ORNL/LTR-2023/2735

Coupon synthesis status report

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Molten Salt Reactor Program

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ABSTRACT

This letter report is in submission of completion of the Level 4 milestone number M4AT-23OR1101023 "Coupon synthesis status report" for the AT-23OR110102 "Beryllium Carbide as moderator for MSRs – ORNL" WBS number 2.04.11.01 within the larger Advanced Reactor Technologies program at Oak Ridge National Laboratory. This effort is an initial study of the viability of beryllium carbide as a future neutron moderator for molten salt reactors and other high temperature reactors. The research was awarded funding in September 2022 and this effort will be completed and reported on as a Level 2 milestone by the end of August 2023. This work is a collaboration between Oak Ridge National Laboratory and the University of Michigan. This report will discuss the status of this effort and planed work before the final reporting.

1. CURRENT PROGRAM STATUS

This program was started under the Advanced Reactor Technology (ART) Molten Salt Reactor (MSR) program in September 2022, with this effort resulting in a Level 2 milestone by the end of August 2023. The initial funding of $500k supports the preliminary studies of the possible use of beryllium carbide (Be_2C) as a future neutron moderator for molten salt reactors. This current work is a collaboration effort between Oak Ridge National Laboratory (ORNL) and the University of Michigan (UofM).

The effort at ORNL is focused on four tasks: Be_2C procurement, high-temperature stability testing, irradiation damage modeling studies, and degradation of Be_2C in the presence of hydrogen. ORNL is in the process of purchasing solid specimens of Be_2C from Materion Brush Inc. (Materion) in Elmore, OH. ORNL and Materion collaborated on the development of a sectioning plan for a solid body of Be_2C. The machining quote was provided to ORNL in early March 2023 and is currently going through the ORNLBuy system. The quote from Materion cites 6 weeks delivery time from the time of purchase. Two of the ORNL tasks are dependent on material acquisition, while the modeling studies will begin in April 2023. ORNL is also in discussion with Argonne National Laboratory about some preliminary thermal properties measurements.

The effort at UofM is focused on two tasks: development of the capability to perform ion irradiations of Be_2C and installation of a hot isostatic press (HIP) to facilitate future production of solid Be_2C bodies from high-purity Be_2C powder. The first task is broken down into multiple sub-tasks including: working with safety personnel at UofM to development of a personnel monitoring plan, development of an encapsulation technique to reduce the risk of exposure to Be during specimen handling and irradiation, preliminary irradiation stage design and proof-of-concept irradiations on non-Be containing samples, and finally preliminary irradiation of Be_2C samples. The UofM work that could be delayed due to material procurement is the irradiation of Be_2C and initial HIP processing of Be_2C powder.

2. BACKGROUND

Be_2C has long been recognized as having high potential to serve as a high-temperature tolerant neutron moderator due to its moderating efficiency and low absorption cross section [1]. Be_2C could serve as an alternate to graphite in many situations due to its improved neutronic performance (greater slowing down power) and potentially much better radiation damage characteristics. Be_2C as a neutron moderator, however, is much less mature than graphite. Graphite is the only proven, fuel-salt compatible moderator. Graphite, however, has both limited displacement damage tolerance and is not a volumetrically efficient moderator. The neutron moderation length in carbon is over 60 cm versus under 6 cm in water [2]. Radiation damage to graphite has long been a known design issue for MSRs. Radiation damage to graphite was central to ORNL's decision in 1967 to shift from a dual to single fluid MSR and was a central rationale in halving the power density of the molten salt breeder reactor's conceptual design [3, 4]. Additionally, graphite that has been exposed to fuel salt represents a significant contaminated waste stream.

Be_2C would require technology development and maturation to become a useful moderator material for MSRs. Available Be_2C pieces are brittle and vulnerable to thermal stress cracking. Moreover, Be_2C is toxic, moisture sensitive, and chemically reacts with uranium. However, potential pathways exist to mitigate or even exploit Be_2C characteristics that have been perceived as disadvantageous (except for its toxicity). Much as with other carbides, fiber reinforcement may reduce brittleness [5]. Be_2C is a methanide meaning that, in the presence of hydrogen, it decomposes into a hydrocarbon gas (methane). One of the most challenging radionuclide containment challenges at MSRs is tritium. Conversion of tritium into methane would be useful at MSRs as tritium is the only radionuclide with significant potential to escape under normal operating conditions. Methane is readily trapped and does not diffuse through structural alloys. Be_2C is chemically compatible with coolant salts but would require a protective layer (like niobium carbide) to be used directly with uranium bearing salts. The most significant remaining uncertainty preventing the widespread use of Be_2C as a high temperature neutron moderator is the lack of information on its radiation damage characteristics.

Beryllium carbide has an antifluorite crystal structure – the same crystalline configuration (with anions and cations reversed) as exceptionally radiation damage resistant fluorite type crystals (e.g., UO_2). A related anti-fluorite crystal (Li_2O) has also been shown to have high radiation damage tolerance [6, 7]. While the analogous material performance information provides a rationale for expending resources to assess of the radiation damage characteristics of Be_2C, the radiation damage characteristics of Be_2C remains speculative with only low-displacement irradiations previously performed [8-10]. Beryllium carbide does not activate substantially, but has multiple, small cross-section, gas generating threshold-reactions (see Figure 1). Consequently, beryllium carbide pieces exposed to energetic neutrons may need to be occasionally baked out at temperatures above 1000°C over the course of the plant lifetime to remove gases that do not release at operating temperature but do migrate to form gas stabilized voids.

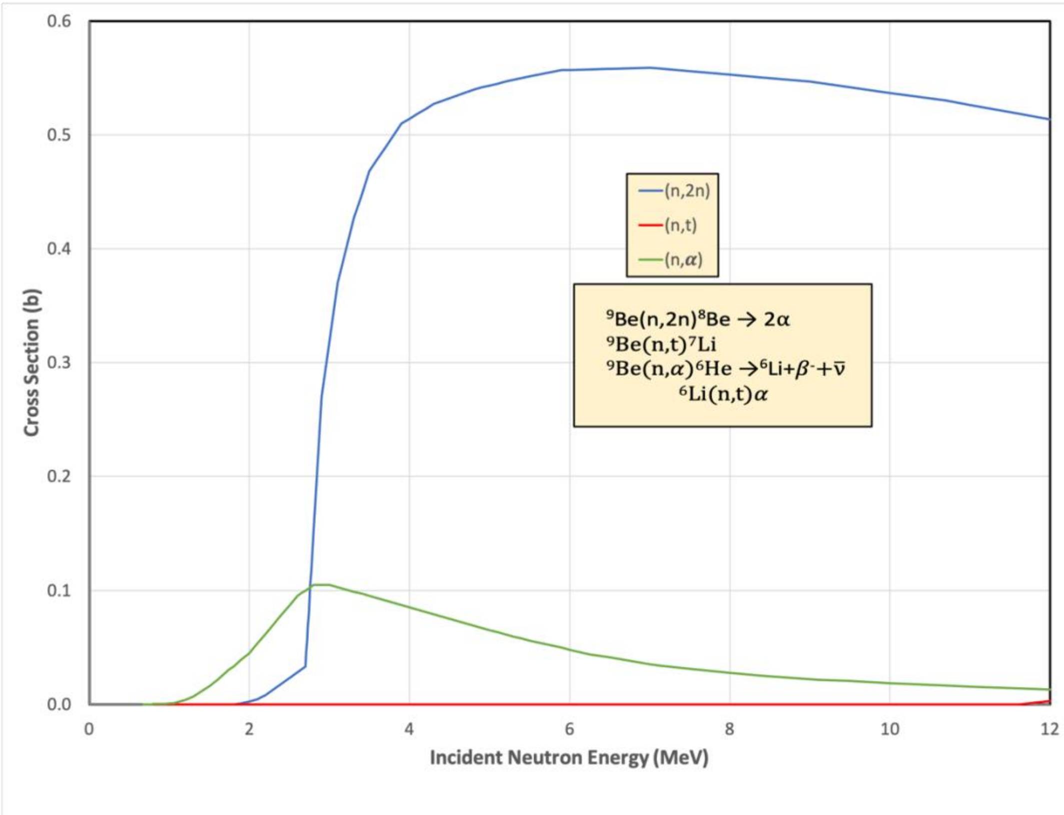

Figure 1. Beryllium gas generating reactions (data from ENDF/B-VIII.0)

Part of the rationale for lack of prior development of Be_2C is the lack of need in gas-cooled reactors. Radiation damage sensitivity of graphite is of less concern to gas cooled reactors due to their lower power density, which results from the decreased heat transfer provided by gas-phase coolants as opposed to halide salts. Be_2C may also be useful as material surrounding fusion plasmas. The major concern for use of Be_2C in fusion is that all fusion neutrons are born with high energy and Be_2C increases meaning that there will be an increase in the formation of tritium resulting in the need of Be_2C to accommodate more energetic neutron gas generation. The major concern in fusion reactors is whether the generated gases are sufficiently mobile at operating temperature to result in gas stabilized voids, but not sufficiently high to release. While gas generation is an issue in MSRs, fission neutrons have an energy distribution of 2-5 MeV and below, resulting in fewer neutrons having sufficiently high energy to generate gaseous atoms.

3. BERYLLIUM CARBIDE PROCUREMENT

Few places have the knowledge or physical capabilities to create solid pieces of Be_2C. Materion recently developed a method to produce a high-purity Be_2C powder, which was formed into a 1.5" diameter by 1" tall puck. Materion has agreed to sell the compacted material to ORNL and UofM in support of this work. The cutting/sectioning plan for this puck was developed by ORNL and sent to the engineers at Materion for feedback and quotation for cutting services. The cutting plan is shown in Figure 2 through Figure 12. Pieces to be cut from the puck include rods with lengths parallel to (Figure 5) and perpendicular to the puck diameter (Figure 9, Figure 11, and Figure 12) which can be used for coefficient of thermal expansion measurements. The small capsule coupons (Figure 7) will be used for experiments studying the high-temperature stability of this material in an inert atmosphere. Small samples will be cut to allow for measurements of the interaction of Be_2C with molten salt in the ORNL skimmer (Figure 8). Finally small square coupons will be cut that will be used by UofM for ion irradiation (Figure 11). In addition to the purchase of this solid piece of Be_2C, 50 g of high-purity Be_2C powder is being purchased that UofM will utilize for hot isostatic press testing. The quote from Materion was received March 6, 2023 and is processing through the ORNL Ariba purchasing system.

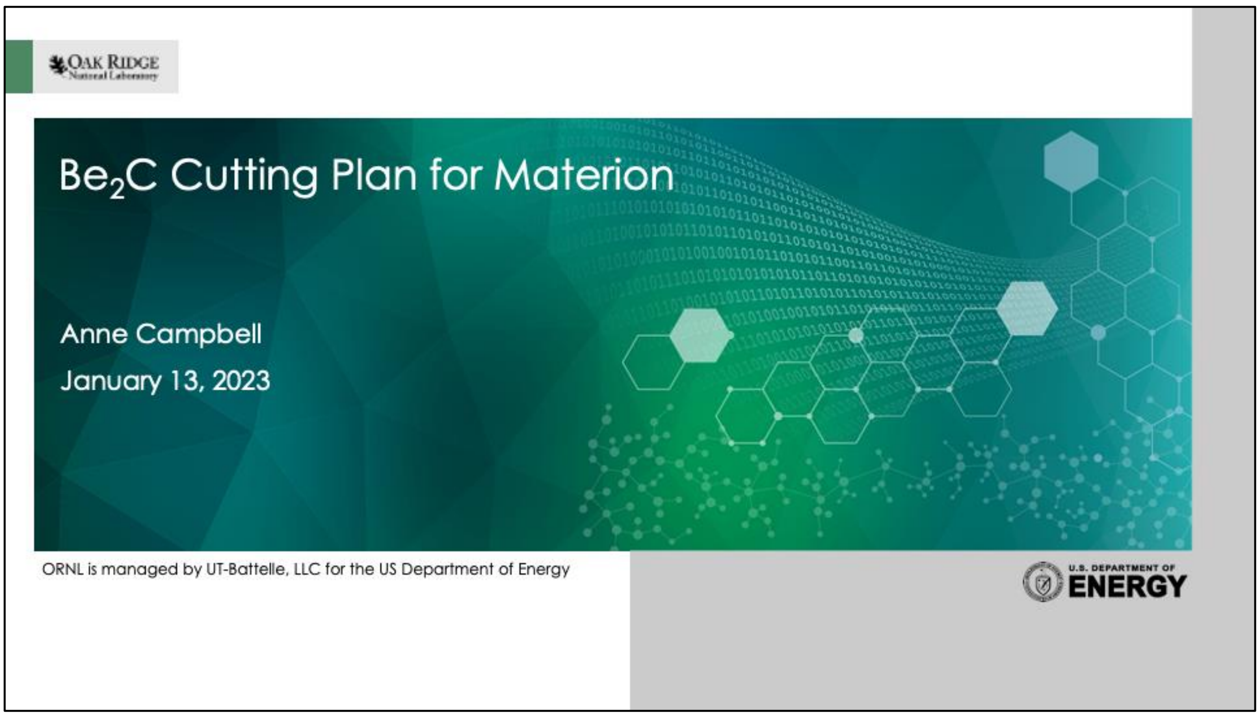

Figure 2. Cutting plan for Be_2C solid puck

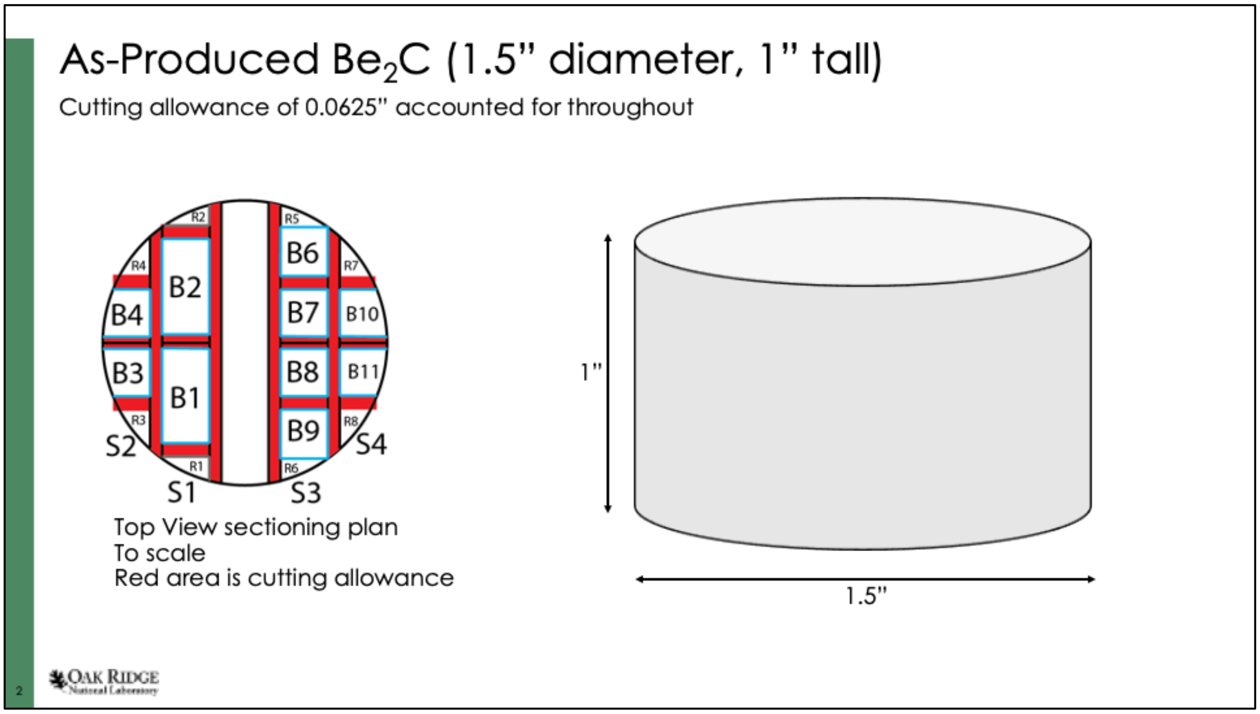

Figure 3. Overview of Be_2C puck and sectioning

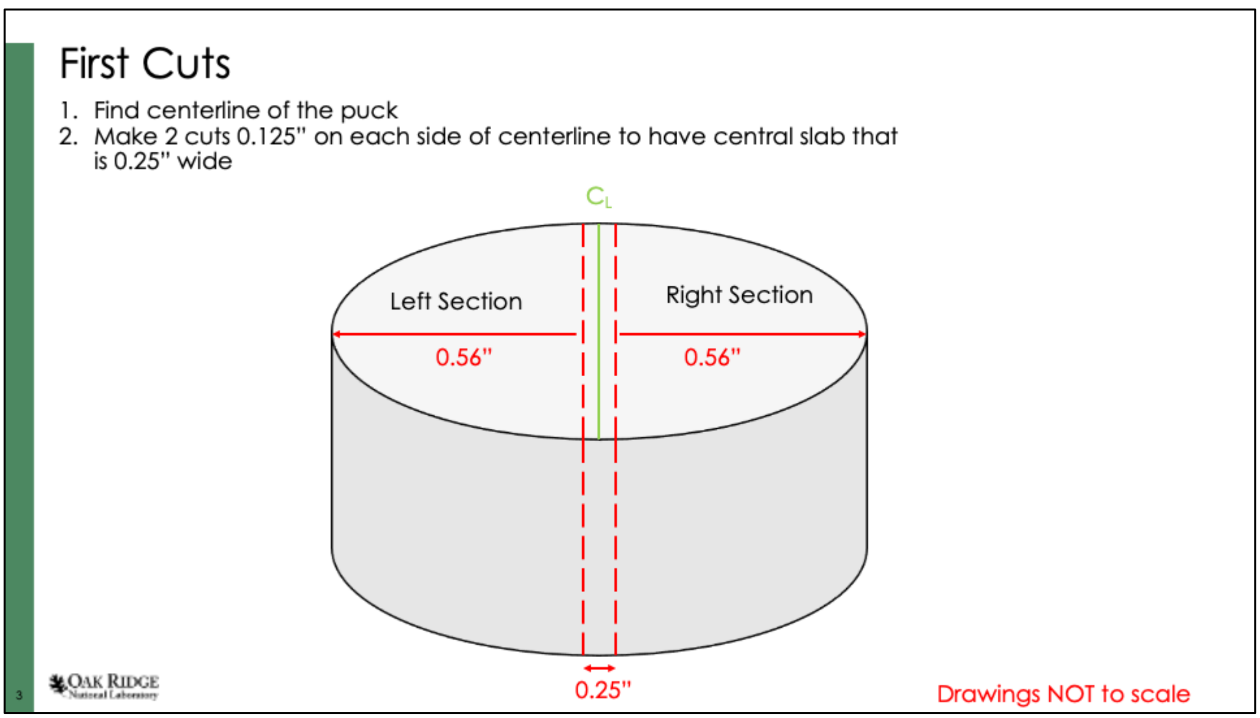

Figure 4. Preliminary sectioning of Be_2C puck.

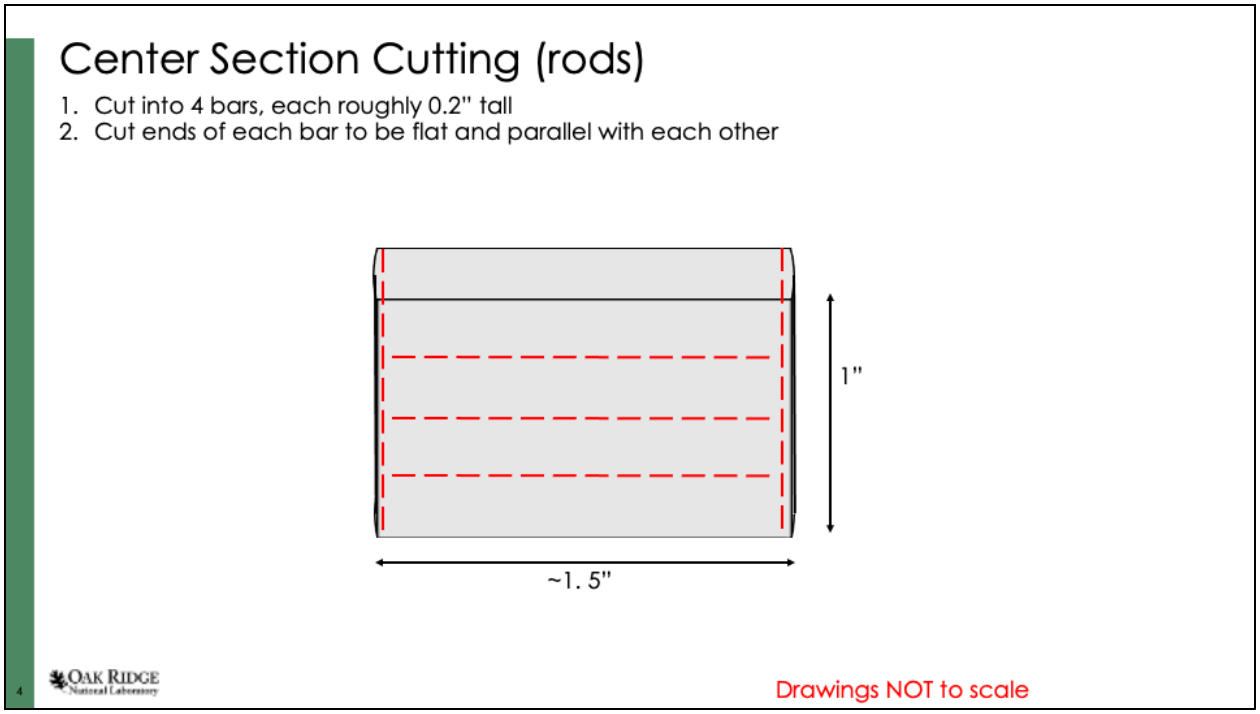

Figure 5. Cutting layout for rods with length parallel to puck diameter for coefficient of thermal expansion measurements.

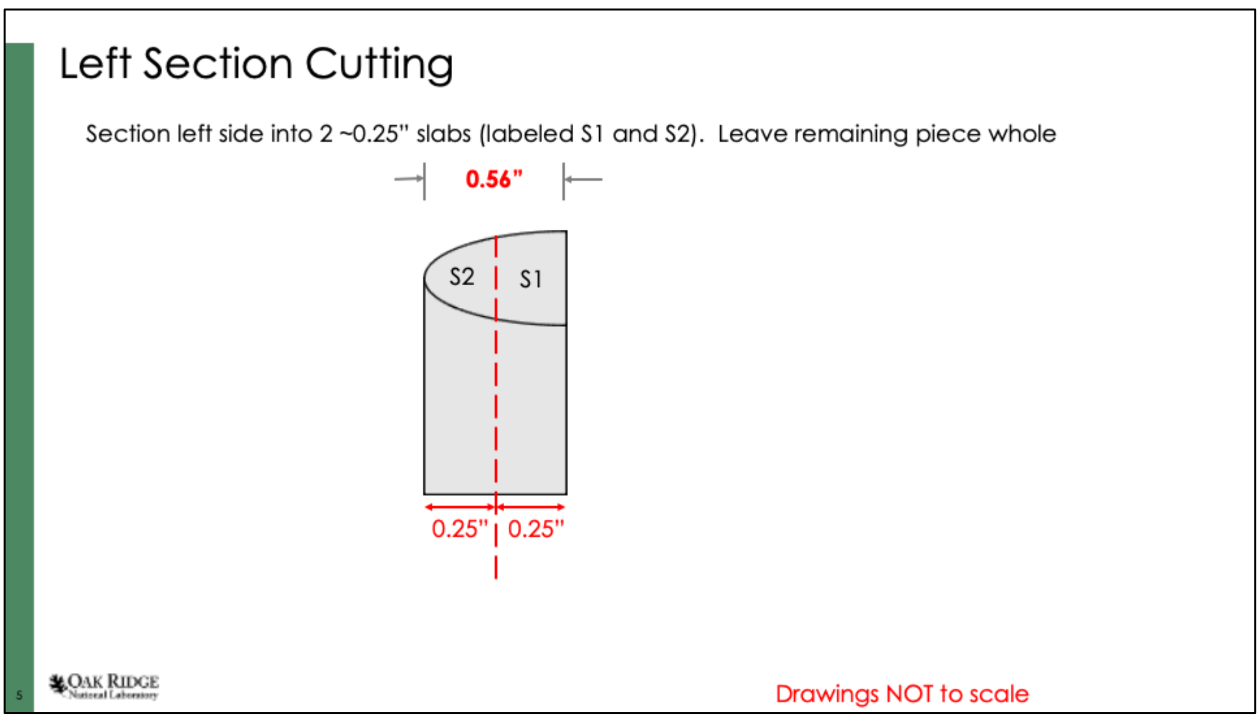

Figure 6. Sectioning of left portion of Be_2C puck.

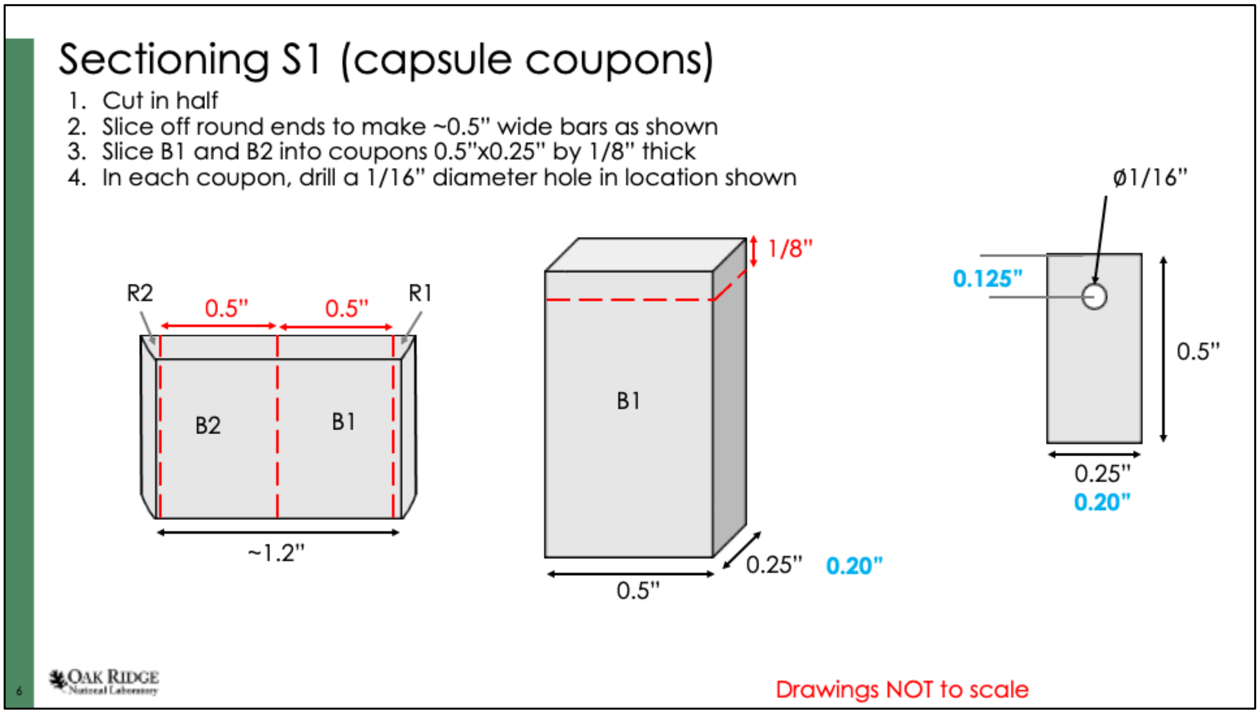

Figure 7. Cutting of coupons for high-temperature stability investigation.

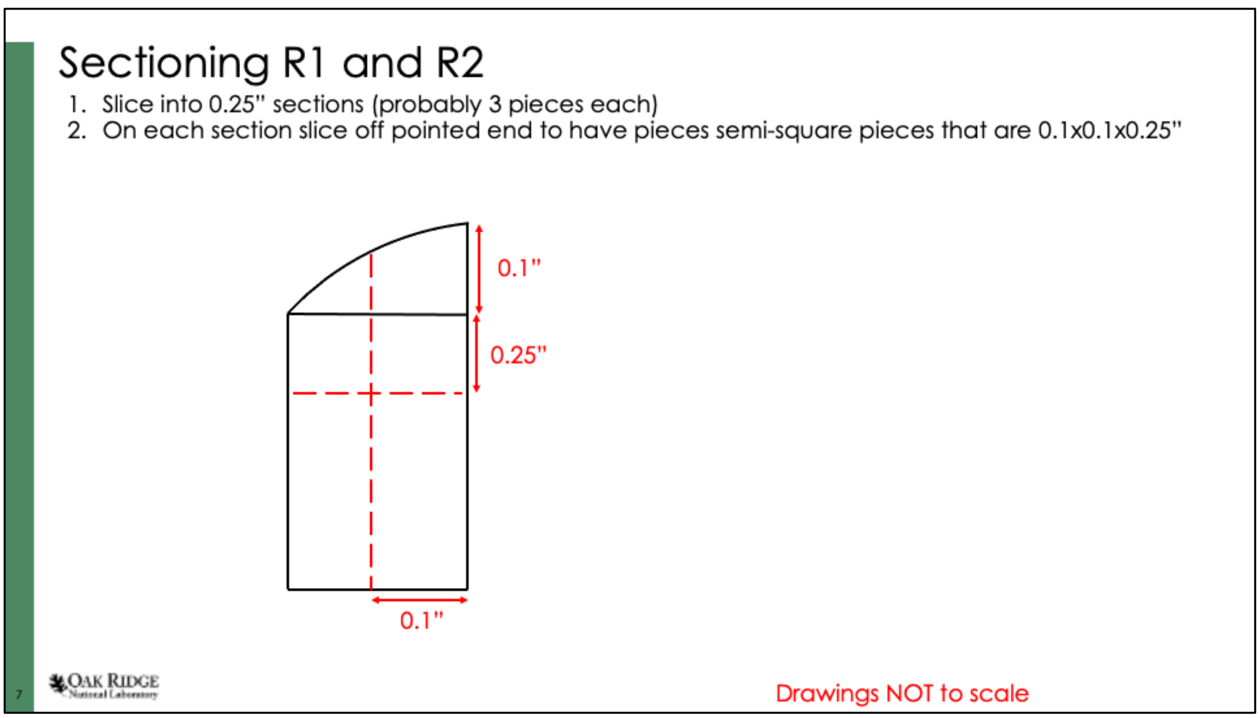

Figure 8. Cutting of specimens for skimmer efforts.

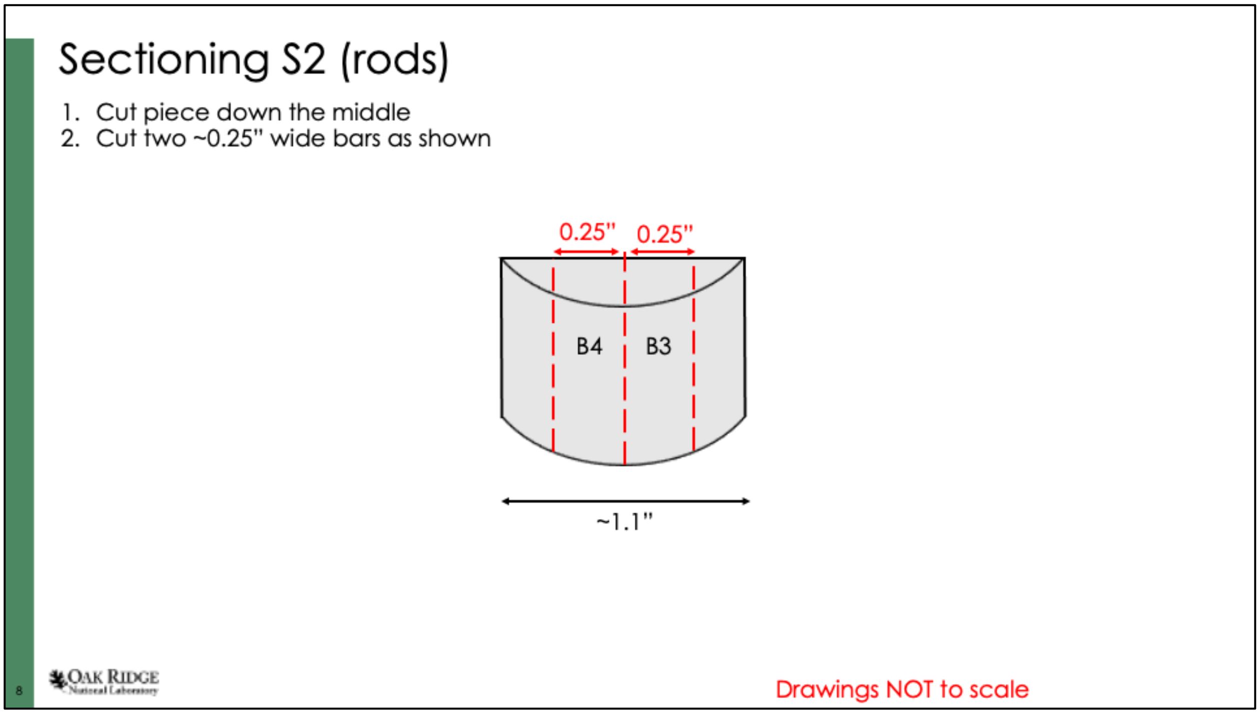

Figure 9. Cutting layout for rods with length parallel to puck thickness for coefficient of thermal expansion measurements.

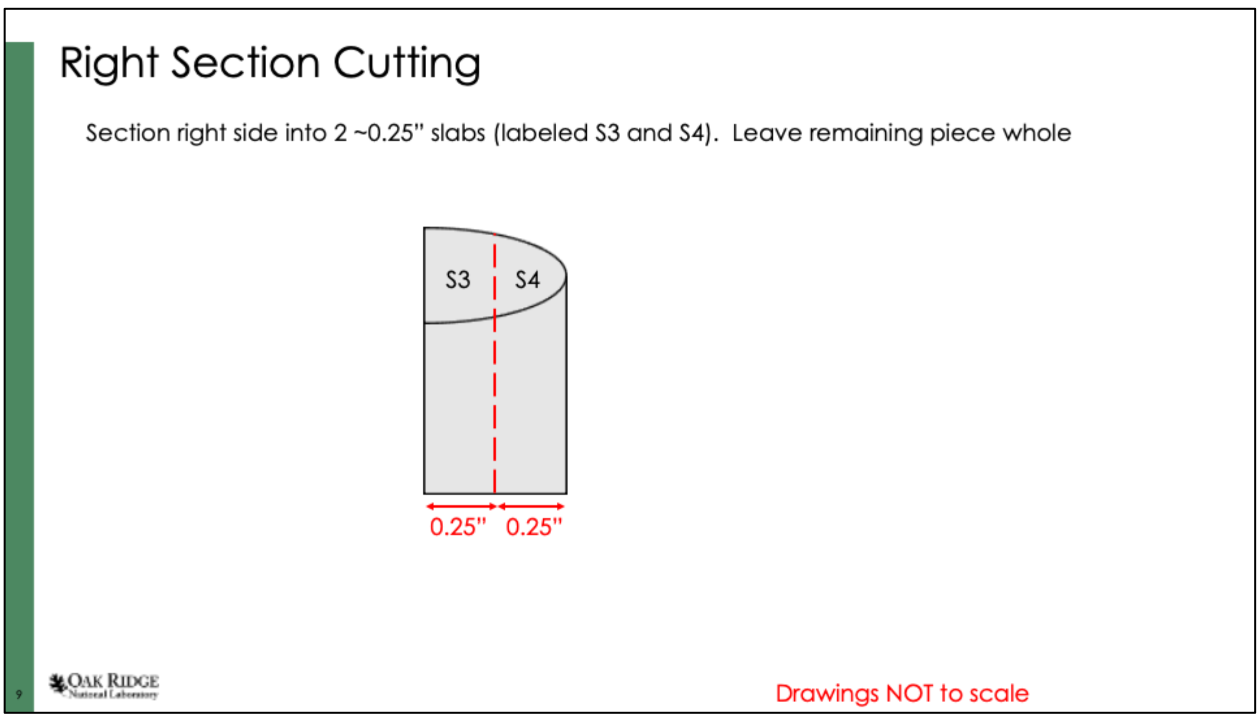

Figure 10. Sectioning of left portion of Be_2C puck.

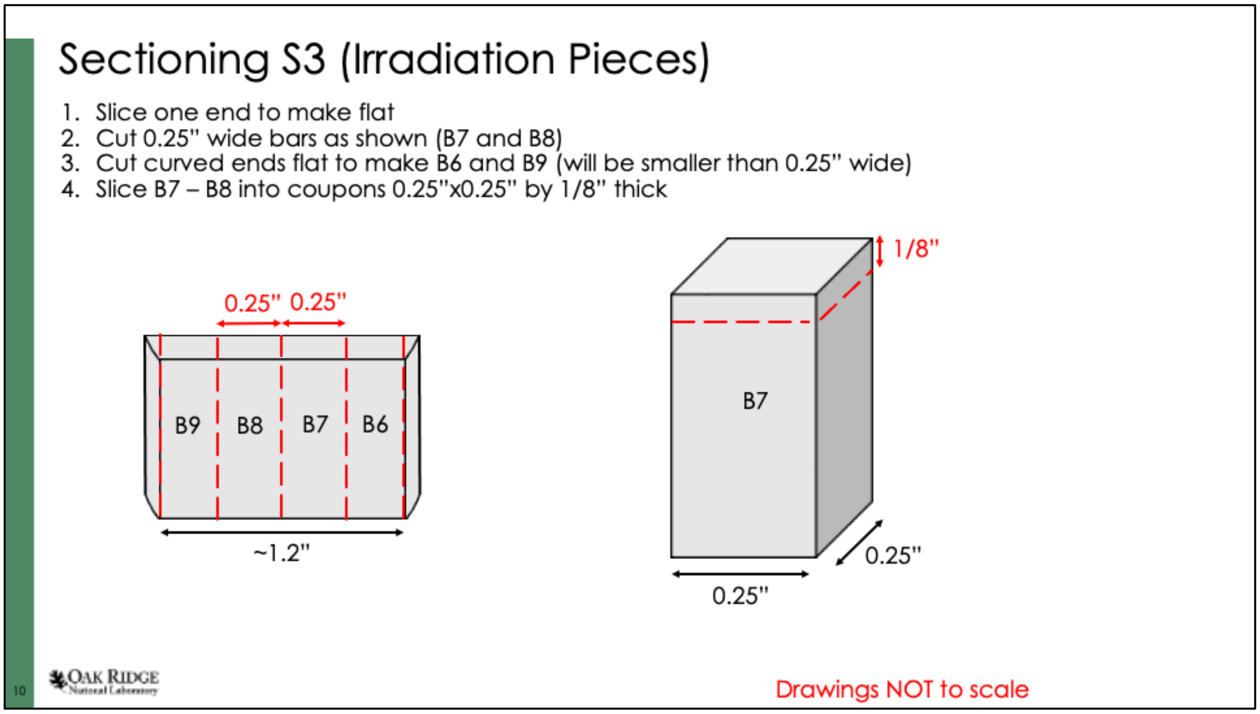

Figure 11. Cutting plan for Be_2C ion irradiation pieces.

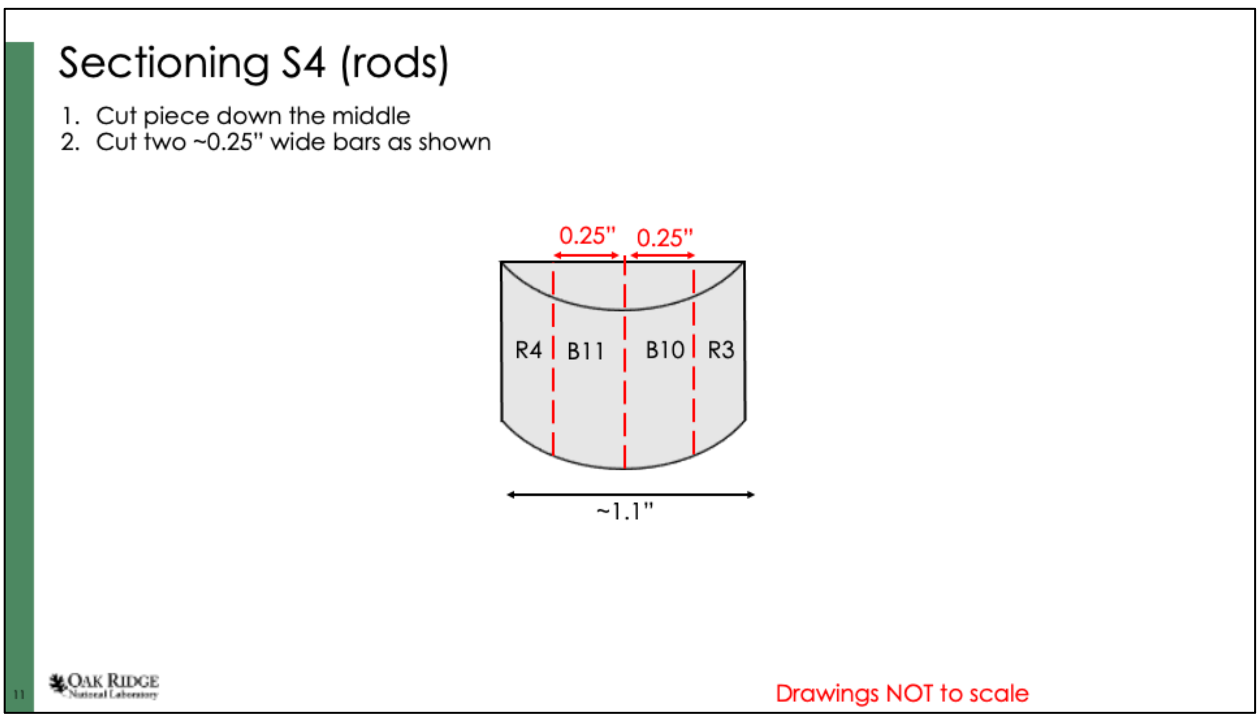

Figure 12. Remaining rod pieces with length parallel to puck thickness.

4. UNIVERSITY OF MICHIGAN EFFORT

Part of the effort in this initial program includes work being performed under the guidance of Prof. Stephen Raiman at UofM. This includes preliminary ion irradiation studies being performed in the Michigan Ion Beam Laboratory (MIBL), and some limited studies on the suitability of hot isostatic pressing (HIP) for forming solid pieces of Be_2C from high-purity Be_2C powder. The original proposal for this work included a $100k subcontract to UofM, which was initiated when the subcontract was awarded in January 2023.

4.1 PRELIMINARY IRRADIATION TESTING

In preparation for the Be_2C tests, two experiments were conducted with lithium oxide (Li_2O) ceramic samples. Li_2O and Be_2C both have a cubic crystal structure and high melting point. The similarities between the two materials allow for the same test parameters to be used and will give valuable feedback on unforeseen hurdles. The main objectives of the preliminary experiments were to choose reliable irradiation constants so that testing could begin as soon as the Be_2C were received.

For the first Li_2O experiment, a target 50 dpa was tested to mark the most damage that would be done. The accelerator proved capable of functioning for the full 69 hour duration along with a reliable source and heating element. The test did reveal that the samples were susceptible to breaking when loading on the stage. This is not acceptable as a fracture of the Be_2C samples could lead to inhalation of particles. To mitigate this, a containment system was designed to prevent this from happening in future tests. No other setbacks were encountered during the experiment. In the second preliminary experiment the irradiation was conducted to 5 dpa. The low damage level provided insight on the results of a quick experiment as opposed to one that is several days long. All parameters worked well with no major problems occurring during testing. All achieved parameters for both experiments can be seen in Table 1. Microscopy including SEM and TEM is planned for the irradiated samples with a large focus being gas generated threshold reactions.

Table 1. Achieved parameters from preliminary ion irradiation tests 1 and 2.

Parameters	Test 1	Test 2
Damage [dpa]	48.69	5.24
Damage Rate [dpa/s]	2.00×10^{-4}	3.31×10^{-4}
Temperature [C]	698.6 ± 3.3	698.0 ± 27.1
Current [nA]	0.244	0.251
Energy [MeV]	1.5	1.5
Time [hr]	69.50	4.58
Beam Area [cm^2]	0.25	0.25
Source	Oxygen	Oxygen

4.2 SAFETY AND CONTAINMENT

Major engineering safeties and procedures were developed for the Be_2C due to its toxic nature. Inhallation, ingestion and even skin contact can lead to chronic beryllium disease which can be fatal. A two-layer containment system was made to protect equipment and personnel from exposure along with a standard operating procedure for how to handle the samples.

The primary containment for the Be_2C will be a gold coating that covers the entire ceramic. Gold will not chemically interact with the sample making it favorable to use. Computational sputter calculations on

SRIM show that a 50 nm thick coating will be sufficient to stop any beryllium sputtering during an irradiation with 3 MeV carbon ions. Plans to conduct an irradiation with a gold coated Li_2O sample are underway to experimentally ensure that the coating will not sputter off and expose the sample.

A secondary containment was made as a failsafe in case the primary containment were to fail. It consists of three layers molybdenum that encloses the coated Be_2C sample in a set of boxex that remain in place during irradiation. Layer one serves as a thermal plate in contact with the heating element of the stage. It is thin enough to allow for proper heat transfer and strong enough to have a thermocouple welded on for monitoring during the experiment. Layer two is a holding plate that the sample will be placed in. The custom shape of the cutouts will allow for an even pressure to be applied to the Be_2C and decrease the chances of a fracture to occur. The final layer is a sputter plate that reduces the number of sputtered particles that are released inside the beamline. A small hole in this layer is the only area of the coated sample that is exposed while the test is in progress. The hole will allow for the ion beam to pass through the outer layers and hit the sample. If the sample were to break during an experiment, it would be contained within the molybdenum box with a minimized number of particles being released though the exposed area of the sputter plate. A full model of the containment can be seen on Figure 13.

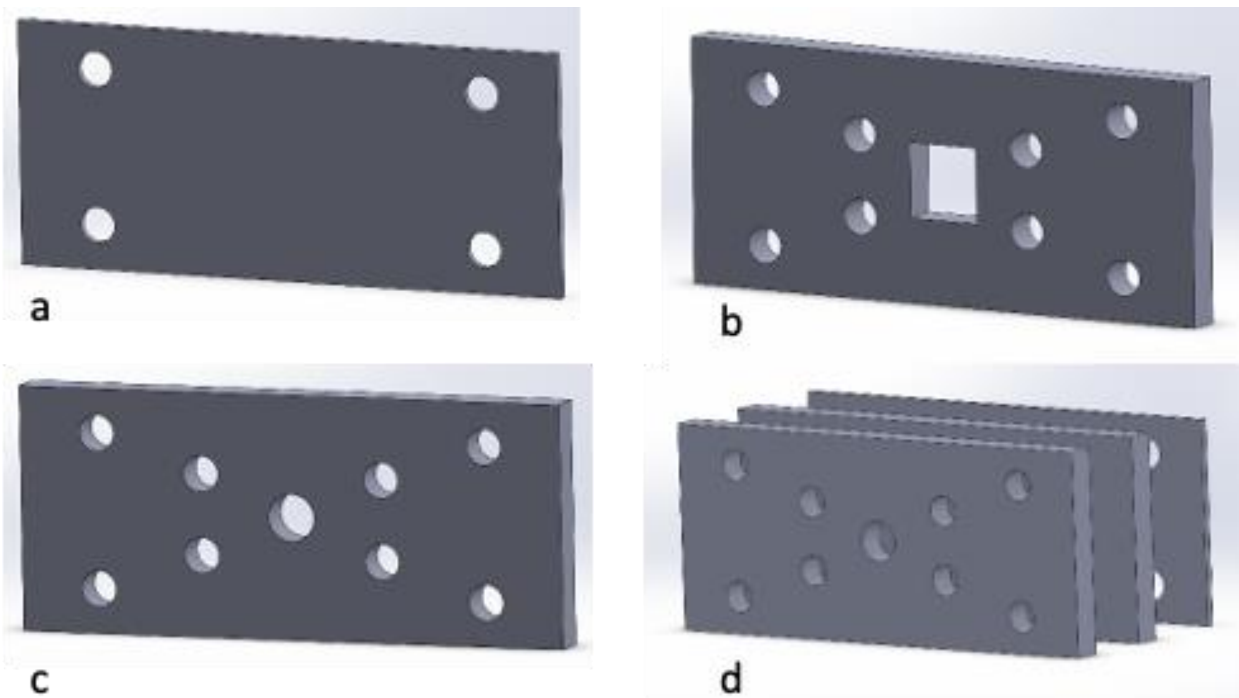

Figure 13. Three-layer physical containment system for Be_2C ion irradiation. (a) thermal plate that will sit between heating element and sample. (b) holding plate with center square cutout where the sample will sit. (c) sputter plate that will sit in front of the sample and define the irradiation area and reduce the amount of gold material that will sputter onto pieces of the vacuum chamber. (d) three plates sitting in order of assembly.

The secondary containment is designed to have a quick stage load process. The thermocouples will be welded and tested beforehand while thermal paste and containment assembly will be done in a glovebox. With most preparation steps done beforehand, the only required process will be to attach wires to the stage and screw all bolts in to place. This will reduce the time that the sample will be in exposed atmosphere and increase safety for all lab workers. Proper personal protective equipment will be utilized when loading and unloading the stage. This includes goggles, gloves, lab coat, and mask to minimize any contact. A blood test will be done before any experiments have been conducted to gather a baseline for beryllium levels. Monthly blood test will be done to check if exposure has occurred unknowingly to add another layer of safety. Swabs will also be done by Environmental Health & Safety (EHS) faculty at the University of Michigan to detect if particles were dispersed during operation.

4.3 FUTURE WORK

To experimentally conclude that the primary and secondary containment are effective, an irradiation will be conducted with both to see how they perform. A Li_2O sample will be coated with gold, heated in the vacuum chamber to 700°C and irradiated with a carbon beam to reach 50 dpa (the highest damage planned for Be_2C experiments). If the coating is too thin, a thicker coating will be applied and tested again until a sufficient thickness has been reached. With computational and experimental test concluding safe test parameters, Be_2C experiments will begin. Microscopy will be conducted before and after all irradiations to document changes that have occurred in the material. Methods for microscopy will include SEM before experiments and TEM/SEM after.

Long term work will include several irradiations of Be_2C samples starting with low doses followed by incremental changes. Solid samples will be irradiated first and continue to be the focus of experiments until installment of the Hot Isostatic Pressure (HIP) unit has been finished. Following this, manufacturing of Be_2C will be done along with irradiation of sintered samples. Be_2C and Be_2C-doped samples will be manufactured and tested with the same parameters to view any changes in behavior.

5. PLANNED ORNL WORK

The investigations at ORNL include multiple efforts to understand the properties of Be_2C on multiple fronts. The first effort will be to understand the thermal stability of solid Be_2C at relevant MSR temperatures. This will be accomplished by measuring the crystal structure of small coupons of Be_2C before and after high-temperature exposure in an inert atmosphere. Crystal structure measurements will be performed via X-ray diffraction (XRD). Kapton film/tape has been previously used for containment of irradiated materials for XRD measurements because it is an amorphous film which doesn't add additional peaks to the XRD spectrum. High temperature exposure of these samples will take place in the welded capsules that have been used for static materials and salt exposures within the MSR campaign, thereby utilizing safety practices that are already approved for this effort. After high temperature exposure the capsules will be opened, samples will be removed, wrapped in Kapton film, and then the XRD measurement will be remeasured.

Another effort at ORNL will be the preliminary steps for modeling interactions of various irradiation species with Be_2C. This process will begin *ab initio* with the development density functional theory (DFT) for atomistic evaluation of radiation defects in Be2C. Next molecular dynamic models will be used to model full collision cascades. Part of this process will require evaluation of the different interatomic potentials that have been developed to determine their suitability for irradiation interaction modeling. Modeling will then progress to kinetic Monte Carlo, which is suited for modeling defect behavior between collision cascades and on longer time scales. Later efforts will utilize cluster dynamics, discrete dislocation dynamics, and crystal plasticity to understand how larger features in Be_2C affects the response to irradiation damage and larger defect behaviors. One of the key modeling efforts will have to focus on the behavior of the gasses produced from neutron capture and transmutation (Figure 1) within the material.

The final effort at ORNL will focus on the degradation of Be_2C due to hydrogen exposure. Small pieces of Be_2C will be exposed to molten salts in a skimmer. This setup will allow for the controlled addition of fixed concentrations of hydrogen gas to quantify the rate of decomposition of Be_2C into methane. This will be a critical knowledge for future use in MSRs where hydrogen and tritium will be produced both by neutron capture in the solid Be, but also from capture within Be containing salts.

ORNL does not currently have equipment for measuring thermal properties of beryllium-containing materials. As such, this program is in discussions with Argonne National Laboratory (ANL) to perform coefficient of thermal expansion measurements on the bar specimens that are cut with their length both parallel to the diameter and parallel to the specimen thickness. This comparison will provide preliminary information about any processing-induced anisotropy. The agreement and subcontract to perform this work is not yet in place with ANL.

ACKNOWLEDGEMENT

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