In-Pile Experiment of a New Hafnium Aluminide Composite Material to Enable Fast Neutron Testing in the Advanced Test Reactor

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Donna Post Guillen
Douglas L. Porter
James R. Parry
Heng Ban

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Idaho National Laboratory

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Donna Post Guillen, Douglas L. Porter, and James R. Parry
Idaho National Laboratory, P.O. Box 1625, Idaho Falls, ID 83415
Tel: (208) 526-1744, Fax: (208)526-3677; Email: Donna.Guillen@inl.gov

Heng Ban
Utah State University, 4130 Old Main Hill, Logan, UT 84322

Abstract – A new hafnium aluminide composite material is being developed as a key component in a Boosted Fast Flux Loop (BFFL) system designed to provide fast neutron flux test capability in the Advanced Test Reactor. An absorber block comprised of hafnium aluminide (Al_3Hf) particles (~23% by volume) dispersed in an aluminum matrix can absorb thermal neutrons and transfer heat from the experiment to pressurized water cooling channels. However, the thermophysical properties, such as thermal conductivity, of this material and the effect of irradiation are not known. This paper describes the design of an in-pile experiment to obtain such data to enable design and optimization of the BFFL neutron filter.

I. INTRODUCTION

The development of advanced nuclear technologies relies on the availability of fast neutron testing facilities for new fuels and materials. Currently, advanced fast reactor fuels and materials being developed by the U.S. Department of Energy (DOE) are sent to France or Japan for irradiation testing in a fast neutron flux environment. Domestic testing options rely upon fast neutron fluxes provided by thermal spectrum test reactors. Since the fast neutron flux component of these reactors is relatively small, the total flux must be augmented and filtered. The lack of domestic fast neutron testing capability hinders the development of advanced fast reactors. To develop such capability, the DOE has examined several options to augment existing nuclear facilities to enable fast neutron testing, which can be brought on line in a few years, much sooner and at a much lower cost than building a new fast-flux test reactor.[1]

A Boosted Fast Flux Loop (BFFL) concept has been proposed to provide fast neutron flux test capability for testing advanced fuel and material specimens in the Idaho National Laboratory's Advanced Test Reactor (ATR), a high power density/high neutron flux research reactor operating in the United States. Design requirements for the testing system specify a fast (E>0.1 MeV) neutron flux of at least 1 x 10^{15} n/cm^2-s with a fast-to-thermal flux ratio in the vicinity of 40.[2] The BFFL concept relies upon booster fuel to enhance the neutron flux and neutron filters to increase the fast-to-thermal flux light water ratio. A new hafnium aluminide (Al_3Hf-Al) composite material has been developed to enable conduction cooling of the specimens, while simultaneously filtering out thermal (lower energy) neutrons and allowing the fast (higher energy) neutrons to pass through the material. Preliminary neutronic calculations and thermal hydraulic analyses indicate that the concept is technically viable.[3,4]

However, the effects of irradiation on the composite material are not yet known and must be determined to enable further development of this fast flux test concept. To determine the thermal heat transfer properties of the Al_3Hf-Al composite and its irradiation performance in ATR, an in-pile experiment will be conducted under the auspices of the ATR National Scientific User Facility (NSUF). The objectives of the experiment are to assess the effect of irradiation on the composite with respect to: (1) physical/morphological, metallurgical and microstructural changes, (2) thermophysical properties, and (3) corrosion behavior in reactor coolant water. Results from the experiment will provide necessary data for the development of fast neutron test capability at ATR, fills a knowledge and information gap in the basic properties of Al_3Hf, and Al_3Hf-Al composite, and advances the scientific understanding of the irradiation effect on these materials. This paper discusses the design, fabrication and analysis of the experiment.

II. EXPERIMENT DESCRIPTION

The experiment is designed to be housed in a small B position (B2) located in the eastern section of the ATR (see Fig. 1). Material specimens fit into holders inside of drop-in capsules. With the exception of a small number of corrosion test specimens, the function of the capsules is to provide a robust barrier between the water coolant and the materials specimens. The capsules will be fabricated to meet the intent of ASME, Section III, Class 1 pressure vessel code requirements. The capsules fit into a basket designed for a small B-position having a diameter of 2.223 cm (0.875 inches). The test train is constructed of aluminum alloy and is conFig.d to hold the specimens for ease of removal following irradiation.

The total fluence the BFFL neutron filter will experience in the ATR is approximately 9 x 10^{21} n/cm^2·s. The neutron filter loses its absorption capabilities due to isotopic changes in the hafnium through the absorption of neutrons. The hafnium absorber will have lost enough of its absorption properties after two BFFL cycles (at 30 days per cycle) to warrant replacement. It is expected that the specimens will require at least 135 effective full power days in the ATR B-2 irradiation position to experience a total fluence of 9 x 10^{21} n/cm^2·s. The length of the ATR irradiation cycle varies from cycle to cycle, but is typically from 40 to 60 days in length. To guarantee the specimens experience a neutron fluence greater than that estimated for the BFFL neutron filter, the specimens will remain in the reactor for up to four consecutive ATR cycles. This allows for unintended shutdowns or shorter cycles and still achieves the minimum neutron fluence expected for the BFFL neutron filter. If the experiment is not ready for insertion at the start of the planned cycle, neutronically equivalent hardware (basket and solid aluminum cylinders) will be available to fill that position. The test train design will provide axial flux profile uniformity, so as not to impact the other experiments in the reactor.

The total duration of the in-pile experiment is four ATR cycles. The experiment assembly will house three capsules per cycle. Four identical capsules, designated A through D, will be assembled. Capsule E is a neutronically equivalent dummy capsule. However, individual capsules will be irradiated for one, two, three or four irradiation cycles to assess the effect of burn-up. Fig. 2 depicts the arrangement of capsules for each of the four cycles. An identical set of specimens will be contained in each capsule. The specimen holders will be numbered, so that they can be tracked during post-irradiation examination (PIE). If sufficient resources are not available to characterize all of the specimens

following irradiation, the specimens will be placed in the ATR NSUF sample library.
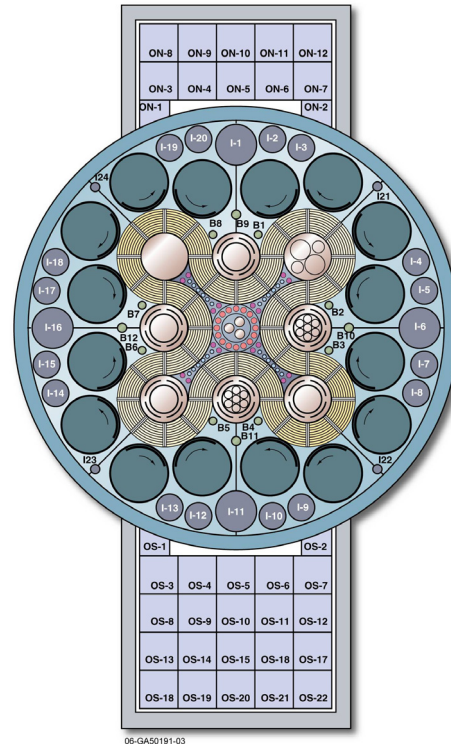
Fig. 1. Diagram of irradiation positions in the ATR.
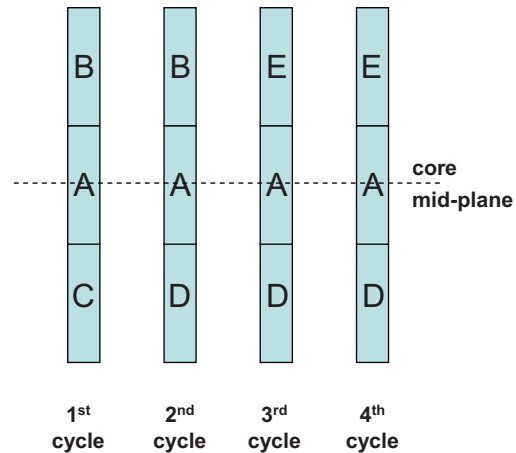

Fig. 2. Capsule loading arrangement by ATR reactor cycle.

Flux wire monitors located within the capsules will be used to quantify the neutron flux at designated locations in the irradiation test vehicle. The flux wire monitors will be incorporated into the test train as follows:

- 1 monitor per capsule to calibrate the Monte Carlo Neutron Particle (MCNP) neutronics code calculations.

Aluminum alloy holders will be fabricated to position the flux wire monitor within the experiment capsule.

- 1 monitor per capsule to assess the neutron flux perturbation of the material. Holders to contain the flux wire monitor will be fabricated from 23 vol% composite material.

The term "capsulette" refers to the container for the flux wires; whereas, the term "capsule" refers to the container for the specimen holders. Two vanadium capsulettes containing flux wires will be incorporated each into the four capsules designated A through D, for a total of eight capsulettes. The flux wire monitor capsulettes are 1.27 mm in diameter by 0.635 cm long. The monitors will not come into contact with the primary coolant. After irradiation, the flux wires will be analyzed for activity levels.

Based upon a preliminary thermal analysis of a candidate neutron filter configuration, the experiment is designed to maintain the encapsulated specimens at a temperature of around 225 ºC. The corrosion test specimens will be cooled by ATR primary coolant. The temperature of the corrosion specimens in contact with the primary coolant will be maintained below 185 ºC. ATR primary coolant water will flow around the capsules inside of the basket and between the basket and the reflector.

The ATR irradiation experiment consists of specimens of the Al_3Hf intermetallic and the Al_3Hf-Al composite material fabricated into various geometries and with different particle sizes, compositions and phases. Four different specimen geometries are specified to accommodate the various pre- and post-irradiation measurements:

1. **5 mm diameter x 5 mm long rod** for thermal expansion coefficient, visual inspection and/or photography, and scanning electron microscopy (SEM) characterization.

2. **5 mm diameter x 0.8 mm thick disc** for thermal diffusivity and specific heat measurements. The two ends of the disc must be parallel for accurate thermal diffusivity measurements.

3. **3 mm diameter x 0.3 mm thick disc** for transmission electron microscopy (TEM) characterization and specific heat measurements. The size of the specimen was chosen based upon the size of the TEM sample holder.

4. **1 cm diameter x 1 cm long cylinder** to serve as a holder and neutron filter for flux wire monitor.

The Al-Hf binary phase diagram indicates that there is very little or no solubility of hafnium in aluminum and intermetallics are seen to form across nearly the entire binary diagram. Compositions comprising Al_3Hf in aluminum are stable up to about 25 at.% Hf and up to the melting temperature of aluminum (about 660 °C).[5] Because of excess aluminum in the composite neutron filter, the intermetallic phase containing the least amount of hafnium (which is in form Al_3Hf) is important. The phase diagram indicates that a 5-10 at. % Hf mixture should consist of Al_3Hf in aluminum, the Al_3Hf being stable. MCNP neutronic calculations indicate that the heating rate saturates at around 6 to 7 at% Hf. A 6.5 at% Hf or greater is necessary to achieve a fast-to-thermal ratio > 40. Therefore, a 7 at% Hf can produce the desired fast-to-thermal ratio and fast neutron fluence for the particular configuration analyzed. This concentration of Hf corresponds to ~23 volume percent of Al_3Hf.

Al_3Hf intermetallic material will be cast from Hf and Al using a centrifugal caster. Some specimens will be comprised solely of intermetallic material cast to the required geometry. Other specimens will consist of the Al_3Hf intermetallic dispersed in an aluminum matrix. To fabricate the composite specimens, the intermetallic will be ground into a powder using a mortar and pestle. The Al_3Hf powder is sorted into size groups using a sonic sifter. Then, the Al_3Hf powder is mixed with aluminum powder and pressed into compacts using a die. Specimens are produced with variations in particle size, volume percent and intermetallic phase as described below:

1. **Particle Size** – The Al_3Hf particles will be sieved into three particle size groups with diameters as follows:

   - Small – < 38 μm

   - Medium – 75 to 105 μm

   - Large – 105 to 149 μm

   A composite specimen contains only one particle size dispersed in an aluminum matrix. Due to specimen thickness requirements of 0.3 mm [300 μm] dictated by the analytical instruments, the Al_3Hf-Al composite specimens for specimen geometry #3 will only contain small particles. If the medium and large particles were used, there would be very few particles in the specimen cross-section and it could not be considered homogeneous.

2. **Volume Percent** – Specimens will be fabricated from pure Al_3Hf intermetallic or as an Al_3Hf-Al composite material. Composite (COMP) specimens will be formed with either 15 vol% or 23 vol% Al_3Hf particles

dispersed in an aluminum matrix. The 23 vol% corresponds to a 7 at% Hf and is the preferred composition. However, due to potential inconsistencies in the fabrication process, a lower at% Hf will be irradiated to determine the performance at a lower at%.

3. **Phase –** X-ray diffraction (XRD) will be performed to confirm the phase of the intermetallic produced by the fabrication process. Either a low temperature (LT) phase Al_3Hf or a high temperature (HT) phase Al_3Hf can be produced. Specimens cast at a pyrometer temperature ~1450 °C are comprised mainly of the LT phase, whereas for specimens cast at a higher temperature of ~1530 °C the dominant phase was the HT phase. The high temperature phase is not stable below 698 °C so it was unexpected that HT phase was retained in the castings made at higher temperature. Because it is expected to be unstable it is expected that the HT phase will revert to LT phase upon irradiation.

All of the thermophysical property measurements will be performed on composite specimens with LT phase, 15 and 23 vol% and both a HT and LT pure intermetallic. All composite specimens are comprised of LT (not HT) phase Al_3Hf particles. Since these measurements are non-destructive, the specimens can be reused for several different measurements to reduce the total number of specimens to be fabricated. For example, the same set of specimens used for the thermal expansion coefficient measurements can also be used for the density measurements. The hardness tests and the isotopic analysis are destructive. When the other measurements are completed, the specimens will be used for the Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS) analysis. However, two sets of specimens are needed for the hardness measurements since these tests are destructive - one set is needed for pre-irradiation characterization and another set for PIE.

III. ANALYSIS

Measurements and analyses will be performed on the specimens before and after irradiation (Table I) to assess thermal, material, and mechanical properties; radiation damage, isotopic evolution and neutron flux; and corrosion effects. Pre-irradiation measurements will be made either at the Idaho Research Center (IRC) or Materials and Fuels Complex (MFC) laboratories. Post-irradiation examination capabilities are available in three primary facilities at MFC:

- The Hot Fuel Examination Facility (HFEF), a large hot cell facility

- The Analytical Laboratory (AL), focused on analysis of irradiated and radioactive materials

- The Electron Microscopy Laboratory (EML), a radiological facility containing optical, scanning, and analytical microscopes

Flux wire monitors will be sent to Pacific Northwest National Laboratory (PNNL) for counting and data analysis.

Thermal and material properties – Differential Scanning Calorimetry (DSC) will be used to measure specific heat, c_p, in a glovebox at MFC if the radioactivity of the specimens is low enough. Thermal diffusivity, α, given as

$$\alpha = \frac{k}{\rho c_p} \qquad (1)$$

where k is thermal conductivity and ρ is specimen density will be measured using a laser flash apparatus for the pre-irradiated specimens. The radiation level of the irradiated specimen will determine whether the analysis can be performed in a glovebox or if it must be examined in a hot cell. If the hafnium activation is sufficiently low, the thermal diffusivity can also be measured after irradiation in a glove box using laser flash. If the specimens are too radioactive, then the Scanning Differential Thermal Microscope (STDM) will be used in the hot cell; additional measurements on pre-irradiation archive specimens will be made for comparison.

Hot cell thermal effusivity characterization will also be done so that thermal conductivity can be extracted without the need to explicitly measure specific heat. A pulsed laser technique will be employed to measure thermal effusivity, e, given as

$$e = \rho c_p k. \qquad (2)$$

The measurement technique uses two lasers to heat the specimen, as the specimen expands the reflected signal changes. Thermal conductivity for highly radioactive specimens can be obtained analytically by multiplying thermal effusivity by thermal diffusivity and taking the square root. As can be seen by the equations above, knowledge of material density is required to calculate specific heat. Density will be quantified by an Archimedes type immersion test in the Analytical Laboratory hot cells at the MFC.

Thermal expansion coefficient will be measured using a dilatometer located in the MFC glovebox. If the radiation level of the irradiated specimens is too high, this measurement will have to be delayed until the specimens can be handled in a glovebox. The maximum dose that can be handled in the glovebox is 10 Rad at 1 cm.

TABLE I.

Pre- and Post-Irradiation Measurements

Measurement	Material	Particle Size	Volume Fraction (%)	Equipment
Thermal diffusivity	HT &LT	N/A	N/A	Laser Flash or Scanning Differential Thermal Microscope
	LT COMP	All Three	15 and 23	
Specific heat	HT &LT	N/A	N/A	Differential Scanning Calorimeter or derived from thermal effusivity hot cell measurement
	LT COMP	All Three	15 and 23	
Thermal expansion	HT &LT	N/A	N/A	Dilatometer
	LT COMP	All Three	15 and 23	
Microstructure	HT &LT	N/A	N/A	SEM/TEM analysis
	LT COMP	Small	23	
Phase composition	HT &LT	N/A	N/A	X-ray diffraction Rietveld analysis
Visual examination, Hydroxide layer characterization, corrosion	HT &LT	N/A	N/A	Optical metallography, photography, SEM
	LT COMP	All Three	15 and 23	
Density	HT &LT	N/A	N/A	Immersion density
	LT COMP	All Three	15 and 23	
Isotopics	HT &LT	N/A	N/A	ICP-MS Gamma counting
	LT COMP	Small	23	
Neutron fluence	LT COMP	Medium	23	Gamma and x-ray counting
Hardness	LT	N/A	N/A	Indentation

Measurements of specific heat capacity, thermal diffusivity and thermal expansion coefficient will be measured from room temperature up to 550 °C in steps of 50 °C, then back down to room temperature again. The density measurement will be made at room temperature.

Mechanical properties – Indentation hardness will be obtained only for the LT Al_3Hf intermetallic. These tests will be performed at room temperature.

Radiation damage – SEM/TEM will be performed to evaluate any microstructural changes resulting from radiation.

Isotopic Evolution – Specimens of the intermetallic material will be dissolved and ICP-MS performed. This test will be done to determine the extent of burn-up and the Hf-179m isotope produced. There are two metastable states for the hafnium decay and the decay chain could produce either Hf-179m1 or Hf-179m2. The particular isotope that is produced determines whether the specimens can be handled in a glovebox or will have to be examined in the hot cell. Isotopic gamma scans will be performed to determine the isotopic distribution of activity over a component's length or width.

Neutron Fluence – Four neutron activation wires will be used to monitor the neutron energy spectrum and fluence during reactor operation. The wires selected produce activation products that are easily measurable and undergo nuclear activation reactions characteristic of different parts of the neutron spectrum. Each flux monitor capsulette will contain 0.1%Co-Al, Fe, Ti, and Nb flux wires inside. Table II shows the reactions and type of flux monitored by wire type. Several activation reactions occur in the wires, allowing the deconvolution of the neutron energy spectrum into three general energy bins – thermal, epithermal, and fast (>1 MeV) since each reaction is sensitive to a different range of neutron energies.[6] The three thermal/resonance neutron detectors can be used to determine the relative thermal and epithermal (resonance) neutron fluences. The three fast neutron detectors each have different threshold energies and are sensitive to different parts of the neutron spectrum.

TABLE II.

Flux Wire Types

Wire	Reaction	Neutron Monitor
0.116% Co-Al alloy	59Co(n,g)60Co	Thermal/resonance
Fe	54Fe(n,p)54Mn	Fast
	58Fe(n,g)59Fe	Thermal/resonance
Nb	93Nb(n,n')93mNb	Fast
	93Nb(n,g)94Nb	Thermal/resonance
Ti	46Ti(n,p)46Sc	Fast

The measured activities of the neutron activation wires are used to determine the neutron fluences experienced by the specimens during irradiation. After removal from the reactor, each capsulette will be opened and the individual wires will be prepared for gamma counting. After gamma counting, the Nb wires will be dissolved and mounted for x-ray counting to determine the activity of Nb-93m. The STAY'SL computer code[7] will be used to adjust the neutron spectrum using a least squares procedure. The input consists of the MCNP-calculated neutron spectrum, the measured reaction rates, and evaluated neutron activation cross sections, along with uncertainties and covariances for all of the input data. The output is the adjusted neutron spectrum with uncertainties based on a least squares adjustment procedure that gives you the best estimate of the neutron spectrum at the location of each flux monitor capsulette.

Corrosion – SEM characterization of specimens will be performed before and after an autoclave treatment to assess the potential for excessive corrosion due to exposure to the ATR coolant. The analysis will confirm whether the material can be exposed as-fabricated to the water. Corrosion testing will be performed prior to irradiation in the small autoclave at MFC on 13 mm diameter x 1.5 mm thick specimens. The corrosion testing will be performed using deionized water at a pressure of 130 ± 30 psig, a temperature of $185 \pm 8°C$, pH of 8.0 ± 0.2 for 18 ± 1 hrs. This treatment procedure is used to apply a uniform, adherent boehmite $(Al_2O_3 \cdot H_2O)$ film on the cladding surface of nuclear fuel plates. LT composite specimens have been fabricated to contain exclusively small, medium or large particles. After autoclaving, the surface of the specimens will be examined using scanning electron microscopy (SEM). Especially of interest is the location where the Hf particles contact the surface of the specimen and any evidence of hydroxide growth deep into the structure. The purpose of the corrosion testing is to assess the severity of the corrosion so that flow-through capsules can be used for certain specimens to be irradiated in ATR. Results from the pre-irradiation corrosion testing are necessary to provide a safety basis for exposing unclad specimens to the primary coolant water. There are concerns with Al_3Hf particles entering the primary coolant stream, the corrosion resistance of the particles themselves, and the creation of electric potentials or stresses due to thermal expansion mismatch that would promote corrosion at the interface. The testing will answer the question of whether or not the surface-connected hafnium aluminides would be tightly bound in the aluminum matrix or hydroxide layer or if they would be released under hydraulic pressure, allowing them to become a source of scouring sand and neutron poison in the primary coolant system. The corrosion behavior of the irradiated specimens will provide valuable information to determine whether the BFFL neutron absorber block must be clad to mitigate corrosion. If cladding the coolant channels is necessary, this could complicate the fabrication of the BFFL neutron absorber.

IV. SUMMARY

The primary goal of the project is to determine the thermophysical properties of Al₃Hf and the Al₃Hf-Al composite and the effect of irradiation in the ATR. New information produced from this research includes:

1. Thermophysical properties of Al_3Hf intermetallic and Al_3Hf -Al composite at different temperatures.

2. Physical/morphological, metallurgical, and microstructural changes of the Al₃Hf-Al composite after different cycles of irradiation.

3. Determine the effect of irradiation on the thermophysical properties of the Al₃Hf-Al composite.

4. Decay products of hafnium (Hf-179m1 versus Hf-179m2).

5. Corrosion behavior of the Al₃Hf-Al composite.

The end result of the project, in terms of data and fundamental understanding obtained, will directly support DOE's mission and benefit the science community in general. The lack of domestic fast neutron testing capability hinders the development of advanced nuclear reactors. For instance, advanced fuels are currently sent to France or Japan for testing. This project would enable the successful development of fast neutron testing capability or similar technologies, which can result in savings of tens of millions dollars over other technical options. Characterization of this new material will provide valuable information to be used for design. The material could also be used as a strong thermal neutron absorber for other tests for advancement of AFCI, GEN IV, and NGNP programs.

ACKNOWLEDGMENTS

NOMENCLATURE

α	Thermal diffusivity
c_p	Specific heat
e	Thermal effusivity
k	Thermal conductivity
ρ	Density

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