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The role of hydrogen in zirconium alloy corrosion

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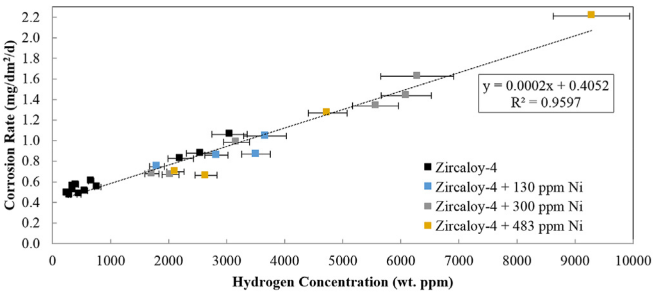
HIGHLIGHTS

- Systematic study of the effects of H concentration on oxide growth in Zircaloy-4.
- The formation of hydrides is associated with accelerated zirconium alloy corrosion.
- H concentrations above the TSS leads to earlier periodic oxide transitions.
- Advanced corrosion into the metal where hydrides precipitated near the MOI.
- Thought that local hardening of the metal matrix leads to earlier oxide transitions.

GRAPHICAL ABSTRACT



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ABSTRACT

Hydrogen enters zirconium metal as a result of the corrosion process and forms hydrides when present in quantities above the solubility limit at a given temperature. Zircaloy-4 coupons of different thicknesses (0.4 mm-2.3 mm) but identical chemistry and processing were corroded in autoclave at 360 °C for various times up to 2800 days. Coupons were periodically removed and weighed to determine weight gain, which allows follow of the corrosion kinetics. Coupon thickness differences resulted in different volumetric concentrations of hydrogen, as quantified using hot vacuum extraction. The thinnest coupons, having the highest concentration of hydrogen, demonstrated acceleration in their corrosion kinetics and shorter transition times when compared to thicker coupons. Furthermore, it was seen that the post-transition corrosion rate was increased with increasing hydrogen concentration. Corrosion rates increased only after the terminal solid solubility (TSS) was exceeded for hydrogen in Zircaloy-4 at 360 °C. Therefore, it is hypothesized that the corrosion acceleration is caused by the formation of hydrides. Scanning electron microscope (SEM) examinations of fractured oxide layers demonstrate the oxide morphology changed with hydrogen content, with more equiaxed oxide grains in the high hydrogen samples than in those with lower hydrogen content. Additionally, locations of advanced oxide growth were correlated with locations of hydrides in the metal. A hypothesis is proposed to explain the accelerated corrosion due to the presence of the hydrides, namely that the metal, locally, is less able to accommodate oxide growth stresses and this leads to earlier loss of oxide protectiveness in the form of more frequent oxide kinetic transitions.

1. Introduction and literature review

Despite having been the subject of extensive research for

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decades, the corrosion of zirconium alloys in nuclear power plants is still not fully understood [1]. As the metal initially rapidly corrodes in the high temperature water present in a nuclear reactor core, the oxide layer that forms is protective and slows down further oxidation. This protective oxide layer is constituted of mostly monoclinic phase zirconium dioxide with some tetragonal phase by the following reaction of Zr metal:

$$Zr_{metal} + 2H_2O_{liquid} \rightarrow ZrO_2 + 2H_2 \quad (1)$$

The kinetics of this oxidation reaction are well described by the power law shown in Equation (2),

$$W = At^n \quad (2)$$

where W is the weight gain, t is the exposure time, A is a constant, and n is an exponent which for autoclave corrosion at 360 °C typically ranges anywhere from 0.2 to 0.5 depending on the alloy [1]. Eventually, the oxide kinetics accelerate during what is known as transition, as depicted in Fig. 1.

Hydrogen can play an important role in the corrosion process of Zr alloys. Because of conservation of mass and charge balance, the oxidation reaction has to be balanced by a reduction reaction, which is generally the hydrogen evolution reaction. Because only a fraction of the hydrogen that is produced by this reaction enters the metal, hydrogen pickup is typically quantified through the hydrogen pickup fraction [2–4]. The hydrogen that enters the cladding material is found in solid solution as long as its concentration remains below the terminal solid solubility (TSS) for hydrogen of the zirconium alloy [2,5–10]. The TSS increases with temperature, such that negligible hydrogen can be dissolved into the metal at room temperature but up to ~120–140 wt ppm can be dissolved at 360 °C, depending on the alloy [2,5–10].

The terminal solid solubility for hydride precipitation (TSS_p) during cooling is different from the terminal solid solubility for hydride dissolution during heating (TSS_d) [5,11]. The difference between these two concentrations is important for many applications, but in the experiment described herein, the quantity of interest is the TSS_d. This is because during autoclave corrosion experiments, the autoclave is cooled down relatively frequently to weigh the samples. During the cool down to room temperature, all of the hydrogen is precipitated out as hydrides. Upon reheating, the hydrides dissolve into the matrix, but only up to the TSS_d. For simplicity, in the remainder of this paper, the relevant concentration limit, TSS_d, will be referred to as the TSS.

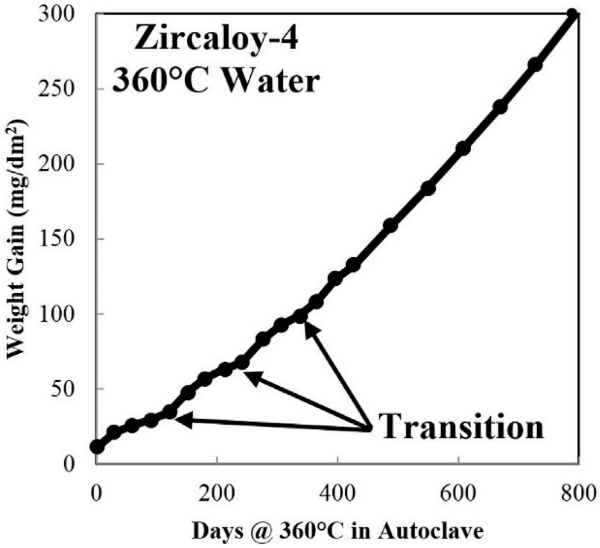

Fig. 1. Weight gain (which is directly correlated with oxide thickness) versus time of a Zircaloy-4 coupon corroded in 360 °C water in autoclave illustrating the cyclic nature of oxide growth and transition cycles.

Fig. 2 shows an example of oxide thickness as a function of burnup for Zircaloy-4 in PWRs and demonstrates the commonly observed accelerated corrosion in commercial reactor claddings subject to high fuel burnup [5,12–16]. One hypothesis to explain this accelerated corrosion is that it is caused by hydride formation at high burnup [12,13,15]. Other factors have been correlated to accelerated in-reactor corrosion, including dislocation formation and accumulation, precipitate amorphization and dissolution, water chemistry (such as the addition of Li), and irradiation growth [12]. However, the observed corrosion rate change at high burnup should be correlated to some parameter that changes at a given exposure, such as hydride formation. Irradiation dissolution and precipitate amorphization, the formation of dislocation loops, water chemistry, and gamma irradiation operate continuously since the beginning of irradiation and in the case of the latter two are present at all times during reactor operation with little change [17]. Since hydride formation can be correlated to accelerated corrosion, it is important to understand the magnitude and onset of this effect, if any, on corrosion resistance of zirconium alloys that are exposed to water for a sufficient duration to cause hydride precipitation.

Initial studies focused on formation of hydrides at the metal-oxide interface (MOI) of Zircaloy-4 [13]. It is known that hydrogen migrates towards regions of high stress and those that are coldest [2,5,13,18,19]. Since in a fuel rod the metal-oxide interface is the coldest location of the metal (farthest from the heat flux of inner fuel pellets and closest to coolant) the hydrogen accumulates there, which leads to hydride formation [13]. This has been verified in many studies [5,18,19].

To study the effect of hydrides on corrosion, researchers performed tests on zirconium alloy samples charged with hydrogen prior to autoclave exposure [12,14,20,21]. Kido demonstrated uniform corrosion acceleration caused by hydrogen in 360 °C water with pre-charged zirconium alloy samples [21]. Results from Blat and Noel from autoclave corrosion tests (under various conditions, including 360 °C primary water, 360 °C heavy water, 400 °C steam, and in furnace with air at 400 °C) on Zircaloy-4 cladding pre-charged with hydrogen using both gaseous and cathodic charging techniques similarly showed accelerated corrosion for samples with more hydrides [14,20]. Of note was that no acceleration of the corrosion kinetics in the pre-transition regime was observed by Kido in materials with higher initial hydrogen concentration [12]. Blat and Noel showed that a thick outer hydride layer (created by cathodic hydrogen charging) was correlated to a significant increase in corrosion as measured by weight gain [14]. Overall, these initial studies indicate that the accumulation of hydrogen can have a deleterious effect on corrosion.

Autoclave tests at 340 °C (water), 360 °C (water), and 400 °C (steam) of Zircaloy-4 tube specimens pre-charged with hydrogen from ~100 to 3000 wt ppm showed that the corrosion temperature affected the onset of accelerated corrosion due to hydrogen, and that this onset correlated with the TSS for those particular temperatures [12]. Once the TSS_P was reached, the corrosion accelerated, as shown in Fig. 3 showing post-transition corrosion rate as a function of hydrogen concentration from the work performed by Kido et al. [12].

A number of possibilities for the mechanism of hydrogen-based accelerated corrosion have been proposed including:

- Faster corrosion of the zirconium hydride as compared to the Zr matrix [14].