



Dynamics of Hydride Formation in Zircaloy-4 for Nuclear Applications

B.S. Rovelo¹, L.H.C. Francisco², N.W.S. Morais³, and J.O.V. Bustillos⁴

¹ brovelo@usp.br, Nuclear and Energy Research Institute (IPEN/CNEN-SP)

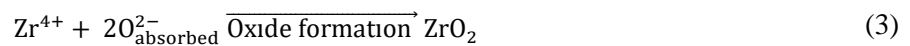
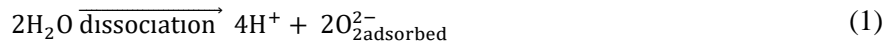
² leo.francisco@usp.br, Nuclear and Energy Research Institute (IPEN/CNEN-SP)

³ nathanaelmorais@gmail.com, Nuclear and Energy Research Institute (IPEN/CNEN-SP)

⁴ ovega@ipen.br, Nuclear and Energy Research Institute (IPEN/CNEN-SP)

1. Introduction

Zirconium alloys (*e.g.*, zircaloy-4) are widely used for nuclear applications, more specifically, in nuclear fuel cladding components (rods) that form the core of pressurized water reactors (PWRs). Properties such as high mechanical, creep, and corrosion resistances and low shock section for absorbing thermal neutrons of zircaloy-4 make it an efficient material for nuclear applications [1]. As the nuclear fuel coating plays an essential role in preventing the escape of nuclear fission products, which are generated in the fission reaction to produce energy and in the transfer of heat to the coolant liquid of the primary circuit that guarantees good functioning and safe operation in PWRs, understanding the mechanisms that can lead zircaloy-4 to weaken and rupture, even outside of its working conditions, is essential to improving its performance [2]. It is known that, in its working conditions, zircaloy-4 absorbs hydrogen from the water present in the primary circuit of PWRs via an oxidation reaction according to equations 1-4 where the diffusion of hydrogen in zircaloy-4 occurs through two simultaneous processes: the discharge of hydrogen from the alloy's oxidation reaction and the metallic absorption of hydrogen and formation of hydrides [3].



With the absorption of hydrogen, zircaloy-4 presents three phases before its saturation: (I) Absorption of hydrogen by the atomic diffusion mechanism, (II) Nucleation of metal hydrides (ZrH_n), and (III) Growth of metal hydrides leading to fissure formation [6]. Hence, in this work, the micromechanics of plastic deformation in zircaloy-4 due to hydrogen absorption were investigated to further understand the effect of PWRs' severe conditions [4] on the alloy's structural and mechanical properties.

2. Methodology

To investigate the effects of hydrogen diffusion in zircaloy-4, the material can be hydrided in a furnace with hydrogen gas pressure. It is known that zircaloy-4 starts absorbing hydrogen at temperatures of around 573 K (under 150 kPa pressure of H_2), and when it reaches ~970 K the material may be completely hydrided so the

sample can be further pulverized [5,6].

The samples of zircaloy-4 used in this work were purchased from Westinghouse Electric Corporation, and are currently utilized to manufacture endcaps in uranium pellet coating tubes in the assembly of the fuel elements for Angra 1 and Angra 2 nuclear power plants. The caps were manufactured at the *Fábrica do Elemento Combustível* (FEC) of the *Indústrias Nucleares Brasileiras* (INB).

The material was first sectioned into 3 mm thick circular pieces (ϕ 8 mm) and washed with a 5% Extran solution in ultrasound for 50 min. Samples were then washed with a 10% HF + 5% HNO₃ aq. solution to remove any superficial ZrO₂ residues. After chemical treatment, the samples were stored and kept under vacuum at room temperature to prevent further oxidation.

To study the dynamics of zirconium hydride formation from zircaloy-4, two thermal treatment steps in a high-temperature tubular furnace with a hydrogen gas pressure setup were performed. In this setup, H₂ gas was first introduced into the furnace to ensure the removal of air before the heating was turned on. Then, the previously treated samples were placed in a ceramic crucible and inserted into the tubular furnace under 150 kPa H₂ gas pressure for a 2-step program: (i) Heating at a rate of 15 K/min starting from room temperature up to 653 K for 1 h. (ii) Further heating at a rate of 5 K/min from 673 K up to 973 K for 2.5 h. After the full program elapsed, the furnace was cooled back to room temperature at a rate of 15 K/min.

Structural analysis of the investigated materials was carried out by X-ray Diffraction (XRD) in a Rigaku Miniflex II diffractometer with a Bragg-Brentano geometry using Cu K α radiation within the 3-80° (2 θ) range with a 0.03°/s step width under 30 kV tension and 15mA current. Scanning Electron Microscopy (SEM) was performed on a JSM-IT700HR/LV microscope under high-vacuum and 10 kV tension *via* secondary electrons to probe surface details. Furthermore, samples were also studied by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) to determine metal concentrations present in the alloy. For this experiment, zircaloy-4 samples were first dissolved in 50% HF aq. Solution. After complete dissolution, residual HF was removed by evaporation and a 2% HNO₃ aq. solution was then added for analysis. Finally, elemental analysis was carried out in a TCHEN600 oxygen/nitrogen/hydrogen elemental analyzer with a setup of 5 kW power and 930 A current to quantify the hydrogen absorbed by the samples as a result of the thermal treatment with H₂ gas and the formation of hydrides. This experiment was performed in triplicate alongside a titanium standard to verify reproducibility, configuring an assertive investigation of the hydrogen content present in the studied materials.

3. Results and Discussion

Structural analysis by XRD (**Fig. 1a**) revealed a predominant tetragonal [Space group: I 4/m m m (139), Z=2] ZrH₂ phase (**Fig. 1b**) obtained from a complete phase transition after the thermal treatment of hcp [Space group: P 63/m m c (194), Z=2] zirconium phase (**Fig. 1c**) of zircaloy-4. Moreover, it is worth mentioning that while literature reports from neutron scattering measurements show the presence of Zr- δ and Zr- ϵ phases in hydrided zircaloy-4 samples [7], no significant amount of metallic zirconium was observed in the hydrided zircaloy-4 materials studied in this work. As no residual ZrO₂ was found in the diffraction data, the XRD results suggest the effectiveness of the chemical treatment used for sample preparation to remove any traces of oxide residues from manufacturing processes, further favoring hydrogen diffusion in the samples and accounting for the absence of the Zr- δ and Zr- ϵ phases in hydrided zircaloy-4.

Additionally, from SEM images (**Fig. 1d, e**) it was possible to visualize brittle-like cracks on the surface of hydrided zircaloy-4 samples due to the formation of ZrH₂ as previously observed by XRD. Such defects weaken the alloy's mechanical properties, further facilitating hydrogen diffusion through the material and being directly correlated with macroscopic fractures to the point the metal structure of zircaloy-4 turns fragile as a result of the phase transition until it is completely pulverized.

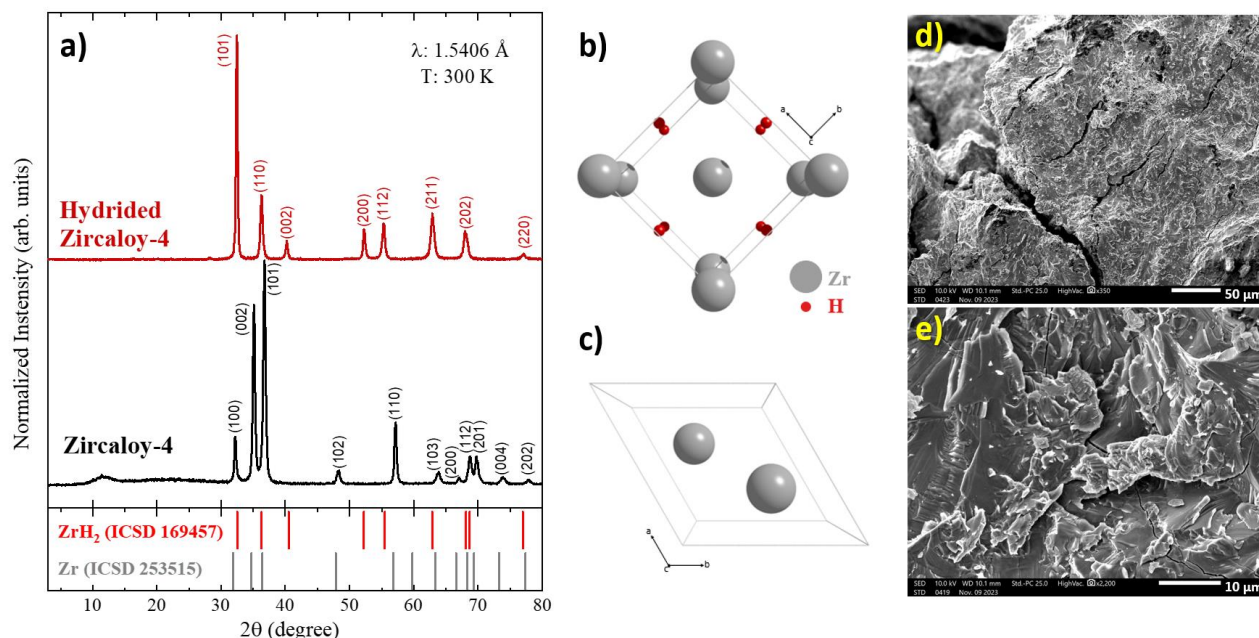


Figure 1: a) Indexed XRD patterns of hydrided and non-hydrided zircaloy-4 materials along with ZrH₂ ICSD 169457 and alpha-Zr ICSD 253515 (*Inorganic Crystal Structure Database*) standards. Crystal structure of b) tetragonal ZrH₂, and c) hcp alpha-Zr phase. SEM images of hydrided zircaloy-4 sample under d) x350 and e) x2200 magnification.

Results from ICP-OES experiments (**Table 1**) ensured a reliable chemical characterization relating to the different metal concentrations present in zircaloy-4. It is observed that the composition and concentration of alloying elements are within expected values according to ASTM B351/351M-13, which amount to a total < 2 % wt. of the material and hence do not constitute a significant amount to impact on the alpha-Zr phase and its transition to ZrH₂ as no impurities were observed in the XRD data. Finally, results for hydrogen elemental analysis (**Table 2**) show that hydrogen concentration in non-hydrided zircaloy-4 range from 0.00382–0.00647%, which is slightly above the standard of ASTM B351/351M-13 (0.0025 %). Still, hydrided samples presented close to a ~200-fold increase in hydrogen concentration (0.774–0.835 %) which was accounted for by ZrH₂ formation and within the range of expected results.

Table 1: ICP-OES results of metal composition in non-hydrided zircaloy-4.

Chemical Element	Zr	Sn	Fe	Cr	Fe+Cr
Composition (%wt.)	98.32	1.48	0.23	0.054	0.357

Table 2: Quantitative hydrogen elemental analysis for non-hydrided and hydrided zircaloy-4 materials.

Materials	Non-hydrided zircaloy-4			Hydrided zircaloy-4		
Mass (g)	0.1624	0.1936	0,1274	0.0200	0.0183	0.0094
H (%)	0.00382	0.00418	0.00647	0.835	0.774	0.807

4. Conclusions

In this work, zircaloy-4 was successfully hydrided using a high-temperature tubular furnace with hydrogen gas pressure. Structural analysis of the studied materials showed that after thermal treatment of up to 973 K under 150 kPa of H₂ gas, alpha-Zr undergoes a complete phase transition to ZrH₂, which in turn results in superficial defects and cracks in hydrided zircaloy-4, severely weakening its mechanical properties until the material is completely pulverized.

As the conditions utilized for hydridation of zircaloy-4 were similar to those this material is submitted when applied in PWRs, this work highlights the mechanisms by which phase transitions and fractures may occur which could potentially cause the nuclear fuel to come into contact with the water in the primary circuit of during operation of said reactors and lead to more serious issues.

Future work on this subject may lean toward the use a of so-called “sacrificial metal” (may it be zirconium itself or another material) to absorb any oxygen present in the tube furnace chamber and delay the diffusion of hydrogen in cladding component materials such as zircaloy-4.

Acknowledgments

The authors would like to acknowledge the Coordination of Superior Level Staff Improvement (CAPES) for financial support (Grant No: 88887.644348/2021-00). The Materials Science and Technology Research Center (CECTM) of the Nuclear and Energy Research Institute (IPEN/CNEN-SP) and Dr. Cristiano Mucsi are also acknowledged for the provided infrastructure and scientific support, respectively.

References

- [1] N. Kumar, A. Alomari, K.L. Understanding thermally activated plastic deformation behavior of Zircaloy-4, *Journal of Nuclear Materials*. vol. 504, pp. 41-49 (2018).
- [2] Y. Yang, X. Song, C. Zhang. Study of cracking in deuterium absorption Zircalloy-4 alloy, *Journal of Nuclear Materials*. vol. 465, pp. 97-103 (2015)
- [3] A. Couet, A.T. Motta, Comstock, R.J. Effect of Alloying Elements on Hydrogen Pickup in Zirconium Alloys, *Proceedings of Meeting Zirconium in the Nuclear Industry: 17th International Symposium*, Robert Comstock and Pierre Barberis, Eds., pp. 1-36 (2014)
- [4] F. Yuan et al., Shear deformation behavior of Zircaloy-4 alloy plate. *Materials Science and Engineering: A*. vol.774, pp. 138914 (2020).
- [5] I.S. Dupim et al., Study on the hydrogenation of Zircaloy-4, *Journal of Nuclear Materials*. vol. 427, pp. 121-125 (2012).
- [6] G. Meyer et al., Hydriding kinetics of zircaloy-4 in hydrogen gas, *Journal of Nuclear Materials*. vol. 229, pp. 48-56 (1996).
- [7] C. Julliet, M. Tupin, F. Martin, Q. Auzoux, C. Berthinier, F. Miserque, F. Gaudier. Kinetics of hydrogen desorption from Zircaloy-4. *International Journal of Hydrogen Energy*. vol.44, pp.21264-21278 (2019).