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# Mechanofusion for Improved Control of Cermet TPBAR Pellet Microstructure

**October 2019**

JS Hardy  
GW Coffey

CA Coyle  
NL Canfield

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Pacific Northwest National Laboratory  
Richland, Washington 99352



## Purpose and Scope

Mechanofusion is an alternative fabrication technique that has the potential to advance cermet TPBAR pellets by producing  $\text{LiAlO}_2\text{-Zr}$  core-shell powders that will provide tighter control of targeted microstructural characteristics such as the presence and thickness of Zr surrounding every  $\text{LiAlO}_2$  particle in the cermet. Significantly enhanced microstructural control will translate to improved control of material properties and characteristics that affect the in-reactor performance of cermet TPBAR pellets. It was the intention of this work to demonstrate the efficacy of mechanofusion for producing precursor powders for TPBAR pellets, however materials procurement issues prevented this objective from being fully realized. In spite of these issues, in the short amount of time during which appropriate materials were available, it was demonstrated that mechanofusion does indeed have promise for producing the desired structures although the process yet requires optimization.



## Acronyms and Abbreviations

ATI	Allegheny Teledyne Inc.
SEM	scanning electron microscopy
TPBAR	tritium producing burnable absorber rod
URN	US Research Nanomaterials Inc.



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# 1.0 Introduction

Mechanofusion is a process technique that is being investigated for its capacity to produce  $\text{LiAlO}_2\text{-Zr}$  core-shell powders as precursor materials in the fabrication of cermet TPBAR pellets. This would provide tighter control of targeted microstructural characteristics such as the presence and thickness of Zr surrounding every  $\text{LiAlO}_2$  particle in the cermet. Significantly enhanced microstructural control would subsequently translate to improved control of material properties and characteristics that affect the in-reactor performance of cermet TPBAR pellets. By encapsulating individual  $\text{LiAlO}_2$  granules in a shell of Zr, mechanofusion increases the likelihood that the tritium produced by irradiation of the  $\text{LiAlO}_2$  is implanted directly into the Zr matrix in the TPBAR pellet. This will also provide the added benefit of preventing grains of  $\text{LiAlO}_2$  from becoming situated at the outer surface of the pellet as can occur in a pellet pressed from cermets made from a random mixture of two uncoated powders, thereby preventing exposed  $\text{LiAlO}_2$  grains from becoming a potential source of gaseous tritium release. The mitigation of  $\text{LiAlO}_2$  clustering in the cermet pellet will also facilitate improved sintering and pellet strength. Additionally, the uniform distribution of ceramic particles in the Zr matrix will allow higher ceramic loadings and may decrease the required sintering temperature. Not only will improved microstructural control improve pellet performance but will also make it possible to better correlate property measurements to microstructural characteristics for an improved understanding of fundamental materials science and chemical behavior. It will also increase confidence in determining and quantifying mechanisms associated with tritium behavior in the cermet and reduce uncertainties in assessing the microstructural evolution related to irradiation damage. Thus, the resulting data will provide more useful input for computational models, including improved models of cermet pellet performance.

As the name implies, mechanofusion is a process that mechanically bonds two materials together, specifically a finer guest, or coating, powder to the surface of a coarser host, or substrate, powder thus forming a core-shell powder. The process is performed in a mill that is similar in appearance to a high speed blender, except that the “blades” are shaped like paddles with press heads near the end that extend out near the walls of the container so as to shear the powder mixture between them. Another difference is that the container rotates as opposed to the paddles, creating a centrifugal force that forces the powder to the outer wall where it must pass between the press head and the wall. This shearing action fuses the smaller particles onto the surfaces of the larger particles to form a shell of some nominal thickness around them. The thickness can be controlled by varying the ratio of core to shell powders. Mechanofusion is most effective when the particle size of the coating powder is at least an order of magnitude smaller than that of the host powder, but this can vary depending on the selected materials. Figure 1 shows a rough representation of the mechanofusion process.

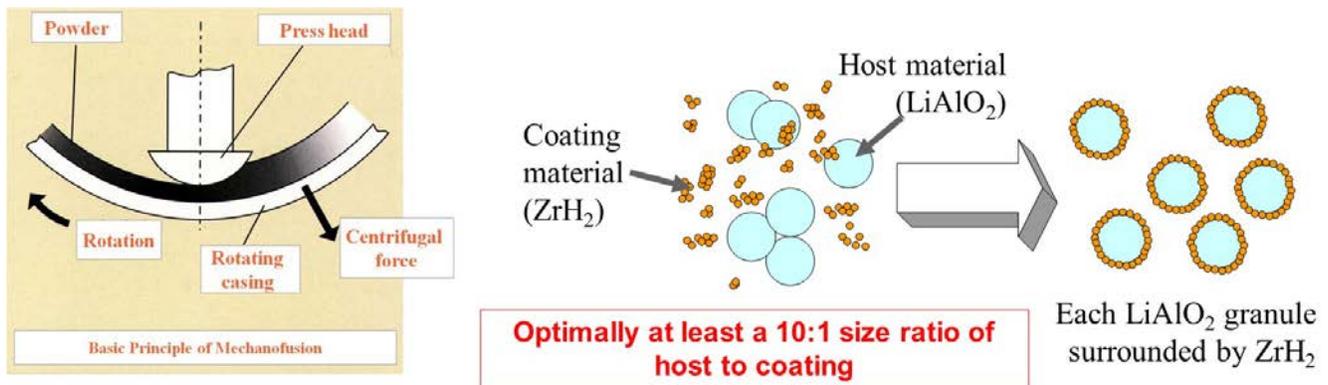


Figure 1. Schematic summary of the mechanofusion process.

The cermet microstructural design effort behind the cermet pellets that recently exhibited promising tritium retention in TMIST-3 tests [1,2] utilized the difference in penetration distances of tritium and helium to strike a balance between maximizing the direct implantation of tritium into the Zr matrix while minimizing implantation of He. It was thereby determined that a  $\text{LiAlO}_2$  particle diameter that is equal to the tritium penetration distance in  $\text{LiAlO}_2$  results in essentially all of the tritium implanting in the surrounding Zr, along with about a third of the He. A further increase in the  $\text{LiAlO}_2$  sphere size would slowly decrease the amount of He that implants in the Zr matrix but would also result in a rapid drop in the amount of tritium that implants in the Zr matrix. Based on the estimated transport distance of tritium in lithium aluminate,  $\sim 30 \mu\text{m}$  diameter spherical particles were targeted for  $\text{LiAlO}_2$ , which translated to a +25-32  $\mu\text{m}$  mesh size fraction. Meanwhile, the expected penetration distance of tritium into Zr indicated that any tritium escaping from the  $\text{LiAlO}_2$  spheres would implant within a  $19 \mu\text{m}$  shell of Zr around the  $\text{LiAlO}_2$  particles and the He would implant in a smaller shell of  $\sim 6 \mu\text{m}$ . An  $18 \mu\text{m}$  layer of Zr between each Li-containing particle was therefore recommended, which equates to  $9 \mu\text{m}$  around each  $\text{LiAlO}_2$  particle. By promoting direct implantation of tritium into the metal matrix, cermet pellets have the potential to simplify the TPBAR design by eliminating separate cracking and gettering components and lead to predictable and uniform distributions of tritium in the cermet.

## 2.0 Groundwork

### 2.1 Materials Procurement

The materials needed for this work were  $\text{LiAlO}_2$  granules on the order of  $30 \mu\text{m}$  in diameter and  $\text{ZrH}_2$  powder on the order of  $3 \mu\text{m}$  in diameter.  $\text{ZrH}_2$  is used because it is much more stable to work with in air at finer particle sizes than Zr metal powder. After mechanofusion, it would then be reduced to Zr metal in a separate step. It was found that a surplus supply of spray dried  $\text{LiAlO}_2$  granules with an average particle size of  $30.9 \mu\text{m}$  was already on hand at PNNL. The  $\text{ZrH}_2$  material was ordered from Allegheny Teledyne Inc. (ATI) because this was one of the  $\text{ZrH}_2$  suppliers used for the original cermet development project [3]. The timeline for procuring this material was as follows:

- Dec 13, 2018: Requested quote from ATI
- March 7, 2019: Quote received from supplier
- March 7, 2019: Requested chemical order be placed
- March 8, 2019: Was notified this order would require a PO
- April 9, 2019: PO was issued
- June 11, 2019:  $\text{ZrH}_2$  Arrives at PNNL

Although this prolonged timeline put the project far behind schedule, previous successes with mechanofusion of several other materials combinations provided confidence that this would not be an insurmountable delay. However, the powder was also found to be too coarse to coat the  $\text{LiAlO}_2$  granules because the wrong particle size was ordered. In scoping tests for the original cermet development project, -325 mesh  $\text{ZrH}_2$  powder was ordered from Chemetall Foote Corp. – Special Metals Division and this powder had a measured average particle size of less than  $3 \mu\text{m}$ , which was the size needed for coating the  $\sim 30 \mu\text{m}$   $\text{LiAlO}_2$  granules. Therefore, for the current project, this same powder specification (i.e. -325 mesh) was ordered without recognizing the fact that -325 mesh can include particle sizes up to  $44 \mu\text{m}$  in diameter despite the fact that the particle size had been much finer in a

previous lot. The material we received had a large fraction of particles in the 5-20 micron range, with the coarsest particles as large as 30-40 microns. Overall, the powder was too coarse for our mechanofusion process.

This sparked another search for a materials supplier able to supply  $ZrH_2$  with the required particle size on a much compressed timeframe as compared to the previous supplier. It was found that US Research Nanomaterials, Inc. (URN) offered a 1-5  $\mu m$   $ZrH_2$  powder. This time, a quote was requested and it was less than a week later that the material was received and ready to use. Unfortunately, it was found that once again, the powder was too coarse to be effective as the coating material in mechanofusion as can be seen in the micrograph in Figure 2.

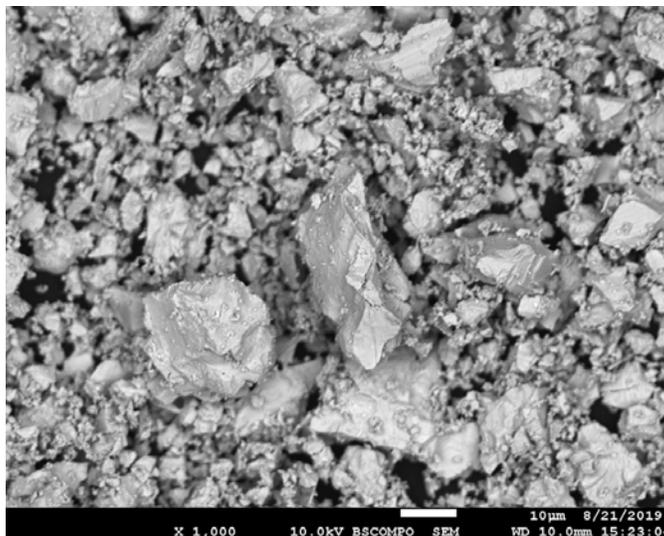


Figure 2. As-received 1-5  $\mu m$   $ZrH_2$  from US research nanomaterials.

The supplier was contacted with the micrograph above attached and notified that the material received did not fall within the advertised size range of 1-5  $\mu m$ . They promptly offered to exchange the powder for material they classified as 1-3  $\mu m$  while commenting that the micrograph was similar to their own micrographs of this product which indicate an average particle size of 5  $\mu m$ . It is apparent from the micrographs that the powder is very bimodal, containing a lot of fines mixed in with the large particles. With all of the fines included, it may very well average to a 5  $\mu m$  powder, but this is not what is generally considered a 1-5  $\mu m$  powder. In any case, the exchange was made very quickly, like the original shipment, but by this time, it was already September 4, leaving less than 4 weeks before the project deadline on September 30. But the material received in the exchange seems to be of an appropriate size for mechanofusion as will be discussed hereafter.

## 2.2 Capability Development

Prior mechanofusion work had only involved stable non-hazardous materials. While more stable the Zr metal powders, fine  $ZrH_2$  powders are still considered to be air- and water-reactive. Thus, in cooperation with the safety and health professionals at PNNL, the project team had to develop a protocol that would enable mechanofusion of reactive materials. This involved installing the mechanofusion mill inside an argon-filled glovebox and porting the cables and cooling lines into the glovebox. The mill requires an uncommon electrical outlet that had to be installed in the lab. Additionally, the mill normally operates with water cooling to keep the bearings from overheating. But because of the water-reactive nature of the  $ZrH_2$ , tests were performed to evaluate whether gas-cooling would be sufficient to replace water-cooling or if milling would have to be performed in intermittent segments with breaks in operation for cooling in between. Temperature monitoring near the bearings during

operation without water cooling indicated that 5 minute segments of operation should be followed by cooling breaks. This is not a significant hindrance to the process since milling generally takes only 5-30 minutes to reach completion. Figure 3 shows the mechanofusion mill set up for processing reactive materials in the glovebox.

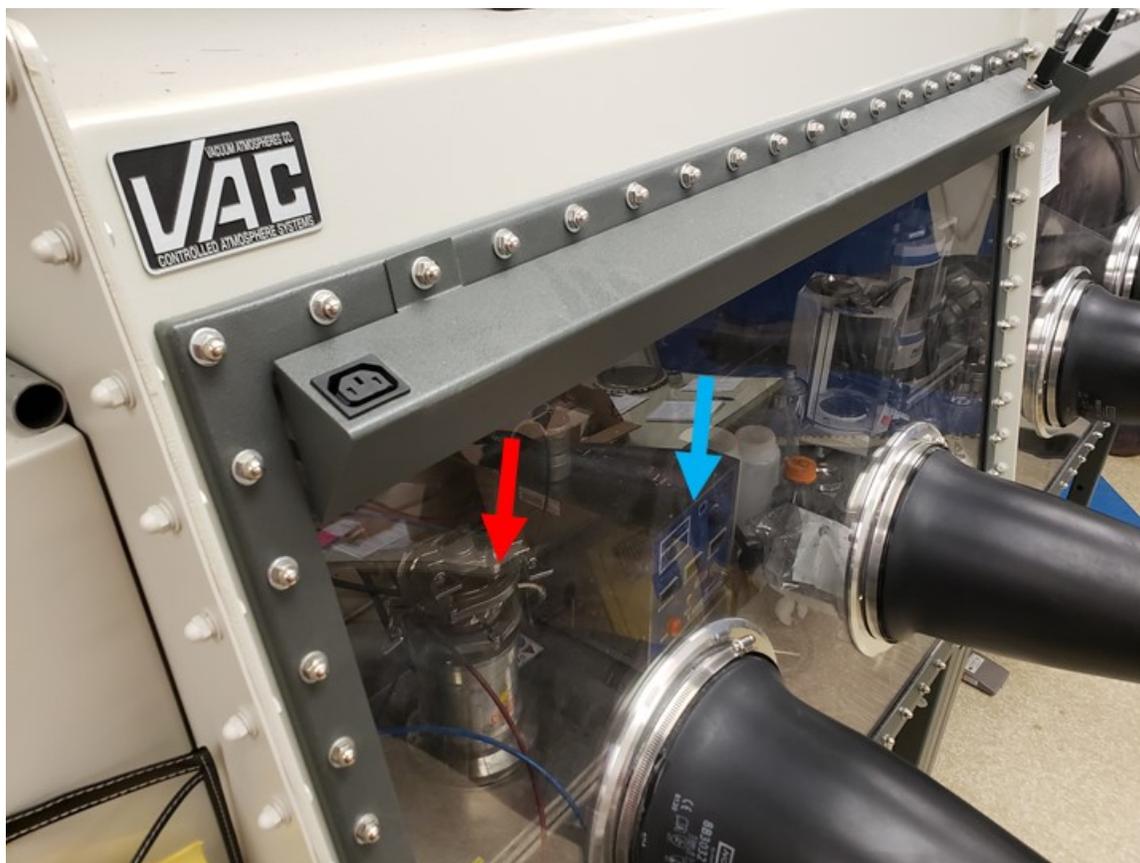


Figure 3. Installed in a glove box, the mechanofusion mill and control box are indicated with red and blue arrows, respectively.

## 3.0 Mechanofusion

### 3.1 Experimental

Prior to milling, the spray dried  $\text{LiAlO}_2$  granules were subjected to a final sintering at  $1265^\circ\text{C}$  for 4 h, followed by breaking up the sintered mass with a mortar and pestle and sieving to a size fraction of -230+500 mesh (i.e. 25-63  $\mu\text{m}$ ). The as-received  $\text{ZrH}_2$  was then manually mixed into the  $\text{LiAlO}_2$  at a mass ratio of between 3:1 and 3.5:1. This powder mixture was mill was placed in the mill and mechanofusion was performed at 3000-3500 rpm for times ranging from 5 to 25 minutes. The processed powder was removed from the mill, mounted in epoxy, and particles were cross-sectioned metallographically for inspection by SEM.

### 3.2 Results with -325 mesh $\text{ZrH}_2$ from ATI

SEM micrographs of a 3:1 mass ratio of -325 mesh  $\text{ZrH}_2$  from ATI to  $\text{LiAlO}_2$  mixture that was milled for 15 minutes are shown in Figure 4. It can be seen that the  $\text{ZrH}_2$  (lighter contrasting material) particle sizes are much

larger than required for coating the  $\text{LiAlO}_2$  (darker contrasting material). Their equivalent diameters should be no more than 10% of those of the  $\text{LiAlO}_2$  host material, but it is evident that the two materials are almost indistinguishable based solely on particle size. Thus, no significant degree of coating of  $\text{ZrH}_2$  on  $\text{LiAlO}_2$  was observed. The closest to the desired outcome is shown in Figure 5, but the coating layer was much thinner than the  $\sim 9\ \mu\text{m}$  anticipated. In many cases, it was found that some of the finer  $\text{ZrH}_2$  particles present in the mixture would be pushed into hollow granules of  $\text{LiAlO}_2$  as shown in Figure 6.

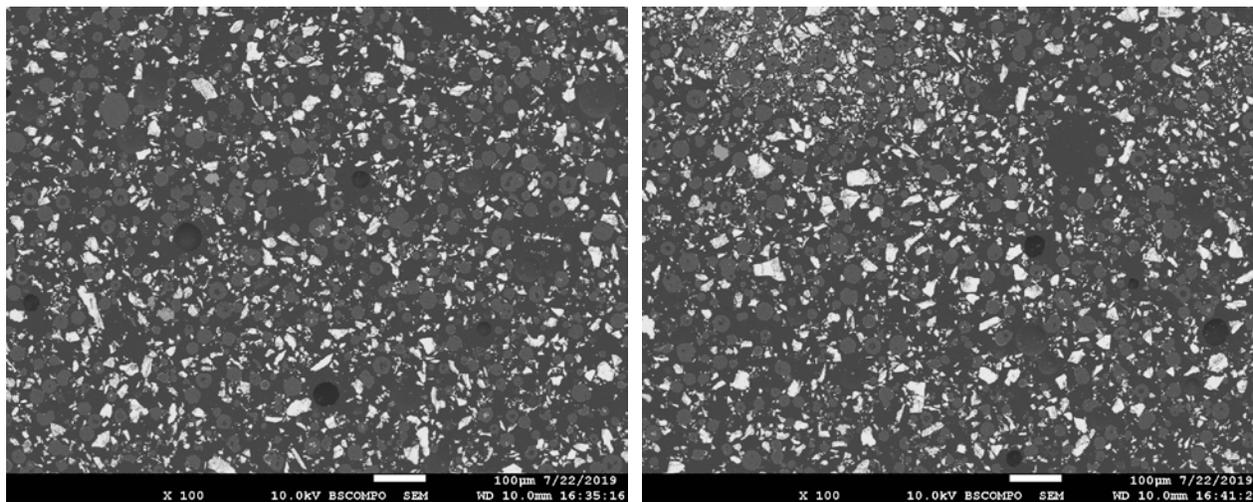


Figure 4. Micrographs of a 3:1 mass ratio of -325 mesh  $\text{ZrH}_2$  from ATI to  $\text{LiAlO}_2$  mixture that was milled for 15 minutes.

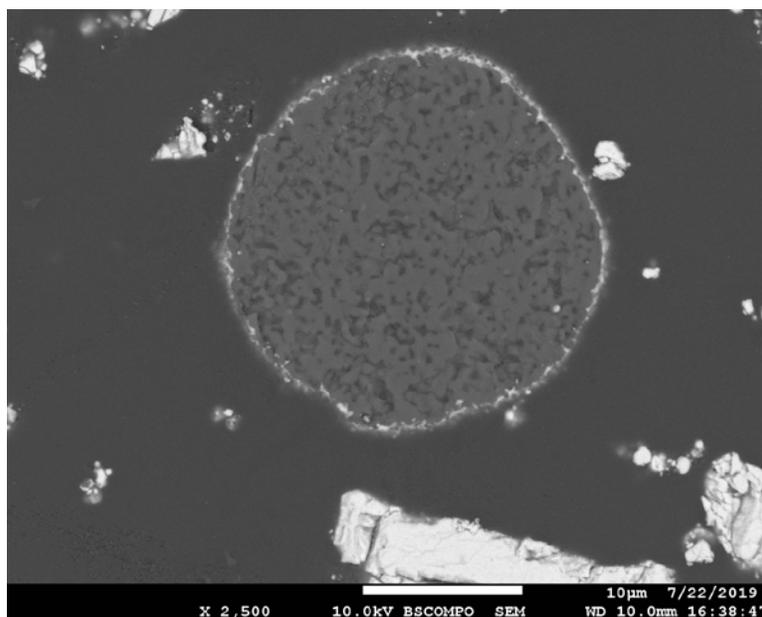


Figure 5. The best coating achieved with  $\text{ZrH}_2$  from ATI was much too thin.

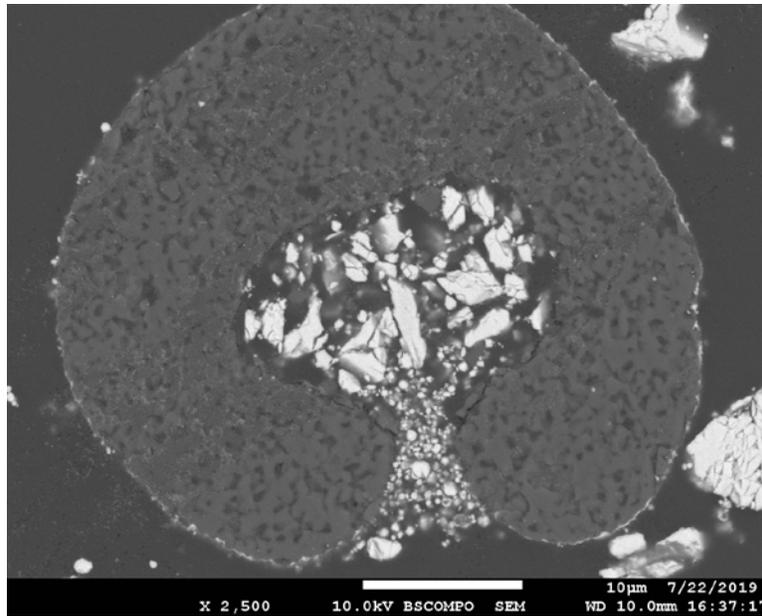


Figure 6. Finer particles of  $ZrH_2$  were pushed into hollow granules of  $LiAlO_2$  during mechanofusion.

### 3.3 Results with 1-5 $\mu m$ $ZrH_2$ from URN

Unfortunately, SEM micrographs in Figure 7 of a 3:1 mass ratio of the  $ZrH_2$  that was advertised to be 1-5  $\mu m$  from URN did not look altogether different from those using the ATI powder after 15 min of milling. Perhaps the lighter contrasting  $ZrH_2$  material was slightly finer than for the ATI powder, but not to the degree required for successful mechanofusion.

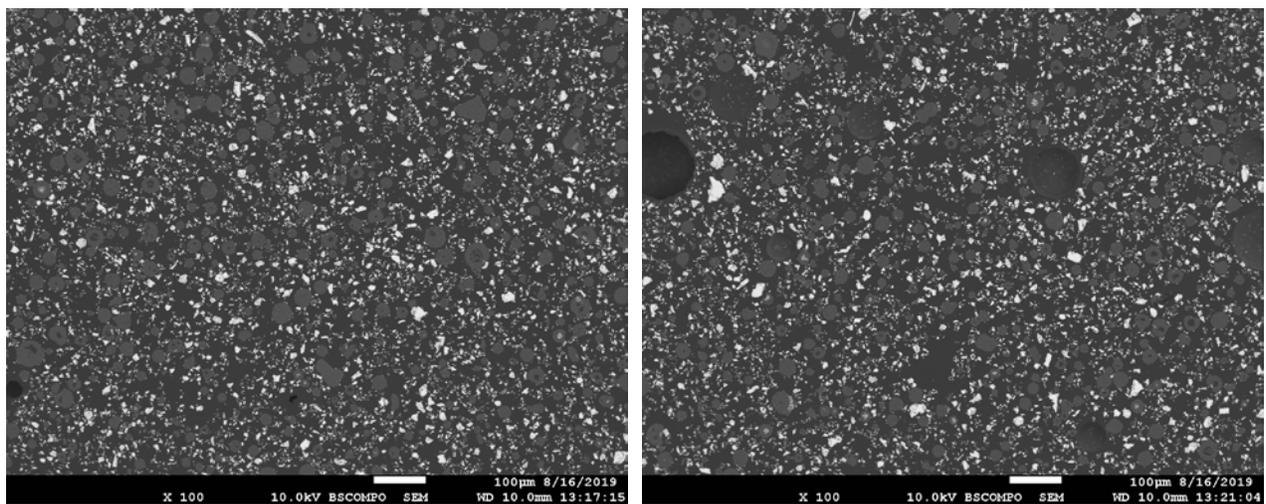


Figure 7. Micrographs of a 3:1 mass ratio of 1-5  $\mu m$   $ZrH_2$  from URN to  $LiAlO_2$  mixture that was milled for 15 minutes.

### 3.4 Results with 1-3 $\mu\text{m}$ $\text{ZrH}_2$ from URN

Although the 1-3  $\mu\text{m}$   $\text{ZrH}_2$  from URN arrived with less than 4 weeks left on the project and the end of fiscal year queue for SEM sample preparation and analysis is long, samples were processed and analyzed with SEM before the project ended. This was fortuitous because the micrographs in Figure 8 of 3.5:1  $\text{ZrH}_2$  to  $\text{LiAlO}_2$  by mass milled for 25 minutes show evidence that with properly sized powders, mechanofusion shows promise for producing the core-shell structures desired for cermet TPBAR pellets. While further work is needed to optimize the materials ratios and processing parameters to achieve higher fractions of coated particles and controlled coating thicknesses, it was demonstrated that mechanofusion has potential for producing precursor powders that will enable increased microstructural control in  $\text{Zr-LiAlO}_2$  cermets.

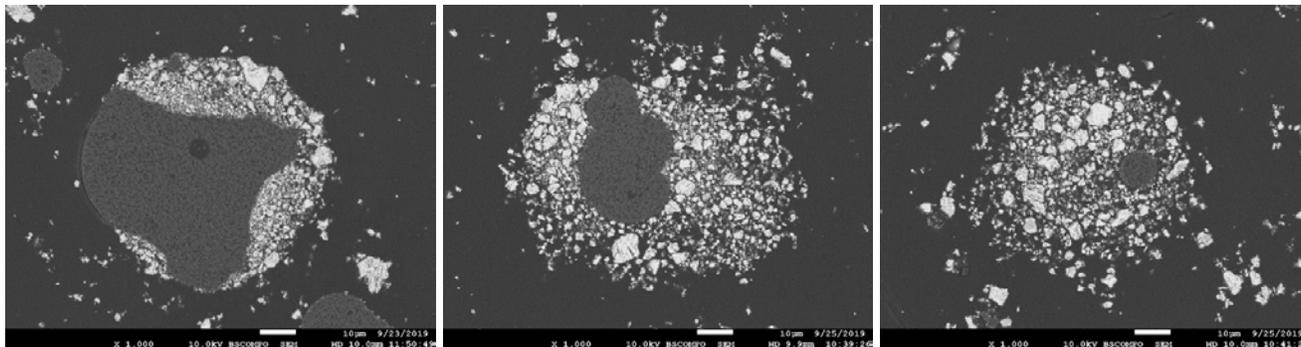


Figure 8. Micrographs of a 3.5:1 mass ratio of 1-3  $\mu\text{m}$   $\text{ZrH}_2$  from URN to  $\text{LiAlO}_2$  mixture that was milled for 25 minutes.

## 4.0 Summary

Capability has been established for performing mechanofusion with reactive materials.

In spite of materials procurement issues causing significant delays, a suitable powder has been obtained and with it, a path forward has been demonstrated showing the potential for mechanofusion to produce  $\text{LiAlO}_2$ - $\text{Zr}$  core-shell precursors for fabrication of cermet TPBAR pellets with improved microstructural control.

## 5.0 Future work

As mentioned above, although evidence of a path forward has been demonstrated, additional work is needed to optimize the particle coatings and determine the fraction of coated particles attainable using this technique. Future work should also include characterization of sintered cermet compacts fabricated using mechanofused precursor powders.

## 6.0 References

[1] M.R. MacDougall, B.A. Collins, T.M. Brewer, D.J. Senior, and W.G. Luscher, Tritium Technology Program TMIST-3A Cycle 161A Data Report, TTP-8-010, Rev. 0.

[2] M.R. MacDougall, B.A. Collins, T.M. Brewer, D.J. Senior, and W.G. Luscher, Tritium Technology Program TMIST-3A Cycle 162A Data Report, TTP-8-018, Rev. 0.

[3] L.M. Bagaasen, R.O. Gates, B.R. Johnson, J.S. Hardy, and D.J. Senior, Tritium Technology Program Cermet Pellet Development Report, TTP-6-008, Rev. 0.





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