Performance Evaluation and Post-Irradiation Examination of a Novel LWR Fuel Composed of $U_{0.17}ZrH_{1.6}$ Fuel Pellets Bonded to Zircaloy-2 Cladding by Lead Bismuth Eutectic

Mehdi Balooch^{a1}, Donald R. Olander^a, Kurt A. Terrania^{a2}, Peter Hosemann^a,
Andrew M. Casella^b, David J. Senior^b, Edgar C. Buck^b

^a *University of California, Berkeley, CA 94720, USA*

^b *Pacific Northwest National Laboratory, Richland, WA 99352, USA*

ABSTRACT

A novel light water reactor fuel has been designed and fabricated at the University of California, Berkeley; irradiated at the Massachusetts Institute of Technology Reactor; and examined within the Radiochemical Processing Laboratory at the Pacific Northwest National Laboratory. This fuel consists of $U_{0.17}ZrH_{1.6}$ fuel pellets core-drilled from TRIGA reactor fuel elements that are clad in Zircaloy-2 and bonded with lead-bismuth eutectic. The performance evaluation and post irradiation examination of this fuel are presented here.

1. Introduction

U_xZrH_y fuel provides a number of design and performance advantages over conventional UO_2 . These advantages include self-moderation (allowing for a more compact core design), enhanced thermal conductivity (~ 18 W/m-K versus 6 W/m-K for UO_2), and a large negative temperature reactivity coefficient. The usefulness of these properties has been observed through decades of optimal performance in TRIGA reactors and from the experience of the Space Nuclear Auxiliary Power (SNAP) program [1].

While U_xZrH_y fuel presents several advantages, it also comes with the concern of anomalous swelling observed early in irradiation (thought to be due to void swelling around the uranium metal particles dispersed within the zirconium hydride matrix) at temperatures above 973 K. In order to prevent the fuel from swelling and potentially rupturing its cladding, the design presented in this paper uses liquid metal (lead-bismuth) eutectic in place of helium in order to take greater advantage of the enhanced fuel thermal conductivity and transport fission heat out of the fuel, thus lowering the operational fuel temperature. Keeping the operational fuel temperature

¹ Corresponding author: mehdi.balooch@gmail.com

² Currently at Oak Ridge National Laboratory

*Corresponding Author at mehdibalooch@gmail.com

low also has the added benefit of drastically lowering the fractional release of fission gases from the fuel [2].

The feasibility and benefits of utilizing hydride fuels in the current fleet of LWRs have been investigated previously in detail using neutronic and thermal-hydraulic calculations as well as laboratory-scale experiments [2, 3] by the materials group within the Nuclear Engineering Department at the University of California at Berkeley (UCB). Recognizing the need to go from laboratory-scale experiments to more relevant environments, a reactor-based irradiation experiment was conducted to evaluate the feasibility of the LWR hydride fuel with initial of 19.95 at% U-235 enrichment.

2. Experimental Material and Methods

2.1 Fuel rodlet fabrication and preparation

Four fuel rodlets were initially fabricated at UCB, with detailed description of fabrication procedure available in an accompanying publication in this journal issue [5]. Three of these rodlets (rodlets 1, 2, and 3) were of the design shown in Fig. 1. Rodlet 4 was similar with the exception that it only contained four pellets as opposed to five. Briefly, the pellets consisted of $\text{U}_{0.17}\text{ZrH}_{1.6}$ and were fabricated by core drilling with diamond bits and smoothed with a centerless grinding apparatus. The two top pellets (nearest the flange) in each rodlet were annular and were formed by core drilling out the pellet centers. The central pellet was half-annular and half-solid. These pellets were annular in order to accommodate the presence of a thermocouple (the bead being located within the cavity of the annular portion of the central pellet) for in-situ temperature measurements.

All pellets were nominally 9.5 mm in diameter and 10 mm in height. These pellets were placed within 75 mm long Zircaloy-2 cladding segments (9.75 mm ID, 11.16 mm OD) along with alumina spacers. The Zircaloy-2 cladding had a roughly 50 μm pure zirconium liner on its inner surface that is the standard mitigation method for pellet-cladding interaction in BWR fuel cladding [4]. Additionally, the cladding surface was purposely oxidized in air (at 350 °C for 24 hours in order to form an estimated one micron thick ZrO_2 scale). This oxide was meant to provide a barrier to hydrogen migration from the fuel matrix to the cladding. A Zircaloy-2 end cap was welded to the bottom of each rodlet and a Zr flange was welded to the top of each rodlet. Solid lead-bismuth chunks were placed within the rodlet between the bottom alumina spacer and the bottom fuel pellet. The rodlets were completed by placement of a compression spring, thermocouples and an upper flange. After the rodlets were completely assembled, they were heated in a helium-filled glove box to allow the lead-bismuth chunks to melt and fill the gap between the fuel and cladding. The elaborate procedure of LM gap-filling to eliminate voids formation is described in detail by Terrani et. al [5] which include multiple cycles of pressurizing the tube to

0.3 MPa using helium gas and subsequently pumping down to vacuum while the tube was mechanically shaken. While the lead-bismuth is solid at room temperature, it was liquid at irradiation temperatures and will be referred to as “liquid metal” (LM) throughout the rest of this paper. Rodlets 1, 2, and 3 were transferred to the Massachusetts Institute of Technology Reactor (MITR-II) for irradiation.

Fig. 1. Schematic of rodlets 1, 2 and 3

2.2 Rodlet irradiation

To meet operational safety requirements within MITR-II, each rodlet was required to be placed within a secondary encapsulation [6]. This secondary encapsulation consisted of a titanium capsule backfilled with lead-bismuth (referred to as outer

liquid metal (LM) throughout the rest of this paper to distinguish it from the inner LM located between the fuel and cladding). The outer LM, initially being compositionally the same as the inner LM, facilitated low resistance heat transport from the cladding to the surrounding water-cooled channel and maintaining a cladding temperature about of 300 °C. In addition, the capsule provided the means to lead the thermocouples wires to outside of the reactor core. It also enabled gas sampling at the plenum region of the capsule above the rodlet to detect possible leakage or fuel failure in real time by monitoring volatile fission products generated within the rodlet. Design and construction of the irradiation capsule was described in detail ref. [6].

The irradiation capsules (3 capsules stacked vertically designated as 1, 2 and 3) were placed in the central region of the core for maximum linear heat rates (LHRs) and minimum axial variation of flux.

Irradiation of the rodlets occurred between May and December of 2011. Due to the detection of fission gas release, reactor operators were forced to remove the rodlets sequentially from the reactor throughout this irradiation period. As a result, rodlet 1 was irradiated for a total of 139 days (715 MWd), rodlet 2 was irradiated for a total of 70 days (353 MWd), and rodlet 3 was irradiated for a total of 82 days (251 MWd). Following irradiation, the capsules containing the rodlets were allowed to cool in the MITR-II pool for 12 month and more than a about year in air storage before being shipped to Pacific Northwest National Laboratory (PNNL) for disassembly and post-irradiation examination.

3. Analytical Methods and Results

The shortened irradiation periods experienced by the rodlets resulted in a fairly small spread in fuel burnup values with estimates of 0.29, 0.19, and 0.17 % fissions per initial metal atom (FIMA) for rodlets 1, 2, and 3, respectively. These values include zirconium as an initial metal atom, as per convention described in ref. [2], and can be perceived as deceptively low for those more acquainted with % fissions per initial heavy metal atom (FIHMA). Excluding zirconium from the calculations, the calculated burnup values are 2.0, 1.3, and 1.2 % FIHMA for rodlets 1, 2, and 3, respectively. The equivalent oxide burnup, to enable easy comparison with commercial fuel, is 4.5, 3.0, and 2.5 MWd/KgU for these capsules, respectively. Due to this small range of burnup values, it was decided to focus available resources on examination of rodlet 1 only, as it achieved the highest burnup.

3.1 Fuel performance as monitored during irradiation

Fig. 2 shows the reactor thermal power along with the fuel centerline and cladding temperatures recorded during irradiation. These temperatures were directly recorded with two thermocouples: one inserted through center holes of top-half of fuel by touching its tip to the center of the whole pellet at midlevel and the other guided along the outer surface of the cladding where its tip was tack-welded to the

cladding with a zirconium foil at mid level as shown schematically in Fig. 1. The gap between the center thermocouple and central void space was filled with LM to minimize the temperature drop across the two. The maximum fuel centerline temperature of 823 K was well below the 973 K threshold at which extensive swelling has been previously observed (1, 2). The fuel centerline temperature rose noticeably with time passed 1200 hours exposure while thermal power kept essentially constant. The cladding temperature was largely held constant, during the irradiation, with small increases correlating directly to jumps in reactor thermal power.

Fig. 2. Reactor thermal power and rodlet 1 thermocouple readings

The increase in centerline temperature while power and cladding temperature remain unchanged suggests the thermal conductivity of the fuel was reduced with burnup. During irradiation, point defects are created by fission spikes and are annealed by recombination, clustering and absorption by permanent sinks. Thermal conductivity deduction from the in-pile temperature measurements requires simultaneous solution of heat conduction and the point defect conservation equation solutions within the fuel. The detailed calculations and deduction of the thermal conductivity are reported in ref. [5].

3.2 Post Irradiation Examination

Upon receipt at PNNL, rodlet 1 was extracted from its titanium capsule. This process required 3 steps; remove the top of the capsule (surrounding the flange) with a pipe cutter, core drill a hole in the bottom of the titanium capsule directly beneath the rodlet, and push the rodlet out the top of the capsule using a pushrod. During the first step, it was discovered that the cladding was broken between the first and second annular pellets (presumably due to fatal cracks developing during irradiation) and the top portion of the rodlet (including the flange and first annular pellet) was extracted, leaving the bottom portion encased in outer LM within the titanium capsule. During

the third step, heat tape was used to soften the lead-bismuth between the cladding and the titanium capsule. Thermocouples were placed between the heat tape and titanium, and within the broken rodlet to make sure that the inner LM was not re-melted in the process. After rodlet 1 had been extracted from its capsule, it was sectioned with a low-speed diamond wheel under flowing argon and submitted to the examinations described in the following subsections. Additionally, rodlet 4, which was not irradiated, was sectioned and examined for direct comparison of pre and post irradiation conditions. As this rodlet was not irradiated, it was never placed within a secondary encapsulation and thus had no outer LM.

3.2.1 Optical Microscopy

Optical microscopy (OM) images for rodlet 4 are provided in Fig. 3. These images do not reveal any evidence of bubbles or voids formation between the fuel and the cladding that may have caused local high resistivity pathway. However, they cannot be used as the evidence for lack of existence in the gap during fabrication or during the irradiation. Metallographic section preparation process may have disturbed the soft bond materials. An attempt was made to use neutron radiography technique to image imperfections in the fuel and the gap. But its resolution was inadequate for detecting possible void in the gap [5].

Some portions of the inner LM were smeared or dislodged during the sectioning and polishing processes, as shown in Figure 3b. This was not entirely unexpected as the LM is much softer than the fuel or the cladding. Fig. 3 also shows that sharp edges and interfaces exist for the fuel, the LM-filled gap, and the cladding inner surface.

Fig. 3. a) sectioning location for the unirradiated sample taken from rodlet 4 b) composite cross section of the rodlet composed of hundreds of high-magnification images stitched together and c) high magnification image of the fuel/inner LM/cladding interface.

Two cross-sectional samples were taken from irradiated rodlet 1. The locations of these samples within the rodlet as well as images corresponding to those in Fig. 3 are displayed for both samples in Fig. 4.

One prominent feature to compare between the sample taken from the midplane of the rodlet (Fig. 4b) and the sample taken from the lower end of the rodlet (Fig. 4d) is the large quantity of outer LM adhered to the outer surface of the cladding on the sample taken from the midplane of the rodlet. During heating as part of the third step of the rodlet extraction process, much of the outer LM liquefied or became soft and was easily removed. However, a large mass of outer LM remained solid and strongly adhered to the midplane section of the rodlet. At this location, the outer thermocouple was tack welded to the cladding with a zirconium foil that was never located during post irradiation examination. It is possible that the zirconium foil dissolved or otherwise reacted with the outer LM.

Light and dark streaks are visible in both the inner LM and outer LM in Fig. 4c and Fig. 4e. These features indicate phase separation within the inner and outer LM that is not present in the unirradiated inner LM.

Fig. 4. a) sectioning locations for the two irradiated samples (midplane and end), **b)** composite cross section of the midplane sample composed of hundreds high-magnification images stitched together, **c)** high magnification image of the fuel/inner LM/cladding/outer LM interfaces of the midplane sample, **d)** composite cross section of the end sample composed of hundreds high-magnification images stitched together, and **e)** high magnification image of the fuel/inner LM/cladding/outer LM interfaces of the end sample.

In Fig. 4, the edges and interfaces of the irradiated fuel, inner LM, and cladding have become rough in comparison to sharp features of Fig. 3. This is evidence of some form of corrosive or erosive attack occurring during the irradiation. The extent of this attack is more clearly seen in Fig. 5. The two black spots on the periphery of the fuel shown in Fig. 4d are missing chunks during the fabrication stage.

Another observation from Fig. 4 and Fig. 5 is that the thickness of the cladding in the irradiated samples is not uniform around the entirety of the sample. In order to quantify the degree to which the cladding has been attacked in each sample, a series of measurements were made with the optical microscope. In order to verify the greatest level of accuracy and precision available, optical measurements were calibrated to an optical ring standard. First, a stitched image of the whole reticle was generated using the same process and number of images used to capture the images of the fuel. Then made sure that in the stitched image of the reticle, the measured diameters of the rings matched the calibrated values. This was done by correcting the corresponding relationship between the physical measured-lengths and pixel edges. Finally the calibration relationship was used to determine lengths in the composite images of the fuel.

Table 1 quantifies the extent of cladding loss observed in Fig. 5. The fuel diameter of the irradiated end section appears to have increased beyond the measurement uncertainties. However, it should be noted that the UCB reported value as measured during fabrication of the fuel is based on average determination over the length of the entire pellet, not at location sectioned at PNNL. Therefore it is not possible to assigned this increase to irradiation induced swelling.

The fuel OD of the midplane irradiated section appears to match the nominal value better than does the fuel OD of the irradiated end sample. As will be discussed in the following subsection, the fuel surface appears to be fractured and partially dissolved into the inner LM. It is possible that this results in a value that does not capture swelling as was the case for the irradiated end sample. The ID, OD, and cladding thickness measurements for the midplane irradiated sample clearly show extensive loss of cladding material both to the inner and outer LM. In fact, within the tolerances of the measurement methods used, the total quantity of cladding material of the irradiated midplane sample has been reduced by 55%. This correlates to a material loss of 40% from the OD and 15% from the ID. It is this loss of material due to interactions occurring at temperature during irradiation that likely led to loss of cladding strength and eventual failure during the experiment.

Fig. 5. a) direct cross-sectional comparison of the unirradiated sample with the irradiated midplane sample, b) direct cross-sectional comparison of the unirradiated sample with the irradiated end sample.

Table 1: Comparison of Measured Dimensions of Fuel Samples

	UCB as-fab fuel OD (μm)	Fuel OD (μm)	Clad ID (μm)	Clad OD (μm)	Clad thick (μm)
Unirradiated Sample	9655 ± 23.8	9654.8 ± 6.4	9786.6 ± 1.3	11178.2 ± 2.9	695.8 ± 3.2
Irradiated End Sample	9655 ± 12.9	9732.0 ± 11.8	9890.3 ± 1.7	11229.0 ± 13.2	669.3 ± 13.3
Midplane Irradiated Sample	9625 ± 19.1	9651.8 ± 19.6	10011.7 ± 3.8	10644.6 ± 53.3	316.5 ± 53.4

3.2.2 Scanning Electron Microscopy

Fig. 6 shows SEM images for the unirradiated sample and the two irradiated samples. The images in the left column of Fig. 6 show the outer cladding surface of the unirradiated sample (6a), unirradiated end sample (6b) and irradiated midplane sample (6c), respectively. Fig 6a shows that a thin oxide layer is present on the unirradiated sample, confirming the presence of the engineered oxide layer. However, this layer is not observed for either of the irradiated samples. The images in the right column of Fig. 6 show the inner cladding/inner LM/fuel interfaces for the

unirradiated sample (6b), irradiated end sample (6d) and irradiated midplane sample (6f) respectively. These images confirm the ordered and clean interfaces of the unirradiated sample and the phase-separated and eroded nature of the irradiated samples as indicated by optical microscopy.

Fig. 6. SEM images of a) Outer cladding surface of the unirradiated sample, b) inner cladding interface of the unirradiated sample, c) outer cladding surface of the irradiated end sample, d) inner cladding interface of the irradiated end sample, e) outer cladding surface of the midplane irradiated sample, and f) inner cladding interface of the midplane irradiated sample.

While the SEM images of Fig. 6 show in extensive detail the physical state of each sample, with phase separations in the LM and attack of the cladding and to a much lesser extent fuel, more detail is provided by elemental mapping of the same areas. Fig. 7, Fig. 8, and Fig. 9 provide EDS elemental maps for the unirradiated sample, irradiated end sample, and irradiated midplane sample respectively. Interestingly, in Fig. 6, the thin oxide layer purposely grown on both inner and outer surfaces for unirradiated case only visible on the outer surface. The elemental mapping, however, clearly confirms the existence of the inner layer oxide [Fig. 7]. Also visible with EDS are structures of Er, which is commonly integrated into the fuel as a burnable poison [7]. The Pb and Bi appear to be well structured within the inner LM, Zr appears to be confined to its expected locations within the cladding and the fuel matrix, and uranium is fairly evenly dispersed within the zirconium hydride (but H is not detectable with EDS) matrix.

Fig. 8 shows that the overall structures are still largely unchanged in the irradiated end sample, but that the inner LM has restructured, the Zr shows some signs of corroding/eroding away, and there are indications of the presence of uniform Zr in the inner LM. The surface of the fuel appears slightly rougher than the surface of the unirradiated sample. Fig. 9 shows significant restructuring around the entire periphery of the pellet at midplane sample after irradiation.. The inner LM is restructured, uranium is moving as a bulk phase away from the fuel toward the cladding, smaller amounts of uranium appear dispersed as micron-size inclusions within the inner LM adjacent to fuel surface, the fuel surface is fractured and penetrated by inner LM, and the attack on the cladding is extensive.

Fig. 7. EDS elemental mapping of the inner cladding/inner LM/fuel interfaces for the unirradiated sample.

Fig. 8. EDS elemental mapping of the inner cladding/inner LM/fuel interfaces for the irradiated end sample.

Fig. 9. EDS elemental mapping of the inner cladding/inner LM/fuel interfaces for the irradiated midplane sample.

Quantitative line plots of Zr, Bi, Pb and U elements across LM/fuel interface are shown in Fig. 10 for unirradiated (left), and irradiated samples (right) at mid-level. In the figure the red dashed- line is representing Bi and the black Pb. No void formation is detected and the interface between LM and fuel is sharp and smooth for unirradiated sample. On the other hand irradiated interface is rougher. It contains different phases than those found in the unirradiated gap LM. The 35%Bi /65 %Pb phase has almost disappeared. The introduction of Zr in the LM resulted in more complicated phases. In addition U phase has appeared near fuel/LM interface as well as in LM adjacent to inner cladding. Further details can be found in the discussion section of this paper.

Fig. 10 SEM and quantitative elemental lines across fuel LM interface of unirradiated and irradiated specimen at midlevel height

3.2.3 Additional Examinations (XRD, H assay, TIMS)

Three additional examinations were performed in order to characterize the state of the fuel. X-ray diffraction patterns indicated that in both the irradiated and unirradiated fuels, the overwhelming majority of the matrix was composed of alpha uranium and delta zirconium hydride. This indicates that while fission is occurring and causing changes in the uranium itself, there does not seem to be evidence of a large migration of hydrogen within or from the zirconium hydride fuel matrix.

Additionally, cross-sectional samples from the irradiated and unirradiated rodlets were sub sectioned to provide samples from three separate radial positions. Each of these three samples was submitted to hot vacuum extraction in order to determine the hydrogen to mass ratio within the fuel at the corresponding radial positions. The results indicated that the radial hydrogen distribution within the fuel did not change significantly as a result of irradiation.

Finally, a small portion of the irradiated rodlet was submitted to thermal ionization mass spectrometry (TIMS) to determine burnup. The fuel started as 19.95 at% U-235 [6] and 0 at% U-236. TIMS analysis indicated that the irradiated fuel was 17.34 at% U-235 and 0.769 at% U-236. Burnup in atom percent of initial available ^{235}U was then calculated using Eq. (1), where all values are in atom % and *BOL* and *EOL* represent “beginning of life” and “end of life”, respectively. The result is a rodlet 1 burnup (*BU*) of 9.25 at%. This corresponds to a % *FIHMA* of 1.85 and a % *FIMA* of 0.27. These values are in good agreement with calculated estimates of 2.0 and 0.29 respectively. The measured values are ~7% lower than calculated estimates.

$$BU = \frac{U_{BOL}^{235} - [U_{EOL}^{235} + (U_{EOL}^{236} - U_{BOL}^{236})]}{U_{BOL}^{235}} \quad (1)$$

Previously FIMA rather than FIHMA has been adopted for hydride fuels [2]. It can conveniently be compared to UO_2 power reactor expressed as MWd/kgU [2, 5]. FIMA in the present work is estimated though total fissions obtained from linear heat rate that in turn derived from MCNP calculation on MIT reactor core for 5 MW power [ref. 5]. It accounts for breeding and burning Pu during the irradiation, even though in this case is insignificant due to high fuel enrichment. BU calculation via TIMS analysis, however, ignores to account for Pu breeding and burning, that may have contributed to lower values compare to the estimated MCNP calculations.

4. Discussion

Previous studies suggest that hydride fuel is prone to undergo a drastic volume change early in irradiation if the temperature is greater than 973 K [1, 2, 8]. Fig. 11 shows the expected swelling behavior of this fuel in general and as a result of the irradiation history realized in this study. The fundamental driver behind the design of the fuel discussed in this paper was to exploit the physical advantages it possesses

while engineering a method of preventing this unwanted swelling. The post irradiation examination evidence presented in this paper indicates that this goal was achieved mainly relative to the swelling issues.

Table 1 indicates that some unexplained changes did occur, but not as an effect of irradiation-induced fuel swelling, characterized as “early” swelling (1,2). The SEM examination of fuel particle size distributions did not indicate any discernable swelling within the fuel, and no detectable cavities were observed (with the micro-examination capabilities that were utilized in this study) adjacent to the α -U/ZrH_x interface. Fig. 12 shows representative SEM images of α -U fuel particles dispersed in the hydride matrix of unirradiated and irradiated pellets. It is worth mentioning that long-term swelling due to fission product accumulation is still reported to be as much as three times faster in hydride fuel than oxide (Fig. 11). This is considered to be a potential disadvantage of hydride compared to oxide fuel. The post irradiation examination, however, provided no indication of changes in any physical parameters of the bulk fuel. No migration of hydrogen within the fuel or from the fuel was observed.

While the fuel design appears to have succeeded in preventing unwanted swelling, other issues were discovered that prevent this fuel design from being feasible in LWR applications at the present. Primarily, there appears to be an unwanted physical or chemical reaction occurring between the LM and both the cladding and to a much lesser extent fuel matrix. Such reactions have been observed previously in the literature [9] for lead-bismuth eutectic and Zircaloy-4 tubing in which contact between the two materials at 672K for 1000 hrs resulted of ~8% loss of the tube wall thickness. Similar exposure with lead-tin-bismuth eutectic reduced the loss to only 0.3%. It was speculated that the chemical compatibility of lead-tin-bismuth with Zircaloy-4 is primarily due to formation of a ZrSn₂ intermetallic layer at the interface of LM and cladding, which limited further interaction. Present work on Zircaloy-2, which contains almost the same percentage of Sn as Zircaloy-4, reveals significantly higher corrosion at mid-plane than that of ref. 9 measured on unirradiated material. However, the irradiated end sample is in fair agreement with values reported previously (9).

Fig. 11. General swelling behavior of this fuel and the expected swelling due to temperatures experienced in the irradiation study described in this paper (ref 1,2).

Fig. 12. SEM imaging of uranium particles dispersed within the zirconium hydride matrix. Left hand column unirradiated, right hand column irradiated.

Further investigation into the properties of the LM provides some insight into the potential mechanisms that can describe the observations made during post irradiation examination discussed here. The phase diagram for lead-bismuth mixtures, presented in Fig. 13 [10], shows the initial eutectic point at 45% lead, 55% bismuth that was used in the design and fabrication of the fuel. The OM and SEM results presented in this paper clearly show that after irradiation, the LM was no longer at eutectic state. In fact, OM and SEM analysis of the unirradiated LM appears to indicate the presence of phase separation. Additionally, the observation during extraction of the rodlet from the titanium capsule at PNNL revealed that the LM surrounding the cladding at midplane did melt at temperatures above the melting point of the eutectic, indicating a significant shift in the material composition. In addition, as the zirconium within the inner and outer LM appeared to be fairly evenly distributed, it is a possibility that LM transformed to a solid solution and that a three-component phase diagram is necessary to truly determine the state of the material. Additionally, as was mentioned earlier, the zirconium foil that was used to secure the outer thermocouple to the outside of the rodlet cladding was never observed in post irradiation examination, indicating that it may also dissolved into the outer LM, creating a new LM composition.

The solubility of Zr and U within pure bismuth and lead are reported decades ago [11-17]. In the literature data are also available regarding the solubility of Zr and U in a lead-bismuth system.

The solubility of Zr in Bi in temperature range 227-725 C is expressed as (12)

$$\log S \text{ (ppm Zr in Bi)} = 6.66 - 2760/T(K) \quad (2)$$

The solubility of uranium in liquid bismuth has been reported at three temperatures. These were 2000 ppm uranium at 400 C, 20,000 at 600 C, and 80,000 at 800 C [13]. Fitting these data, following expression for solubility of U in Bi with temperature is derived:

$$\log S \text{ (ppm U in Bi)} = 7.59 - 2892/T(K) \quad (3)$$

The solubility of Zr in LBE reported in the literature is given by [18]

$$\log S \text{ (ppm Zr in LBE)} = 6.15 - 3172/T(K) \quad (4)$$

From eqs. 2 and 3, the solubility of Zr and U in liquid metal Bi at 300 C are 70 and 350 ppm, respectively. The solubility of Zr in LBE from Eq. 2 suggests a value of 4 ppm, appreciably less than pure Bi at this temperature.

Fig. 13. Phase diagram for a lead-bismuth mixture [10]

The extensive loss of the cladding thickness near the midplane of the fuel into inner LM suggests that more zirconium loss was observed than would have expected for dissolution to the levels just discussed. Previous experiences with Zr LBE systems reveal corrosion can easily be detected when the temperature during operation is 400 °C or higher [9]. It is known from corrosion tests that Zircaloy-2 is not attacked by LBE at 350 °C but dissolved rapidly at 450 °C [19]. These observations confirm that corrosion rate should have been acceptably low around 300°C, but could become unacceptable at higher temperatures. As seen from Fig. 2, the measured outside clad temperature stayed fairly constant around 300 C during operation for rodlet #1 examined here. This value is about 75 degree lower than the early-performed thermal simulation in ref. 6, however.

Another important consideration is the fact that new intermetallic phases such as $ZrBi_2$, $ZrBi$, Zr_3Bi , Zr_5Pb_3 , $Zr_{3.33}Pb_{0.67}$ and UBi_2 are being formed [11-16].

Due to the lack of phase diagrams for Pb-Bi-U-Zr, Pb-Bi-Zr, and Pb-Bi-U systems, existing diagrams for the binary systems Pb-Zr, Bi-Zr, U-Bi, and Pb-U are used as guiding tools for insight into the behavior of the ternary and quaternary systems. It can be seen in the Bi-Zr and Pb-Zr binary systems that intermetallic phases can form and that they are stable at room temperature [11, 14]. Five distinct intermetallic phases are recognized to form in the Bi-Zr system as opposed to two for the Pb-Zr system. While the phase diagram for the ternary system is not available, it is likely that the system will have more intermetallic product possibilities than the sum of the two binary systems. Similarly, several intermetallics are possible when considering the Bi-U and Pb-U systems [16, 17]. Application of the CALPHAD method for calculating composition and number of the phases over a large composition such as system discussed above would be highly beneficial.

Unless a uniform intermetallic barrier forms between the cladding and the liquid metal, it is possible that large quantities of cladding and fuel matrix can be incorporated into these high-melting phases. There are several fundamental implications of this reality. First, portions of the LM may have in fact precipitated out as solid intermetallic particles during the irradiation. Second, the formation of any such solid precipitates will affect the density of the LM, leading to potentially fluctuating mechanical stresses at irradiation temperatures. Third, the solid Zr in both the cladding and the fuel matrix may be consumed beyond expected solubility limits, resulting in thinning of the cladding and potentially causing the failure of the rodlet observed in this study.

Examination of Figs. 8, 9 and 10 indicate that the Zr tends to be more evenly distributed throughout the inner LM than does the U. In fact, the U tends to form individual particles near the fuel surface and bands near the cladding surface. While only speculative, it is possible that this is caused by a greater affinity of the system for the formation of Zr-containing intermetallics and forcing the U to persist in elemental form. Additionally, temperature differential across the LM may cause the U particle to migrate toward the cladding and collect into the higher concentration “banding” observed in Fig. 9. A large temperature drop across the inner LM is not expected, but it is possible that this may have developed in some locations due to the formation of the intermetallics just discussed.

Another unknown is what role the presence of O and H plays within the Pb-Bi-Zr-U system. Recent laboratory tests at UC Berkeley reveal that the corrosion rate of Pb-Bi on Zircaloy cladding is much less in a reducing atmosphere ($\text{Ar}+10\%\text{H}_2$) than within an oxidizing atmosphere. However, one major concern with the current fuel design was the possibility of hydrogen transport from the fuel matrix to the Zircaloy-2 cladding. Experiments have been undertaken to determine the effectiveness of a thin oxide layer on the Zircaloy surface to prevent hydrogen transfer. In these experiments, zirconium hydride matrix fuels were placed in compression against bare Zircaloy and oxidized Zircaloy for extended periods. The results indicated that the oxide layer was an effective barrier to hydrogen uptake by the Zircaloy [20]. The

hydriding of the Zircaloy created a high enough level of concern that an attempt was made to purposely oxidize the inner and outer surfaces of the cladding during rodlet fabrication. Fig. 6 and Fig. 7 indicate that only a small fraction of the quantity of oxidation expected was formed on the cladding OD and much less on the ID (perhaps due to oxygen starvation within the tube during oxidation). It is possible that the level of oxidation observed in the post irradiation examination presented here is present in all Zircaloy and that the attempted oxidation during fabrication had no effect at all. In the end, it is possible that this oxidation layer on the cladding ID facilitated a faster and more extensive reaction between the LM and cladding. In fact investigation of compatibility of Zr, Nb, Mo, and Ge in liquid LBE has been carried out recently using at 550 °C with an oxygen concentration of 1×10^{-6} wt.% for 312 hours [21]. The result, at first glance, showed only a trace of zirconium oxide formation on the surface of the sample. Further investigation, however, revealed that in this relatively short time the zirconium alloy constantly consumed oxygen in liquid LBE to form zirconium oxide. As the oxide thickened, the scale was spalled off from the surface of the sample, thinning Zr sample.

The exact nature of the thinning and failure of the rodlet at mid-level is still unclear. However, the geometrical arrangement and experimental setup in the reactor provides additional factors for consideration. For example, the tantalum sheathed thermocouple for measuring cladding temperature was tightly attached to the outer surface of the cladding by a spot-welded Zr strip. This process may have contributed to changes in cladding mechanical properties as well as thinning. It is worth mentioning again that the midplane sample revealed no evidence of Zr strip, and it was likely totally dissolved during the irradiation experiment. Even though no evidence on possible existence of voids formation resulted during sample preparation or bubble formation during irradiation, it is conceivable that their existence close to mid-level had caused local higher temperature formation that could not be detected by averaged-measured surface thermocouple. As a result local accelerate corrosion may have resulted excessive thinning. It has been realized that mechanical damage sustained during irradiation in the reactor. During a reactor outage, an inspection of the hydride fuel capsules revealed mechanical damage to the bottom spacer in the fuel capsule stack (5) and the two of three capsule positioning pins were missing. This condition was attributed to inadequate welds on the pins, which may have resulted in unexpected vibration of the capsule stack within the channel. It is conceivable that combined accelerated thinning around midlevel and vibration that caused the rodlets to swing back and forth within outer LM resulted in catastrophic failure of the Zircaloy tube.

5. Conclusions

The fuel design evaluated in this paper appears to have succeeded in finding a way to exploit the advantages of uranium zirconium hydride fuels while avoiding the undesired swelling that has historically occurred early in life. However, other issues

were discovered that prevent this fuel design from being feasible in LWR applications at the present. Many improvements are required in the choice and design of the cladding material and/or LM. Previous studies have indicated that using lead-tin-bismuth eutectic in place of lead bismuth could reduce some of the potential materials incompatibility issues observed in the current experiment [9]. It is hypothesized that the formation of a ZrSn_2 layer at the interface of the LM and the cladding is the reason for this increase in compatibility. If this were true, then potentially coating Zircaloy cladding with a Sn layer or a SnZr_2 layer would provide the necessary environment for desired materials performance. Additionally, there is the option of moving to another cladding, such as a ferritic steel materials that possess a reasonable level of materials compatibility with the liquid metal of choice. Finally, the compatibility of the hydride fuel with LM needs to be investigated in significant details. In any case, some encouraging performance results were observed, but further engineering and testing is necessary to determine the potential utility of this fuel in light water reactors.

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