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Study of stainless steel corrosion by hydrogen measurement under deoxygenated, low-temperature and basic repository conditions

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ABSTRACT

Spent fuel assemblies comprising Zircaloy and stainless steel pieces are expected to be disposed of in a deep underground repository. Corrosion is considered to be a leaching source of activated radionuclides such as C-14. Japanese safety assessment has estimated the corrosion rate of stainless steel as 2×10^{-2} μm a^{-1} based on limited experimental results at 308 K in the presence of 3200 ppm chloride. This corrosion rate corresponds to a leaching period of 8500 years.

In the present study, corrosion tests of 18Cr–8Ni austenitic stainless steel were performed under assumed disposal conditions (dilute NaOH solution, pH 12.5, 303 K, Ar environment) by continuous measurement of gaseous hydrogen over 6.5 years through use of the gas flow system. The cumulative amount of hydrogen shows a good parabolic relationship against time until one year, followed by an approximately linear relationship. This suggests that the corrosion kinetics changes from an initial diffusion process to a linear rate law that holds for a long time. Assuming a corrosion reaction of $3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$, the corrosion rate decreases with time but after one year the rate remains constant at approximately 4×10^{-4} μm a^{-1} over the 6 next years.

1. Introduction

In the nuclear fuel cycle, it is a challenging issue to implement a safe and rational management of waste generated from a fuel reprocessing. After the nuclear fuel is reprocessed, the wreckage of spent fuel assemblies are mixed and compressed, and then the compacts are stuffed into stainless steel canisters. The activated metals wastes, called the hulls and endpieces, are expected to be disposed in a deep underground repository as Group 2 category of TRU waste in Japan (Federation of Electric Power Companies (FEPC) and Japan Atomic Energy Agency (JAEA), 2007). Carbon 14 is a typical activated product in metals and is mainly generated by the $^{14}N(n,p)^{14}C$ reaction. Stainless steel nozzles account for 16% by weight of the hull and endpiece waste, and their C-14 corresponds to 28% of the total C-14 inventory (Sakuragi et al., 2013). An important issue in disposal safety is radionuclides leaching and hydrogen gas generation as a result of metals corrosion.

Numerous studies have been focusing the stainless steel corrosion under alkaline condition and on a reinforce in concrete (Fajardo et al., 2014; Abd El Haleem et al., 2010) or durability under caustic environments (Speller and Texter, 1924; Bhattacharya and Singh, 2011; Gras and Spiteri, 1993). Most of these studies were investigated under oxygenated conditions and discussed the corrosion rate in the range of around several μm a^{-1}. However, the corrosion behavior of stainless steels under the anticorrosive repository conditions (low oxygen, high alkaline and low temperature) is not clear because the corrosion rate is very slow and the oxide films are very thin (International Atomic Energy Agency, 1998). Aqueous corrosion of stainless steels is generally described by a model in which the formation of passive Cr oxide limits the transport of Fe ions. Robertson published parabolic corrosion rate constants at high temperatures down to 423 K and presented a high-temperature corrosion model of stainless steels from the point of view of oxide characterizations based on several studies involving measurement of electrochemical and weight changes (Robertson, 1991). A Japanese safety assessment has regarded the congruence of radionuclides leaching and metal corrosion and estimated the uniform corrosion rate of stainless steels as 2×10^{-2} μm a^{-1} (Federation of Electric Power Companies (FEPC)

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and Japan Atomic Energy Agency (JAEA), 2007). This estimation is based on experimental results (without peer review) at 308 K in the presence of 3200 ppm chloride ions by measuring the evolved hydrogen gas and an assumed reaction as $3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$. Based on the above hypotheses and the thickness of structural material, the leaching period of radionuclides in waste stainless steels has been assumed to be 8500 years (Federation of Electric Power Companies (FEPC) and Japan Atomic Energy Agency (JAEA), 2007).

The purpose of the present study is to show the long-term corrosion behavior of the austenitic stainless steel in the absence of chloride. High pH and deoxygenated conditions were selected to simulate the typical underground repository environment, and the gas flow system was used to measure the amount of gaseous hydrogen that evolves from the corrosion reaction. The corrosion reaction follows the previous study (Federation of Electric Power Companies (FEPC) and Japan Atomic Energy Agency (JAEA), 2007) for comparison of the corrosion rate. Uniform corrosion kinetics can also be evaluated by long-term continuous monitoring of hydrogen gas.

2. Experimental

The 18Cr–8Ni austenitic stainless steel with a thickness of 0.1 mm was obtained from Nilaco Corporation (Product No. 753323). The inspection data for the chemical composition is shown in Table 1. The stainless steel sheet was polished with 0.02 mm alumina powder and then cut. Figs. 1 and 2 shows the cross section of the specimen after chemical etching with 10% oxalic acid aqueous solution and the TEM observation with EDX analysis. The average diameter of the grains is approximately 15 μm. The initial oxide thickness is approximately 3 nm.

The experimental setup for the gas flow corrosion system is shown in Fig. 3. This system is capable of simultaneously measuring the 15 reaction vessel units connected in parallel. Hydrogen contamination from the atmosphere (hydrogen concentration approximately 0.5 ppm) was avoided by using the double container system. Test solutions were deoxygenated before use. The stainless steel sample (20 sheets, 100 mm × 100 mm × 0.1 mm, surface area of 0.40 m^2) were immersed in 2.5 dm^3 of dilute NaOH solution (initial pH = 12.5) in the inner glass flask and kept at 303 K for 6.5 years. An argon carrier gas with oxygen concentration less than 1 ppb was passed through the inner flask at a flow rate of 0.9 $dm^3\ min^{-1}$, and the hydrogen concentration in the carrier gas was measured periodically using atmospheric pressure ionization mass spectrometry (API-MS, Hitachi Tokyo Electronics, UG-400). Vapor in the Ar carrier gas was recovered by a water cooling condenser. Three test vessels were prepared for this study: two for stainless steel corrosion and one for a blank run. Details for the test immersion vessel are illustrated in Fig. 4.

Surface oxide characteristics after corrosion were examined in samples that were immersed in a glass ampoule for two years. The condition is equivalent to that for the gas flow experiment as in a dilute NaOH solution of pH 12.5 at 303 K. The cross section of the oxide layer was observed by TEM (JEOL, JEM-2010F) and analyzed by EDX (NORAN Instruments, Vantage EDX) for a sample prepared by FIB (Hitachi, FB2000A) after the vacuum deposition of carbon. The elemental distribution of the surface was measured by XPS (Physical Electronics, Quantera SXM).

Table 1
Composition of stainless steel used in corrosion tests (in wt%, from inspection data). Values in parenthesis represent the specification (Japanese Industrial Standards G 4305).

C	Si	Mn	P	S	Ni	Cr
0.07 (<0.08)	0.45 (<1.00)	0.79 (<2.00)	0.028 (<0.045)	0.005 (<0.030)	8.29 (8.00–10.50)	18.14 (18.00–20.00)

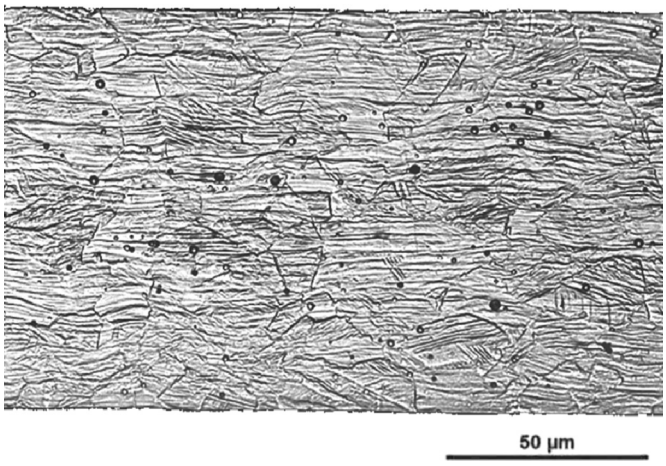

Fig. 1. Optical micrograph of a chemically etched cross-section of stainless steel.

Absorption of hydrogen into stainless steel was measured by the inert melting system coupled with a gas chromatography (LECO, RH-404). Measurements were taken on a specimen with a thickness of 0.02 mm that was placed in an ampoule and underwent corrosion for 90 days at 353 K in a dilute NaOH solution of pH 12.5. The ampoule method is described in detail in a separate study (Sakuragi et al., 2012).

3. Results and discussion

The results of hydrogen absorption into the stainless steel obtained from the batch ampoule method were shown in Table 2. It was a slight increase in the hydrogen concentration in metal after 90 days corrosion at 353 K. Then, the hydrogen pick-up ratios, x (%), obtained from the equation below were less than 3%.

$$x = \frac{A_{abs}}{A_{gas} + A_{abs}} \times 100 \quad (1)$$

where A_{abs} is the atomic molar amount of absorbed hydrogen per unit surface area (mol m^{-2}) and A_{gas} is the atomic molar amount of gaseous hydrogen per unit surface area (mol m^{-2}). Therefore, it is approved to count the gaseous hydrogen for evaluating the stainless steel corrosion in this system.

Fig. 5 shows the change in gaseous hydrogen concentration in the argon carrier gas for the gas flow experiment. The evolved hydrogen decreased over time from 15 to 1.5 ppb in the initial year. After that the hydrogen concentration can be considered to be constant: average values of Run 1 and Run 2 are 1.50 ± 0.34 ppb and 1.67 ± 0.42 ppb, respectively. This amount is adequate for the blank test, which shows a nearly constant value around 0.32 ± 0.06 ppb.

The cumulative atomic molar amount of gaseous hydrogen per unit surface area, A_{gas} (mol m^{-2}), can be obtained from

$$A_{gas} = \frac{2}{S}\sum \frac{C_t i + C_{t_{i-1}}}{2} \cdot \frac{v}{V^\circ} \cdot (t_i - t_{i-1}), \quad (2)$$

where C_{ti} is the net concentration of H_2 gas (ppb) at time t_i, t_{i-1} is one time increment before t_i, v is the gas flow rate (0.9 $dm^3\ min^{-1}$), V° is the molar volume of a perfect gas (22.4 $dm^3\ mol^{-1}$), and S is the surface area (0.4 m^2). The results of A_{gas} as a function of time and the least square fit in accordance with the following allometric