys in 5 percent nitrogen-95 percent argon and 100 percent nitrogen atmospheres.

The nitridation studies with irradiated Fissium III alloy did not provide an unequivocal result as to the effect of irradiation on the rate. It is believed that two different effects related to irradiation may be important. One is a possible acceleration of the reaction, resulting from ionization of the gas at the metal surface, where an intense radiation flux exists. The other effect is related to irradiation damage to the alloy, which produces an increased surface area of the metal through the formation of microcracks.⁽⁷⁵⁾ The polishing procedures did not remove the

microcracks or irregularities. Below 600 C, however the effect of irradiation on the nitridation rates was modest (see Figures 7 and 8)

In the ignition experiments however, it is strongly suspected that the ignitions were related to the rapid swelling of irradiated uranium-fissium alloys which occurs between 600 and 700 C whether nitrogen is present or not. In these experiments the ignition temperature correlated reasonably well with the temperature at which a large increase of surface area occurs and fission product krypton and xenon are released.⁽⁷⁶⁾

V. CONCLUSIONS

By means of the nitridation rate data presented in this report, the thicknesses of nitride films to be expected on fuel pins and ingots at various stages in the EBR-II fuel cycle have been calculated by Hesson and Feldman,⁽¹⁾ who assumed the reaction occurring is

and a density of 11.24 g/cc for the uranium nitride. The results are given in Table 5.

Table 5

CALCULATED NITRIDATION OF UNIRRADIATED FISSION PINS AND
INGOTS IN ARGON-5 PERCENT NITROGEN ATMOSPHERE

	197 C	308 C	504 C
K, (g/sq cm) ² /min × 10 ¹¹			
Uncoated pins	0.236	5.60	186
Sodium-coated pins	0.958	15.2	325
Grams nitrogen reacted per sq cm in 100 min × 10 ⁵			
Uncoated pins	1.53	7.5	43
Sodium-coated pins	3.06	15.3	57
Nitride thickness in 100 min, mils			
Uncoated pins	0.008	0.039	0.224
Sodium-coated pins	0.016	0.099	0.296
Percent of total uranium nitrided in 100 min			
Uncoated pins (0.144-in. dia)	0.011	0.053	0.304
Sodium-coated pins	0.021	0.108	0.403
6-kg ingots (square)	0.002	0.011	0.040

One of the most difficult problems is to relate these data in a reliable manner to melt refining yields. The effect on melt refining yields of storing unirradiated Fission II fuel pins in a crucible at various temperatures and under various atmospheres has been investigated by Bennett.⁽⁷⁷⁾ His results, based on 2-kg melt refining runs, are presented in Table 6. Two hours of exposure of unirradiated uranium-fission alloy to five percent nitrogen in argon at 650 C did not produce sufficient nitridation to cause a reduction in the melt refining yield. In Figure 11, the nitridation rates observed by Bennett are compared with the data for irradiated Fission III and for unirradiated Fission II with and without sodium coatings.

*X-ray diffraction results indicate that the major phase is U₂N₃ or UN₂ and that the minor phase is UN on the surface of the nitrided samples.

Table 6

**EFFECT ON MELT REFINING YIELD OF STORING UNIRRADIATED EBR-II FUEL PINS
AT 350 AND 650 C IN NITROGEN-CONTAINING ATMOSPHERES**

Storage Conditions					
Time:		2 hr			
Temperature:		as indicated			
Atmosphere:		as indicated			
Melt Refining Conditions					
Temperature:		1400 C			
Time:		3 hr			
Atmosphere:		argon			
Crucible:		pressed lime-stabilized zirconia			
Description of Charge			Conditions of 2-hr Storage		
Run No.	Weight (g)	Form	Average Percent N ₂ Present in Argon ^a	Temperature (C)	Melt Refining Yield (%)
340	1986	Massive U	0.03	650	96.3
347	1964	U-fissium pins + ~0.7 w/o Ce	0.02	650	95.5
-	1961 ± 3	U-fissium pin + ~0.5 w/o Ce	5.43 ^c	350	95.6 ^b
345	1964	U-fissium pin + ~0.7 w/o Ce	5.25 ^c	350	94.6
346	1964	U-fissium pins + ~0.7 w/o Ce	4.98 ^c	650	94.7

^aAs the mass spectrometer cannot distinguish between nitrogen and carbon monoxide at these concentrations, a small amount of the latter may be present.

^bAverage of two runs from previous series (see ANL-6477, page 35).

^cAverage of nitrogen concentrations at start and end of storage period. The maximum decrease was approximately 2 percent for the storage runs.

Figure 11

COMPARISON OF NITRIDATION RATES

- 1 Irradiated Fissium III alloy
 - 2 Sodium-coated, unirradiated Fissium II alloy
 - 3 Uncoated, unirradiated Fissium II alloy
- Alloy Compositions: Fissium II (see page 5);
Fissium III (see page 11)

Bennett's results showed no decrease in melt refining yield when the calculated amount of uranium nitride (U_2N_3) produced was 0.064 gm/cm^2 . If it is assumed that the fuel temperature in the Fuel Cycle Facility is held below 600°C at all times to avoid fission gas release and swelling which may lead to ignition, a minimum of 40 hr of exposure to five percent nitrogen in argon should be required to form 0.064 g of uranium nitride per square centimeter on irradiated, sodium-coated fissium alloy. Because these experiments could not be conducted under exact plant conditions, however, this result should be regarded as a guide and not as a guarantee that the melt refining yields will be unaffected under these circumstances.

The amount of nitridation that can be tolerated in other phases of the fuel cycle, such as injection casting of new pins, is not known at the present time. However, the information now available on nitridation rates should aid in finding a solution to difficulties which may arise.

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APPENDIX

Calculation of the Fission Product Concentrations in
Irradiated Uranium-Fissium Alloys

The following assumptions were made in computing fission product concentrations and activity levels

1. one gram of fuel;
2. seven cycles of MTR irradiation; one MTR cycle is 15 days of irradiation followed by 6 days of cooling;
3. one atom percent burnup and
4. thermal fission yield data from Katcoff (78)

The rate of production of an isotope is given by the equation

$$R = AB \quad , \quad (1)$$

where $A (= 2.59 \times 10^{-7}$ atoms fissioned/day) is the number of atoms fissioned per day and B is the fission yield. The rate of decay of an isotope is

$$R = N\lambda \quad (2)$$

where N is the number of atoms present and λ the decay constant. The decay constant may be calculated from the equation

$$\lambda = 0.693/t_{1/2}(d) \quad (3)$$

The net rate of production of an isotope is

$$\frac{dN}{dt} = AB - N\lambda \quad (4)$$

or

$$N = \frac{AB}{\lambda} [1 - e^{-\lambda t}] \quad (5)$$

The number of total atoms N_T present per gram of fuel at discharge may be calculated from the equation

$$N_T = N [e^{-12\lambda} + e^{-10\lambda} + e^{-8\lambda} + e^{-6\lambda} + e^{-4\lambda} + e^{-2\lambda} + 1] \quad (6)$$

The number of curies per gram at discharge is

$$C = \frac{N_T \lambda (d^{-1})}{3.2 \times 10^{15}} \quad . \quad (7)$$

The general equation for the number of curies per gram of fuel at any time t for an isotope is given by the equation

$$C_T = C e^{-\lambda t} \quad . \quad (8)$$

Substituting Equations 5, 6, and 7 in Equation 8, we obtain

$$C_T = 80.9 e^{-\lambda t} B [1 - e^{-15\lambda}] [e^{-126\lambda} + e^{-105\lambda} + e^{-84\lambda} + e^{-63\lambda} + e^{-42\lambda} + e^{-21\lambda} + 1] \quad . \quad (9)$$

The equation for the computation of the number of grams of fission product per gram of fuel based on the above assumptions is

$$G_T = (4.3 \times 10^{-7} \text{ Mw}) B \frac{e^{-\lambda t}}{\lambda} [1 - e^{-15\lambda}] [e^{-126\lambda} + e^{-105\lambda} + e^{-84\lambda} + e^{-63\lambda} + e^{-42\lambda} + e^{-21\lambda} + 1] \quad , \quad (10)$$

where Mw is the atomic weight. For stable elements,

$$G_T = (4.3 \times 10^{-7} \text{ Mw}) B (105) \quad . \quad (11)$$

Values for C_T and G_T may be calculated by varying t for each set of λ and B .

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