Metallic residues after hydriding zirconium

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Abstract
As a part of the production of nitride nuclear fuel for use in fast nuclear reactors, zirconium is hydrided followed by nitriding and mixing with uranium nitride. This work concludes a study of unwanted metallic particles present in a powder that is supposed to be a zirconium hydride. Sponge zirconium was hydrided at different temperatures and different time intervals, and the resulting hydride was milled into a powder. The powders were analyzed using SEM and XRD after which the powders were pressed into pellets for light optical microscopic study. The primary goals were determination of the structure of the particles and thereafter elimination of them. It was seen that hydriding at 500 °C results in less metal particles but more experiments need to be conducted to confirm this.
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Appendices
1 Introduction

During the 1960s it was important to decide upon which type of nuclear fuel to use in commercial nuclear power plants. Among the different types of uranium based compounds were metallic uranium, uranium dioxide (UO₂) and uranium nitride (UN) [4]. All of them had promising properties preferable for effective production of energy, such as a high melting point and thermal conductivity. While the nitride had superior properties it could not be used in a reactor cooled by water, such as a BWR (Boiling Water Reactor). Therefore, the uranium oxide was chosen. This type of fuel has been in use all over the world since.

Today there are several project groups, for example the Swedish ELECTRA, developing so-called Generation IV Fast reactors that do not use water as the cooling agent – these will instead be cooled by for example gas or liquid metals, such as sodium or lead. Since the neutrons are slowed down by water, these new reactor types will be more efficient for conversion of U²³⁸ to Pu²³⁹ which is a fissile fuel useable in a nuclear reactor. Another advantage and means of a possible drastic increase of efficiency is the ability to use nitride fuels because water is not present.

At KTH, research is being conducted regarding the use of nitride based nuclear fuels. A lot of this research is done in their nuclear fuel lab where different compounds – not only uranium nitride – are synthesized and their properties tested. Zirconium nitride is added, forming (U-Zr)N. One reason for this is that the UN becomes more thermally stable. The synthesis of this compound is divided into separate steps, as shown below.

![Diagram of fuel synthesis](image)

**Figure 1: The steps for creating (U-Zr)N fuel**

A metallic sample is hydrided in an environment of argon and hydrogen, after which the hydrogen is switched to nitrogen and a nitride is produced from the hydride. This product is preferred to be in the shape of a fine powder which can be pressed and sintered into a nuclear fuel pellet. One method of synthesizing (U-Zr)N is, as shown in Figure 1, to separately produce UN and ZrN before mixing these into a powder that is pressed and sintered into (U-Zr)N pellets.
At KTH, some difficulties have been encountered in the process of producing ZrH₂. First of all, a fine powder is not achieved directly from the hydriding of zirconium in contrast to the case of forming UH₃. The ZrH₂ must be removed from the furnace and milled separately before the nitriding step. ZrH₂ is pyrophoric, so taking the sample out of the furnace without exposing it to air is troublesome. Secondly, metallic residues have been found in the resulting ZrH₂ powder. These residues render the powder unsuitable for pellet production for a number of reasons. The pressing of pellets from powder containing significant amounts of zirconium particles resulted in the pressing tools becoming coated with zirconium so that they required cleaning. Also, sintering of a zirconium nitride pellet containing metallic particles resulted in diffusion of zirconium towards the surface, forming a layer of metallic zirconium. Finally, the addition of zirconium resulted in the end product being a cermet instead of a ceramic, giving it other properties such as a lower melting temperature.

This report concludes a project of analyzing the unwanted particles in an attempt to determine their composition, structure and thereafter cause of existence. As this has been the primary goal, the secondary one was to find a way of eliminating these particles from the process. These particles have been encountered before, and repeated hydriding of the material has been found to not be a reliable method for eliminating them [6]. Another report notes that a possible cause of their existence is the high transformation rate from β-Zr to hydrides [2]. This was useful during the investigation of these particles.
2 Theory

2.1 Reactions
Zirconium hydride is in theory formed by the reaction

\[ \text{Zr} + \text{H}_2 \leftrightarrow \text{ZrH}_2 \]

which can be achieved by heating a sample of zirconium in an environment of hydrogen. In practice it is more complicated than that. The product is generally not simply one stoichiometric phase. Furthermore, the production of ZrH\(_2\) involves the material undergoing several phase transitions, with variations depending on circumstances such as temperature.

2.2 Phases and structure
As mentioned before, there are several different phases of zirconium hydride. Figure 2 shows the Zr-H phase diagram that was generated using the Thermo-Calc Binary Solutions Database from 2006.
The hydriding process can be performed by setting a synthesis furnace containing solid zirconium and hydrogen gas to a specific temperature until the formation of ZrH₂ is finished. Depending on reaction temperature the sample can undergo different phase transitions before the final product is acquired.

At low temperatures the stable zirconium phase is α-Zr, an HCP lattice structure with low solubility of hydrogen. The high-temperature stable phase is β-Zr, a BCC structure that has much higher hydrogen solubility than the α-phase. The hydride phases are the δ-phase, which is an FCC zirconium hydride of slightly varying composition (ZrH₂₋ₓ), and the ε-phase, an FCT hydride that is nearly stoichiometric (ZrH₂) and exists as a twin structure. It can be formed by martensitic transformation [1].

If the sample, originally made up of α-Zr, is hydrided above the eutectoid temperature (549°C) then β-Zr will form. As seen in Figure 2, this phase can absorb a lot of hydrogen before transforming into δ-ZrH₂₋ₓ and ε-ZrH₂. If synthesized below 549°C the sample will transform from α-Zr, with a much lower absorption of hydrogen than the β-phase, into δ-ZrH₂₋ₓ and then into ε-ZrH₂ [2].

There are two competing mechanisms during these reactions. The first one is a formation of an external hydride layer, dominating in low temperature ranges. Increasing the temperature towards and beyond the eutectoid temperature will increase the rate of hydrogen diffusion through grain boundaries, the second mechanism. A low-temperature transformation from α-Zr to δ-ZrH₂₋ₓ will result in a great volume expansion [2] that increases the pressure on the grain boundaries, making diffusion of hydrogen through them more difficult. Thus an external layer is formed. With increasing temperature, the grain boundary diffusion mechanism dominates. While cooling a sample subjected to this high-temperature treatment, the β-phase will quickly transform into the δ- and/or ε-phases. This has in earlier work been noted as a possible explanation for finely dispersed phases of metal and hydride in the hydride product [2].

### 2.3 Shape and handling

Due to volume expansion, and the fact that it is a ceramic material, the hydride product is very brittle. It can easily be broken into pieces which makes it easier to mill into a fine powder. This shape is preferred because the large reactive area of many small particles makes the nitriding step easier. The milling part of the nitride fuel production is troublesome because of the fact that zirconium hydride, among other substances handled in the process, is pyrophoric; it might self-ignite at room temperature and normal air conditions. The milling cups (see section 3.3) are air tight and the lab is equipped with glove boxes in which pyrophoric powders can be handled safely. It is the transfer between furnace and inert atmosphere containers that may subject samples to air. Safety precautions are taken during these procedures. Design of a compact furnace insert to be transferred unopened into the glove box is in progress, but certain construction material issues remain.
3 Execution

3.1 Materials
Sponge zirconium was used because it is porous and thus reacts faster because of the increased reaction area and decreased material thickness through which hydrogen must diffuse. The sponge zirconium was stored in a protective argon atmosphere to minimize oxidation.

The hydrogen gas reacting with the zirconium sample was AGA Laboratory Hydrogen 5.5 of 99.9995% purity. Argon gas was used as a moderator to make sure that the reaction did not go too fast. Too fast hydrogen uptake may result in suction of atmosphere through the end filter and into the furnace. The presence of a non-reacting gas makes sure that in the event of a backflow the amount of hydrogen around the sample decreases until the gas flow stabilizes. This non-reactive gas was AGA Argon ICP 5.0 of 99.999% purity.

The argon gas was further purified by passing it through a heated gas cleaning system consisting of magnesium and copper turnings. Both gases passed through another system of silica gel, Ascarite and magnesium perchlorate that removed oxygen, moist and other contaminants before they reached the reaction chamber.

3.2 Synthesis furnace and Data Acquisition Laboratory (DASYLab)
The synthesis was done in a vertical furnace into which a quartz or alumina tube is inserted. The furnace is fed with gas through two pipe systems, one with argon (Ar) or nitrogen (N₂) gas, one with hydrogen (H₂) gas.

For small samples a quartz tube was used. Centered inside the tube is a porous quartz filter that can support the sample while letting gas flow through. Since the quartz tube is thin and very brittle it had to be protected from the pressure applied to the tube by the expanded hydride. This was done by surrounding the sample with a wire mesh of copper to ensure good clearance of the quartz walls. For larger batches of zirconium, a bigger alumina tube was inserted instead. To hold the sample in place in the middle of the furnace, it was placed inside a steel crucible hanging from the top of the tube by a wire of molybdenum. When using this tube there is no need to be concerned about cracking from the expansion of the sample. On the other hand, a drawback with the alumina tube is that the crucible hinders gas flow around the sample. This was countered by adding ventilation holes in the bottom of the crucible.

The entire synthesis system is controlled by a computer through the use of the DASYLab software interfacing with data acquisition hardware. The control program used in DASYLab was created by Tobias Hollmer [3]. Using the program, it is possible to control furnace temperature ramps by changing voltage input to a thyristor while the temperature is measured by a thermocouple. Two Bronkhorst EL-FLOW F-201CV-2K0 flow controllers are used to set the flow into the furnace, one for the argon and nitrogen, one for the hydrogen. A third Bronkhorst component, EL-FLOW F-111B-5K0, measures the gas flow out of the furnace.

The program measures the net flow difference with good accuracy, thus indicating any reaction consuming or releasing gas. With a sensitive thermocouple, the occurrence of exo- or endothermic reactions can be noted by observing non-linear changes in temperature. This data is saved in a log file that was used to create the diagrams shown in section 4.1.
The setup with furnace and controller can be seen in Picture 1

Milling was done to get a powder that can later be pressed into a pellet for sintering. Because zirconium is a metal it is ductile and therefore not very suitable for milling, but zirconium hydride is. The milling was done in a shaking cup mill, seen in Picture 3, with a vacuum tight steel cup and steel milling-balls of three different sizes, two 20mm, two 10mm and eight 5mm ones. The pieces of zirconium hydride were loaded into the cup in a Labconco Precise Controlled Atmosphere Glove Box, shown in Picture 4 to avoid oxidation. After the milling the resulting powder was kept in the glove box. This was also to avoid oxidation.

3.4 X-Ray Diffraction

One of the methods used to investigate the composition and structure of the samples was X-ray diffraction (XRD). A spectrum of X-rays is generated and scattered off the surface of a sample. A specific crystal lattice structure will generate maxima of scattered X-rays at specific angles. By comparing the intensity of detected wavelengths at these angles with a database, the lattice parameters of the sample can be determined.

The XRD used was a Siemens DS00 X-Ray Diffractometer, as seen in Picture 2. The sample is not held in a protective atmosphere, which was a problem because the analyzed powder was pyrophoric. To protect the powder from air it was mixed with small amounts of paraffin oil to form a moist paste. As seen in Figure 12 the paraffin oil does not cause too much disturbance to the readings because it has an amorphous structure, and XRD only detects reflections off a crystal lattice.
However, by making the sample a paste it became harder to get the smooth surface required to get clear readings from the XRD. This is a lesser problem than not being able to get any readings at all so it was accepted. If the paste was dry enough, the oil did not interfere much with the results. The program used to read the data from the XRD machine was Diffrac plus XRD Commander which recorded detected X-ray spectra. These were then analyzed with Socabim EVA software to quantify the discovered compounds. It should be noted that compounds making up less than 1% of the sample will not show in XRD analysis.

### 3.5 Scanning Electron Microscope (SEM) with Energy-dispersive X-ray spectroscopy (EDS)

The second method of determining the composition of samples was by using Scanning Electron Microscopy (SEM) that utilizes a beam of electrons to produce high-resolution pictures of a wide range of magnifications. Many SEM apparatus are also installed with Energy Dispersive X-ray Spectroscopy (EDS) equipment used to determine composition of analyzed areas, points or lines of choice. It is difficult to identify light elements though, which in this case is troublesome since it has been of interest to analyze hydrides as a great part of this project. During this project a Hitachi S-3700N SEM was used and it can be seen in Picture 5

Since the samples analyzed are in the shape of a powder, it could prove difficult to embed them into a conductive polymer matrix as is usually done before SEM analysis. Particles may also fall off during the polishing of the sample. This was attempted in addition to using conductive tape instead, onto which the powder simply sticks.
3.6 Samples

Three samples were prepared. The first was a reference using the same synthesis method that had been used earlier, and the rest using two different “recipes”. Table 1 gives a short description of the different syntheses used and Table 2 through 4 in the following sections describe them in detail. After synthesis of all samples, they were milled for 2x10 minutes and the resulting powder was analyzed by SEM and XRD.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZP120201</td>
<td>Reference, Three cycles of hydriding/dehydriding between 550°C and 800°C</td>
</tr>
<tr>
<td>ZP120316</td>
<td>As reference but with very slow cooling</td>
</tr>
<tr>
<td>ZP120319</td>
<td>Hydriding at 500°C followed by slow cooling</td>
</tr>
</tbody>
</table>

Table 1: Summary of sample processing

3.6.1 ZP120201

This sample was synthesized using a recipe with cyclic hydriding. This was because such a synthesis may result in increasing expansion and embrittlement with each cycle. This may lead to cracking and thus increasing the reactive area and therefore also reaction rate. Cyclic hydriding was also thought to give a more pulverized sample.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>600</td>
<td>0,5</td>
<td>0,5</td>
<td>58</td>
<td>Hydriding</td>
</tr>
<tr>
<td>600</td>
<td>600</td>
<td>0,5</td>
<td>0,5</td>
<td>50</td>
<td>--&quot;--</td>
</tr>
<tr>
<td>600</td>
<td>900</td>
<td>0,5</td>
<td>0</td>
<td>30</td>
<td>Dehydriding</td>
</tr>
<tr>
<td>900</td>
<td>900</td>
<td>0,5</td>
<td>0</td>
<td>10</td>
<td>--&quot;--</td>
</tr>
<tr>
<td>900</td>
<td>550</td>
<td>0,5</td>
<td>0,5</td>
<td>70</td>
<td>Hydriding</td>
</tr>
<tr>
<td>550</td>
<td>550</td>
<td>0,5</td>
<td>0,5</td>
<td>50</td>
<td>--&quot;--</td>
</tr>
<tr>
<td>Repeat following twice</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>550</td>
<td>900</td>
<td>0,5</td>
<td>0</td>
<td>35</td>
<td>Dehydriding</td>
</tr>
<tr>
<td>900</td>
<td>900</td>
<td>0,5</td>
<td>0</td>
<td>10</td>
<td>--&quot;--</td>
</tr>
<tr>
<td>900</td>
<td>550</td>
<td>0,5</td>
<td>0,5</td>
<td>70</td>
<td>Hydriding</td>
</tr>
<tr>
<td>550</td>
<td>550</td>
<td>0,5</td>
<td>0,5</td>
<td>50</td>
<td>--&quot;--</td>
</tr>
<tr>
<td>550</td>
<td>100</td>
<td>0,5</td>
<td>0,5</td>
<td>120</td>
<td>Cooling</td>
</tr>
</tbody>
</table>

Table 2: Synthesis recipe for sample ZP120201

3.6.2 ZP120316

This sample follows the reference with the exception that the cooling rate is slower. As mentioned before, a high cooling rate may be the cause of metallic residues in the sample. The slower cooling rate gives more hydrogen time to diffuse into the sample during cooling.
### Table 3: Synthesis recipe for sample ZP120316

<table>
<thead>
<tr>
<th></th>
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<th></th>
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<tbody>
<tr>
<td>20</td>
<td>600</td>
<td>0,5</td>
<td>0,5</td>
<td>58</td>
<td>Hydriding</td>
</tr>
<tr>
<td>600</td>
<td>600</td>
<td>0,5</td>
<td>0,5</td>
<td>50</td>
<td>--&quot;--</td>
</tr>
<tr>
<td>600</td>
<td>900</td>
<td>0,5</td>
<td>0</td>
<td>30</td>
<td>Dehydriding</td>
</tr>
<tr>
<td>900</td>
<td>900</td>
<td>0,5</td>
<td>0</td>
<td>10</td>
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</tr>
<tr>
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<td>550</td>
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<td>0,5</td>
<td>70</td>
<td>Hydriding</td>
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<tr>
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<td>--&quot;--</td>
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<td></td>
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<td></td>
<td>Repeat following twice</td>
</tr>
<tr>
<td>550</td>
<td>900</td>
<td>0,5</td>
<td>0</td>
<td>35</td>
<td>Dehydriding</td>
</tr>
<tr>
<td>900</td>
<td>900</td>
<td>0,5</td>
<td>0</td>
<td>10</td>
<td>--&quot;--</td>
</tr>
<tr>
<td>900</td>
<td>550</td>
<td>0,5</td>
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<td>70</td>
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</tr>
<tr>
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<td>550</td>
<td>0,5</td>
<td>0,5</td>
<td>50</td>
<td>--&quot;--</td>
</tr>
<tr>
<td>550</td>
<td>100</td>
<td>0,5</td>
<td>0,5</td>
<td>300</td>
<td>Cooling</td>
</tr>
</tbody>
</table>

**3.6.3 ZP120319**

To avoid the possibility that β-zirconium degrades into α-zirconium and δ-hydride this sample was hydrided at a lower temperature.

### Table 4: Synthesis recipe for sample ZP120319

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>500</td>
<td>0,5</td>
<td>0,0</td>
<td>48</td>
<td>Heating</td>
</tr>
<tr>
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<td>500</td>
<td>0,5</td>
<td>0,5</td>
<td>60</td>
<td>Hydriding</td>
</tr>
<tr>
<td>500</td>
<td>100</td>
<td>0,5</td>
<td>0</td>
<td>120</td>
<td>Cooling</td>
</tr>
</tbody>
</table>

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3.7 Pressing and optical inspection

The last experiment was conducted to determine which method leads to the lowest amount of zirconium particles. By pressing the zirconium hydride powder into a pellet and then examining it in a microscope the metal particles could be identified.

To help the powder stay together a binder, zinc stearate of technical grade from Sigma-Aldrich, was added to the powder. The powder was then pressed at 3.5 tons of pressure for 5 min in the press shown in Picture 6.

The green pellets were then carefully ground on grit 280, 360 and 1200 grinding paper to bring out the metal particles.

A Wiki Digital Microscope, shown in Picture 7, was used to take pictures of all the samples.

![Picture 6: The press](Image)

![Picture 7: The microscope used to take the pictures](Image)

4 Results

4.1 Synthesis results

4.1.1 ZP120201

This synthesis went without incident and the synthesis log is shown in Figure 3. It can be noted that the rate of the hydrogen uptake increases with every hydriding/dehydriding cycle. This was both wanted and expected, since the formation of hydride during every cycle embrittles and cracks the material, thus increasing the reactive area prior to the next cycle. It can also be seen that the uptake did not return to the same level at the end of every hydriding sequence indicating that the hydriding was not completed. The reason for this is probably that the pieces of zirconium were rather large,
thus the sample needed more time to react. The very high spikes in flow difference were due to changes in the inflow of hydrogen.

4.1.2 ZP120316
This synthesis did not go as planned because of recurring problems with the control program. Somehow the program, or hardware, stopped changing the signal to the control equipment. Among other things, the temperature exceeded the planned dehydriding temperature of 900°C until the furnace was manually switched off at 1000°C. The synthesis had to be restarted which led to the synthesis log being fractured into multiple files. When the problem occurred again the synthesis was terminated before any serious deviations from the planned ramps of temperature and time could happen. These partial logs can be seen in Figure 4a through 4e. In Figure 4a the temperature peak from the control problem can be seen. Compared to the synthesis of ZP120201 the flow difference returns to a stable level during each cycle indicating that the reaction was completed. The peaks in flow difference were also smaller probably because the sample was smaller and therefore had less reacting area.
4.1.3 ZP120319

This synthesis had the same problem with the control equipment as ZP120316 but the problems were discovered, and handled, before complications occurred. The logs for this experiment can be seen in Figure 5a and 5b. The gas uptake declined to the same level as for ZP120316. The dip in flow at the end of figure 5a could be from further uptake during cooling but it is very small and could be a result of the change in temperature.
4.2 Synthesis products
There were large differences in the coloration and appearance of the different samples after syntheses.

4.2.1 ZP120201
The sample was of a grey and yellow color, and slightly cracked. This can be seen in Picture 8. The zirconium hydride pieces also had different colors depending on where they had been in the reaction chamber. Areas where the pieces rested against each other were closer to their original metallic color.

4.2.2 ZP120316
In Picture 9 it is seen that the sample was cracked and colored similarly to ZP120201, but was more yellow where the melted copper net had been in contact with it. The peak in temperature during the program malfunction caused the copper net to melt and cling to the sample.
4.2.3 ZP120319
The last sample had larger cracks than the others, it was more brittle than ZP120316 and it was of grey and blue color as slightly seen in Picture 10. It could be broken into pieces by hand.

4.3 Milling
All the samples had similar appearance after milling. They were all a fine black powder that, when removed from the milling cup, clung to the walls in a thin layer that was easily scraped off. In the bottom of the milling cup the powder had been compacted into a chunk that easily crumbled back into powder. In the case of ZP120201, there were two relatively big, solid metal pieces left from the milling. This confirms what the synthesis logs indicated, that the reaction might not have gone to completion.

4.4 Pressing and optical inspection
The powders were pressed into pellets that held together well, very little flaking was observed. During the grinding pellet ZP120201 was observed to be softer than the others because of its smaller powder particle size.
The pellet cross sections can be seen in Picture 11 through 13. The metal particles can be seen as brighter spots.
Comparison between ZP120316 and ZP120319 shows that the latter had less metal particles in the cross section. The ZP120201 pellet had significantly lower amount of metal particles but this could be a result of its smaller particle size because the powder was sieved in the search for large, metallic particles. When it came to pressing the powder into a pellet, a greater fraction of larger particles had been used up for other tests than the fraction of smaller ones. Simply put, the larger ones were a bit underrepresented in the ZP120201 pellet.

4.5 SEM
The results from the SEM analyzes of all samples are described below. The full SEM reports can be seen in the appendix.

4.4.1 Elemental Analysis
The content of the samples from an ESD area analysis is shown in Table 5. It should be noted that hydrogen cannot be detected by ESD and that quantification of lighter elements like oxygen will not yield accurate results. This is why relative frequency was used in the other analyses.

<table>
<thead>
<tr>
<th>Element</th>
<th>Series</th>
<th>Norm. C [wt.%]</th>
<th>Atom. C [at.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>K-series</td>
<td>5,60</td>
<td>25,29</td>
</tr>
<tr>
<td>Zirconium</td>
<td>L-series</td>
<td>94,40</td>
<td>74,71</td>
</tr>
<tr>
<td>ZP120201</td>
<td></td>
<td></td>
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Table 5: Results of element analyses

4.4.2 Mapping
By using an EDS element mapping or a line-scan the relative frequency of the different elements can be shown. It would be optimal if the relative frequency of hydrogen and zirconium could be compared but, as noted before, the inability of ESD to detect hydrogen prevents this. Instead the relative frequency of zirconium was used because zirconium hydride has a lower concentration of
zirconium than metal zirconium. This difference should make the metal particles show as bright spots in the mappings and as high peaks in the line scans.
But as seen in the element mappings in Figure 6 through 8, no significant differences in zirconium concentrations can be seen within the samples, not even between them. The inconsistency in concentration through the samples can be credited to the rough surface of the powder. As different slopes will scatter the electron beam differently, hills will shield other parts from the beam and more compacted powder will show an increase in zirconium concentration. Because of this it was not known if a maximum on the relative scale indicated a metal particle or a hydride in a favorable angle.
This was further supported by the line-scans seen in Figure 9 through 11. In all the line scans there was often a correlation between drops in relative frequency of both zirconium and oxygen. These variations could be due to different amounts of hydrogen. However, it is more likely that the
differences in intensity are because of packing and orientation of the material. The problems stated
above can be alleviated by introducing an internal standard of artificial zirconium granules mixed
with the sample that act as a reference for full zirconium concentration. The relative scale could then
be calibrated by this.

4.6 XRD
The results from the XRD analyses can be seen in Figure 13 through 15 below. See the appendix for
larger and more detailed figures. The same peaks are present in all three of the diagrams. These
were compared with databases of characteristic peak positions and sizes for different compounds. All
of them seem to correspond well to the close-to stoichiometric $\varepsilon$-$\text{ZrH}_2$, shown by the purple peaks.

![Figure 12: determination of the background spectra of paraffin oil](image)
One thing of interest is that the relative peak sizes were not correct for a compound only made up of ZrH₂ – there is also some hydride of different composition that shares a peak with ZrH₂, thus making it appear higher. A possible match for such a compound was found to be ZrH_{1.8} (still tetragonal though), shown by the green peaks.

Strangely enough, no obvious oxide presence was noted. Even if there is some, the characteristic peaks lay too close to other peaks to be significant. This is a good thing since it proves that the paraffin oil was enough to protect the pyrophoric powder from oxygen. Neither could any significant trace of metallic zirconium be found. One must be reminded about the fact that if there is less than one weight percent of a compound, it can barely be seen in an XRD analysis. This may also be the reason why copper was not found in ZP120316.
Figure 14: XRD results from sample ZP120316

Figure 15: XRD results from sample ZP120319
Another thing the three diagrams had in common was two to three rather distinct peaks in the beginning of the diagram. These could never be accounted for – either they are artifacts or an unknown compound.

The only thing that really differs between the three samples is a minor variation in relative peak heights, as seen in Figure 16, indicating different hydride quality (more or less pure ZrH₂).

Figure 16: The XRD results of all samples, for comparison
5 Conclusions and Discussion
The cyclic hydriding did not lead to crumbling as described in [5]. This is probably because the samples Parkison & McDeavitt hydrided had pipe geometries, while the ones hydrided in this project were bigger. The fractures that developed during hydriding were not large enough to break the material apart. The porous nature of sponge zirconium might have given the material more room to expand internally resulting in less fracturing.

It seems like ZP120319 contained less metal particles than ZP120316 but more syntheses should be made to confirm this.

The SEM was insufficient for analyzing the samples because of the fact that it cannot identify hydrogen and ideally the concentration of zirconium and hydrogen should be compared relative to one another. The EDS line scan analyses showed varying amounts of zirconium, but this was mainly because the packing and orientation of the powder affected how the signals reached the EDS receiver.

All the samples have been confirmed to contain mainly ε-phase zirconium hydride, in addition no large amounts of oxygen or nitrogen contamination could be found. This shows that paraffin oil protects samples from atmosphere during transport and XRD analyses.

The cooling rate can have an effect on the formation of metal particles because the hydrides absorb more hydrogen at lower temperatures. If the cooling rate is so fast that the rate of hydrogen diffusion into the sample is insufficient, the shortage of hydrogen may result in metallic residues in the product. A very logical explanation is that the metallic particles consist of α-Zr, and that these exist due to diffusion of hydrogen from areas nearby the growing hydride phases. Diffusion of hydrogen through the hydrides is difficult, making sure the metallic phases do not receive any more hydrogen during cooling.

6 Future work
While it was stated that ZP120319 appeared to have the least amount of metallic particles this should be confirmed further by making more detailed light optical analyses.

For further investigation of this problem it is recommended to hydride below the eutectoid temperature and cool the sample slowly afterwards. This is to prevent the formation of β-Zr as the high transformation rate from β-Zr into hydrides may be the reason for having metallic particles left in the sample. It is also to make sure that the rate of diffusion keeps up with the increasing need for hydrogen while transforming the metal into hydrides. In addition, more syntheses should be made to compare high versus low temperature hydriding, and fast versus slow cooling rate.

It could also be interesting to study the effects of the metal particles on the end product to see if they have any benefits.

Methods of separating the unwanted particles from the hydride powder should be tested. This would aid in the quantification and analysis of them. In the final weeks of this project it was discovered that the powder responds to magnetic fields. Magnetic separation should therefore be considered. There
is also a difference in density between the hydride and the metallic residues, and there are several methods that can be used to sort samples by density. Flotation and air current sorting are examples. The later has the advantage that it sorts by both density and particle size.

Using a SEM installed with an EBSD (electron backscatter diffraction) can be used to determine the crystal structure of a sample at higher magnification than the XRD. This is an advantage as analyses of individual metal particles can be done. There are even more accurate ways of determining the structure of a material, although requiring expensive equipment, for example Selective Area Electron Diffraction (SAED) performed with a Transmission Electron Microscope (TEM). Focusing on a very small area this can be used to determine the structures of single crystals.

7 Acknowledgements

We would like to thank

Simo Saarinen for partaking in the creation of our MATLAB-program used to plot synthesis logs.
Pertti Malkki for teaching us how to use most of the lab equipment and helping us with XRD and SEM analyses.
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Wen Li Long and Ljubov Belova for assisting us with SEM analyses.
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And of course the Dpt. of MSE and the Dpt. of Physics for giving us access to the lab, necessary equipment and useful resources.
8. References

[1] Zirconium Hydride (ZrH), Postgraduate Course Seminar, Prof. Dr. Radomir Ilić, U of Maribor, Ljubljana (14 March 2000)


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