Corrosion tests of non-irradiated stainless steel by hydrogen measurement system (WP2)

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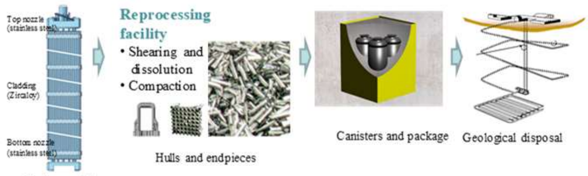
SUMMARY

The aqueous corrosion behavior of non-irradiated stainless steel under simulated repository conditions was studied. A sensitive hydrogen measurement was selected to evaluate the very low rate of stainless steel corrosion based on the reaction of $3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$. The long-term observations on the corrosion behavior demonstrated that the corrosion rate decreased with time during the initial first year. This initial corrosion rates showed a tendency to be higher at higher test temperatures. The corrosion behavior in the NaOH solution was comparable to that in pure water. Detailed kinetics on the initial behavior suggested that the stainless steel corrosion follows a parabolic rate law, which implies that the initial corrosion process is under diffusion control. The surface oxide films after each corrosion test consisted of Fe, Cr and Ni oxides. However, the passivation was not clear because the oxide film was very thin and amorphous. After the first year, the constant corrosion rate, approximately 0.4 nm/y at 303 K, was observed during 6 years and more. This corrosion rate is 1/50 slower than that of the conventional evaluation and can bring a significant impact on the estimation of radionuclide leaching and gas generation in the safety assessment on the disposal of stainless steel waste.

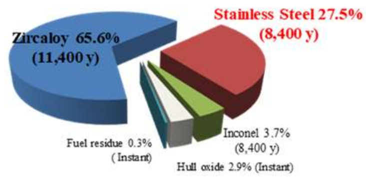
OBJECTIVES

- **Experimental set up for metals corrosion by sensitive hydrogen measurement**
- **Short and long-term corrosion behavior of stainless steel (unirradiated) under deoxygenated conditions**
- **Challenges for passive oxide film characterization**

After reprocessing in Japan, the wreckage of spent fuel assemblies are mixed and compressed, and then disposed in a deep underground repository. C-14 is a typical activated product in metals. An important issue is radionuclides leaching and hydrogen gas generation as a result of metals corrosion.



Processing and disposal concept for hull-endpiece waste in Japan



C-14 inventory for hull-Endpieses waste in Japan [3].
In brackets represents leaching time.

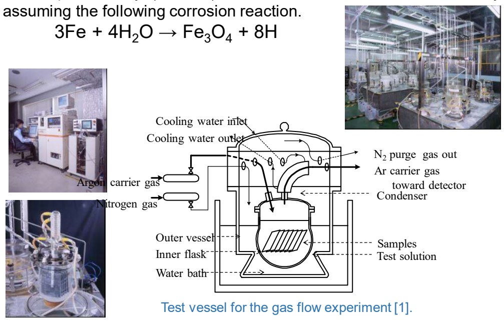
Specimen

The 18Cr-8Ni austenitic stainless steel of 0.1 mm thick was used after polished with 0.02 mm alumina powder.

Gas Flow Experiment

Double vessels were used to avoid contamination by atmospheric oxygen and hydrogen. Specimens were immersed in 2.5 dm³ solution in the inner glass flask kept at 303 K. An argon carrier gas was passed through the inner flask, and the hydrogen in the carrier gas was measured periodically using atmospheric pressure ionization mass spectrometry (API-MS). The corrosion rate was obtained by assuming the following corrosion reaction.

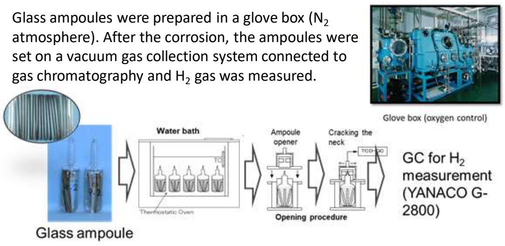
$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 8H$$



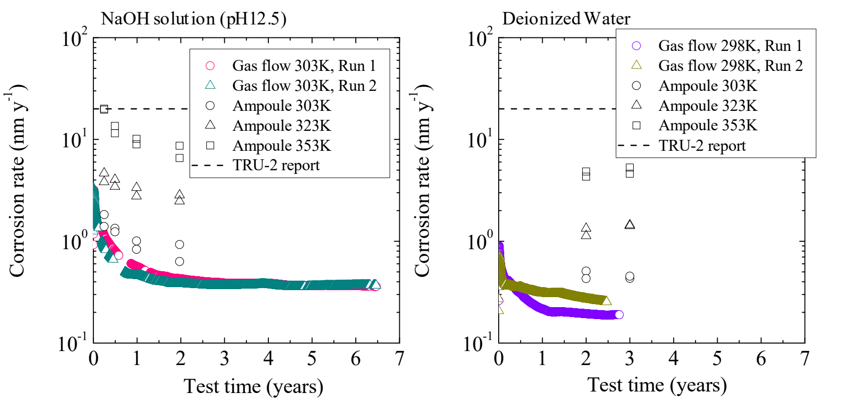
Test vessel for the gas flow experiment [1].

Glass Ampoule Method

Glass ampoules were prepared in a glove box (N_2 atmosphere). After the corrosion, the ampoules were set on a vacuum gas collection system connected to gas chromatography and H_2 gas was measured.

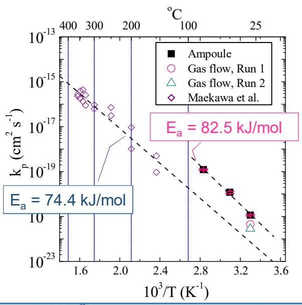


Long-term Corrosion Rate



Corrosion rate of stainless steel as a function of time and temperature in NaOH (left) and pure water (right).

Short-term Corrosion Kinetics (~ 365 days)



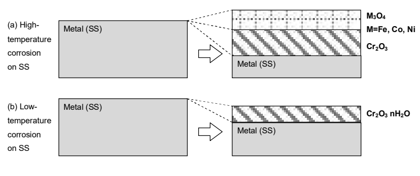
The parabolic corrosion rate constants, k_p ($cm^2 \cdot sec^{-1}$) can be defined as,

$$x^2 = k_p \cdot t$$

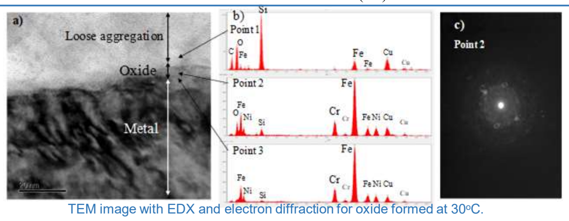
- x is the thickness of magnetite (Fe_3O_4)
- t is the test time

- The corrosion kinetics follows a parabolic rate law.
- The k_p values are larger than those at high temperatures [4].
- The activation energy is 82.5±6.2 kJ/mol, which corresponds to the energy for high temperature. Suggesting that the basic corrosion mechanism is similar at both high and low temperatures.
- At high temperature, the kinetic behavior has been discussed by Robertson [4], who explained that the formation of duplex oxide on a metal surface and the diffusion of Fe ions through the oxide are considered to be rate controlling for the corrosion.

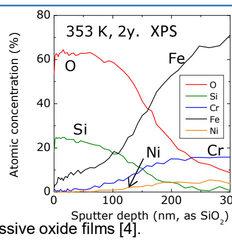
Oxide Film Characteristics



Corrosion films suggested on stainless steel [4].



TEM image with EDX and electron diffraction for oxide formed at 30°C.



Depth profile by XPS

- Generally, the corrosion resistance of stainless steels is due to the formation of Cr_2O_3-base passive oxide films [4].
- In this study, the oxide consists of iron and chrome, and is amorphous.
- Detailed characteristics of the oxide is not clear (Magnetite? Chrome base passive oxide?) and is a future challenge.
- Silicon oxide is observed at surface as a loose aggregation (due to dissolution of the glass ampoule), but may not affect the corrosion rate.

CONCLUSIONS

- Hydrogen measurement systems demonstrated to allow to obtain extremely low corrosion rate.
- Long-term corrosion rate of stainless steel is constant and around 0.4 nm/y at 30°C.
- The oxide film characteristics controlling to the corrosion kinetics is a future challenge.

REFERENCES

1. Sakuragi, T., Tanabe, H., Hirose, M., Sakashita, A., Nishimura, T. 2013. Estimation of Carbon 14 Inventory in Hull and End-Piece Wastes from Japanese Commercial Reprocessing Operation, *Proceedings of the ICEM2013*. Brussels, Belgium.
2. Sakuragi, T., Yoshida, S., Kato, O., Tateishi, Y. 2016. Study of stainless steel corrosion by hydrogen measurement under deoxygenated, low-temperature and basic repository conditions. *Progress in Nuclear Energy* 87, 26-31.
3. Sakuragi, T., Yoshida, S., Kinugasa, J., Kato, O., Tateishi, Y. 2016. Corrosion Kinetics of Stainless Steel by Hydrogen Measurement under Deep Geological Repository Condition. *Proceedings of Waste Management 2016 Conference*.
4. Robertson, J. 1991. The mechanism of high temperature aqueous corrosion of stainless steel. *Corrosion Science 32*, 443.

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