# COMMERCIAL INTRODUCTION AND EXPERIENCE WITH THE ADVANCED HIGH IRON CLADDING HiFi® IN BOILING WATER REACTORS

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## ABSTRACT

The high iron cladding material, **HiFi®**, was selected as the next generation BWR cladding material to meet the increasing demands for higher fuel duties and burnup. It increases the safety margins compared to the current standard Zircaloy-2 based BWR claddings by further reducing the hydrogen uptake. A range of hydrogen pickup data from autoclaves, coupons and more recently from end of life commercial rods is presented. Initially developed by NFI in Japan, **HiFi®** is now being introduced globally as the next generation cladding material to be used in the Westinghouse 11x11 BWR fuel product **TRITON11™**. Historically, BWRs have used the Zircaloy-2 cladding specification. The **HiFi®** alloy has an iron content significantly higher than the 0.2 wt% upper limit in the Zircaloy-2 specification, whilst all the other alloying elements are inside it. Initial autoclave results suggest further **HiFi®** modifications will result in even lower hydrogen pickup.

## 1. Introduction

In order to meet evolving requirements imposed on fuel cladding materials for boiling water reactor (BWR) nuclear fuel, Nuclear Fuel Industries Ltd. (NFI) developed HiFi cladding, a zirconium-based cladding material that builds on the extensive performance experience acquired with Zircaloy-2 cladding, but with a relatively minor change of the chemical composition [1] [2]. Zircaloy-2 cladding is currently the industry standard for BWR fuel. In particular, HiFi cladding was designed to improve resistance to hydrogen uptake, intended to maintain and increase safety margin, to meet increasing demands for higher fuel duties and burnup, as well as new cladding hydrogen-based criteria for reactivity insertion accidents (RIA) and loss-of-coolant accidents (LOCA).

## 2. HiFi and Alloy 2 development

Starting in the mid-1980s, NFI developed an advanced cladding material with high corrosion resistance and reduced hydrogen pickup for next generation high burnup BWR fuel, with average discharge burnup greater than 60 GWd/tU. This advanced cladding material has a nominal iron content of 0.4 wt%, which exceeds the upper limit of the ASTM specification for Zircaloy-2 cladding. The final chemical composition of HiFi cladding was determined following extensive ex-core testing, aiming to optimize manufacturability, mechanical properties, corrosion and hydrogen pickup. In addition to higher iron, other variants considered during development of HiFi cladding included low tin and added traces of niobium. All the variants demonstrated good fabricability, without significant differences observed during processing. Finally, the composition chosen is that listed in Table 1, which only changes the iron level compared to Zircaloy-2 cladding. All other alloying elements and impurities remain unchanged. Processing of HiFi cladding has only minimal differences in the specifications of heat treatments and cold pilgering reductions, which have been tailored to the modification in chemical composition, in order to optimize the microstructure for robust performance. It has been found that the larger amount of iron in HiFi produces secondary phase particles which have a larger number density, mean particle size, and particle volume fraction compared to Zircaloy-2 [3].

Whilst NFI were developing HiFi, Westinghouse were in parallel independently developing three different high iron cladding materials. One of them, referred to as “Alloy 2”, was very similar to HiFi. The chemical composition of Alloy 2 is within the specifications for HiFi with the only exception being a chromium content of 0.17 wt% versus the upper limit for both HiFi and Zircaloy-2 of 0.15 wt%, as shown in Table 1. This slightly elevated level of chromium present in Alloy 2 compared to HiFi is not expected to have any detrimental effects on performance. The Alloy 2 experience is thus relevant when evaluating the beneficial effect of small variations in the alloy composition without diverging significantly from the performance experience acquired with Zircaloy-2 in Westinghouse BWR fuel up to end-of-life (EOL) burnup levels.

| **Element (wt%)** | **Alloy 2** | **Specifications** | |
|---|---|---|---|
| | | **Zircaloy-2** | **HiFi** |
| **Sn** | 1.3 | 1.20 - 1.70 | 1.20 - 1.70 |
| **Fe** | 0.33 | 0.07 - 0.20 | 0.25 - 0.50 |
| **Cr** | 0.17 | 0.05 - 0.15 | 0.05 - 0.15 |
| **Ni** | 0.06 | 0.03 - 0.08 | 0.03 - 0.08 |

Table 1: Summary of alloy compositions

## 3. Irradiation experience and introduction timeline

Side-by-side out-of-pile testing comparing HiFi and Zircaloy-2 cladding demonstrates that most of the properties are equivalent between the two materials. This includes thermal properties, mechanical properties, corrosion properties, and LOCA properties as evaluated in integral burst tests [4]. The exception in equivalence between Zircaloy-2 and HiFi cladding is the hydrogen pickup fraction observed in HiFi cladding, being significantly lower than that of Zircaloy-2 cladding [5][6].

Table 2 summarizes the extensive irradiation testing performed by both NFI and Westinghouse, starting with coupons in 1992. The Oskarshamn 3 in-pile verification was with

Alloy 2 whilst all other material was the standard HiFi. In addition to the already achieved end-of-life burnup, HiFi rods are currently loaded in Westinghouse 10x10 BWR fuel assemblies in three commercial plants. The poolside and post-irradiation examination (PIE) data from these early loadings is being used to support the introduction of the first commercial TRITON11 lead test assemblies which are currently in production. HiFi will be used in the future for all 11x11 cladding tubes.

| Plant | Fuel vendor | Type | Comments |
|---|---|---|---|
| **Europe 1** | NFI | Coupons | - |
| **Japan 1** | NFI | Coupons | 6 cycle irradiation to 70 GWd/tU. |
| **Halden** | NFI | Fuel rods | - |
| **Europe 2** | NFI | Fuel rods | 7 cycle irradiation to 76 GWd/tU. |
| **Oskarshamn 3** | Westinghouse | Fuel rods | Irradiation to 60(1) GWd/tU. |
| **Europe 3** | Westinghouse | Fuel rods | Loading 2012. Irradiation ongoing. |
| **Europe 4** | Westinghouse | Fuel rods | Loading 2014. Irradiation ongoing. |
| **Europe 5** | Westinghouse | Fuel rods | Loading 2018. Irradiation ongoing. |

1) Average burnup in lower half of the rod was measured as 56.2 GWd/t, local burnup where the measurements were made was approximately 60 GWd/t.

Table 2: Summary of HiFi irradiation experience

## 4. Alloy 2 irradiation data

In 2001 a lead rod fuel assembly was loaded in Oskarshamn 3 that included one fuel rod with Alloy 2 cladding, together with Zircaloy-2 references. Both types of cladding were manufactured with the same process parameters, including pilgering steps and annealings. The fuel assembly was irradiated for two 12-month cycles. After two cycles the Alloy 2 fuel rod along with a Zircaloy-2 reference rod were rebuilt into a fresh assembly. In the second life the fuel assembly was irradiated for additional cycles. The two-life rods reached a final rod average burnup of 56 GWd/tU in 2008, with a total operating time of approximately 2230 days. Throughout the irradiation program, the fuel rods have been inspected on several occasions, as shown in Table 3 below.

| Year | Visual | Rod growth | Corrosion |
|---|---|---|---|
| **2003** | X | X | X |
| **2004** | X | X | |
| **2005** | X | X | X |
| **2007** | X | X | X |
| **EOL** | X | X | X |

Table 3: Poolside inspection scope of Alloy 2 lead rod in Oskarshamn 3

The oxide thickness on the outward facing surface (towards the channel) of the fuel rods was measured by EC-liftoff. The rod average oxide thickness for the Alloy 2 rod and the reference rod with Zircaloy-2 cladding is shown in Figure 1. It can be seen that the Alloy 2 corrosion was similar to that of Zircaloy-2.

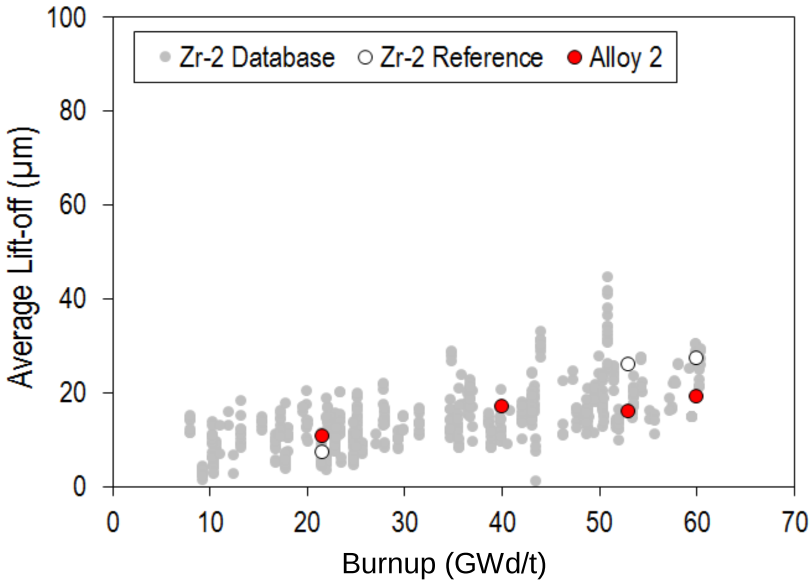

Figure 1: Poolside lift-off data for Alloy 2 and Zircaloy-2 in Oskarshamn 3

The rod with Alloy 2 cladding and the reference rod with Zircaloy-2 cladding were shipped to the Studsvik hot cell laboratory for PIE. The scope of the PIE included puncturing and fission gas analysis, visual inspection, profilometry, EC lift-off measurements, gamma-scanning, cladding hydrogen measurement by hot vacuum extraction (HVE) and scanning electron microscopy examinations.

Figures 2 and 3 show the oxide thickness in the lower part of the two rods, in particular the spacer shadow corrosion at the positions of the two lowest spacers (the shadow corrosion is usually most extensive in the lower part of the fuel). It can be seen that the shadow corrosion is almost identical in the two rods, indicating that there is no difference in the shadow corrosion behaviour of Alloy 2 and Zircaloy-2.

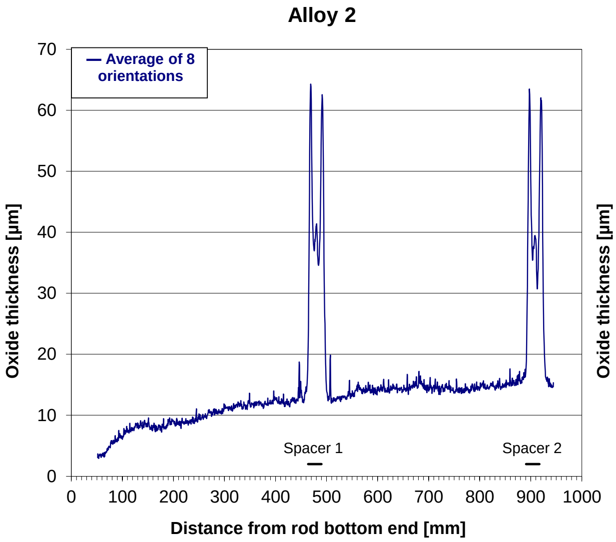

Figure 2: Alloy 2 oxide thickness,
lower part of rod.

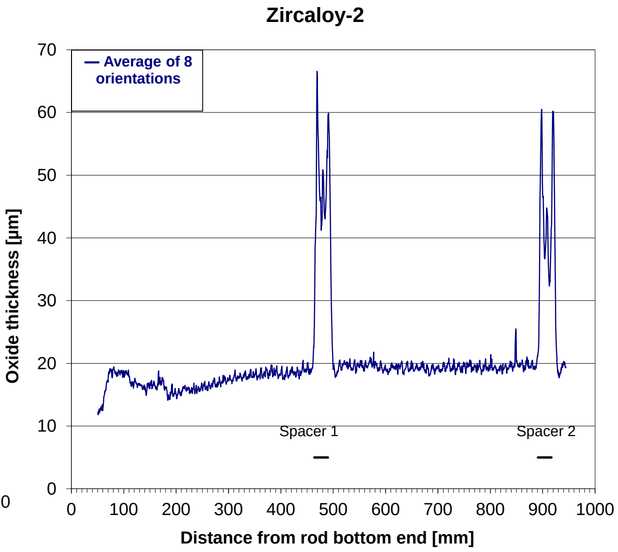

Figure 3: Zry-2 oxide thickness,
lower part of rod.

Metallographic samples of the cladding were examined by scanning electron microscopy (SEM), where the local hydrogen content through the wall thickness could be quantitatively evaluated from backscattered electron imaging (BEI). It was found that for both cladding materials a significant portion of the hydrogen in the cladding (essentially all in the form of hydrides at room temperature) was located in the liner, adjacent to the liner-base material interface. It was apparent that the hydriding was heavier in the Zircaloy-2 sample than in the Alloy 2 sample at the same elevation, see Figures 4 and 5.

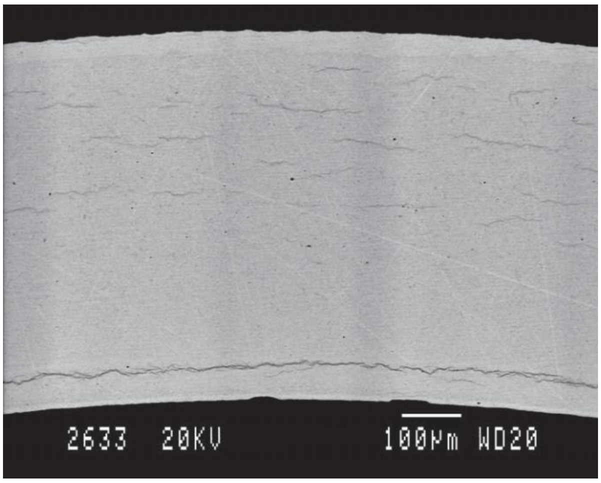

Figure 4: Alloy 2 SEM-BEI image
2676 mm from bottom of rod.

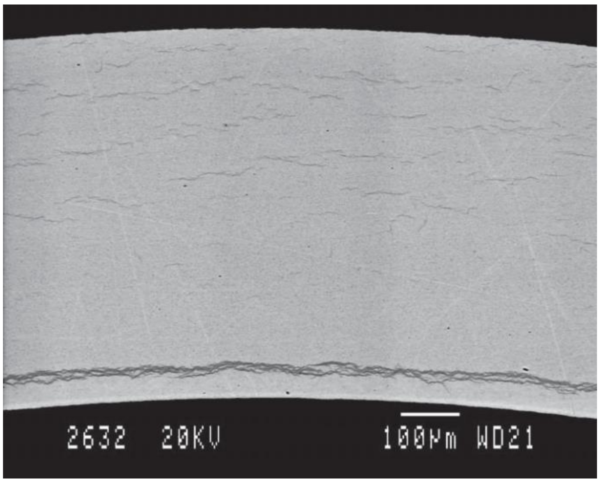

Figure 5: Zircaloy-2 SEM-BEI image
2642 mm from bottom of rod.

The wall-average hydrogen concentration in the cladding was determined at different elevations, both by HVE and by SEM-H analysis. At all elevations the hydrogen level was lower in the Alloy 2 samples than in the corresponding Zircaloy-2 samples, see Figure 6.

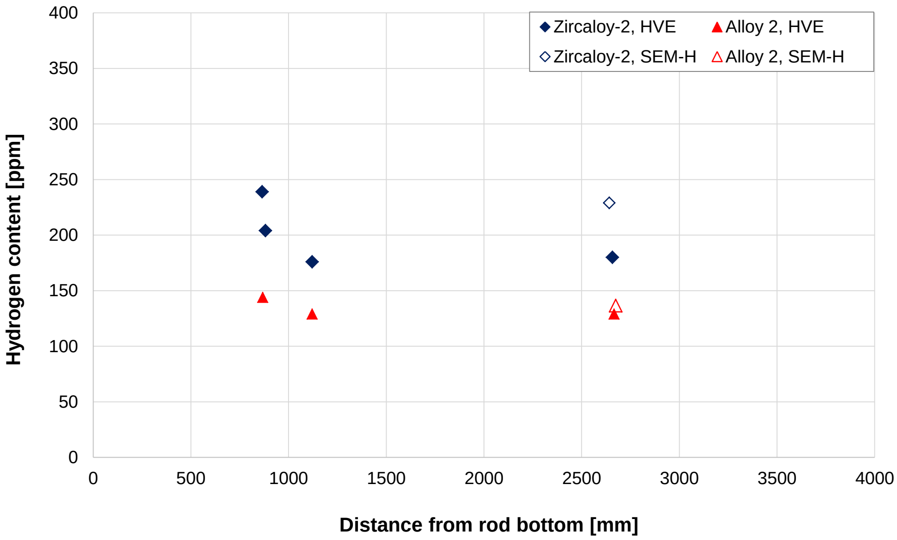

Figure 6: HVE and SEM hydrogen measurements

## 5. Hydrogen pickup data

The HiFi coupons and fuel rod cladding in the testing reported here have always been loaded together with Zircaloy-2 reference material in both reactor irradiations and autoclave testing. This enables a direct comparison of the different materials under identical conditions. The hydrogen pickup data is summarized in Figure 7. The data is plotted in order of increasing hydrogen content of the reference Zircaloy-2 cladding.

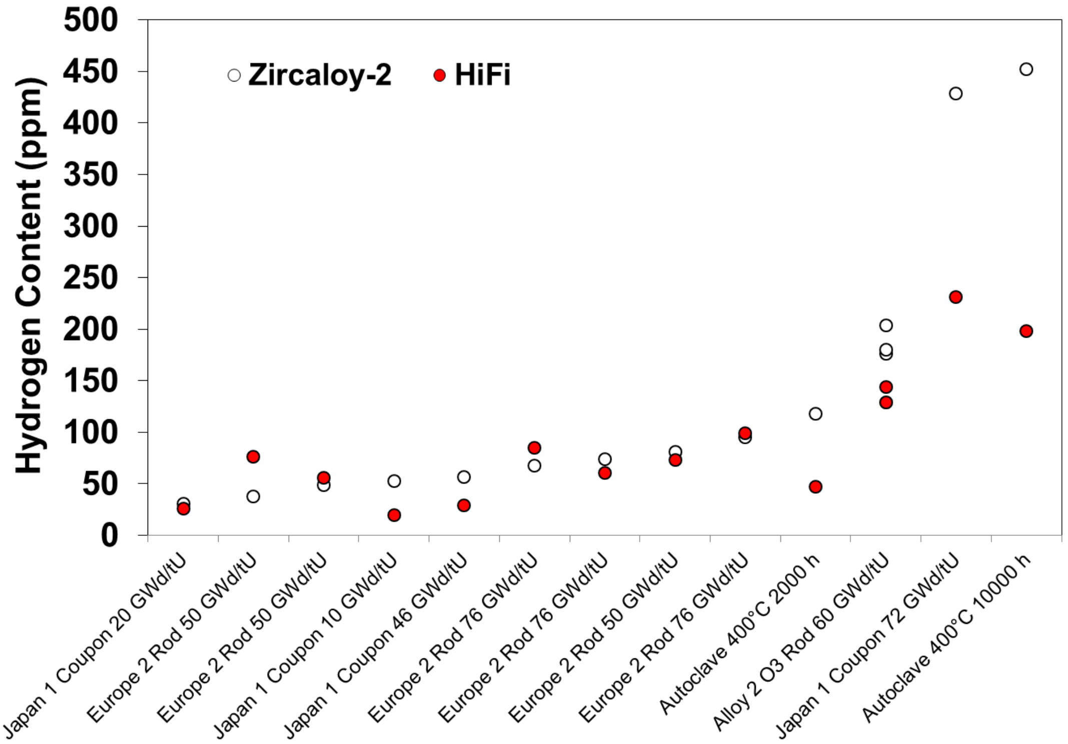

Figure 7: Summary of hydrogen pickup data.

The benefit of a lower hydrogen pickup with HiFi cladding becomes apparent in conditions where the Zircaloy-2 cladding has greater than approximately 100 ppm hydrogen. In lower hydrogen pickup conditions such as those found in “Europe 2” both HiFi and Zircaloy 2 behave similarly. The measurement uncertainty also has a larger contribution to the scatter at low hydrogen content levels.

When compared to the Westinghouse hydrogen pickup database shown in [7] and more recent data in [8] the “Europe 2” data for both HiFi and Zircaloy-2 appears as quite exceptional in that, after 7 cycles of irradiation to 76 GWd/tU, the hydrogen content remains less than 100 ppm [4]. Corresponding 7 cycle rods with Zircaloy-2 cladding at a burnup of 55-60 GWd/tU operated in the Leibstadt BWR had 170-275 ppm hydrogen whilst 9 cycle rods, with a similar rod average burnup to “Europe 2” of 71-79 GWd/tU had 575-640 ppm [8]. The rods from “Europe 2” do not show the accelerated end of life hydrogen pickup observed in Leibstadt.

Two possible explanations for the lower H pickup in “Europe 2” are considered. Firstly it is known that hydrogen pickup is not just a simple function of burnup and that residence time in core is also important. The burnup accumulation rate was higher in “Europe 2” than either Leibstadt or Oskarshamn 3, Figure 8. It required nine annual cycles in Leibstadt to reach rod average burnups of 70.7 to 78.7 MWd/kg whilst the “Europe 2” irradiation achieved 76 MWd/kg after only seven cycles. Typical seven cycle hydrogen pickup data from Leibstadt is however still higher than that observed in “Europe 2” and the second factor which may be more important is the power history, particularly towards the end of life. “Europe 2” rods were operated at high powers throughout the irradiation whilst Leibstadt rods, which form the majority of the Westinghouse database, were operated at low powers towards the end of life. Low power operation later in life has been shown to promote high hydrogen pickup [9]. The hydrogen pickup in both Leibstadt and "Europe 2" is therefore entirely consistent with observations from other fuel vendors.

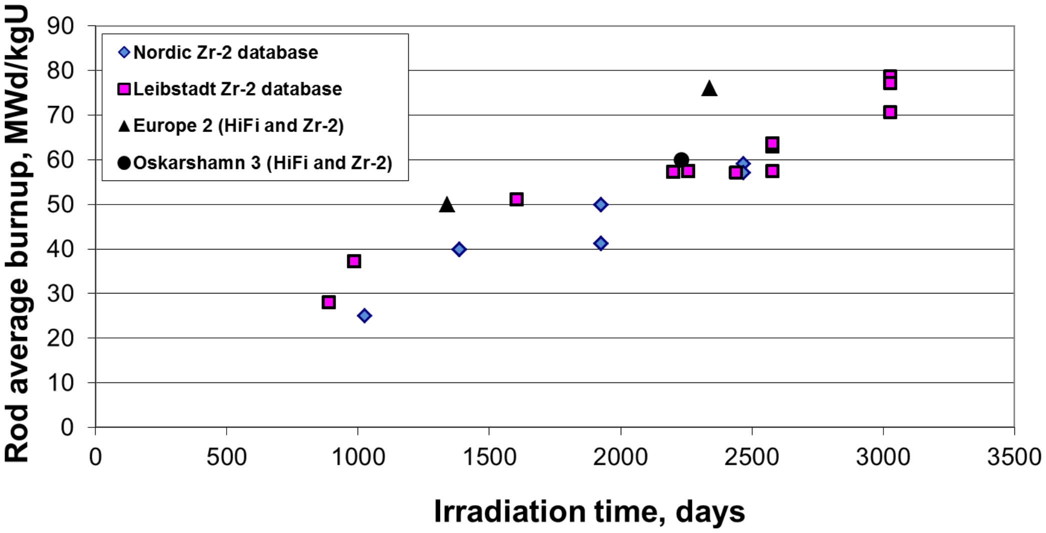

Figure 8: Rod average burnup versus irradiation time.

Due to the low hydrogen content found in rods irradiated in "Europe 2" subsequent HiFi rods were loaded in commercial plants with lower burnup accumulation rates. Hot-cell PIE from these rods will be performed as the rods are unloaded in the next few years.

## 6. Further optimization of HiFi

The HiFi loadings summarized in Table 2 were all of "standard HiFi", with the exception of the Alloy 2. They had an essentially identical manufacturing process and, apart from iron, had routine target levels of all other elements as used in the manufacture of Westinghouse LK3 Zircaloy-2 cladding. Today's versions of Zircaloy-2 are far superior to the initial versions produced many decades ago; however, after half a century of optimization there was little scope for further improvement in Zircaloy-2. NFI have already shown that HiFi can be manufactured with higher sigma A (annealing parameter) values without encountering nodular corrosion [1]. In addition to heat treatments the HiFi specification has some room to adjust and further optimize the target levels of Fe, Cr and Ni compared to the standard HiFi. Some additional modified HiFi variants have recently been produced and initial double side autoclave testing at 415 °C indicates that further improvement and reduction of the hydrogen pickup is possible. As expected from earlier data the standard HiFi has less hydrogen pickup than Zircaloy-2 whilst all the modified HiFi variants show even greater improvement, Figure 9. The autoclave testing is ongoing and will continue to higher hydrogen levels.

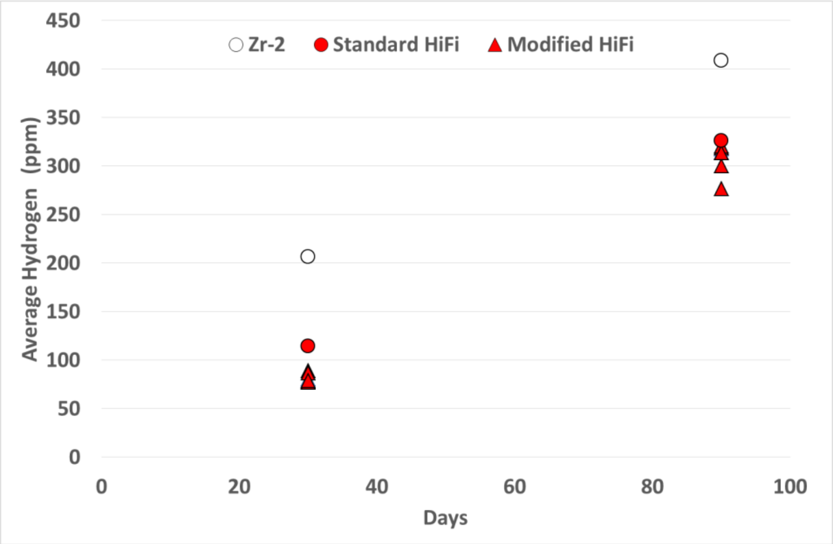

Figure 9: Comparison of hydrogen pickup in autoclave tests on standard Zircaloy-2, standard HiFi and a variety of modified HiFi materials including Alloy 2.

## 7. Conclusions

Extensive characterization tests performed on Zircaloy-2 and HiFi cladding demonstrate that, with similar heat treatment and processing, the differences in chemical composition between the materials do not appreciably alter the physical, mechanical, microstructural or LOCA properties from those known for Zircaloy-2 cladding. Whilst the corrosion performances of Zircaloy-2 and HiFi are similar, the benefit of HiFi's high iron content results in a significantly lower hydrogen pickup fraction. Initial autoclave results suggest further HiFi modifications will result in even lower hydrogen pickup. A range of hydrogen pickup data from autoclaves, coupons and more recently from end of life commercial fuel rods is presented which clearly shows this benefit of high iron claddings in BWR applications. Data is being gathered across a range of operating conditions such as different water chemistry, burnup and power histories.

## 8. Acknowledgements

The Alloy 2 hot-cell data which was obtained at Studsvik within the Fuel Program Group (PGB) with support from the participating organizations OKG, Vattenfall and Westinghouse is gratefully acknowledged.

## 9. References

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