Technology Enabling Zero-EPZ Micro Modular Reactors

Milestone M2.2.1

Stability of Zirconium Hydride

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SUMMARY

This reports complete Milestone M2.2.1 *Stability of zirconium hydride*: Experimental investigation of the hydrogen concentration of encapsulated zirconium hydride before and after joining.

In this milestone, we first report the successful fabrication of crack-free bulk zirconium hydride by using the ORNL static hydriding system. The fabricated hydride was characterized by using X-ray diffraction (XRD) and X-ray computed tomography (XCT). XRD results showed that the δ-phase zirconium hydride, α-zirconium, and ε-phase hydride were present. XCT confirmed the absence of the internal cracking. The hydrogen concentration was determined by the weight change before and after hydrogen loading, given the fact that the oxide phase was not found during XRD analysis. Two metallic cladding materials, i.e., molybdenum and FeCrAl, were selected to encapsulate the fabricated zirconium hydride pellets. Demonstration capsules were designed and machined. Mo crucible was successfully sealed by using a combination of electron beam welding and gas tungsten arc welding. Due to the undesired neutronics property of Mo, further investigation of this cladding material was not pursued. Electron beam welding and laser beam welding were employed to seal the FeCrAl capsules. XRD were performed on the zirconium hydride before and after the sealing. The results showed that the welding process has negligible impact on the hydrogen content in the FeCrAl-canned zirconium hydride. The presented work fulfilled the proposed work under this milestone and paves a pathway to fabricate single-phase zirconium hydride and to develop robust cladding materials to can bulk zirconium hydride.

CONTENTS

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ACRONYMS

ARPA-E	Advanced Research Projects Agency-Energy
BCC	Body-centered cubic
EBW	Electron beam welding
FCC	Face-centered cubic
GTAW	Gas tungsten arc welding
H	Hydrogen
HCP	Hexagonal closest packed
LAMDA	Low activation materials development and analysis
LCAC	Low carbon arc cast
LW	Laser Welding
MEITNER	Modeling-Enhanced Innovations Trailblazing Nuclear Energy Reinvigoration
Mo	Molybdenum
ORNL	Oak Ridge National Laboratory
XCT	X-ray computed tomography
XRD	X-ray diffraction
Zr	Zirconium

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1 Fabrication of crack-free zirconium hydride

1.1 Introduction

Metal hydrides are particularly well suited to thermal reactor system in which core weight and volume need to be minimized, where they serve as a constituent in fuels and in moderator and shield materials. Given that zirconium has very low neutron absorption cross section, zirconium hydride is particularly attractive for the high-performance moderator application. There is a need for thermally and chemically stable zirconium hydrides. It is well known that the common method of preparing metal hydrides is by direct reaction of the metal with hydrogen, guided by the phase diagram and the pressure-composition-temperature relationship. The reaction of hydrogen with the metals (e.g., Zr, Y, Ti, Th) is a diffusion-controlled exothermic process that normally results in expansion of the metal lattice as the hydrogen enters portions of the lattice. This gives rise to a substantial decrease in density and represents a significant volume expansion during the hydriding process (e.g., 17% in the case of ZrH_2). Such changes produce severe stresses in the massive metal hydrides since the diffusive nature of the hydriding process results in a large hydrogen concentration gradient. During the hydriding process, a hydride case forms on the surface and hydrogen is in solid solution in the interior of the specimen. At the interface between the hydride case and the interior, the growth accompanying hydride formation generates stresses that can easily exceed the fracture strength of the hydride and cause extensive cracking. Therefore, to prepare massive single-piece forms of metal hydride forms, this cracking must be avoided—which is challenging [1] [2].

In this report, we first summarize our efforts to develop the capability to fabricate crack-free zirconium hydride.

1.2 Thermodynamics of the Zr-H binary system

The zirconium-hydrogen (Zr-H) binary phase diagram and the pressure-composition-temperature relationship are the two most important pieces of information needed to guide the fabrication of crack-free zirconium hydride. Figure 1 shows the phase diagram for Zr-H system. The zirconium hydrogen solid solution (α and β phase), the δ phase-hydride, and the ε phase-hydride are present. In the α-phase region, the hydrogen atoms reside in the lower energy tetrahedral interstitial sites of the hexagonal closest packed (HCP) zirconium lattice (a=0.32333nm, c=0.51523nm). The β phase at high temperature has a body-centered cubic (BCC) crystal structure with a lattice parameter of 0.3614nm. The δ phase-hydride has a face-centered cubic (FCC) crystal structure (a=0.4779nm) with a CaF_2 prototype structure (space group: Fm-3m). In the ε phase region, hydrogen atoms occupy all available interstitial sites in the HCP structure of ZrH_2 (a=0.35179nm, c=0.4779nm).

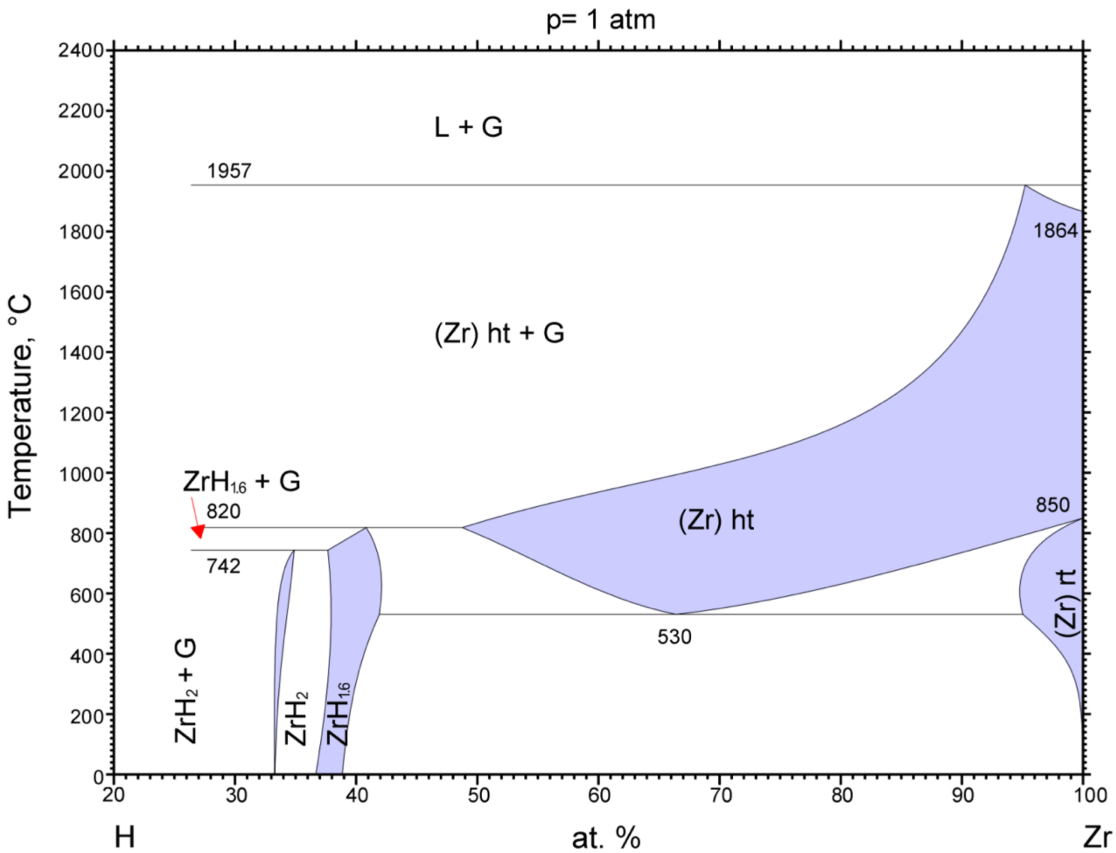


Figure 1. Phase diagram of Zr-H system

The equilibrium hydrogen pressure as a function of temperature and H/Zr ratio was also established, expressed by Eq. (1), where C is the H/Zr atomic ratio [3].

$$p_{\mathrm{H_2\text{-}eq}}\ [\mathrm{MPa}] = \left(\frac{C}{2-C}\right)^2 \exp\left(5.72 + 5.21C - \frac{172\ [\mathrm{kJ\ mol^{-1}}]}{RT\ [\mathrm{K}]}\right) \tag{1}$$

1.3 Hydriding process

As stated in the Introduction, fabrication of metal hydrides is achieved through the direct reaction of metals and hydrogen at high temperature. Zirconium hydrides with desired H/Zr atom ratios may be fabricated in a variety of ways, e.g., by introducing measured amount of hydrogen into small-volume retorts or by carefully matching retort temperature and hydrogen pressure. In the current work, the first method was employed.

A hydriding system (Figure 2) with an ultra-high vacuum level of 1×10^{-7} torr was established by modifying the permeation testing station [4] located at the ORNL Low Activation Materials Development and Analysis (LAMDA) laboratory for the fabrication of zirconium hydride. The maximum temperature of the furnace in this system is 1100°C. A quartz retort was used to minimize the permeation of hydrogen at elevated temperatures.

The most significant challenge in fabricating massive crack-free bulk metal hydride is that the hydrogen concentration gradient across the sample body resulting in differential strain and stress, and ultimately may result in cracking. The prevention of cracking then would appear to be clearly a matter of preventing large concentration gradients within the sample. Therefore, hydriding was initiated at the desired final equilibration temperature; but the rate of hydriding at said temperature was limited to allow more time for hydrogen redistribution (via bulk diffusion process) within the workpiece and thus avoid an adverse hydrogen concentration gradient in the sample. Uniformity of retort temperature is generally of primary importance in producing sound massive metal hydrides with uniform hydrogen/metal atom ratios.

A typical example of the use of the hydriding system is described as follows. A metal zirconium sample is cleaned and then inserted to the quartz tube. After the system is evacuated to a vacuum level of 1×10^{-7} torr, the metal zirconium sample is heated in vacuum to a high temperature for a couple of hours. This high temperature is maintained in the subsequent hydriding process. Then a predetermined amount of hydrogen, corresponding to the wanted H/Zr atom ratio of final ZrH_x product, is introduced to the quartz tube at a slow flow rate. Following the consumption of hydrogen, when the equilibrium hydrogen pressure is established in the system, additional annealing time is applied to ensure the homogeneous distribution of hydrogen within the sample. The hydride sample is extracted following a rapid temperature decrease of the system.

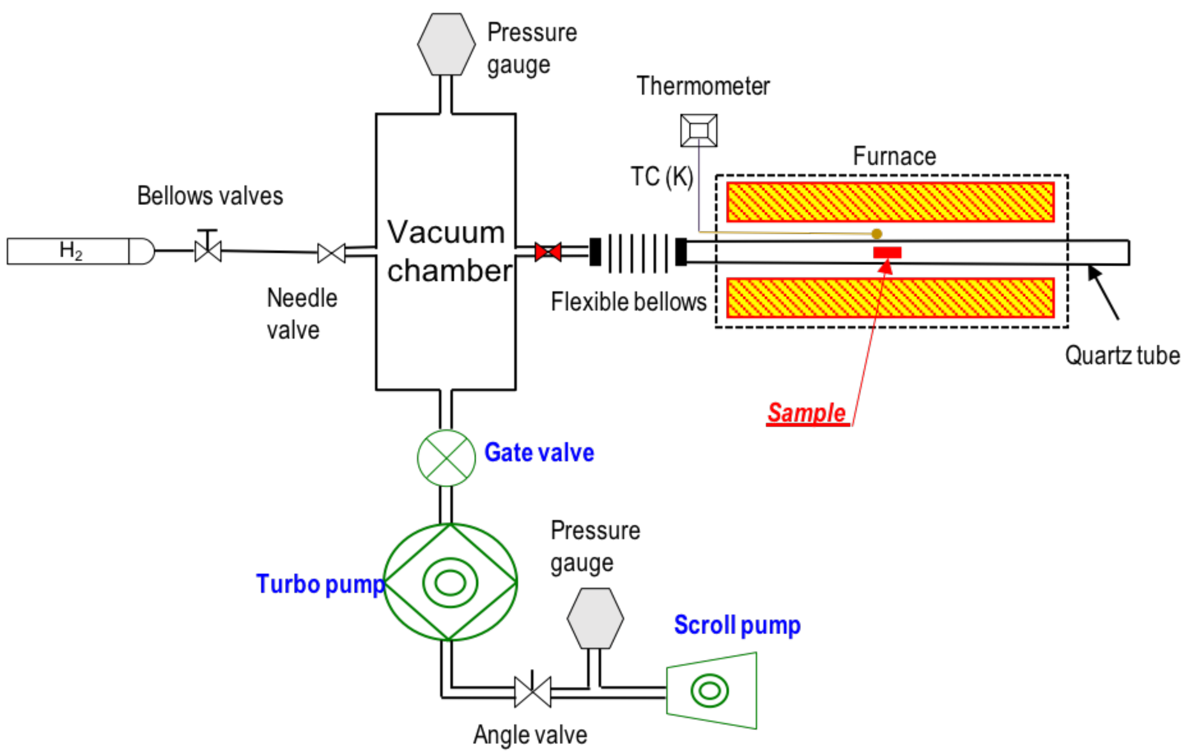


Figure 2. Schematic plot of the static hydriding system.

1.4 Crack-free zirconium hydrides

Following the above-mentioned fabrication procedure, we have successfully fabricated crack-free zirconium hydride pellets through carefully controlling the hydrogen flow rate. The starting material is zircaloy-4 rod with a diameter of 10 mm and a height of 20 mm. Figure 3(a) shows the picture of 3 zirconium hydride rods with H/Zr atom ratios of 1.352, 1.575, and 1.609, respectively. No visible cracking was observed on the surfaces. We also demonstrated the fabrication of crack-free large zirconium hydride rods with H/Zr ratio of 1.56 and 1.60, respectively, as shown in Figure 3 (b). The hydrogen content of the as-fabricated zirconium hydride samples was determined based on the weight change, which was assumed to be due to the absorption of hydrogen during the hydriding process.

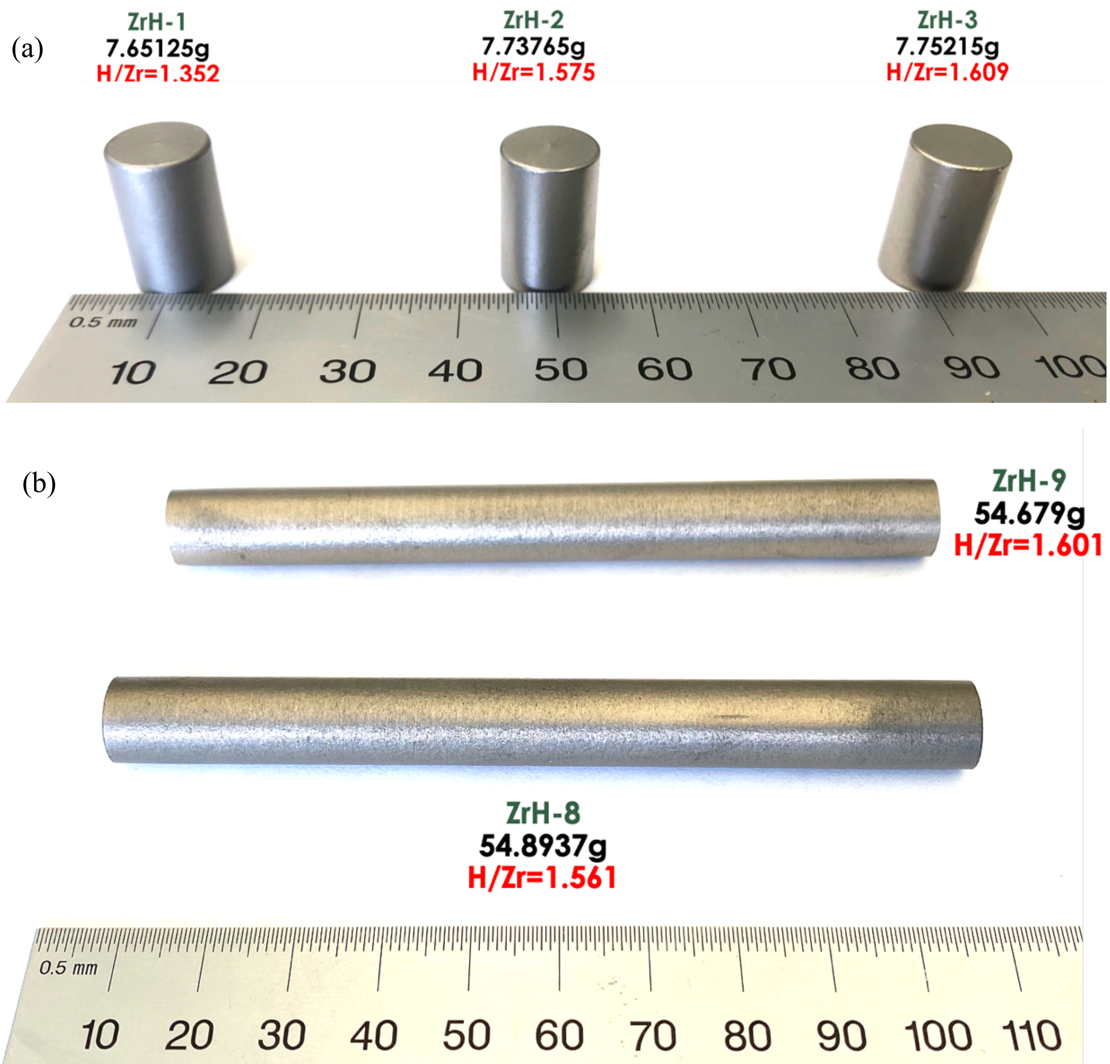


Figure 3. As-fabricated (a) zirconium hydride pellets and (b) long rods by using the ORNL hydriding system.

Table 1 lists the weight change and the calculated H/Zr atom ratio of eight ZrH_x pellets. LECO oxygen and hydrogen analyzer was initially planned to directly measure the hydrogen concentration in as-fabricated hydrides. However, the detection limit of LECO is 2000ppm for 1 g sample. Even when we reduced the weight of the testing sample to be 0.05g, the significant amount of released hydrogen saturated the non-dispersive infrared detector and yielded the unphysical outputs. Therefore, we will use the H/Zr atomic ratio obtained based on the weight change throughout this report.

Table 1. ZrHx fabricated by using the ORNL hydriding system

Sample	Weight of starting yttrium metal (g)	Weight of as-fabricated ZrH_x (g)	Absorbed H amount (mol)	H/Zr atom ratio
ZrH-1	7.65124	7.76326	0.11202	1.352
ZrH-2	7.73765	7.86965	0.132	1.575
ZrH-3	7.75215	7.88726	0.13511	1.609
ZrH-4	5.76820	5.85348	0.08528	1.365
ZrH-5	5.77184	5.85940	0.08756	1.401
ZrH-6	5.79036	5.87806	0.0877	1.398
ZrH-7	53.9813	54.8937	0.9124	1.561
ZrH-8	53.7468	54.6790	0.9322	1.601

No surface cracking was observed on the as-fabricated ZrH_x pellets. X-ray computed tomography (XCT) was employed to investigate any possible internal cracking of the fabricated zirconium hydrides. XCT measurements were conducted using a ZEISS Metrotom M800 (200 kV/14 W power). A single scan (1 hour) was conducted to evaluate the whole volume of the specimen. The resolution varies from 9~13 voxel size. Figure 4 shows the XCT images of ZrH-2 with a H/Zr atom ratio of 1.575. No internal cracking was observed in the studied materials.

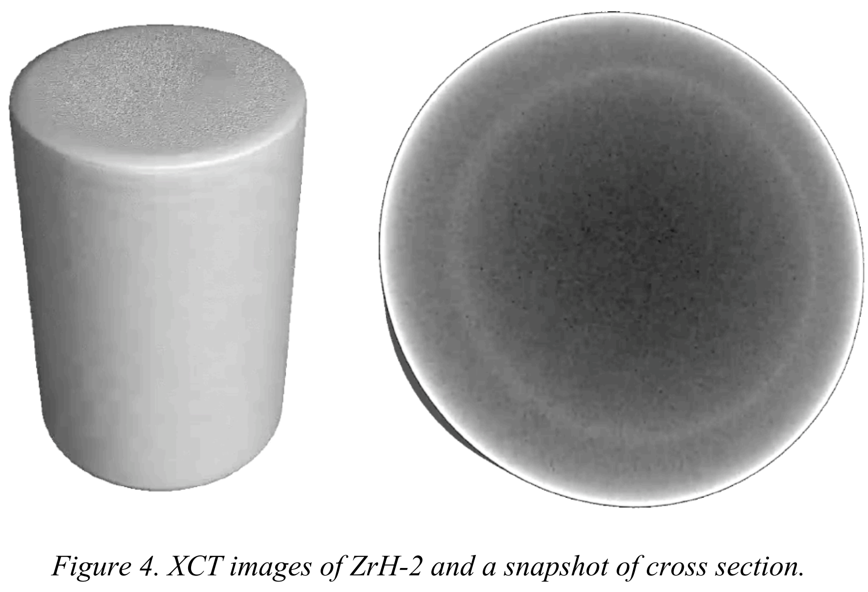


Figure 4. XCT images of ZrH-2 and a snapshot of cross section.

X-ray diffraction analysis was employed to confirm the phases present in the fabricated hydride samples. XRD samples were prepared by depositing ZrH_x powder on a low-background silicon single-crystal sample holder. Samples were also mixed with lanthanum hexaboride (LaB_6) powder, used as an internal standard during pattern refinement. High-resolution diffraction patterns were obtained using a Bruker D2 Phaser benchtop X-ray diffractometer of 0.30 kW with Cu Kα radiation. Rietveld refinement was performed on the experimental patterns using General Structure Analysis System [5]. XRD analysis of ZrH-2 (Figure 5) indicated that both epsilon-phase and delta-phase hydride present in the fabricated hydride rod. More efforts are needed to fabricate single phase zirconium hydride, which will be reported in the next milestone report.

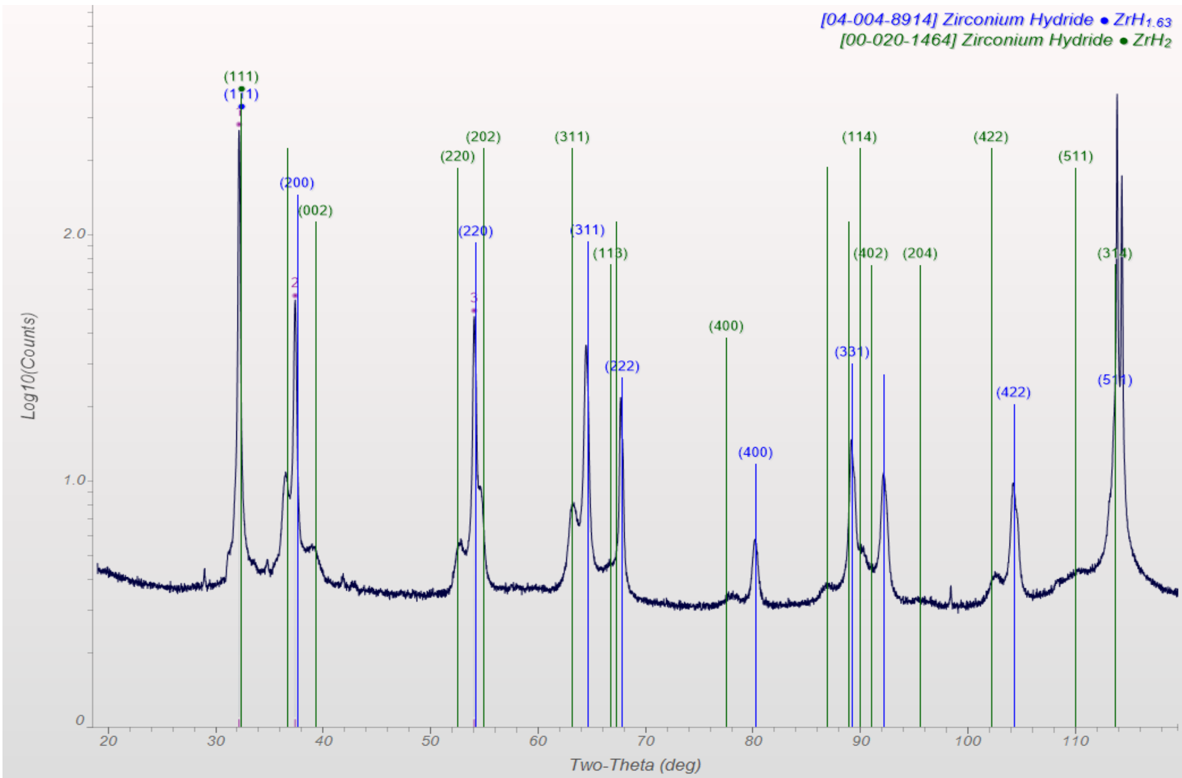


Figure 5. XRD pattern of ZrH-2 (H/Zr=1.575).

2 Cladding ZrHx pellets

2.1 Machining and welding Mo and FeCrAl crucibles

The deployment of zirconium hydride moderator at high temperature is challenging due to the thermally driven hydrogen desorption. Cladding zirconium hydride with materials having low hydrogen permeability is proposed here to mitigate the hydrogen loss from hydrides. In addition to the low hydrogen permeability, other factors considered include neutronics, chemical compatibility, radiation stability, and machinability. We are evaluating different material systems (i.e., molybdenum, FeCrAl, SiC) for their application as cladding materials, supported by the Resource

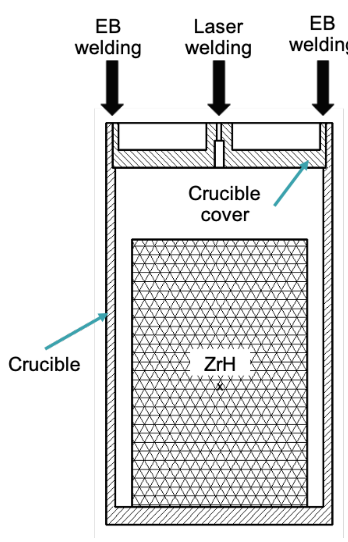
Team. Up to now, we have focused on the two metallic cladding materials, i.e., Mo and FeCrAl. In this study, low carbon arc cast (LCAC) unalloyed molybdenum was used due to its good machinability and low hydrogen permeation. FeCrAl has been developed at ORNL for the application as accident tolerant fuel cladding. C26M2 with a nominal composition of Fe-12Cr-6Al-2Mo-0.2Si-0.03Y, in weight percent, was used. Table 2 lists the analyzed composition of the material.

Table 2. Analyzed composition of C26M2 (heat #17025001), balanced Fe.

	Composition, wt.%						
	Cr	Al	Mo	Si	Y	C	S
Nominal	12	6	2	0.2	0.03	-	-
Analyzed*	11.87	6.22	1.98	0.20	0.03	<0.01	<0.005

* By an induction coupled plasma optical emission spectroscopy (ASTM E1097-12, for major elements) and a combustion analysis (ASTM E1019-11, for C and S)

Two Mo crucibles were machined from LCAC pure Mo bars, with dimensions of 12.9 mm outer diameter, 0.5 mm wall thickness and 22.5 mm height. Two Mo covers were also machined from LCAC pure Mo bars, with a center hole in the middle. Covers were designed to fit in crucibles precisely and the center hole was designed to fill crucibles with helium after the cover and the crucible were welded along the circumference. The schematic of the crucible design and two machined pure Mo crucibles and covers are shown in Figure 6.



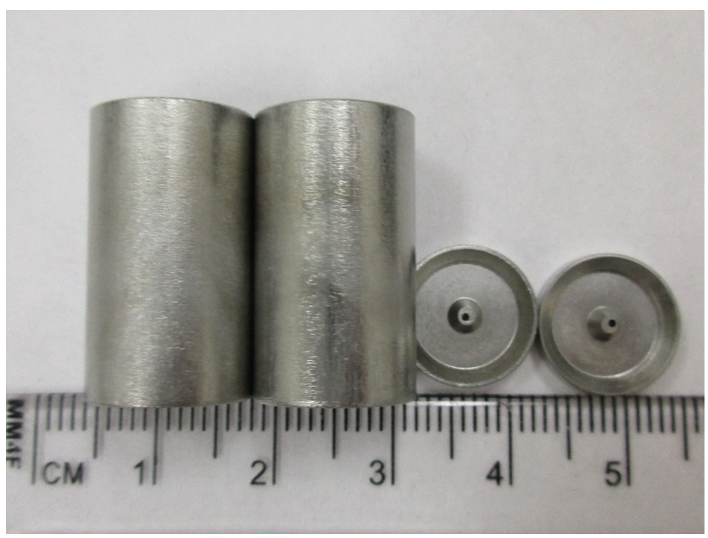


Figure 6. Crucible design schematic (Left) and machined L/C A/C pure Mo crucibles and covers (Right)

Two FeCrAl crucibles were machined from 10.25 mm outer diameter and 0.4 mm wall thickness FeCrAl tubes, and their heights were 24 mm. Two top covers with through thickness center holes and two bottom covers were machined from FeCrAl bars. Two sets of machined FeCrAl crucibles and covers are shown in Figure 7. Note that there were no center holes on the bottom covers in Figure 7.

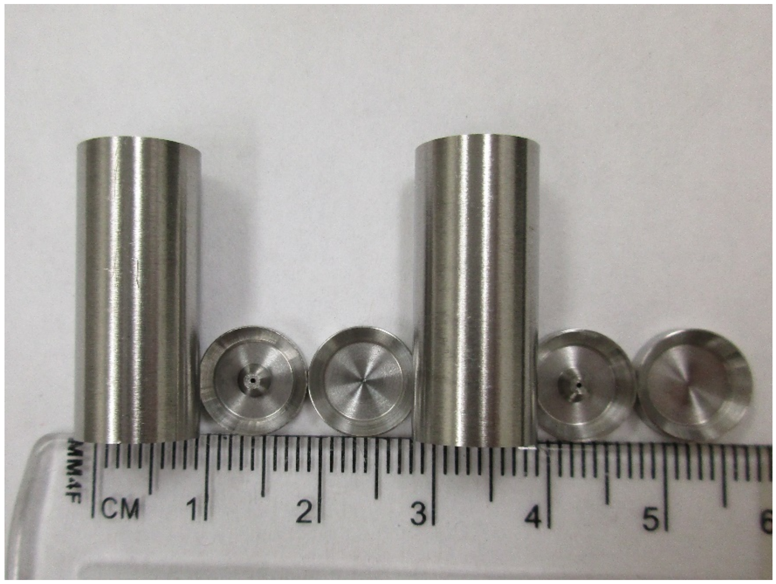


Figure 7. FeCrAl crucibles and covers

Two sets of Mo crucibles, one empty and the other containing ZrH-2 rod, were welded using a combination of electron beam welding (EBW) and gas tungsten arc welding (GTAW). The EBW was employed first to weld covers to crucibles along circumference directions under vacuum condition. Then crucibles were moved into an environment-controlled glove box with 1 ATM helium pressure for GTAW welding. Figure 8 showed the welded empty crucible and the one containing ZrH-2 pellet. After welding, leak tests were carried out on these two crucibles. The leak test contained two experiments, the helium leak test for minor leakage and the bubble test for major leakage. Both crucibles passed leak test with the criteria of 1 x10^{-8} cc/sec leak rate. The large-scale material melting by GTAW secured the center hole seal for pure Mo crucibles.

Figure 8. Welded Mo crucibles with and without zirconium hydride

Although we successfully demonstrate machining and welding Mo crucible to encapsulate zirconium hydride, the Resource Team suggested that Mo is a strong resonant neutron absorber and is not an ideal cladding material from the standpoint of neutronics. Therefore, future characterization of the Mo cladding was not pursued in this project.

In addition to Mo, FeCrAl was also investigated as the candidate cladding material. One set of FeCrAl crucible containing ZrH-6 was successfully welded. Similar to the Mo crucible, EBW was employed first to weld covers to crucibles under vacuum condition. Instead using GTAW following EBW, laser welding (LW) was employed to seal the center hole in helium environment. The LW chamber was vacuumed first then filled with helium with 1 ATM pressure. After the pressure maintained at 1 ATM, LW was used to melt materials around the center hole and seal it. The local heating of LW will minimize the thermal impact on the contained zirconium hydride pellet. Figure 9 showed the welded FeCrAl crucible containing ZrH-6. It is noted that in order to fit the fabricated FeCrAl crucible, the height of the ZrH-6 was reduced by ~1.5mm by polishing the two ends. After welding, leak test was performed. Results showed that the welded FeCrAl crucible passed the leak test with a helium leak rate less than 1×10^{-8} cc/sec.

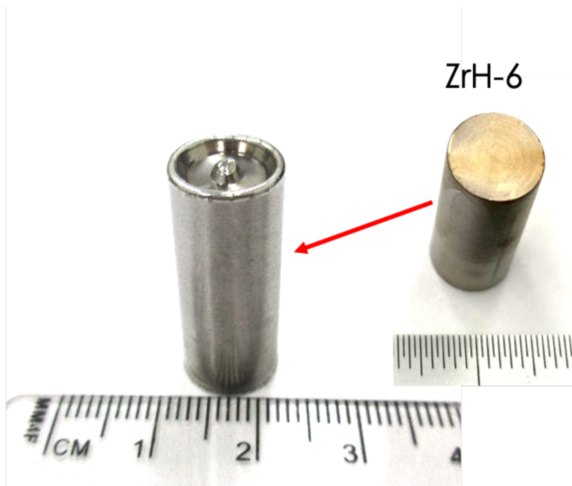


Figure 9. As-welded FeCrAl crucible containing zirconium hydride rod.

2.2 Impact of welding on encapsulated zirconium hydride

A concern during sealing the FeCrAl crucible is how the heat generated from welding will impact the hydrogen content of the zirconium hydride, considering the sensitivity of hydrogen desorption to heat. However, this impact is expected to be very limited, since the welding process is in a short time period, less than several minutes. After the leak test of the welded crucible, the top cover of the FeCrAl crucible was cut open and the contained zirconium hydride pellet was extracted for weight measurement and XRD analysis. Figure 10 showed the opened crucible and the extracted hydride sample. The weight of the contained ZrH-6 was changed from 5.06946g before welding to 5.06679g following welding. ~0.05% weight change was found, corresponding to 0.7% hydrogen loss. The XRD patterns of ZrH-6 before and after welding are shown in Fig. 11. It is apparent two patterns are highly overlapped. XRD analysis showed that as-fabricated ZrH-6 has δ-phase zirconium hydride, γ-phase zirconium hydride (a metastable phase), and α-phase zirconium with the phase fractions of 77.0% 20.1%, and 2.9%, respectively. Following welding the phase fractions of the three present phases changed to 73.2%, 13.5%, and 3.3%, respectively. It indicates that the welding process has negligible impact on the hydrogen content of the encapsulated zirconium hydride pellets.

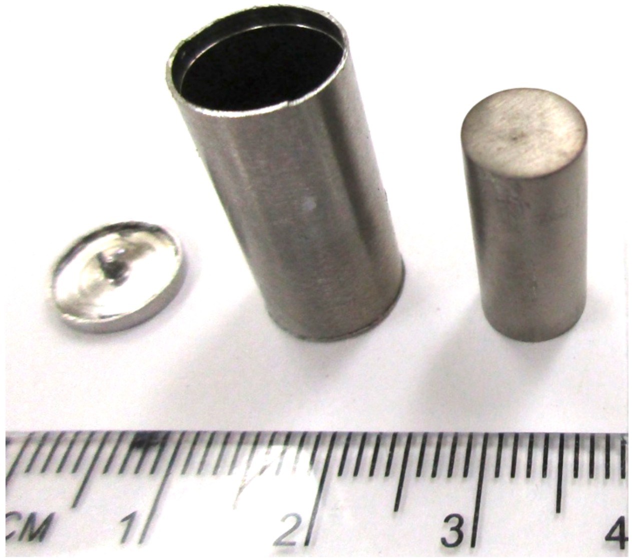


Figure 10. Opened FeCrAl crucible and the extracted zirconium hydride pellet following welding.

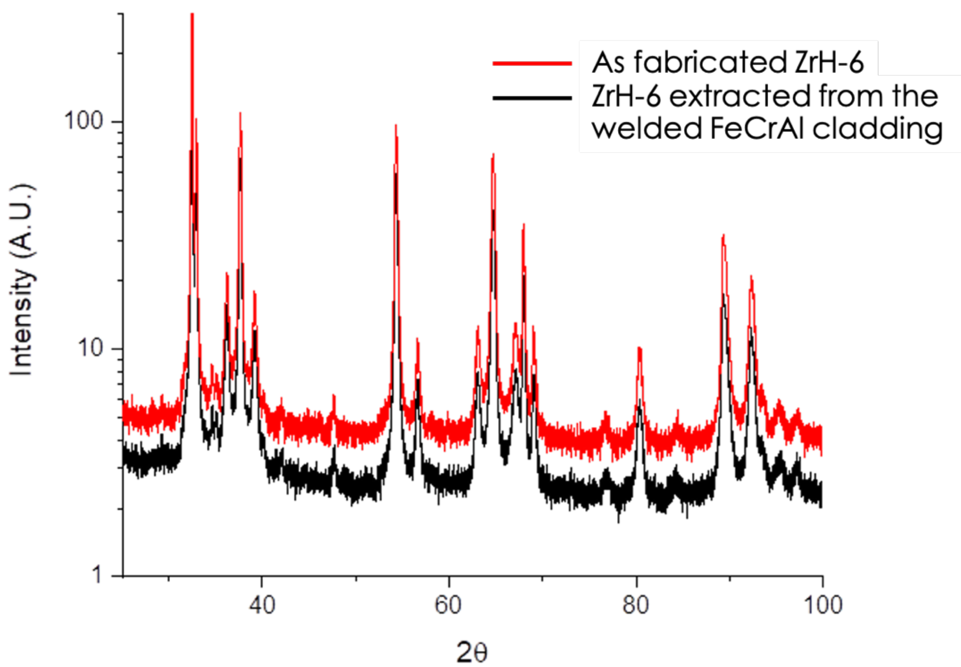


Figure 11. XRD pattern of as-fabricated ZrH-6 and ZrH-6 extracted from the welded FeCrAl cladding .

3 Summary

In this report, we summarized our efforts to develop bulk zirconium hydride moderator. The challenges in fabricating crack-free zirconium hydride are discussed. Using a modified static hydriding system, we have successfully demonstrated the fabrication of crack-free zirconium hydride pellets and rods. The machinability and weldability of two candidate cladding materials were also investigated. The crucibles made from Mo and FeCrAl were successfully fabricated and welded. Characterization of the contained zirconium hydride in FeCrAl cladding before and after welding indicates the impact of welding process on hydrogen content in zirconium hydride is very limited.

As to the future work, we will focus on the fabrication of crack-free single-phase zirconium hydride. The thermal stability of zirconium hydride as well as the hydrogen permeation through cladding materials at elevated temperatures will be studied in coordination with the Resource Team.

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