Effect of surface roughness on the oxidation and hydriding behaviour of Zircaloy-4

H. Akhiani[1], J. A. Szpunar[1]
[1] Department of Mechanical Engineering, University of Saskatchewan, Canada
(hamed.akhiani@usask.ca)

Abstract

Fuel cladding tube is one of the most critical parts in the core of a nuclear reactor. It should be manufactured to satisfy very strict clearances and quality requirements. In conventional pressure water reactors like CANDU, Zircaloy-4 is being used for fuel cladding. In the reactor`s environment, Deuterium or Hydrogen can ingress and form hydrides in the cladding tube. The hydrogen solubility in α-zirconium decreases dramatically from 6 at.% at 550˚C, to 0.7 at.% at 300˚C, and 10^{-4} at.% at room temperature. The excess hydrogen is precipitated in the form of zirconium hydrides [1]. There is no in-depth study of surface roughness effects on the properties of cladding tubes, however surface condition may affect oxidation, hydride formation and mechanical properties. In this study, the effect of surface oxide layer on hydride formation and morphology has been studied. Kinetics of oxidation was measured by TGA in air. It was demonstrated that the surface of oxide layer might act as a protective layer against hydrogen ingress. It has a significant effect on the hydrides morphology.

1. Introduction

Zirconium alloys have been used extensively as structural materials in nuclear reactors. Low neutron absorption, good mechanical properties, and superior corrosion resistance that results from protective Zirconium oxide layer are very important in reactor environment [1,2]. Cladding tubes are manufactured by extrusion-like process called Pilgering, in which the tube rotates during mandrel penetration. This is a cold deformation process with high strain applied to the tube during manufacturing. In fact surface structure is affected during this multi pass process. Surface roughness has influence on oxidation kinetic, affinity to react with contaminations, and coolant flow [3,4]. The effect of surface profile on the fluid turbulence has been studied elsewhere [5].

It is well-known that Zirconia oxide layer can act as a barrier against hydrogen penetration; therefore it will avoids hydrides formation. As the hydrides are brittle, they would deteriorate the mechanical properties of the cladding tubes. In this study, the effect of surface roughness on the oxidation kinetic, hydrogen ingress and hydride formation of Zircaloy-4 cladding tube has been investigated.

2. Experimental

The materials used in this study were supplied by Cameco. In order to study the effect of surface roughness, various surface conditions were applied. The conditions of the samples are illustrated in Table 1.

Table 1. Surface condition of Zircaloy tube

Samples name	Applying route	R_a (µinch)
G	Grinded by 60 grit SiC paper	110
U	Unpolished	15
P	Polished	8.5
K	Pickled (aqueous solution of Nitric and Hydrofluoric acid)	6

Polished samples are the final surface finished that is used in the CANDU reactors. Other surface roughnesses were applied using various grit SiC abrasive papers. Surface properties were measured using Mitutoyo SJ-400 profilometer. After applying the surface treatment, one set of samples were oxidized at 400 °C in air atmosphere for 24hr. In order to investigate the protectiveness of oxide layer against hydrogen ingress and hydride formation, the oxidized as well the non-oxidized samples with various surface roughness were subjected to hydriding process.

Thermo Gravimetric Analysis (TGA) was carried out on Grinded (60 grit), polished and unpolished tube surfaces at 500,700 and 1100˚C. The samples were analyzed using a TA Instruments Q600 at 10 °C/min ramping regime. All samples were cleaned with Acetone for 3 minutes in an Ultrasonic bath and dried with a heat gun prior to TGA. The sample was purged with air at a flow rate of 500 mL/min.

Hydriding experiments were carried out in a quartz tube furnace at 400 °C for two hours. A noncombustible mixture of Ar-2.5% H_2 was purged in to the tube at approximately 1.0 L/min. After temperature has dropped below 100 °C, they were removed from the quartz tube. After that, the sample were cut from cross section, cold mounted and etched using 50 mL nitric acid (70%) and 2 drops of HF (48%).

3. Results and Discussion

3.1 Surface Profile and Roughness

The measurement of various surface roughness parameters is illustrated in Table 2. Ra, Rq and Rz are arithmetic average, root mean square and JIS roughness of surface asperities and valleys, respectively. Rsk (Skewness) shows the number of peak and valleys regarding each other while Rku (Kurtosis) indicates their sharpness. If Rsk is negative the surface has more valleys than the peaks (asperities) and vice versa. Rku below 3 is for dull and flat surface while higher than 3 is for sharp and pointed peaks and valleys. The surface profile includes the waviness and roughness while roughness by definition is enclosed to short wavelength irregularities. Further surface parameters and formula can be found elsewhere [3]. Fig. 1-4 shows surface profile and roughness of polished and unpolished samples respectively.

Table 2. Surface roughness parameters of Zircaloy tubes

abrasion paper/polisher	measured surface roughness				
	Ra	Rz	Rq	Sk	Ku
400	17.90	113.40	23.26	0.15	3.80
600	10.24	69.10	13.48	0.67	4.24
800	9.24	62.80	12.24	0.54	4.60
unpolished	15.14	98.73	21.23	-1.87	7.27
3 micron SiC	7.02	44.60	9.00	-0.08	3.49
0.04 micron Alumina	6.79	45.45	9.25	-0.75	5.84
polished	8.14	55.80	10.54	-0.51	2.65

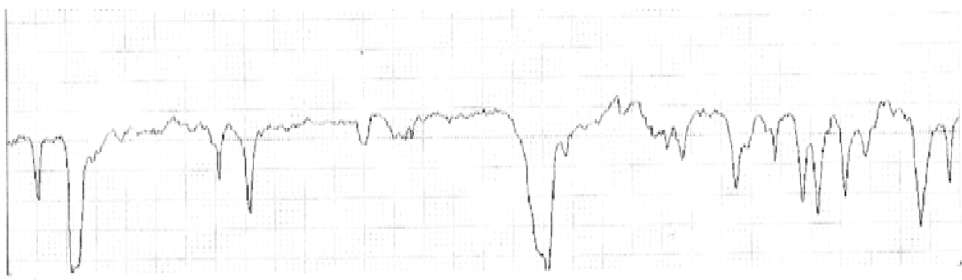


Fig 1. Surface profile of Unpolished zircaloy tube.

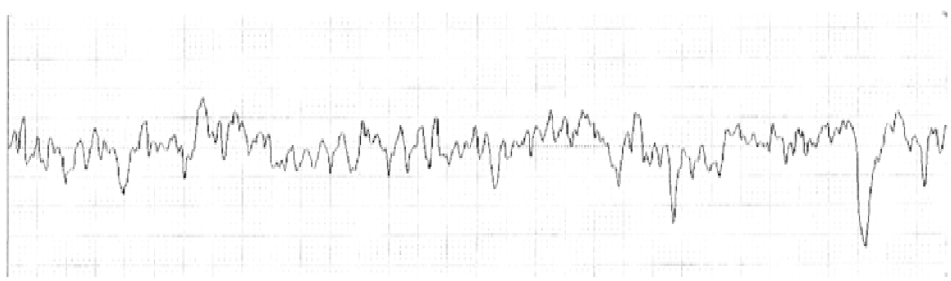


Fig 2. Surface profile of polished zircaloy tube.

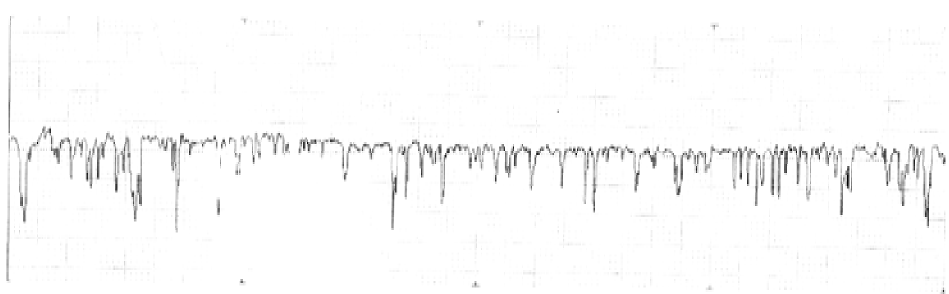


Fig 3. Roughness profile of Unpolished zircaloy tube.

Fig 4. Roughness profile of polished zircaloy tube.

By investigating the roughness parameters, some interesting points can be depicted; Ra, the most common parameter which indicates the roughness, is higher in unpolished samples; ~16 µinch against ~9 µinch in polished sample.

In as received polished samples, the Skewness (Rsk) is slightly negative (~-0.5) but for unpolished samples it is more negative (~ -2). It showed that there are more valleys in unpolished samples. On the other hand, the kurtosis (Rku), for unpolished sample is ~7 which compare to polished tube (~3) shows very sharp peaks and valleys.

These results and also the surface profiles are completely in accordance with the grooves and morphology that were observed in SEM images (explained posteriori in Section 3.3).

3.2 Thermo Gravimetric Analysis (TGA) Tests

The TGA tests were carried out for polished (P), unpolished (U) and a very rough grinded surface (G), which was grinded with 60 grit abrasive paper. These tests were conducted at 500, 700 and 1100 °C isothermally for 24, 4 and 1 hour(s) respectively. The results are shown in Fig. 5-7. The two letters abbreviation that used for the samples, shows the surface condition and the temperature that were tested. For example U5 is unpolished sample that has been tested in 500 °C.

At 500 °C, there are some spikes in the weight gain curves. Especially with G sample, sudden increase seems odd. These tests were repeated three times. While the result`s trend were the same for polished and unpolished samples, the sudden increase in the weight of G sample were repeated each time but not at the same exact time.

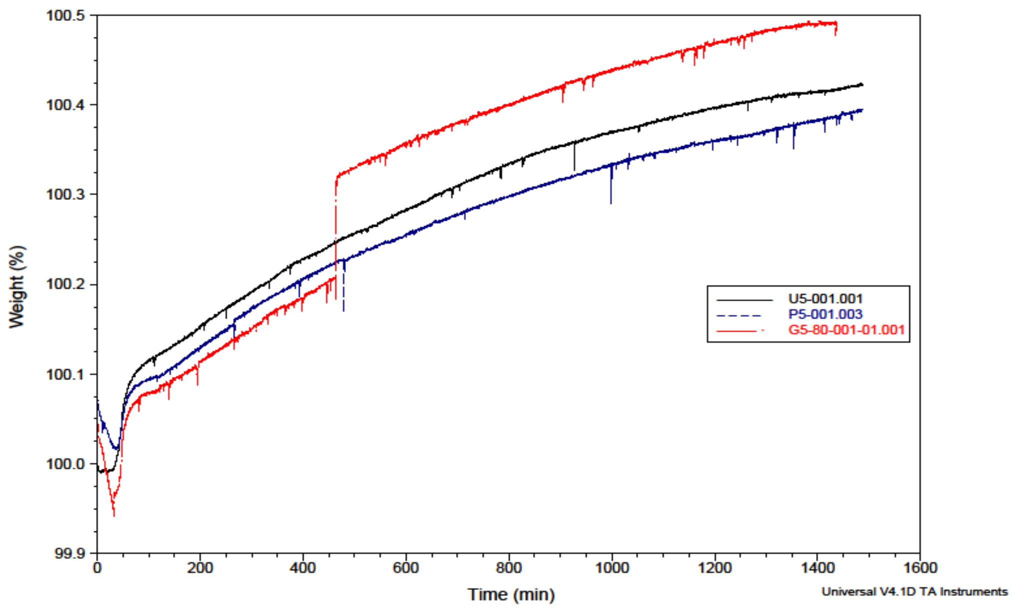


Fig 5. Thermogram overlay of samples U5, P5 and G5 run at a ramp rate of 10 °C per minute to a maximum temperature of 500 °C and held at maximum temperature for 24 hours. Furnace purge gas was air at 500 mL/min.

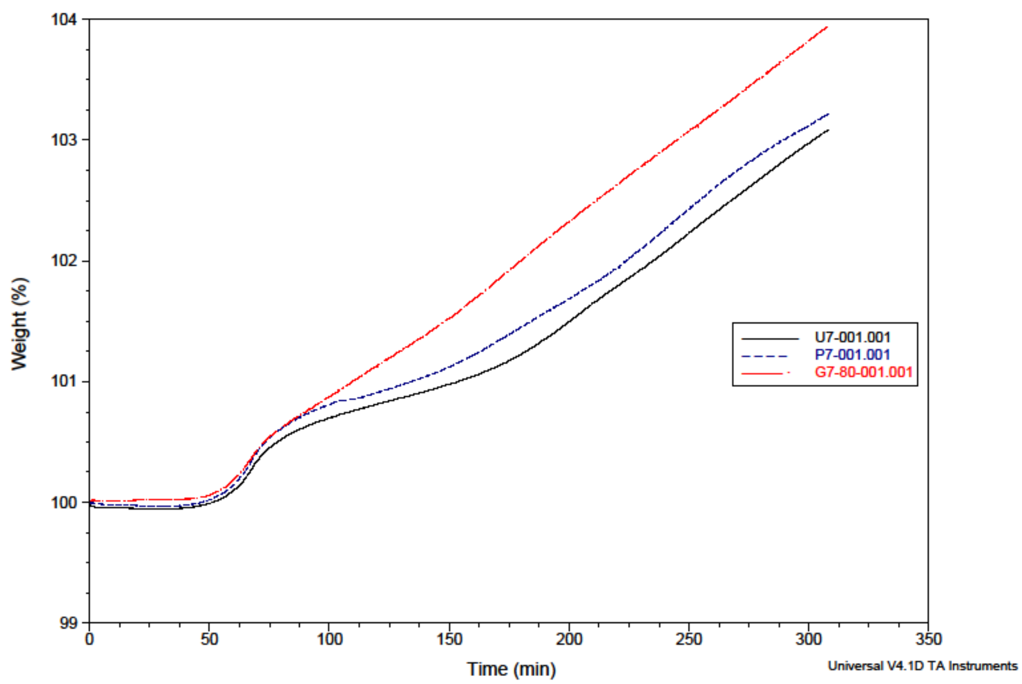


Fig 6.Thermogram overlay of U7, P7 and G7 samples, run at a ramp rate of 10 °C/min to a maximum temperature of 700 °C and held at maximum temperature for 4 hours. Furnace purge gas was air at 500 mL/min.

The oxidation mechanism at all the temperatures is expected to be the same for each of the surfaces, since oxidation is a thermally activated phenomenon. Grinded (G) sample exhibited the highest oxidation rate while polished (P) and unpolished (UP) samples showed lower rate with minor differences.

The insignificant effect of surface roughness on the oxidation behavior as determined from TGA can be attributed to the small sample size (3 mm x 3mm) that was exposed to the test environment which could not probably capture the overall oxidation behavior that surface roughness has induced.

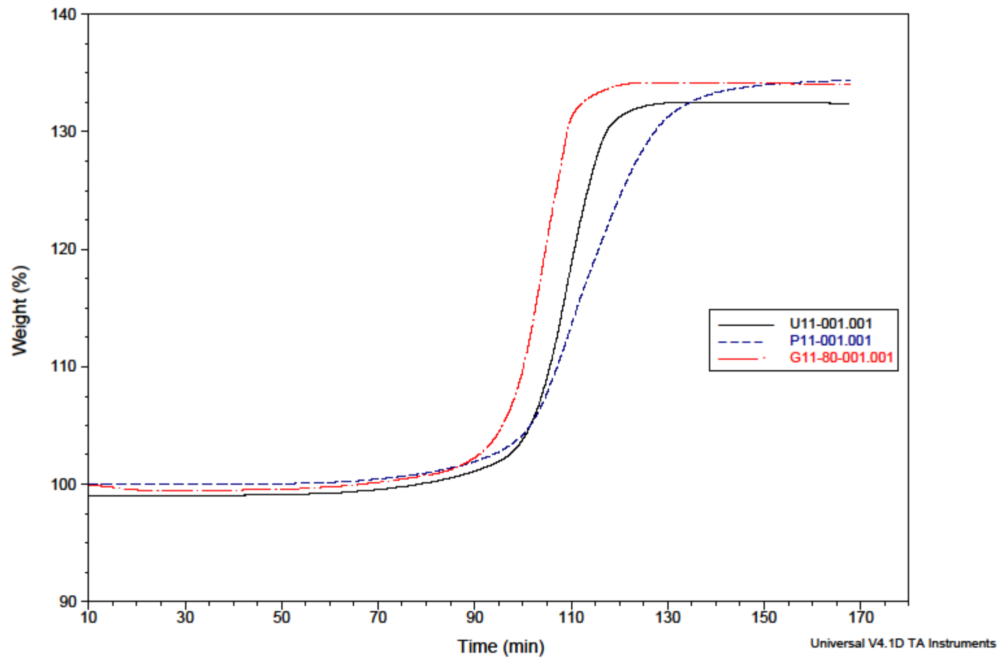


Fig 7. Thermogram overlay of U11, P11 and G11samples, run at a ramp rate of 10 °C/min to a maximum temperature of 1100 °C and held at maximum temperature for 1 hour. Furnace purge gas was air at 500 mL/min.

3.3 Hydriding

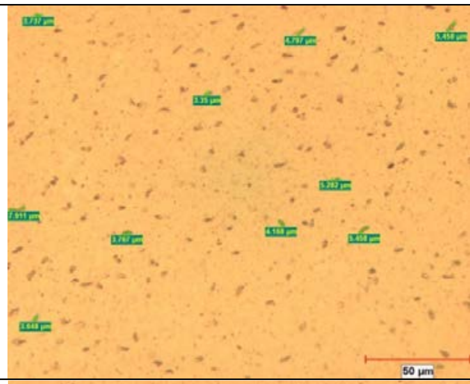
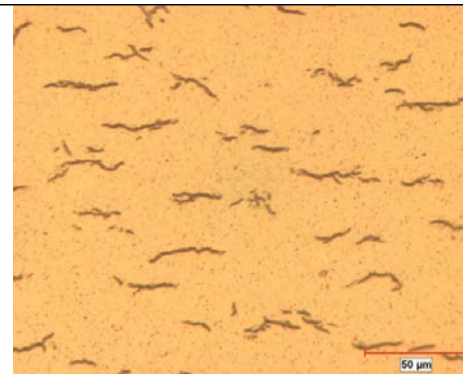
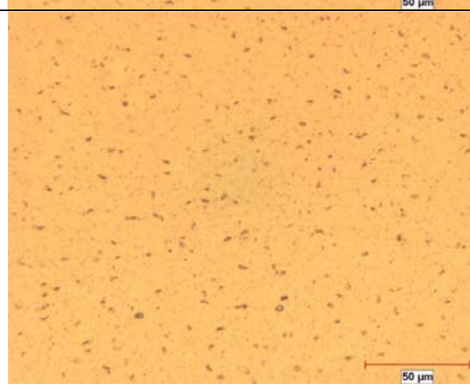
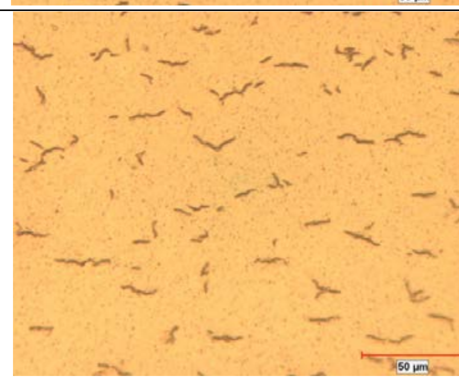
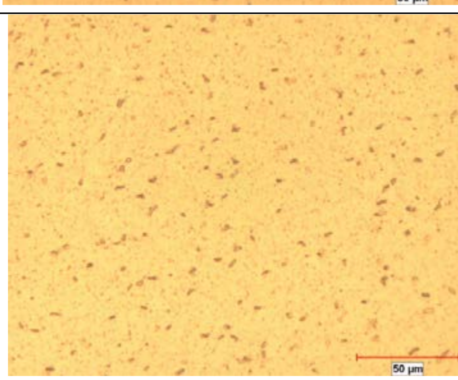
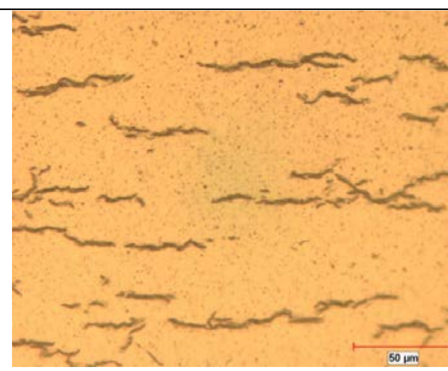
Two sets of samples were prepared from polished and unpolished tubes; a set with thin oxide layer on the surface which were oxidized at 400 °C for 24 hours in air and the other without any oxidation on the surface. These samples were then subjected to hydriding tests. As received unpolished, polished, grinded and pickled constitute the different surface conditions that were investigated by hydriding tests. Pickling was carried out in 45/45/10 mL, nitric acid/deionized water/ HF for the pickled sample. This condition was applied because the pickling can remove a very thin layer from the surface including contaminations and oxides. Also the surface roughness of the pickled sample is smoother than the as received polished sample.

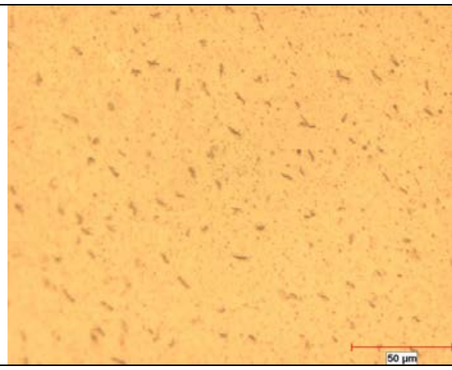
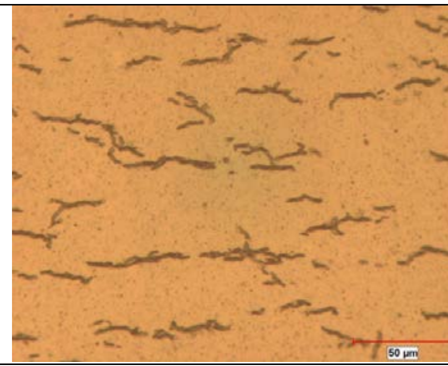
The etched cross sections of hydrided samples are illustrated in Fig 8. The morphology of hydrides is different in samples with oxide layer. Smaller hydrides with higher aspect ratio appeared in pre-oxidized samples while platelet-like hydrides are typical in non-oxidized tubes. For quantification of hydrides, two approaches were used; first, the amount of hydrogen in the hydride samples was measured by an inert-gas-fusion process with LECO hydrogen determinator. Also, using Clemex image processing software, the amount of hydrides in different region on the cross section was calculated. The software identifies the hydrides and then calculates the surface area occupied by the hydrides. Also it is capable of measuring F_n[1], which is the index for hydrides orientation. Fig. 9 shows how the software

[1] Fraction of hydrides with more than 40 degree from radial direction, F_n= radial hydrides/ total hydrides

can find and calculate the radial and non-radial hydrides. Radial and circumferential (non-radial) hydrides are shown in green and red respectively.

Fig 8. Cross sectional morphology of hydrides in samples with different surface condition.

Surface condition	**X (Pre-oxidized at 400 ˚C/24 hours)**	**H (w/o oxidation)**
Grinded (with 60 grit paper)		
Unpolished		
Polished		

Pickled		

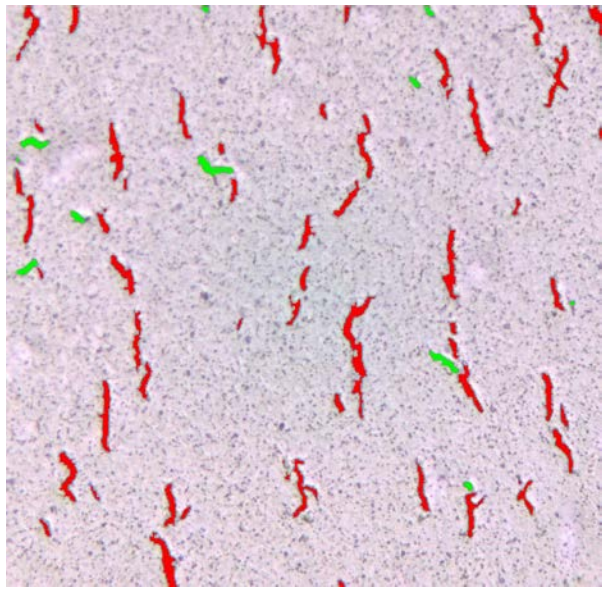


Fig 9. Hydrides measurement using the Clemex software

The results of LECO analyzer and Clemex software are illustrated in Fig. 10 and Table 3, respectively. Each measurement is the average of two samples.

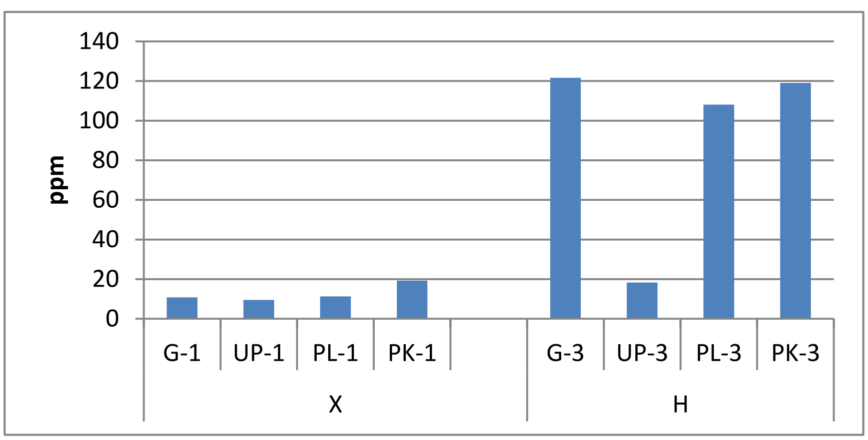


Fig 10. Hydrogen amounts in the Zircaloy tube in different surface condition

It seems that the oxide layer alleviate the hydrogen ingress and thus less hydride with smaller sizes formed in the samples with oxide layer rather than non-oxidized samples. Unpolished samples, even without the pre-oxidized layer, have the lowest hydrides. It seems that because of surface condition after pilgering in unpolished samples, the hydrogen absorption of these samples is different from others. Fig. 11 shows the difference between polished and unpolished surface morphology of Zircaloy-4 tube. Large valleys and grooves which are related to pilgering process are smeared in polishing process and most of them are filled with the material by polishing. It is clear that due to polishing, surface morphology has changed. Perhaps these grooves can help the hydrogen escape from the tubes easier. In other words it can act as a short path for hydrogen escape. On the other hand polished tube has less grooves on its surface thus less hydrogen can be escaped and more would be trapped.

Table 3. Average of the measured hydrides various parameters using Clemex software

Sample preparation conditions		**code**	**ave. total hydrides**	**ave. hydrides size**	**ave. Fn**
H	grinded	G-3	973.20	12.83	0.78
	unpolished	UP-3	674.17	7.56	0.71
	polished	PL-3	1750.29	21.92	0.80
	pickled	PK-3	1646.67	24.84	0.77
X	grinded	G-1	451.26	3.29	0.61
	unpolished	UP-1	157.67	1.89	0.65
	polished	PL-1	575.40	3.28	0.56
	pickled	PK-1	475.73	3.18	0.57

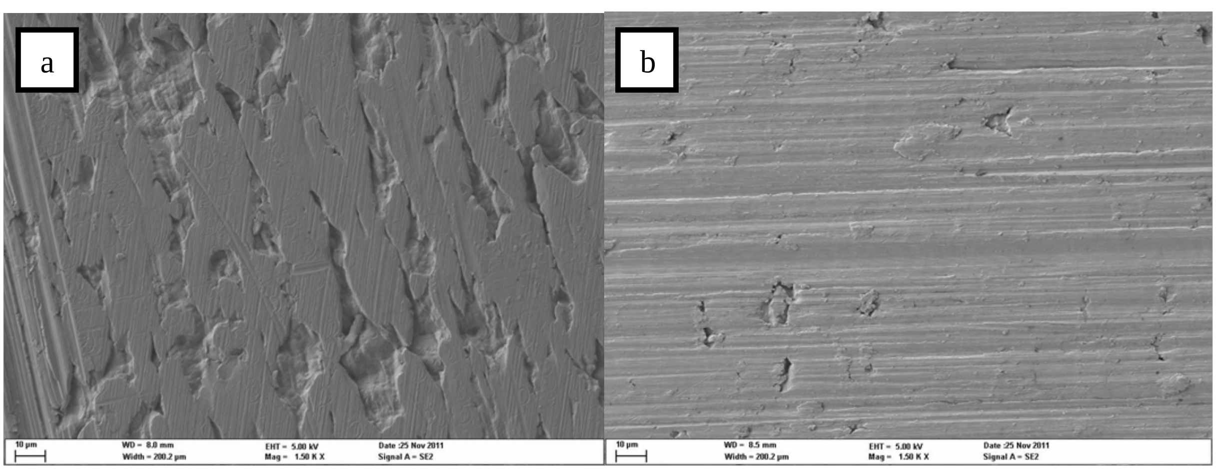


Fig 11. SEM image of a) unpolished, b) polished surface of Zircaloy tube

The amounts of hydrogen in pre-oxidized samples are below 20 ppm, while it is over 100 ppm for the samples without the oxide layer on the surface except the unpolished one. The low hydrogen amount in unpolished samples might be correlated to the surface morphology as mentioned before.

4. Conclusion

The surface roughness effects on the air oxidation at specific temperatures were studied. Some slight differences regarding oxidation kinetic and weight gain were observed. Also hydriding were studied with different surface roughness with and without the surface oxide layer. Hydrides were quantified using LECO analyzer and image processing techniques. It is found that surface oxide layer acted as a barrier against hydrogen ingress. In both pre-oxidized and non-oxidized surface, unpolished samples propose much less hydrides than polished surface. It seems that the surface treatment (grinding, polishing and pickling) does not significantly affects the protectiveness of the oxide layer, although there are slight differences between the amounts of hydrogen in these samples. More investigation is conducting on this area to find clear correlations between the surface roughness and oxide protectiveness.

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5. References

[1] N. A. P. Kiran Kumar, J. A. Szpunar, Z. He, “Preferential precipitation of hydrides in textured zircaloy-4 sheets”, Journal of nuclear materials, 403, 2010, pp. 101-107.

[2] N. A. P. Kiran Kumar, J. A. Szpunar, Z. He, “Microstructural studies and crystallographic orientation of different zones and δ-hydrides in resistance welded Zircaloy-4 sheets”, Journal of nuclear materials, 414, 2011, pp. 341-351.

[3] D. Post Guillen, T. S. Yoder, “Thermal hydraulic effect of fuel plate surface roughness”, Nuclear engineering and design, 238, 2008, pp. 2480-2483.

[4] A.M. Huntz, B. Lefevre, F. Cassino, “Roughness and oxidation: application to NiO growth on Ni at 800°C”, Materials science and engineering A, 290, 2000, pp. 190-197.

[5] P. As. Krogstad, R. A. Antonia, “Surface roughness effects in turbulent boundary layers”, Experiments in Fluids, 27, 1999, pp. 450-460.

[6] Degarmo, E. Paul; Black, J T.; Kohser, Ronald A. (2003), Materials and Processes in Manufacturing (9th ed.), Wiley, p. 223, ISBN 0-471-65653-4.

[7] H. H. Hsu, L.W. Tsay, “Effect of hydride orientation on fracture toughness of Zircaloy-4 cladding”, Journal of nuclear materials, 408, 2011, pp. 67-72.

[8] J.D. Irish and S.R. Douglas, “Validation of WIMS-IST”, Proceedings of the 23rd Annual Conference of the Canadian Nuclear Society, Toronto, Ontario, Canada, 2002 June 2-5.