Corrosion behavior of irradiated and non-irradiated zirconium alloys: investigations on corrosion rate, released ^{14}C species, and IRF (WP3)

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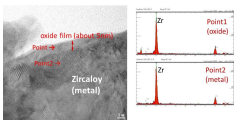
SUMMARY

The long-term aqueous corrosion of irradiated and non-irradiated zirconium alloys was studied. A sensitive hydrogen measurement was selected for the non-irradiated alloy based on the reaction of Zr + $2H_2O \rightarrow ZrO_2 + 2H_2$. The corrosion rates decreased with time and increased at a higher temperature, but the influences of pH and other chemical properties of the solution on the rate were not significant. The equivalent corrosion rates obtained from the leached ^{14}C were less than that of non-irradiated Zr alloys. The fraction of leached ^{14}C from irradiated Zircaloy-2 (BWR) as gas, dissolved organics and dissolved inorganics was obtained. The fraction in the liquid phase increased with time and reached over 90% after 2 years. The inorganic/organic ratios of the liquid were around 1/3 and seemed to be not depending on time. Instant release fraction (IRF) for spent claddings was also discussed. The inventory measurement shows that the abundance of ^{14}C in the oxide was only 7.5%, and the leached ^{14}C from the irradiated cladding with oxide was found to be 0.0038%. These understandings should be reflected in the future safety assessment so that a lower, or potentially negligible, IRF can be supported.

OBJECTIVES

- **Long-term corrosion rate of Zr alloys obtained by hydrogen (gas + absorbed), and affecting factors as temperature, pH, and Na/Ca, and congruence of ^{14}C release.**
- **Released ^{14}C fraction from irradiated cladding as gas, dissolved organics, and dissolved inorganics.**
- **Discussion on the instant release fraction (IRF) for irradiated cladding with regards to oxide inventory and ^{14}C release from oxide.**

Corrosion Test for Non-irradiated Zr alloys



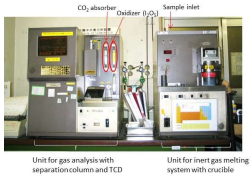
TEM image before corrosion

- The glass ampoule method
- The gas flow experiment

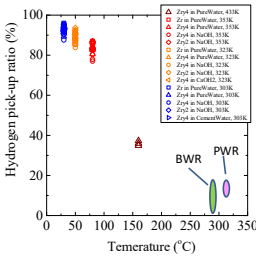
- The initial oxide is 3nm
- Corrosion reaction; Zr + $2H_2O \rightarrow ZrO_2 + 2H_2$

Hydrogen Absorption

- Absorbed hydrogen was measured by the inert gas melting system coupled with GC (Japanese Industrial Standard Z 2614)
- Initial hydrogen content is 10 ppm

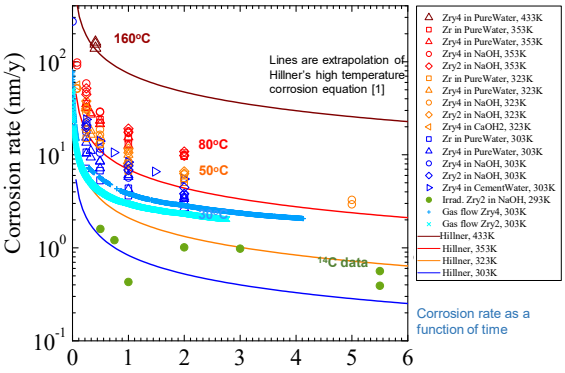


Absorbed hydrogen measurement system



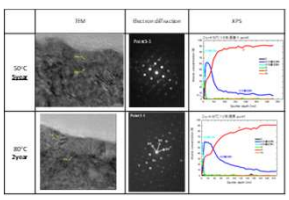
Hydrogen absorption ratio

Long-term Corrosion Rate



Corrosion rate as a function of time

- Corrosion rate decreases with time (close to the Parabolic law [2])
- The data higher than Hillner's equation
- ^{14}C data lower than hydrogen data
- Oxide is well crystalized and the tetragonal structure can be confirmed



Oxide film characterization

CONCLUSIONS

- Long-term corrosion rate decreases with time and is around 4 nm/y at 30°C (after 2 years).
- Leached ^{14}C from irradiated cladding is mainly dissolved organics.
- Instant release fraction (IRF) is suggested negligible or at least less than 20% assumed in the safe case.

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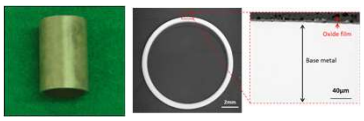
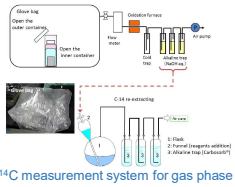
Corrosion Test for Irradiated Zircaloy-2



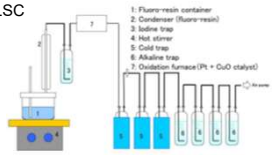
Observation of cladding

- BWR Zircaloy-2 (Burnup; 41.6 and 39.7 GWd/t)
- Cladding with and without oxide film for immersion test
- Container of glass inner vial and gas tight outer SS vessel
- NaOH solution at pH 12.5
- Room temperature
- ^{14}C is recovered as $^{14}CO_2$ and measured by LSC

Immersion of cladding

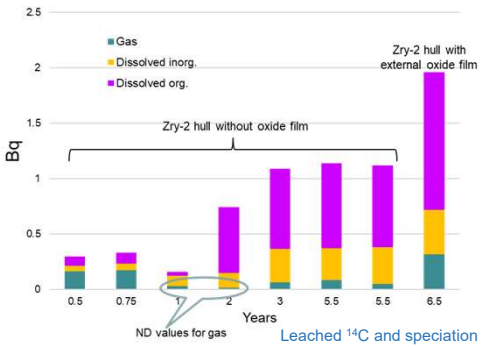


^{14}C measurement system for gas phase



^{14}C measurement system for inventory and liquid phase

Leached ^{14}C



- The total leached ^{14}C is small up to 1- 2 Bq.
- Released of ^{14}C as gas is a significant fraction (53-55%) during the first year. After 1 year, the gas fraction decreases.
- In the dissolved fraction, the organics are high proportion to the inorganics.
- For sample with oxide, the total leached ^{14}C is relatively higher than without oxide.
- The overall trend is similar between with and without oxide.
- Except data up to 1 year, the gas is a minor fraction.
- The dissolved organic is major around 60-70%.

Leached ^{14}C and speciation in gas and liquid phases

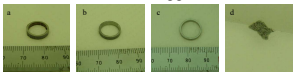
Instant Release Fraction (IRF)

Preliminary safety case in Japan [3]

- Hull oxide is regarded as a source of IRF and the oxide inventory is assumed to be 20% for hull waste

Inventory measurement [4]

- ^{14}C specific activity for oxide is larger than metallic part
- But ^{14}C abundance for oxide is 7.5%
- ORIGEN calculation suggests 3.5% for oxide [5]

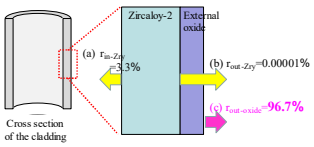


Thickness (μm)		Specific activity (Bq/g)			
Base metal	Oxide layer	(a) Cladding with internal and external oxide	(b) Cladding with external oxide	(c) Cladding base metal	(d) External oxide*
704.7	25.3	1.54×10^4	1.53×10^4	1.49×10^4	4.25×10^4
		1.49×10^4		1.50×10^4	3.83×10^4
		1.43×10^4		1.47×10^4	

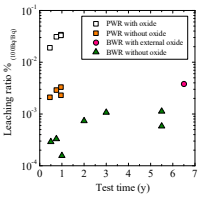
* Units of grams in the oxide are converted to grams of zirconium, not grams of ZrO_2.

Leaching experiment using cladding with oxide [4]

- Oxide should be a main leaching source
- However, leaching ratio (total leached Bq / inventory) is only 0.0038% after 6.5 years



Estimated leached ^{14}C from oxide based on the corrosion-related congruent release.



Leached ^{14}C ratio

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