EVOLUTION OF HYDROGEN PICKUP FRACTION WITH OXIDATION RATE ON ZIRCONIUM ALLOYS

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ABSTRACT

Hydrogen pickup during aqueous corrosion of zirconium-based alloys is currently the most important life-limiting phenomenon for operation of cladding and structural components of fuel in light water reactors, especially at high burnup where embrittlement due to hydriding becomes a significant factor. A fraction of the hydrogen generated by the corrosion reaction is absorbed by the metal, which is known as the hydrogen pickup fraction. The current understanding of the fundamental mechanisms driving hydrogen absorption and governing the hydrogen pickup fraction, and crucially its relationship with the oxidation rate, is very limited and semi-empirical at best. For many practical purposes and analytical methods it has been assumed that the hydrogen pickup fraction of zirconium-based components is constant over the entire in-reactor exposure. In this study, tubing and strip specimens of zirconium alloys, using a wide range of commercial and model chemical compositions and final heat treatments to produce different microstructures, have been subjected to long-term autoclave testing simulating in-reactor conditions. Alloy systems studied include Zircaloy-2, Zircaloy-4, ZIRLO®+ and zirconium-niobium. The corrosion kinetics and the hydrogen content and pickup fraction were closely followed during exposure. A consistent correlation between the oxidation rate and the hydrogen pickup fraction has been observed whereby the hydrogen pickup fraction increases when the corrosion rate decreases, such that the hydrogen pickup fraction is not constant during exposure. The hydrogen pickup fraction evolves following a correlation with the oxidation rate, while being strongly influenced by alloy composition and final heat treatment of the material. The correlation between hydrogen pickup fraction and oxidation rate has been attributed to changes in the electronic conductivity of the zirconium oxide, which in turn is linked to the characteristics of the oxide and the base metal. The results from this study are consistent and supported by observations made under a broader research program to understand the fundamental mechanisms of hydrogen pickup in zirconium alloys, called MUZIC-2. MUZIC-2 is led by Westinghouse in collaboration with industrial partners: EPRI, EDF, Rolls-Royce, Amec Foster Wheeler, Sandvik, Vattenfall, Studsvik, Paul Scherrer Institute and NNL; as well as academic institutions: University of Oxford, University of Manchester, Imperial College London, Chalmers Institute of Technology and Pennsylvania State University. Under this collaboration program, the samples produced in this study are being characterized with state-of-the-art techniques, aiming to understand the interaction and evolution of oxidation rate, chemistry/microstructure/conductivity of the oxide, transport paths and eventually the evolution of the hydrogen pickup fraction. In this paper these interactions are put into context by reporting and analyzing industry relevant oxidation rates and hydrogen pickup data produced by Westinghouse.

1. Background

Zirconium-based alloys are widely used for fuel cladding and structural components in light water nuclear reactors. For these components, hydrogen pickup due to aqueous corrosion during operation is currently the most important life-limiting phenomenon. This is most

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noticeable at high burnup towards the end of life of the fuel, where embrittlement of the material due to hydriding becomes a significant factor for its performance. It is therefore of utmost importance to the nuclear industry to optimize materials to minimize hydrogen pickup during operation.

The propensity of a material to absorb hydrogen is commonly expressed as the hydrogen pickup fraction, defined as the ratio of the hydrogen absorbed by the metal to the total amount of hydrogen generated during corrosion. The hydrogen pickup fraction of zirconium based materials is affected by multiple factors. The current understanding of the fundamental mechanisms driving hydrogen absorption and governing the hydrogen pickup fraction, and crucially its relationship with the oxidation rate, is very limited and semi-empirical at best.

In order to gain understanding on the fundamental mechanisms involved during aqueous corrosion of zirconium alloys, a large international collaborative research program started in 2006. The program is called Mechanistic Understanding of Zirconium Corrosion, abbreviated as MUZIC. The first phase of MUZIC provided important insights into corrosion mechanisms and the evolution of the zirconium oxide during transition of oxidation kinetics, examples of publications in [1,2].

The second phase of MUZIC, which started in 2010, is focused on hydrogen pickup mechanisms. MUZIC-2 is led by Westinghouse in collaboration with industrial partners: Electric Power Research Institute, Electricite de France, Rolls-Royce, Amec Foster Wheeler, Sandvik, Vattenfall, Studsvik, Paul Scherrer Institute and National Nuclear Laboratory; together with academic institutions: University of Oxford, University of Manchester, Imperial College London, Chalmers Institute of Technology and Pennsylvania State University. The approach of MUZIC-2 is a combination of experimental and theoretical/modeling studies using complementary techniques.

For many practical purposes and analytical methods for nuclear fuel design it has been assumed that the hydrogen pickup fraction of zirconium-based components is constant over the entire in-reactor exposure. Recently within MUZIC-2, it has been demonstrated that the hydrogen pickup fraction is not constant during the corrosion process and has a close relationship with the corrosion kinetics. A correlation between the oxidation rate, the onset of corrosion transitions and the hydrogen pickup fraction has been consistently observed whereby the hydrogen pickup fraction increases when the corrosion rate decreases, such as the hydrogen pickup fraction is not constant during exposure. The correlation between hydrogen pickup fraction and oxidation rate has been attributed to changes in the electronic conductivity of the zirconium oxide, which in turn is linked to the characteristics of the oxide and the base metal. Indeed, the pickup of hydrogen has been hypothesized to have an inverse relationship to the rate of electronic conductivity of the oxide, i.e. the higher the electronic conductivity of the oxide, the lower the hydrogen pickup fraction [3,4].

The study reported in this paper consists of long-term autoclave testing of tubing and strip material of zirconium-based alloys using a wide range of commercial and model chemical compositions and final heat treatments to produce different microstructures. During testing, the corrosion kinetics and hydrogen pickup fraction were closely followed as a function of exposure, aiming to independently test the hypothesis that the hydrogen pickup fraction has an inverse relationship with the oxidation kinetics, and that different conditions in the base metal affect the hydrogen pickup fraction, most probably due to changes in the conductivity of the oxide.

The samples produced in this study are being characterized using state-of-the art techniques, with results reported elsewhere [5,6], aiming to understand the interaction and evolution of oxidation rate, chemistry/microstructure/conductivity of the oxide, transport paths and eventually the evolution of the hydrogen pickup fraction. In this paper these interactions are put into context by reporting and analyzing oxidation rate and hydrogen pickup data produced by Westinghouse.

2. Autoclave Testing

In order to test the multiple factors that affect the hydrogen pickup fraction in zirconium-based alloys, a selection of materials and conditions was made using the following criteria:

- Include industry relevant alloy systems such as Zircaloy-2 (Zr-Sn-Fe-Cr-Ni), Zircaloy-4 (Zr-Sn-Fe-Cr), ZIRLO (Zr-Nb-Sn-Fe) and Zr-Nb. Alloying elements are likely to segregate in the zirconium matrix and in the oxide, and also form second phase particle (SPP) precipitates in the metal (e.g. Laves phases and β-Nb). Some elements (e.g. Nb and Sn) may distribute in solid solution. Different chemical compositions were included to confirm and gain insights on known effects such as the beneficial effect of Nb and Fe, and the detrimental effect of Ni on hydrogen pickup.
- Some of the materials were obtained as strip and others as cladding tubes. The type of specimen is indicated in Table 1 below. All the specimens were tested in as-fabricated condition. Buffed surface for strips and belt polished outer diameter with grit blasted inner diameter for tubing were employed.
- All the materials studied were obtained in fully recrystallized condition. To study the effect of SPP size/density and phase transformation, some of the materials (designated as -A) were subjected to an additional anneal at 720°C for 24 hours.

All the materials listed were subjected to corrosion testing in pure water at 360°C in static stainless steel autoclaves. The tubing and strip specimens were tested in two separate autoclaves. The number of coupons in each autoclave at a given time was limited to maintain the level of hydrogen dissolved in the water below 40 cc/kg H_2O. Enough coupons were prepared to extract samples after 1, 3, 7 and then approximately every 15 days until a total corrosion time of 225 days was achieved. After extraction, specimens were weighed and hydrogen content measurements were performed using inert gas diffusion.

3. Corrosion Kinetics and Hydrogen Pickup Fraction

For all the specimens tested, the weight gain as a function of exposure time follows a power law of the form $W = At^n$ from the start, where W is the weight gain, t is the exposure time, and A and n are constants. The value of n, in particular, is characteristic of each material and condition. Table 1 presents a summary of the specimens tested and the overall results for the pre-transition regime. At different points during the tests all the specimens reached a corrosion transition, where the oxidation rate increases. In some cases the post-transition oxidation reproduces the initial kinetics with periodicity, while in others the oxidation kinetics deviate from a power law after the first transition. An example of this is shown for ZIRLO, with and without the additional heat treatment, in Figure 1.

Table 1 shows the constants describing the pre-transition oxidation kinetics for all the materials tested, as well as the total hydrogen pickup fraction at the end of the test. The main observations from this table are the following:

- The pre-transition oxidation kinetics and onset of corrosion transition for the LK2+ and LK3 variants of Zircaloy-2 are very similar.
- All the Zr-Nb specimens without additional anneal showed corrosion transition late in the tests.
- For all the alloy systems, the annealing treatment accelerates the onset of the corrosion transition, and increases the oxidation rate post-transition. In some cases, for example for ZIRLO-A in Figure 1, the corrosion rate is almost constant after the first transition.

Table 1 Pre-transition oxidation kinetics and total hydrogen pickup fraction

			Pre-transition oxidation kinetics			Hydrogen pickup fraction at end of test (225 days)
Alloy	**Designation**	**Heat treated (720°C/24hrs)**	***A***	***n***	**Oxide thickness at transition (μm)**	
Zircaloy-2	LK2+(1)	-	6.9	0.29	2.2	20%
	LK3(1)	-	7.1	0.28	2.1	20%
	LK3-A(1)	Yes	6.7	0.33	2.2	25%
Zircaloy-4	Zr-4(2)	-	8.1	0.29	2.1	20%
	Zr-4-A(2)	Yes	6.9	0.32	1.9	17%
ZIRLO	ZIRLO(2)	-	7.0	0.34	2.5	16%
	ZIRLO-A(2)	Yes	5.5	0.41	2.1	10%
Zr-Nb	Zr-0.5Nb(1)	-	6.9	0.36	3.1	9%
	Zr-1.0Nb(1)	-	5.7	0.41	3.4	12%
	Zr-1.0Nb-A(2)	Yes	5.9	0.47	3.1	9%
	Zr-2.5Nb(1)	-	7.7	0.34	3.2	11%

(1) Cladding Tube (2) Strip

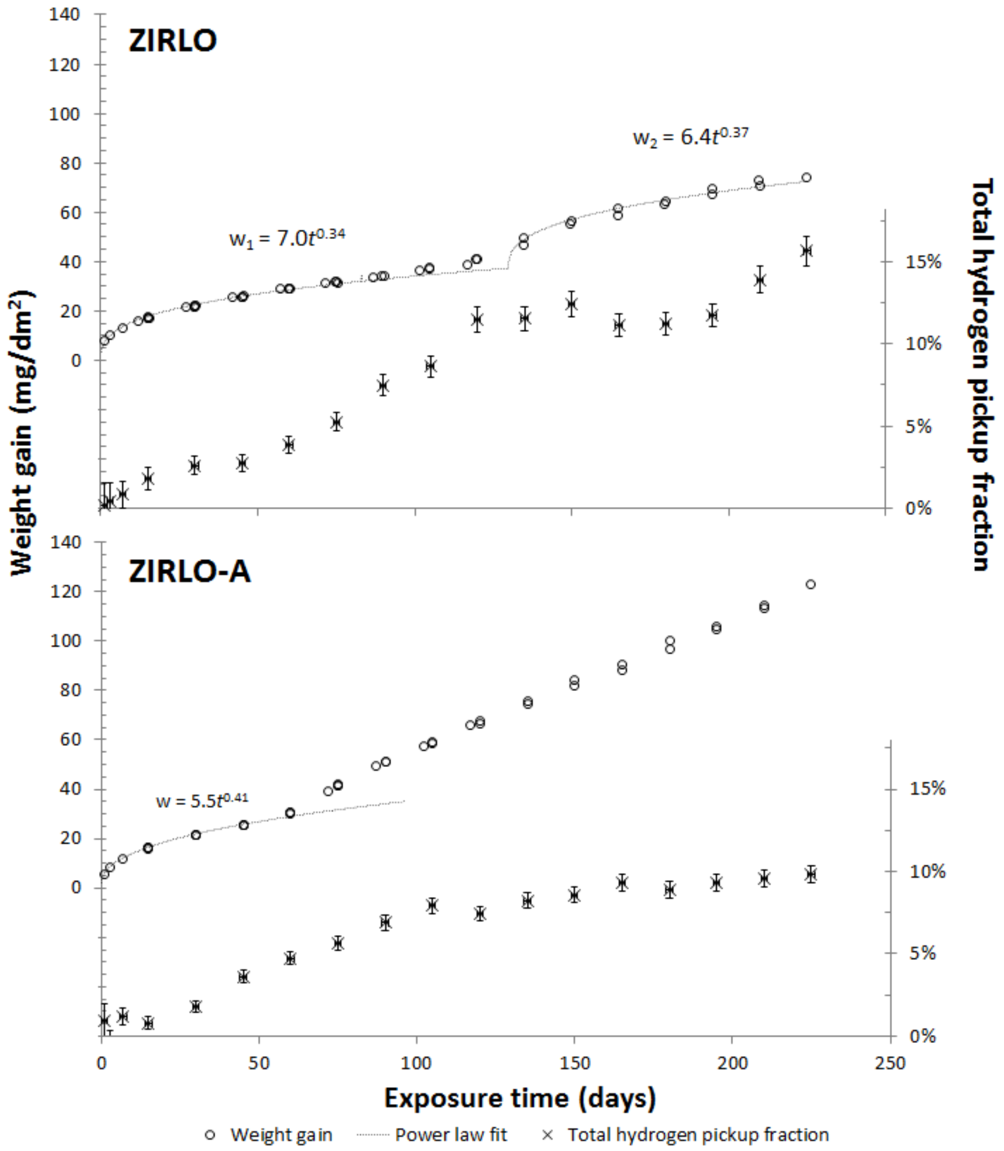

Figure 1 Weight gain and total hydrogen pickup fraction of ZIRLO tubes (with and without additional anneal) as function of exposure time. Regimes where a power law applies are indicated

Figure 1 shows the oxidation kinetics for ZIRLO specimens with and without the additional anneal. In the initial pre-transition regime and in some samples in a second pre-transition regime, the kinetics can be described by a power law. The total hydrogen pickup fraction at different exposure times is also shown in the figure. Crucially, the total hydrogen pickup fraction varies as a function of exposure time. Annealed samples of Nb-containing alloys (ZIRLO-A and Zr1.0Nb-A), show oxidation kinetics approximately linear after the first transition, while the hydrogen pickup fraction remains reasonably constant.

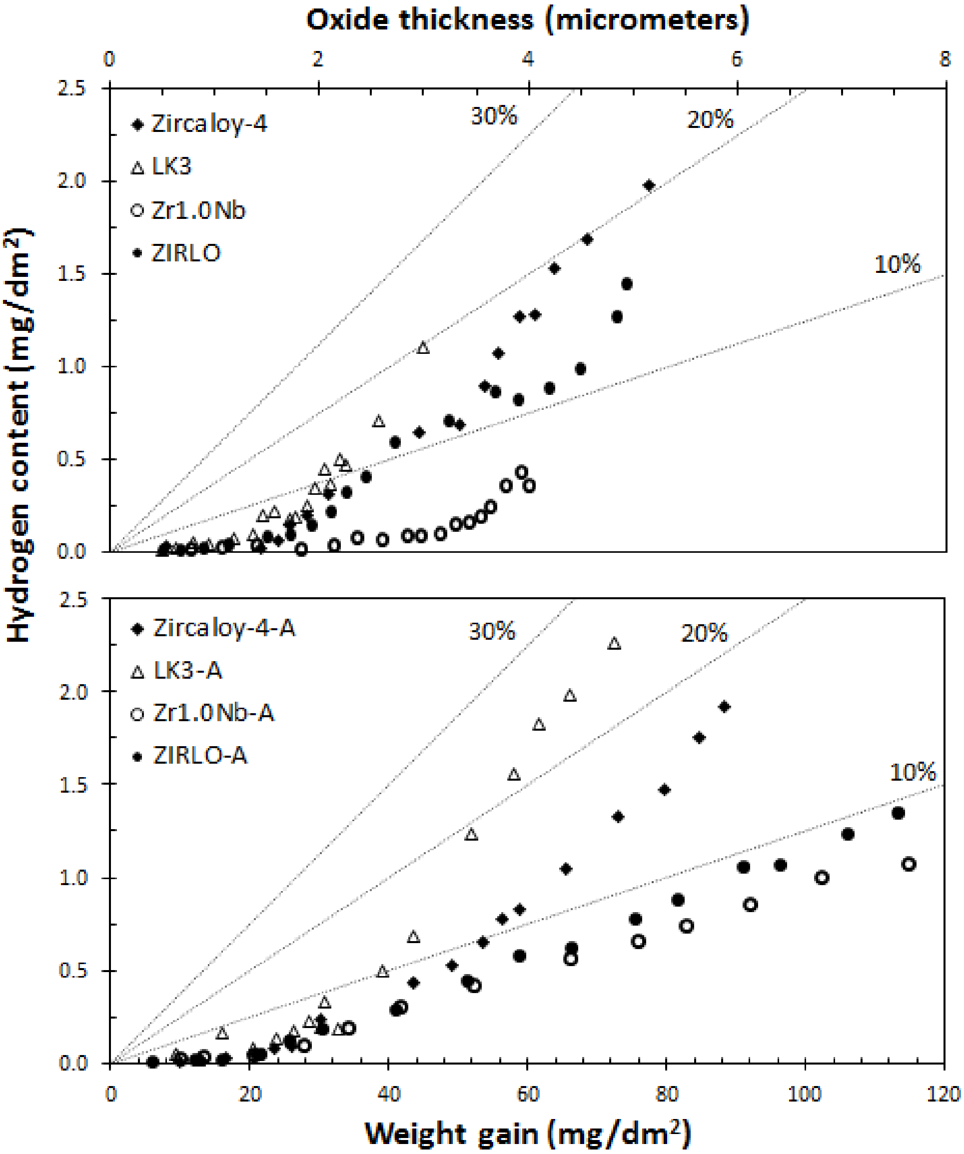

Figure 2 Hydrogen content as a function of weight gain (and oxide thickness) for different alloys. Materials with additional anneal (designated as –A) at the bottom. The straight dashed lines correspond to constant total hydrogen pickup fraction of 10%, 20% and 30%

Figure 2 shows the hydrogen content in each alloy tested versus total corrosion weight gain and oxide thickness. In such a graph, if the hydrogen pickup fraction is constant during corrosion the data points should follow a straight line. Constant hydrogen pickup fractions of 10, 20 and 30% are indicated in the figure. The data shows that the hydrogen pickup does not follow a straight line, and increases as the corrosion proceeds. For example, Zircaloy-2 (LK3) has a total hydrogen pickup fraction of less than 10% at 20 mg/dm^2 (about 1.4 micron thick oxide layer) but about 20% at 40 mg/dm^2 (2.8 microns). The differences between the alloys are clear, with Zr-1.0Nb showing the lowest hydrogen pickup fraction, followed by

ZIRLO and Zircaloy-4. Zircaloy-2 (LK3) shows the highest hydrogen pickup fraction. The additional annealing treatment does not change this ranking, but modifies the distance between alloys with the hydrogen pickup fraction of LK3-A remaining high, while that of ZIRLO-A decreases. The figure illustrates that the hydrogen pickup fraction increases with exposure time for all the materials. For the specimens without anneal the hydrogen pickup fraction steadily increases following the periodicity of the corrosion kinetics. The additional anneal makes the evolution of hydrogen content after the first corrosion transition more linear, resulting in an almost constant hydrogen pickup fraction. At the same time the oxidation rate deviates from a power law and also remains relatively constant. ZIRLO-A and Zr-1.0Nb-A show a hydrogen pickup fraction close to constant after the first oxidation transition, just below 10%.

It is important to note at this point that the testing conditions for the autoclave tests performed are most relevant for in-reactor performance of pressurized water reactor (PWR) materials. Relevance of the observations reported here for boiling water reactor (BWR) phenomena such as nodular or shadow corrosion remains to be tested.

To illustrate the correlation between oxidation kinetics and hydrogen pickup fraction and confirm the observations in [3], the total hydrogen pickup fraction is plotted in Figure 3 as a function of the exponent n, which describes the change in corrosion rate when a power law applies before the first corrosion transition. Although specimens with additional anneal (-A) do not show periodic power law oxidation kinetics, the correlation remains valid since the hydrogen pickup fraction remains reasonably constant after the first transition. The figure clearly illustrates the inverse relationship between the hydrogen pickup fraction and the oxidation kinetics for the wide range of alloy systems tested in this study. For example, most Zr-Nb alloys have kinetics close to parabolic (n close to 0.5) and show the lowest hydrogen pickup fraction.

The results support the notion in [3] that a common oxidation and hydrogen pickup mechanism exists for all the alloys, and that the hydrogen pickup must be described within a general corrosion mechanism. The correlation between hydrogen pickup fraction and oxidation rate has been attributed to changes in the electronic conductivity of the zirconium oxide, which in turn is linked to characteristics of the oxide and the base metal [7]. All the samples produced in this study have been made available to the MUZIC-2 program to study the interaction of chemistry, microstructure and conductivity of the oxide with the oxidation rate and the hydrogen pickup fraction.

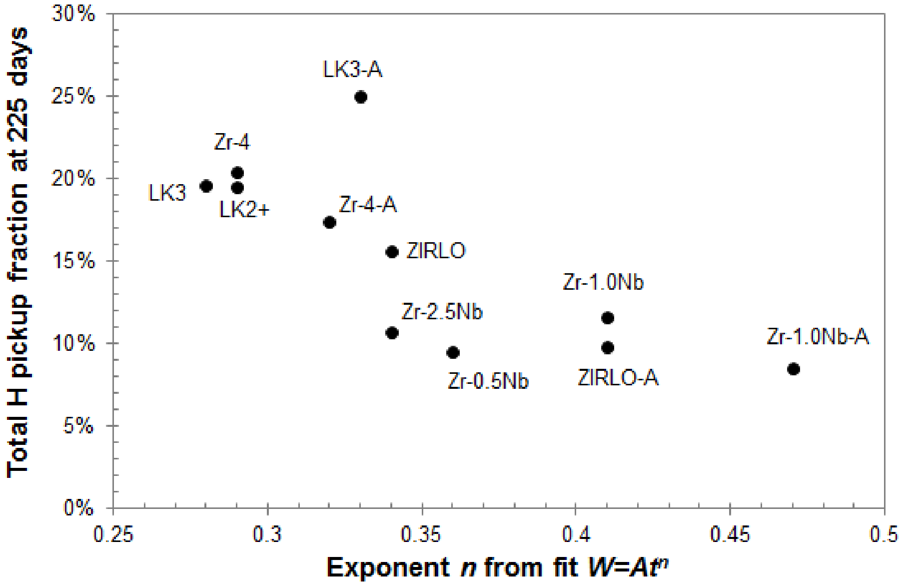

Figure 3 Total hydrogen pickup fraction at the end of autoclave tests (225 days) as function of the exponent *n* from the power law fit of the pre-transition weight gain $W=At^n$ for various zirconium alloys

4. Conclusion

A wide range of industry-relevant alloys have been tested in identical conditions to closely follow oxidation kinetics and hydrogen pickup. The study confirms that the hydrogen pickup fraction is clearly not constant throughout the corrosion process of zirconium-based alloys and correlates with oxidation kinetics. The hydrogen pickup fraction decreases with increasing the exponent n, such that it is the lowest for materials with oxidation kinetics close to parabolic, consistent with the observations in [3].

The base hydrogen pickup fraction and its variation during corrosion both depend on the composition of the material, with the highest fractions observed in Zircaloy-2 and the lowest in Zr-Nb systems. Thermal treatments, which increase the size of second phase particles in Zircaloy-2 and Zircaloy-4, and induce phase transformations in ZIRLO and Zr-Nb; accelerate the onset of the oxidation transition, increase the oxidation rate after transition, and change the subsequent evolution of the hydrogen pickup fraction.

The results obtained in this study are consistent with the hypothesis in [3] and [7] that the mechanisms for oxidation and hydrogen pickup are the same for all the alloys, and that they are closely coupled, so a mechanistic model of zirconium corrosion must include both phenomena.

Acknowledgement

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