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Irradiation Induced Changes to Zircaloy-4: A Final Report to PNNL for FY16

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Abstract

Understanding the stability of the zircaloy-4 liner, which is used in the Tritium-Producing Burnable Absorber Rod, is important for predicting the maximium reasonable life time and failure mechanisms of this essential component for tritium production. In this year-long study, a combination of in-situ ion irradiation transmission electron microscopy and thermal desorption measurements were used to explore the structural stability of Zr-4 as a function of sequential and concurrent displacement damage, helium implantation, and molecular deuterium implantation at the temperature of interest for reactor operation. Under the limited conditions explored, the liner alloy appeared to be relatively stable based on the direct TEM observation of the microstructure.

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NOMENCLATURE

NG	Neutron Generator
GTS	Gas Transfer System
SNL	Sandia National Laboratories
SRNL	Savannah River National Laboratory
PNNL	Pacific Northwest National Laboratory
TPBAR	Tritium Producing Burnable Absorber Rod
I^3TEM	In-Situ Ion Irradiation Transmission Electron Microscope
TPD	Temperature Programmed Desorption
EFPD	Effective Full Power Days
RGA	Residual Gas Analyzer

1. INTRODUCTION

Sandia National Labs is responsible for two NW components that utilize tritium, Neutron Generators (NG) and the Gas-Transfer Systems (GTS). It is critical to Sandia's mission that the supply of tritium be uninterrupted and available when needed. To support the tritium supply mission of both the Savannah River National Lab (SRNL) and the Pacific Northwest National Lab (PNNL), we have conducted fundamental research using two unique facilities here at Sandia National Labs (SNL).

1.1. Project Overview

1.1.1 TPBARs

Tritium-Producing Burnable Absorber Rod (TPBAR)s are used to breed and extract tritium for use in NW and commercial components. Tritium is the radioactive isotope of hydrogen and decays into ^{3}He with a half-life of 12.3 years. The Lithium Aluminate Pellet in Figure 1 is made with the ^{6}Li isotope which interacts with a neutron via the reaction $^{6}Li + n \rightarrow Tritium + {}^{4}He$. When inserted inside a nuclear reactor with a large flux of neutrons large quantities of tritium are produced. The role of the TPBAR is not only to produce but capture the tritium, which it does inside the Zircaloy-4 Tritium Getter, also shown in Figure 1. The behavior of the Zircaloy-4 is of critical importance to the performance of the TPBAR and is the focus of this work.

Table 1: List of major components and impurity maxima for the Zircaloy-4 alloy.[Whitmarsh]

Element	Weight (%)
Major Components	
Sn	1.2-1.7
Fe	0.12-0.19
Cr	0.05-0.15
Ni	0.007
Impurity Maxima	
Al	0.0075
B	0.00005
C	0.0270
Cd	0.00005
Co	0.0020
Cu	0.0050
H	0.0025
Hf	0.0200
Pb	0.0130
Mg	0.0020
Mn	0.0050
N	0.0080

Si	0.0120
Na	0.0020
Ti	0.0050
W	0.0100
U(Total)	0.00035
U-235	0.0000025

The major constituents of Zircaloy-4 are listed in Table 1. Zircaloy-4 was developed for use in water reactors to minimize corrosion.[Whitmarsh] The basic properties of Zircaloy-4 have been measured and studied by many people.[Whitmarsh] However, the properties of Zircaloy-4 are time-varying due to the dynamic environment inside of a nuclear reactor and the decay of the generated tritium.

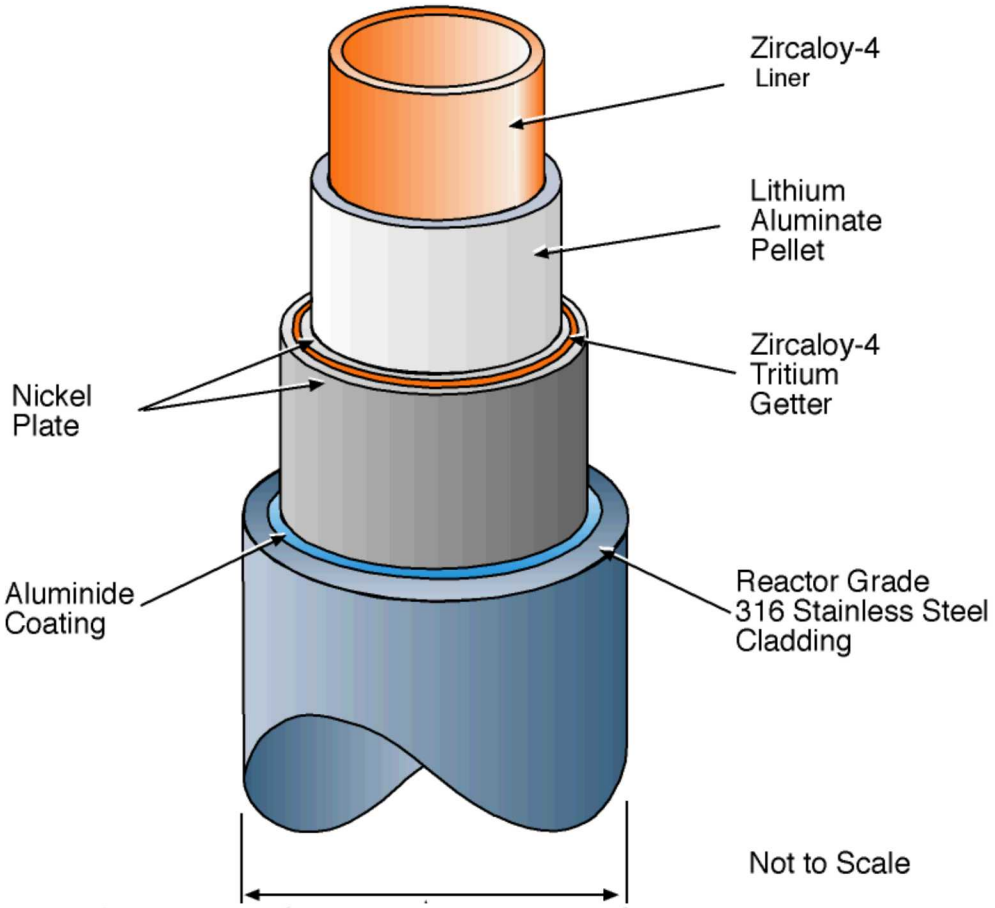

Figure 1: Diagram of the internal structure of the TPBAR. Note that Zircaloy-4 is used in two locations, as an inner liner and as the tritium getter.[Whitmarsh]

1.1.2 Ion Induced Damage as a Surrogate for Reactor Induced Damage

This work is a first attempt to simulate the radiation damage the Zircaloy-4 encounters while in the nuclear reactor. The damage is simulated using the unique facilities located in building 720 and run by the Ion-Solid Interactions Department.

There are two time-dependent damage mechanisms that the Zircaloy-4 encounters inside of a nuclear reactor. One, the tritium generated by the n+Li reaction decays into ^{3}He. The ^{3}He is mostly captured by the Zircaloy-4 and is stored in helium bubbles under pressure on the the order of GPa . Second, the neutron flux will also create displacement damage by knocking atoms out of their lattice sites creating self-interstitials and a damage cascade.

Table 2: Total helium atom accumulation per inch of TPBAR calculated in intervals of 50 days.

Days	50	100	150	200	250	300	350	400	450	500
He Atoms	3.8E-7	9.4E-7	3.8E-6	8.6E-6	1.5E-5	2.4E-5	3.4E-5	4.6E-5	6.0E-5	7.6E-5

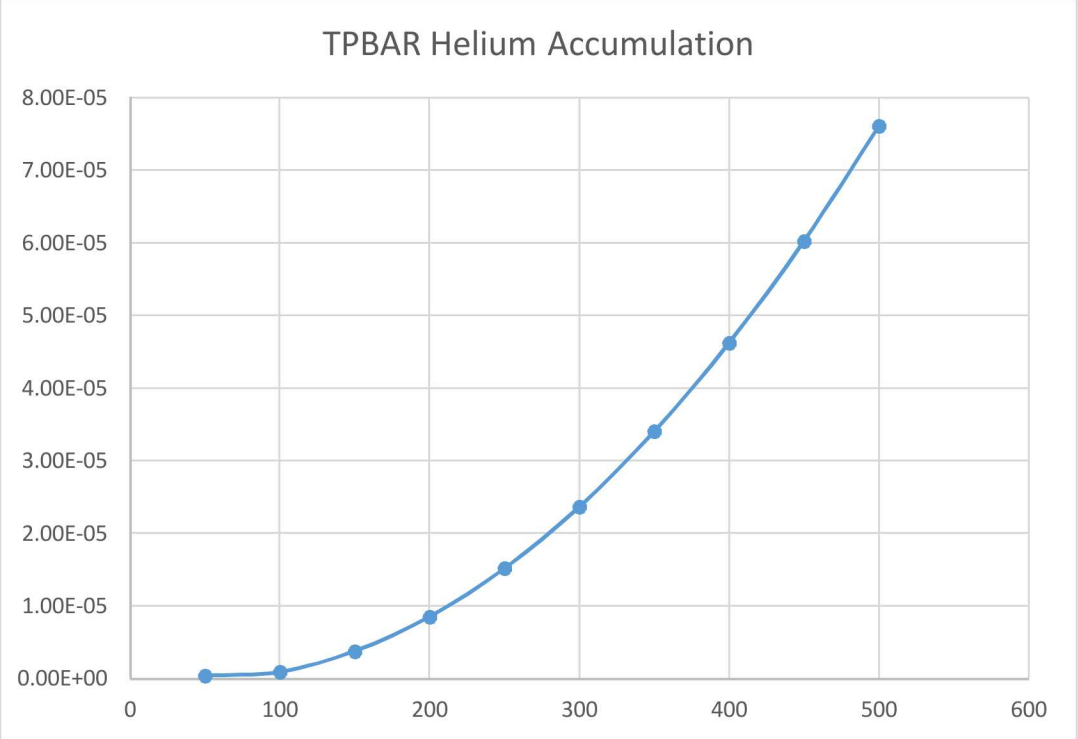

Figure 2: Helium accumulation versus time for 1 inch of TPBAR.

Dave Senor at PNNL reported tritium production in the TPBAR of 1.5E-5 grams of T_2/EFPD/gram of pellet. Table II shows the total accumulation of helium atoms per inch of TPBAR for intervals of 50 days. Figure 2 shows the exponential nature of the helium accumulation due to tritium decay with continuous tritium production. After 50 days in the reactor 3.86E-7 moles of Tritium should be present per gram of pellet while after 500 days (the nominal end of the cycle) there should be 7.67E-5 moles of tritium per gram of pellet.

It is possible to implant Helium into small Zircaloy-4 samples to achieve levels of helium accumulation equivalent to 50 and 500 days in the reactor in a matter of hours utilizing ion accelerators. A question during any implantation experiment is the degree to which the implantation mechanism mimics a decay process. In the case of tritium, the decay product Helium is only imported 1 eV during the tritium decay process, far less than what is needed to cause any lattice damage. To simulate conditions experienced by zircaloy in reactor, helium was implanted at 350 keV into bulk samples and 10 keV into TEM samples (to simulate tritium decay into helium). In addition, 3.25 MeV Zr ions were used to simulate lattice displacement damage caused by neutrons. The computational code TRIM[Zeigler TRIM] can be used to calculate the impact of ions in materials. Figure 3 shows the expected damage distribution for zirconium ions implanted into zirconium at 3.25 MeV using TRIM. For a 100 nm-thick TEM sample of zirconium, a zirconium ion accelerated to 3.25 MeV is expected to create ~1300 displacements/ion, while helium ions accelerated to 10 keV will produce ~40 displacements/ion. Interestingly, for Zirconium ions into a 100 nm-thick TEM foil, 99.93 % of the incident ions will pass through the sample leaving minimal implanted self-interstial. The majority of the vacancies and interstials produced will be the result of primary and secondary knock-on events and not the projectile ion itself. Thus, the damage induced by neutrons should be very similar to the damage induced in TEM samples at these energies for a heavy ion like Zirconium.

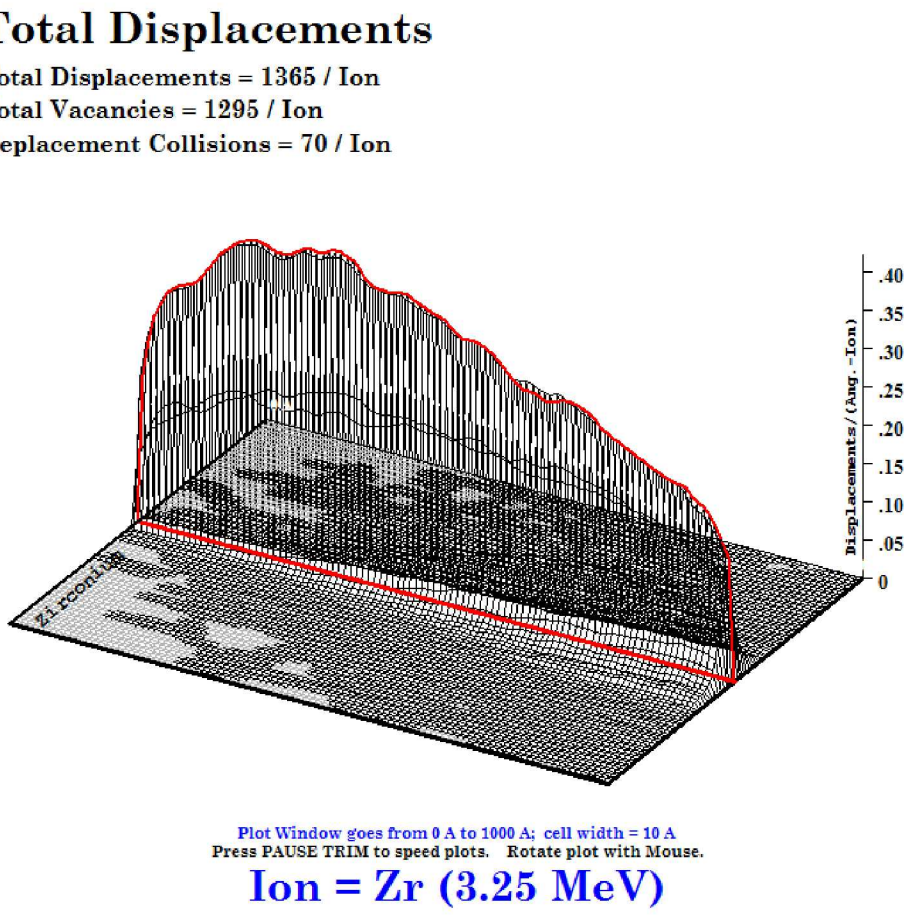

Figure 3: TRIM calculated damage profile for 3.25 MeV Zr ions implanted into a 100 nm Zirconium TEM sample.

1.2. Sandia Capabilities

1.2.1 I^{3}TEM (In-Situ Ion Irradiation Transmission Electron Microscope)

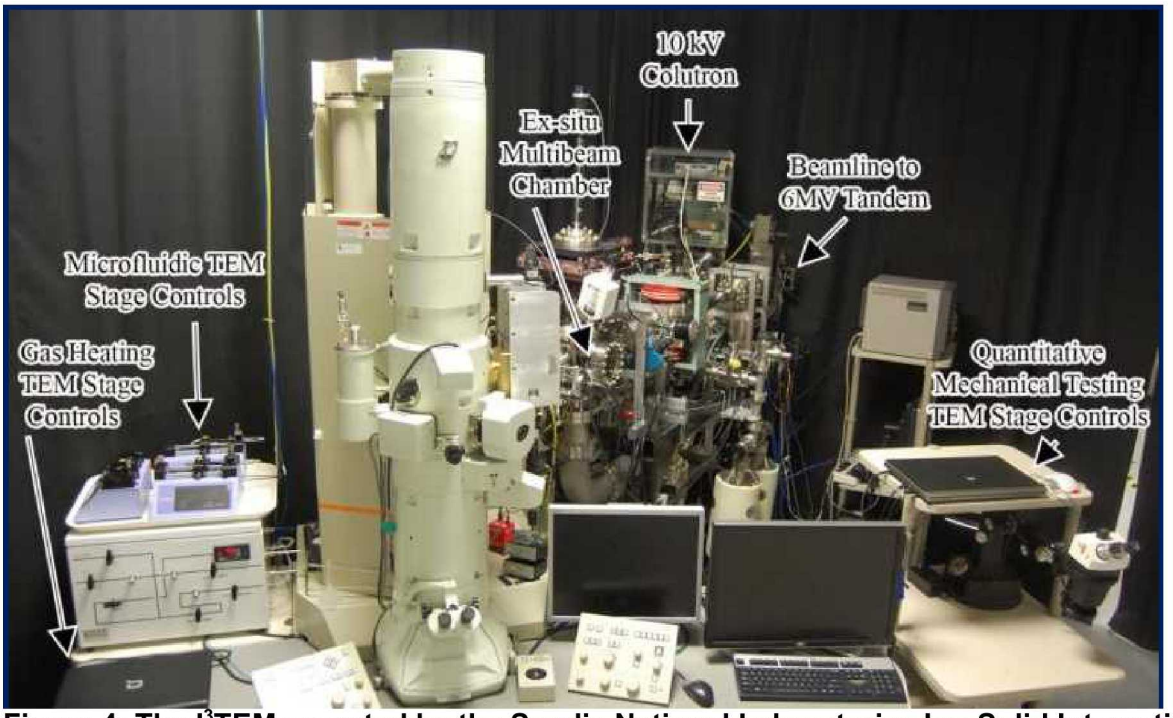

Figure 4: The I^{3}TEM operated by the Sandia National Laboratories Ion-Solid Interactions Department located in Building 720. The TEM is a 200 kV JEOL 2100 TEM with a LaB_6 filament.

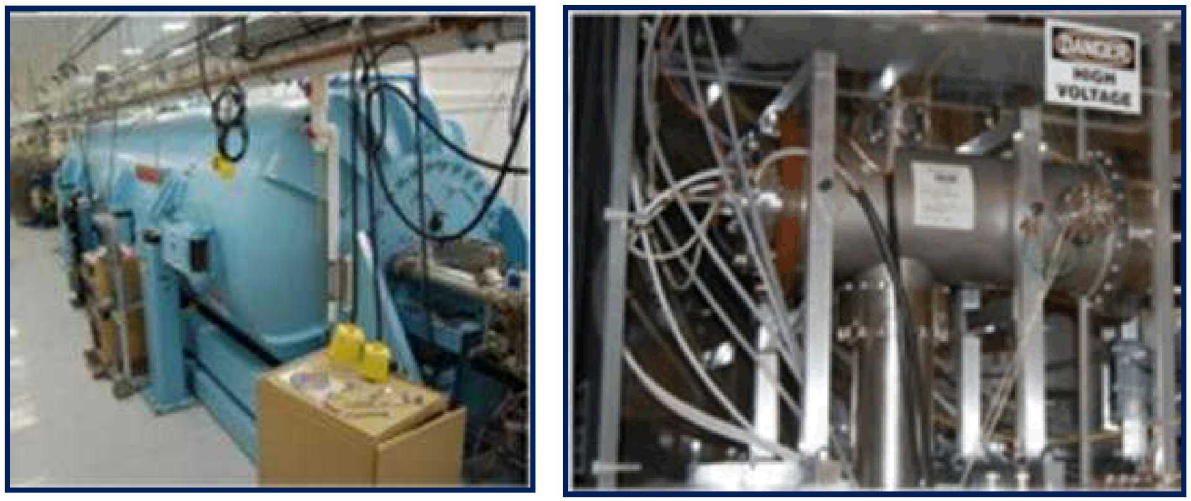

Figure 5: (Left) The 6 MV Tandem Van de Graff Accelerator used for accelerating heavy ions and (Right) the 10 kV G-1 Colutron used for gaseous implantation.

Sandia operates a unique facility in building 720, the Ion Beam Laboratory, where microstructural evolution of samples can be studied in a 200 kV JEOL TEM while simultaneously being irradiated with ions from both a 6 MV Tandem Van de Graff accelerator and a 10 kV G-1 Colutron (see Figure 4). This facility enables the simulation of atomic level damage that occurs over many years in nuclear environments to be simulated with days to week long exposures. This compression of the time scale of the experiment is critical to the understanding of currently used materials and greatly increases the prospects of developing new materials.

1.2.2 Temperature Programmed Desorption (TPD) to determine diffusion parameters

TPD has often been used in surface science to measure surface binding energies of atoms. However, the technique can also be used on bulk samples to determine changes in diffusion of dissolved gas species. The use of TPD on hydrogen storage materials is by now well documented. The technique is rather simple, the sample is heated usually with a linear ramp of a few C/second while a residual gas analyzer (RGA) measures the evolved gas species. TPD allows the observation of changes in the number of binding sites and the binding energy of various sites, which all impact atomic motion.

1.3 Scope of this Work

This proposal had two main goals. One, to establish the equivalency of microstructural defects caused by irradiation inside a nuclear reactor and that caused by a high energy heavy ion beam. Two, as a test case to measure the diffusion of H, D, or He in implanted Zircaloy-4 samples using TPD. For the TPD measurements the following 8 samples were made with varying Zr, D, and He implantation levels as listed in Table 3. Table 4 lists the energies used for the implantation into the TEM foils

Table 3: TPD sample implantation schedule.

Sample Number	3.25 MeV Zr	160 keV D	350 keV He
1	Yes	Yes	
2	Yes		Yes
3	Yes	Yes	
4	Yes		Yes
5		Yes	
6		Yes	
7			Yes
8			Yes

Table 4: Implantation energies used for implantation into TEM foils.

Ion Species	Implantation Energy
Zirconium	3.25 MeV
Helium	10 keV
Deuterium	10 keV

2. RESULTS

2.1 Irradiation Simulation in the I3TEM

Thin foils of Zircaloy-4 were made into TEM samples via thinning and jet polishing for the monitoring of microstructural changes due to ion irradiation. Figure 6 shows the damage in the sample before (Left) and after (Right) Zr ion irradiation. The damage is visible as the black spots and the general darkening of the sample. Because of the extent of the damage no specific dislocations were observed.

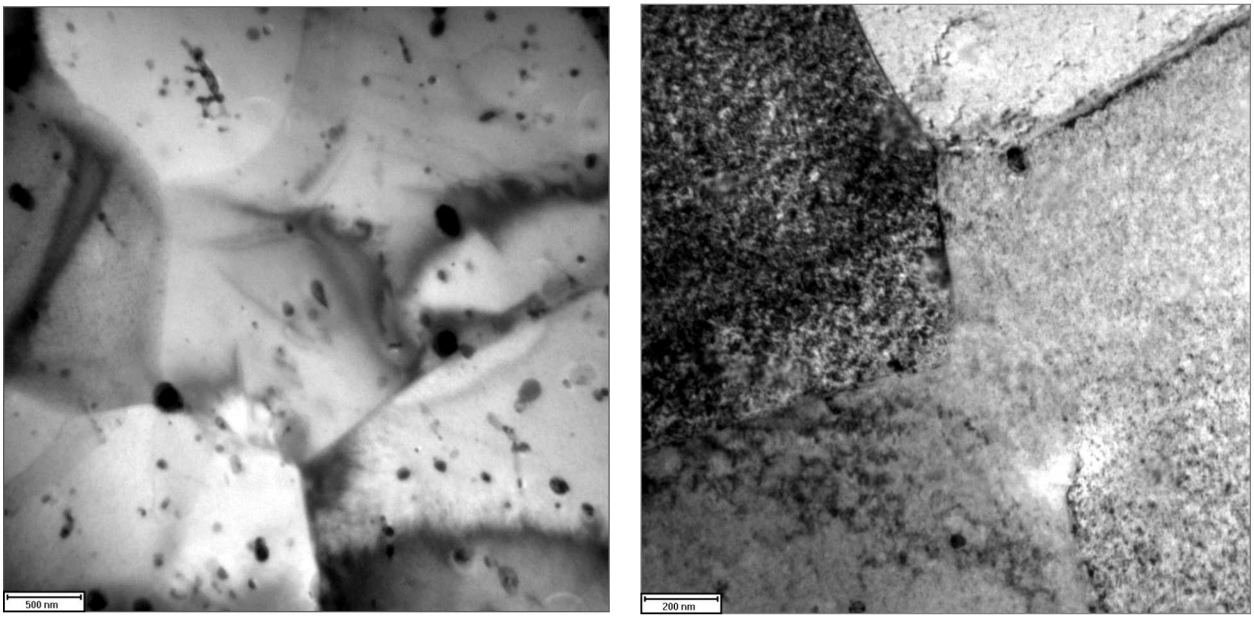

Figure 6: (Left) Before irradiation and (Right) after Zr ion irradiation into Zircaloy-4 TEM samples to level of ~7 dpa.

Figure 7 shows the impact of He ion irradiation followed by Zr ion irradiation. Figure 7A shows the damage immediately after the irradiation. High a high density of black spot damage is present; however, through focus imaging did not reveal the presence of any cavities immediately after irradiation. Figure 7B, C, and D are a series of through focus images acquired 30 days after irradiation. Interestingly, helium bubbles were observed after 30 days. Helium obviously diffused enough in the sample to accumulate into helium bubbles which were not present immediately after irradiation. This same phenomena was observed in samples which were bombarded in the sequence of Zr ions first, followed by He ions. The order of the irradiation doesn't seem to matter.

Figure 8a demonstrates the damage from overnight concurrent irradiation by Zr, Deuterium, and Helium ions. Similar black spot damage is observed as in Figure 6. Through-focus imaging did not reveal the presence of any cavities immediately after irradiation. The samples were imaged 30 days later, and large helium bubbles (up to 15 nm in diameter) were present. Figures 8 b-d are a series of through-focus images showing the helium bubbles.

These measurements provide a proof of concept for the ability of the I^3TEM to simulate the radiation environment of the TPBARs in a nuclear reactor. More work is needed to determine

the impact of fluence, sample temperature, and ion energy on the microstructure and see which combination provides the best match with the neutron induced microstructural changes.

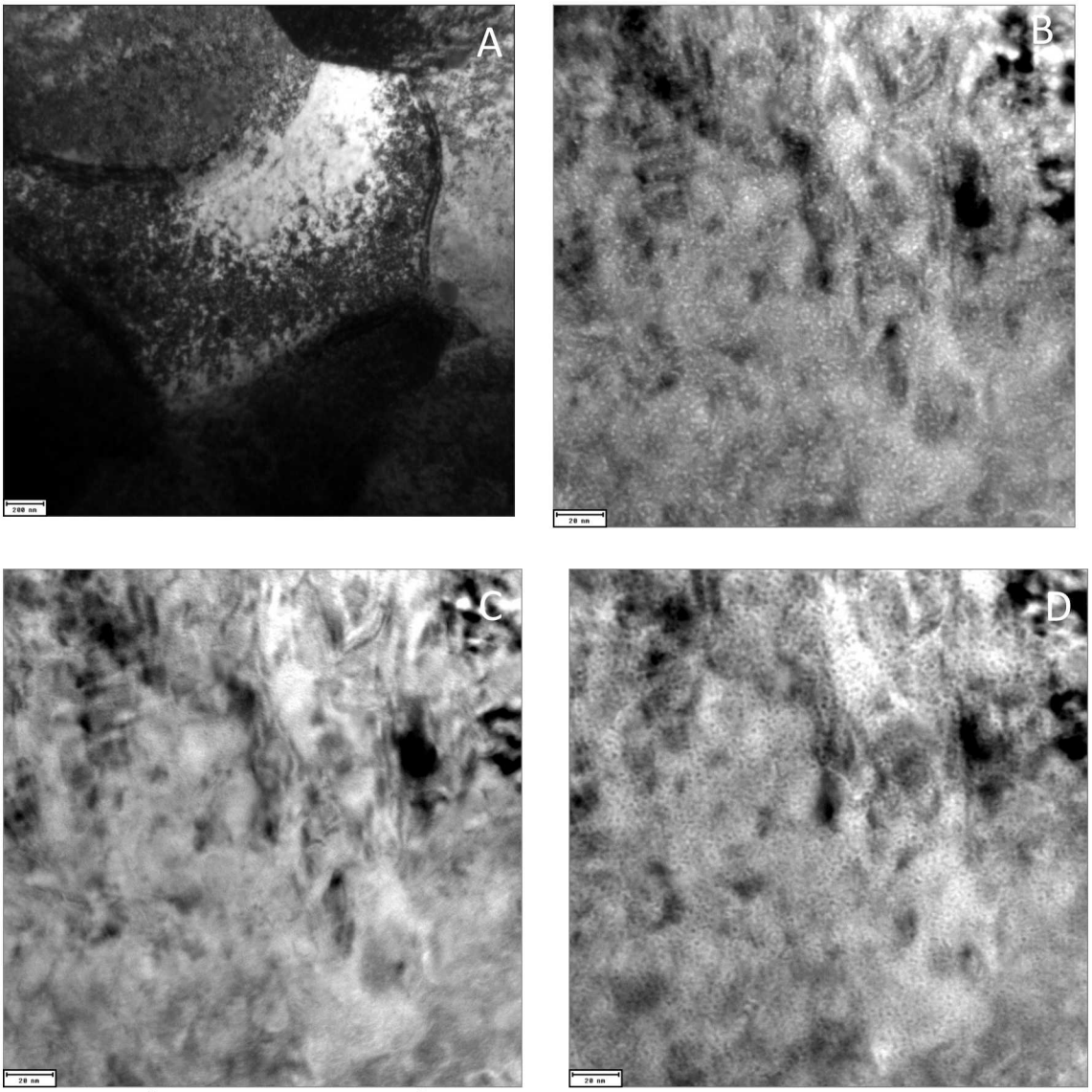

Figure 7:A) He ion irradiation followed by Zirconium ion irradiation. Figures B, C, and D taken 30 days later in the B) Under focus, C) In Focus, and D) Over Focus conditions.

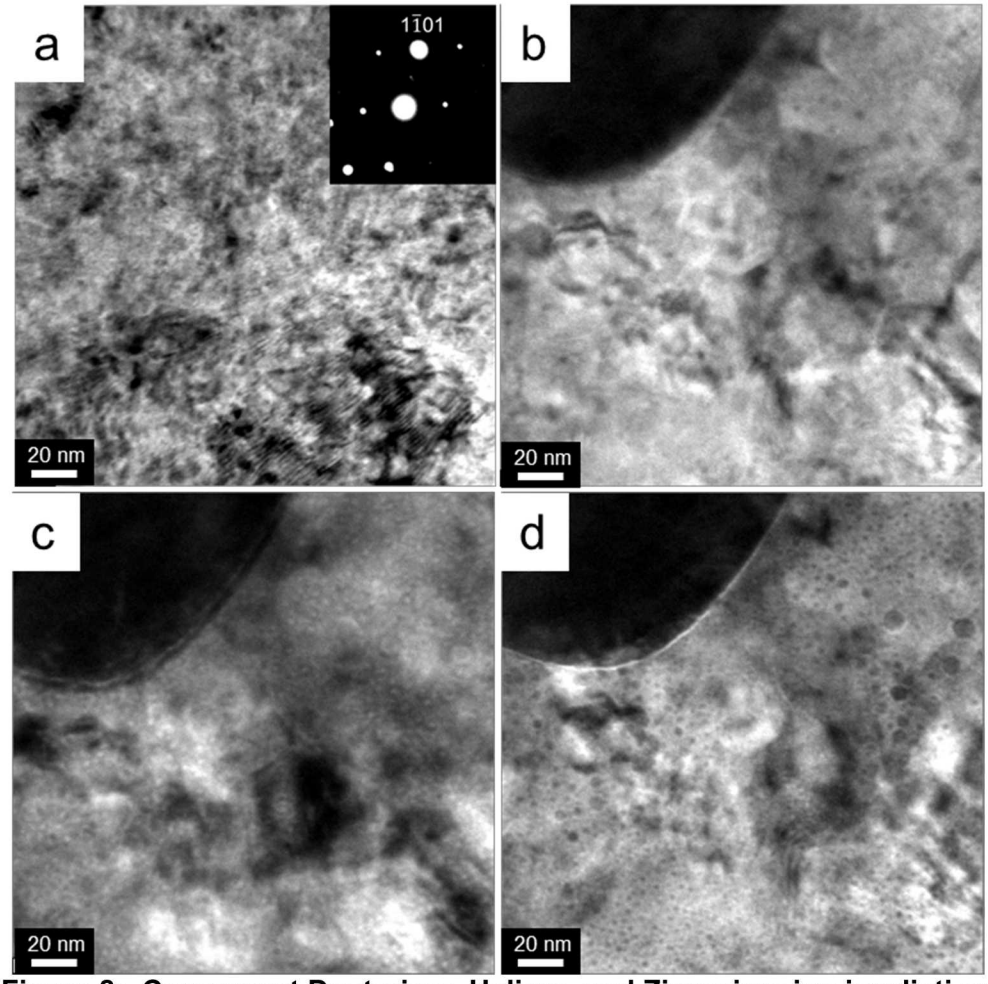

Figure 8: Concurrent Deuterium, Helium, and Zirconium ion irradiation. a) immediately after irradiation. A high density of black spot damage is visible, but no bubbles are seen. b) in-focus image 30 days after irradiation. c-d) over and under focus image 30 days after irradiation shows the presence of helium bubbles ranging from nanometers to over 15 nm in size.

2.2 Thermal Desorption Measurements

The thermal desorption measurements were performed as a means of determining the binding energies of hydrogen, deuterium, and helium in Zr-4 as a function of ion irradiation. Unfortunately, this aspect of the work was not terribly successful. As shown in Figure 9, no correlated differences are observed as a function of ion irradiation. In fact, we were not able to observe Helium or Deuterium at all. Both Helium and Deuterium will be mass 4 which can't be separated with our RGA but no mass 4 peak is observed.

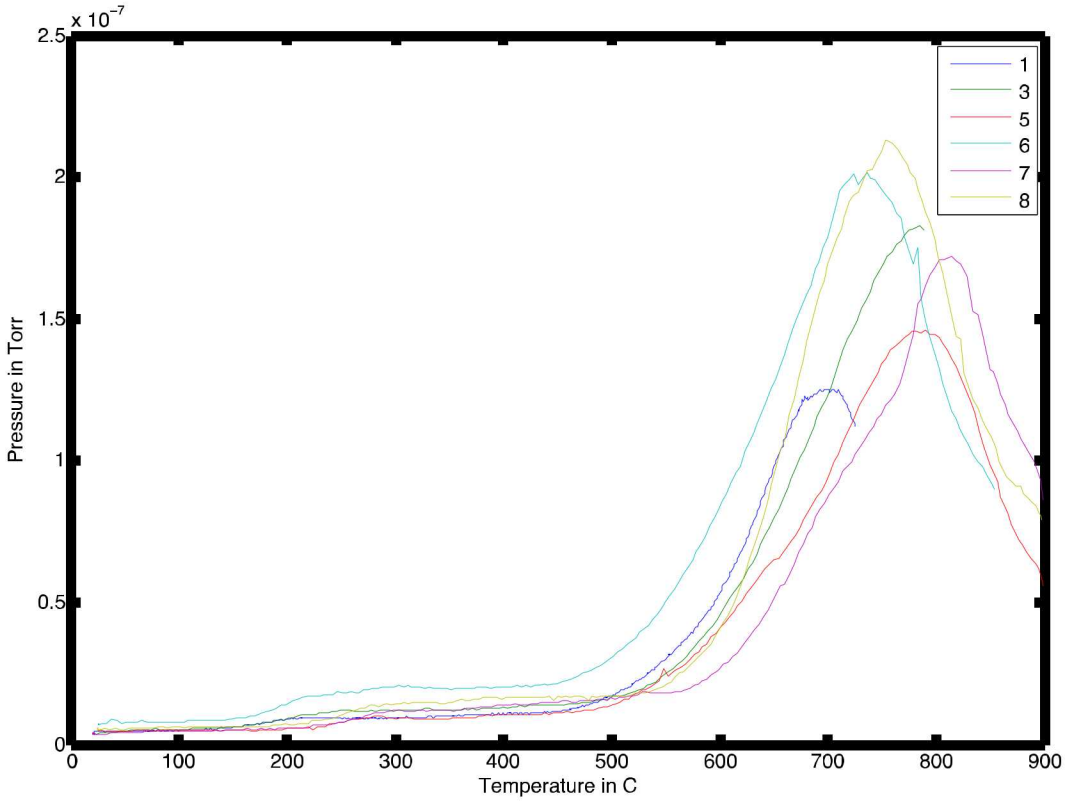

Figure 9: Summary plot of TPD data from Deuterium implanted data. The signal in plot is of Mass 2, H2. No D2 signals were observed from these samples.

3. CONCLUSIONS AND FUTURE WORK

The I^3TEM was able to simulate the radiation environment of TPBARs using Zr, D, and He ions. Black spot damage was observed, as a consequence of the irradiation. 30 days after irradiation helium bubbles are observed independent on whether the helium ions are implanted before or after the Zr ions.

Follow on work should study the impact of sample temperature, fluence, flux, and Zr ion beam energy on microstructural changes. A collaboration with an atomistic modeling group would also allow the determination of the type and number of dislocations created by Zr ion irradiation.

4. REFERENCES

1. C. L. Whitmarsh, *Review of Zircaloy-2 and Zircaloy-4 Properties Relevant to N. S. Savannah Reactor Design*, ORNL-3281, Oak Ridge National Laboratory, Oak Ridge, TN, July 1980.
2. James F. Ziegler, SRIM.org

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