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IRRADIATION PERFORMANCE OF NITRIDE FUELS

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IRRADIATION PERFORMANCE OF NITRIDE FUELS

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INTRODUCTION

The properties and advantages of nitride fuels are well documented in the literature. Basically the high thermal conductivity and uranium density of nitride fuels permit high power density, good breeding ratios, low reactivity swings, and large diameter pins compared to oxides. Nitrides are compatible with cladding alloys and liquid metal coolants, thereby reducing fuel/cladding chemical interactions and permitting the use of sodium-bonded pins and the operation of breached pins. Recent analyses done under similar operating conditions[1,2,3] show that - compared to metal fuels - mixed nitrides operate at lower temperatures, produce less cladding strain, have greater margins to failure, result in lower transient temperatures, and have lower sodium void reactivity. Uranium nitride fuel pellet fabrication processes were demonstrated during the SP-100 program[4], and irradiated nitride fuels can be reprocessed by the PUREX process[5]. Irradiation performance data suggest that nitrides have low fission gas release and swelling rates thereby permitting favorable pin designs and long lifetime. The objective of this report is to summarize the available nitride irradiation performance data base and to recommend optimum nitride characteristics for use in advanced liquid metal reactors.

MIXED NITRIDE IRRADIATION

Over 140 (U,Pu)N fuel pins were irradiated as part of the U.S. Liquid Metal Fast Breeder Reactor (LMFBR) program[6,7] with the following variables:

Design Features

Cladding: 7.87 - 9.40 mm-o.d./304 & 316 ss
He- and Na-bonded (with and without shroud tubes)
MN density: 80 - 90 %TD
Smear density: 75 - 86% TD

Irradiation Conditions

Power: 67 - 107 kW/m
Temperature: 825 -950 K cladding
Burnup: 3 - 8 at.%

Early mixed nitride (NM) irradiation tests showed a relatively high failure rate as summarized in Table 1. Although the complete data sets have not been

TABLE 1. (U,Pu)N Irradiation Test Summary

Test	# Pins	Bond	Burnup (at.%)	# Failures
BMI-50	49	Na&He	16	9
BMI-1,2,3	16	Na	8	10
C-5	12	Na	7.6	1
C-6,7,8	61	He	8.8	4
K-4	8	Na	9.6	0

analyzed and fuel characteristics and operating conditions are not well documented; some trends are apparent. For example, mixed nitride fuel showed relatively low fission gas release, and swelled at approximately 1.5- $\%\Delta V/V_0$ per atomic % burnup. Fission gas release from these pins was generally around 10%, therefore failures were probably not caused by high gas pressure. In addition, no evidence of nitrogen interaction or fuel/cladding chemical attack was found, suggesting that failure was either caused by fuel/cladding mechanical interaction or by defective welds. A large percentage of the failures were in pins with small gaps and high smear density, and some of the early failures apparently were related to high temperature fuel swelling. Microstructural analysis of irradiated MN showed that the fuel pellets tended to crack into large pieces, and the fuel swelled to strain and deform the cladding. Although these characteristics did not always result in failures; the observations lend credence to failure by fuel/cladding mechanical interactions.

The K-4 was the most successful (U,Pu)N irradiation test[6]. The K-4 test contained both mixed carbide and nitride fuel pins irradiated in the EBR-II reactor; test parameters are summarized in Table 2. The MN pins achieved over 9 at.% burnup with no failures. This success was attributed to a large fuel/cladding gap, shroud tubes to contain cracked pellets, and low smear density. The K-4 pins were examined in detail but the results are not published in the open literature.

TABLE 2. K-4 Test Parameters

# Pins	Fuel Composition	Fuel Density(%TD)	Smear Density(%TD)
4	(U,Pu)C (4%M_2C_3)	98.9	81.2
4	(U,Pu)C (16%M_2C_3)	98.9	81.1
8	(U,Pu)N (0%M_2N_3)	96.8	79.4

Design Features

Cladding: 7.87 mm-o.d. 316 ss
Shroud tubes: 0.076 mm thick 316 ss

Irradiation Conditions

Power: 85 kW/m
Temperature: 825 K cladding
Burnup: 9.6 at.% peak
Fast fluence: 6×10^{22} n/cm^2

URANIUM NITRIDE IRRADIATION

Uranium nitride was developed and tested during the 1960s for space nuclear power reactors[8,9], and over 100 helium-bonded pins were irradiated in thermal reactors with various parameters including: tungsten, tantalum, molybdenum, and niobium alloy cladding; cladding temperatures ranging from 1100 - 2200 K; burnups to 4.5 at.%; fuel densities ranging from 80 - 96 %TD; and various UN grain sizes and stoichiometries. The results from these irradiations varied greatly, but general trends can be summarized as follows:

- Niobium alloys were the most viable cladding for operation below 1400 K; however, tungsten liners were required to prevent fuel/cladding/ chemical interactions.
- Fission gas release rates were low.
- The high creep strength of UN resulted in swelling that is not constrained by niobium cladding at high temperatures.
- Low amounts fission gas were released from large grain size UN.
- Swelling and fission gas release were very high from hypostoichiometric UN.

Based on this early experience, the U.S. selected UN as the reference fuel for the SP-100 space nuclear power reactor. Approximately 90 fuel pins were tested in the Experimental Breeder Reactor and the Fast Flux Test Facility fast spectrum reactors with the following variables:

Design Features

Cladding: 5.84 - 7.62 mm-o.d./Nb-Zr or PWC-11
Liner: Tungsten, rhenium, and bonded-rhenium
UN density: 87 -96 %TD

Irradiation Conditions

Temperature: 1200, 1400, & 1500 K cladding
Burnup: 1 - 6 at.%

Many of the details of these irradiations are not currently available; however some performance trends can be found in the literature. First, even though the SP-100 pins were tested at relatively high temperatures - up to 1900 K fuel centerline - no failures occurred; therefore the fuel pin design is very robust. Second, metallic fission products, especially ruthenium[4], were found to migrate down the thermal gradient to the fuel pellet surface and into the cladding. Third, no breakaway swelling or fission gas release was observed, and high density fuel released less fission gas than low density fuel[10]. Fourth, large fission gas pores formed in the center of the low density UN fuel pellets, while the high density fuel showed no evidence of restructuring or cracking. Finally, chemical vapor deposited tungsten liners cracked during irradiation but a thin liner of wrought rhenium metallurgically bonded to the inside diameter of Nb-1Zr cladding was found to be an effective barrier to fuel/cladding/chemical and mechanical interactions.[11] Irradiation performance models, predicting the performance of UN fuels for space reactors have been developed.[12]

Microstructural analysis on irradiated UN showed that low density fuel tended to restructure and form center voids. Transport of UN from the fuel centerline to the cladding walls was seen, suggesting dissociation of UN from hot regions and reformation in cold regions. Chemical interactions between fuel, fission products, liners, and cladding was also found in the low density fuel. High density UN displayed rather innocuous changes in microstructure; classical fission gas bubbles formed and migrated to the grain boundaries with increasing burnup. Very little cracking was observed, but the pellets sintered together at high operating temperatures. Figure 1 graphically displays the hypothetical performance of UN fuel pellets based on the observations from the U.S. space reactor fuel development program. The black marks represent metallic fission products migrating to the pellet surface and into the cladding. The voids represent the formation of center line fission gas pores. High density UN (>95 %TD) operating at moderate temperatures (fuel center line <1650 K, cladding <1400 K) has low swelling, low fission gas release, no fission product interaction, and the potential of operating to high burnups. Low density, hypostoichiometric UN, and high operating temperatures are undesirable characteristics that will limit the useful lifetime of UN fuel. As a consequence of these observations, UN fuel pellets for the SP-100 reactor were fabricated to the following specification:

Density:	96.5 ±1.5 %TD
Stoichiometry:	1.00 -1.05 (N+C+O)/U
Grain Size:	>30 μm
Carbon:	<3000 ppm
Oxygen:	<1000 ppm

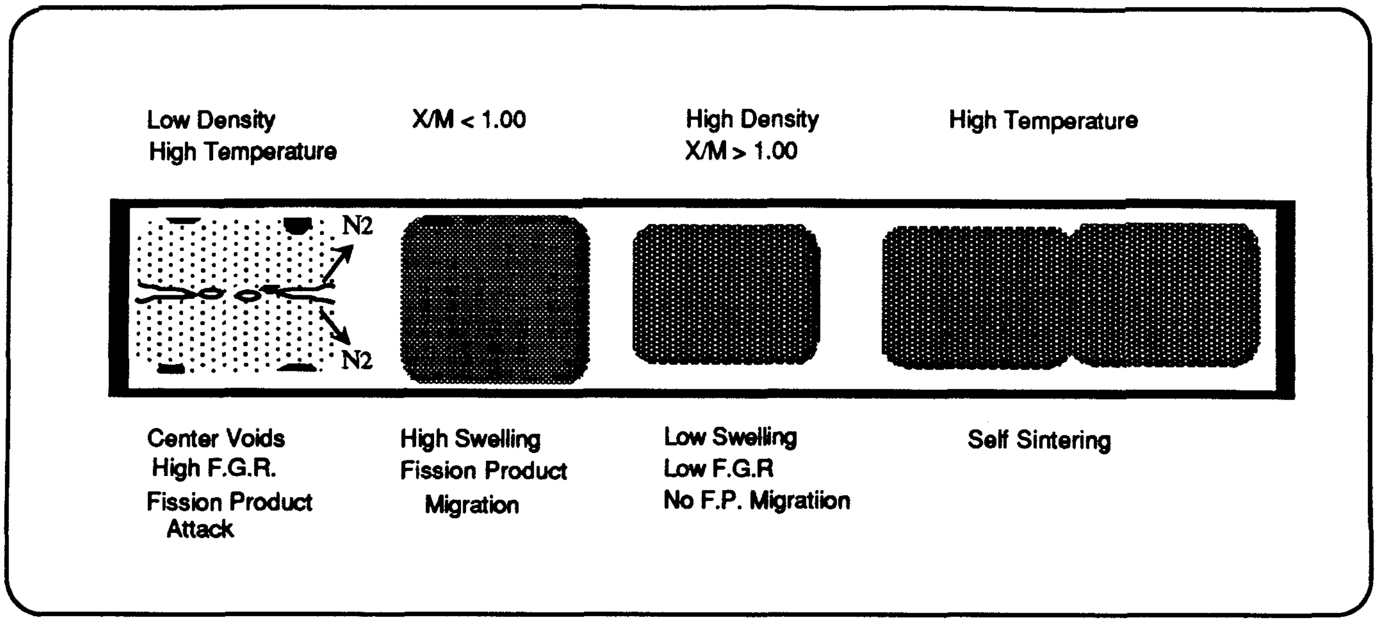

Figure 1. Schematic representation of UN fuel pellet performance.

FISSION GAS RELEASE

Variables influencing irradiation induced fission gas release include temperature, burnup, fuel density, temperature gradient, fuel stoichiometry, impurities, and grain size. Unfortunately, the only reliably reported variables are burnup and starting density; operating temperatures are estimated and the other variables are generally not reported in the literature. However, sufficient information is available to determine trends. Figure 2 is a summary plot of the available fission gas release data as a function of calculated average fuel temperature from the UN irradiation data base generated during the SNAP program.[8,9]

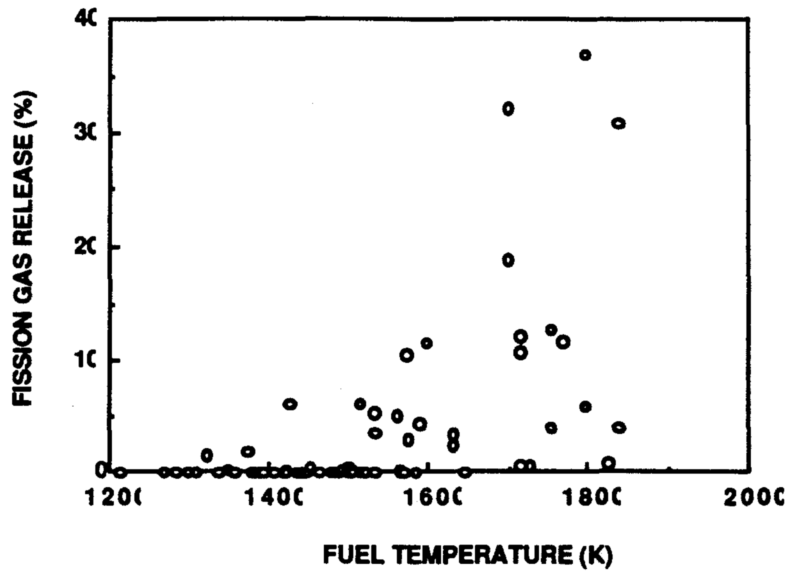

Figure 2. Uranium nitride fission gas release as a function of fuel temperature from the early irradiation data base. [8,9]

The fission gas release rates are very variable primarily because all burnups and fuel variables are plotted together. The very high fission gas releases are probably from either high burnup tests or hypostoichiometric UN_{1-x}. The very low fission gas releases are probably from loss during measurement. Nevertheless, the results suggest UN fission gas release can be kept very low at temperatures up to 1600 K; higher temperatures clearly result in increasing release rates.

Fission gas release from the SP-100 UN irradiation tests is plotted as a function of temperature in Figure 3-a and burnup in Figure 3-b. The gases were determined by puncturing fuel pins after irradiation, measuring volume of gas in the pin, and analyzing for Xe and Kr. The high density UN released considerably less fission gas than low density fuel as would be expected because of the greater open porosity and free access to the plenum gap from low density fuel. The fission gas release rate appears to increase linearly with burnup to 5 at.%, and the release rate from low density fuel is approximately three times that for high density UN.

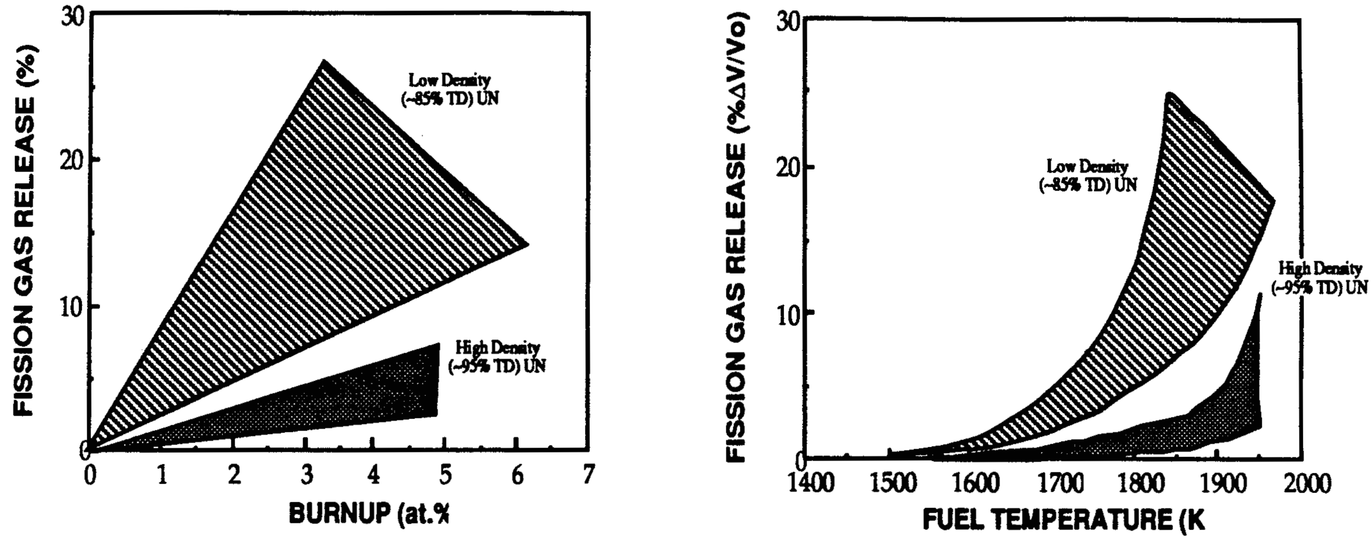

Figure 3. SP-100 UN fission gas release; (a) as a function of burnup, and (b) as a function of temperature.

The temperature tends in Figure 3-b suggest that low density UN begins to release fission gas at temperatures greater that 1600 K, while high density UN appears to retain significant amounts of fission gas up to 1800 K.

Storms [13] proposed a fission gas release equation of the form:

$$FRG = 100/[\exp(0.0025\{TD^{0.77}/BU^{0.09} - T\}) +1]$$

where FGR is the percent of fission gas released, TD is the percent of theoretical fuel density, BU is burnup in atomic percent of uranium, and T is the average fuel temperature in degrees Kelvin. Predicted fission gas release curves, shown in Figure 4, suggest that release rates decline with increasing burnup, accelerate rapidly with increasing temperature, and are sensitive to fuel density.

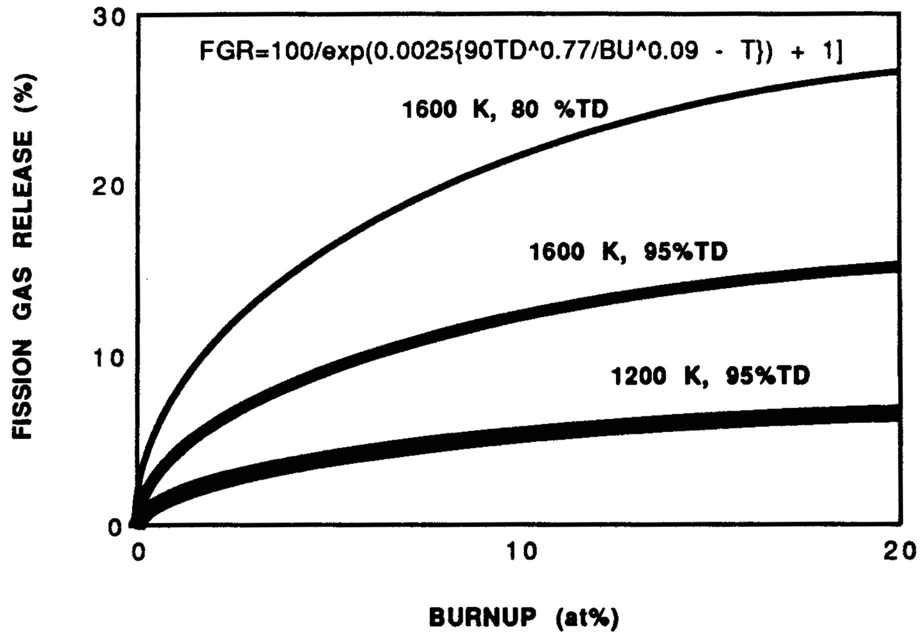

Figure 4. Predicted effects of burnup, temperature, and density on uranium nitride fission gas release.

A comparison of available (U,Pu)N fission gas release data is plotted as a function of burnup and temperature in Figures 5 and 6. Although the data contain many unannotated variables - for example, power density, burnup rate, smear density, temperature estimates, stoichiometry, grain size, and impurity characteristics - there is a relatively good consistency, and the figures tend to validate Storms' correlation. This correlation is strictly an empirical fit to the available fission gas release data as function burnup, temperature, and fuel density.

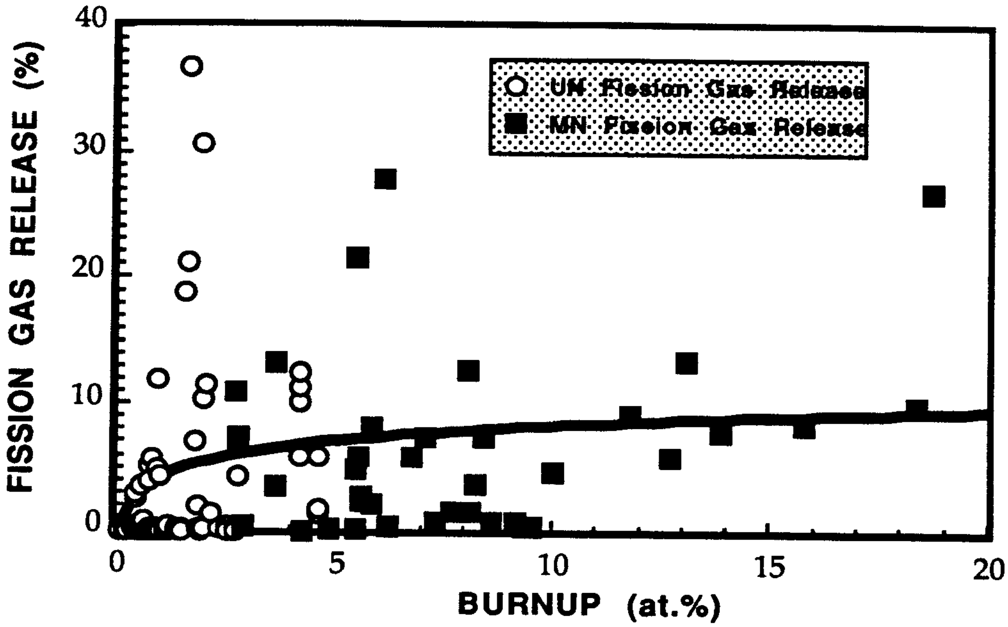

Figure 5. Mixed nitride fission gas release as a function of burnup. Differences in temperature, density, and fuel characteristics are not considered.

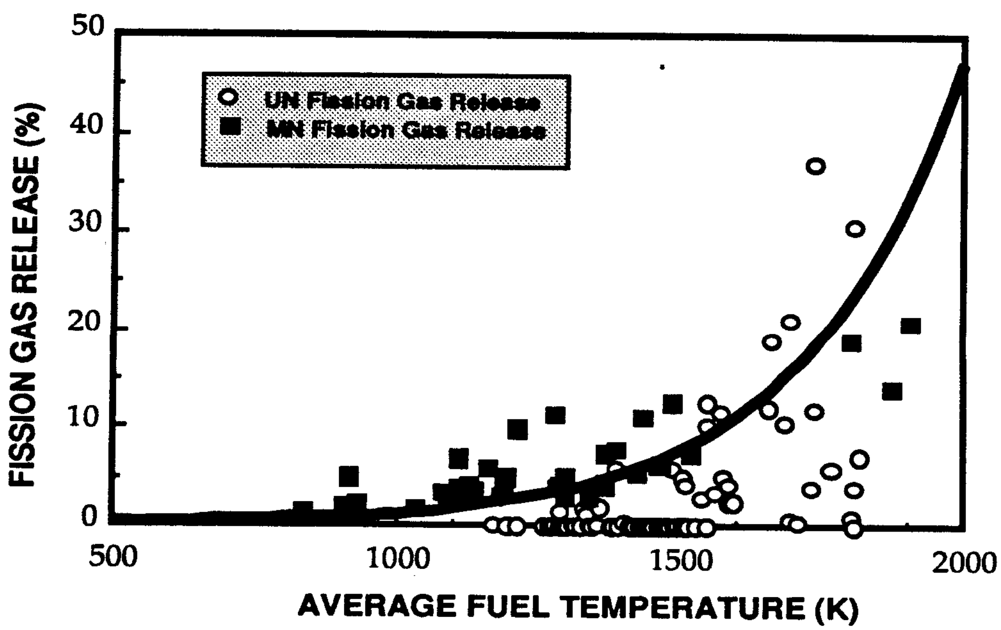

Figure 6. Mixed nitride fission gas release as a function of temperature. Differences in temperature, density, and fuel characteristics are not considered.

Two UN swelling correlations have been published[14,15] of the form:

$$\Delta V/V_0 = a \times 10^{-b} \cdot (T)^{c} \cdot (BU)^{d} \cdot (TD)^{d},$$

where a,b,c, & d are fit constants.

The fits to these correlations are not particularly good because of the number of variables in the irradiation data base, the uncertainty of temperature measurements, and various swelling measurement techniques. Uranium nitride swelling has been measured on 45 fuel pins irradiated during the SP-100 program. Fuel pellet dimensional changes were measured by digitizing densitometry traces of neutron radiographs of the irradiated pins. The swelling data of the SP-100 UN plotted in Figure 7 includes cladding temperatures from 1250 to 1550 K and high (open points) and low (shaded points) density UN. The decrease in swelling rate with burnup is probably caused by resistance of the cladding, and the initial high swelling is the unrestrained UN swelling rate.

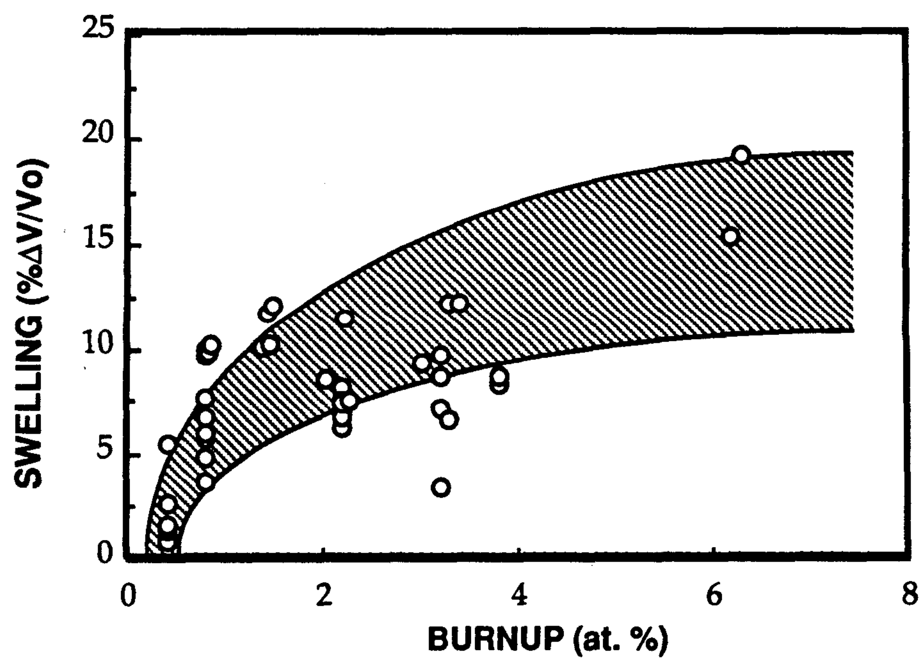

Figure 7. Swelling rate of SP-100 UN fuel irradiated in FFTF and EBR-II.

The influence of other variables are not considered in these correlations. Probably the greatest uncertainty is in the actual operating fuel temperature because the test data only report cladding temperatures estimated from reactor coolant temperatures. The average fuel temperatures are then calculated based on uncertain fuel/cladding gap size, gap conductivity, and fuel thermal conductivity information. A review of detailed test characteristics followed by consistent temperature calculations might help narrow down the scatter in the data and permit more accurate predictions of mixed nitride fission gas release and swelling.

Stoichiometry is the most important nitride fuel characteristic to regulate because UN, and to a lesser extent (U,Pu)N, dissociates at high temperatures. Uranium metal reacts with metallic fission products to form low melting alloys that increase atomic mobility in the fuel thereby greatly increasing fission gas release, swelling, and fuel/cladding chemical interactions. Gradual loss of nitrogen from nitride can produce the following hypothetical reaction:

$$UN_{1+x} + (Ru,Pd,Mo,Rh) \rightarrow U(Ru,Pd,Mo,Rh)liquid + UN_{1-x} + N_2$$

Formation and migration of metallic fission product inclusions have been observed[4,16] in both UN and (U,Pu)N at high powers and temperatures. Therefore, it is important to maintain a low temperature gradient and control stoichiometry. Excess carbon in the form of M_2C_3 has been found to be effective in maintaining hyperstoichiometry during (U,Pu)C irradiations.[16] Similarly excess nitrogen in the form of M_2N_3 might help stabilize nitride fuels during irradiation. The effects of excess N_2 on gap conductivity and internal pin pressure would have to be considered in the fuel pin design. In addition, new fabrication techniques, such as high pressure sintering, would have to be developed to fabricate nitride fuels with excess M_2N_3.

SUMMARY

Probably the greatest uncertainty in these fission gas release and swelling correlations is in the actual operating fuel temperature because the test data only report cladding temperatures estimated from reactor coolant temperatures. The average fuel temperatures are then calculated based on uncertain fuel/cladding gap size, gap conductivity, and fuel thermal conductivity information. A review of detailed test characteristics followed by consistent temperature calculations might help narrow down the scatter in the data and permit more accurate predictions of uranium nitride fission gas release and swelling. Nevertheless, by applying the performance trends described in this review of nitride fuel irradiation data, a reliable nitride fuel pin with high burnup capability can be postulated based on the following constraints and recommendations:

- Fuel density greater than 95 %TD to reduce restructuring and fission gas release,
- Peak fuel operating temperature less than 1600 K to reduce fission gas release, swelling, and fission product migration,
- Hypostoichiometric MN_{1+x} to eliminate metallic fission product formation,
- Sodium-bonded fuel pins to minimize fuel/cladding mechanical interactions,
- Pin diameter, cladding thickness, fuel/cladding gap thickness, plenum volume based on performance requirements but constrained by Storms' fission gas release correlation and swelling at 1.5 % $\Delta V/V_0$ per at.% burnup.

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