Development of Metal Corrosion Testing Method Simulating Equipment of Reprocessing of Spent Nuclear Fuels

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Abstract

In the PUREX reprocess method, spent nuclear fuels are dissolved and chemically treated with nitric acid media. The reprocessing solution containing Fission Products derived from spent fuels is very corrosive to metal materials, the corrosion problem often appears on the surface stainless steel devices. The presence of oxidizing metal ions such as ruthenium (Ru) and Neptunium (Np) in the process solution is the key reason for severe corrosion of stainless steel. In order to obtain the corrosion rate of stainless steel for evaluation of the corrosion of real reprocessing plant devices, we installed the corrosion test apparatus inside an airtight concrete cell in a hot laboratory (the WAste Safety TEsting Facility (WASTEF) of the Japan Atomic Energy Agency), and performed the corrosion tests of stainless steel in the heated nitric acid solution containing Np. The corrosion tests were performed in the temperature range from room temperature to boiling point for 500 hours per batch. The results show that the presence of Np accelerate the stainless steel corrosion in the nitric acid solution.

1. Introduction

In the Plutonium Uranium Redox Extraction (PUREX) process, which is used as a reprocessing method in Japan, spent nuclear fuels are dissolved and chemically treated with nitric acid media. These reprocessing devices are made from metals; stainless steels, zirconium and so on which are corrosion-resistant materials in nitric acid solutions. It has been reported that this nitric acid solution containing Fission Products (FP) derived from spent fuels is very corrosive to metal materials, the corrosion problem often appears on the surface of devices in contact with the nitric acid solution. A typical corrosion phenomenon is an intergranular corrosion of stainless steel. The presence of oxidizing metal ions such as Ruthenium(Ru) and Neptunium(Np) in the process solution is the key reason for severe corrosion of stainless steel[1]. For stable operation management and to predict the lifetime of reprocessing devices, it was necessary to quantify the corrosion rate of stainless steel in nitric acid solutions containing oxidizing metallic ions and to clarify the corrosion mechanism.

Therefore, to obtain the corrosion rate data of stainless steels in the nitric acid solution containing Np, we installed the corrosion test apparatus in a hot laboratory (WAste Safety TEsting Facility (WASTEF) of Japan Atomic Energy Agency).

This report describes the details of the corrosion test apparatus, experimental procedure and the results of the corrosion tests.

2. Corrosion test apparatus and procedure

2.1 Corrosion test apparatus

The corrosion test apparatus possessed the following capability;

- A high resistance to concentrated boiling nitric acid solution.
- The ability to precisely control the temperature and pressure of the test solution for more than 500 h.
- A sealing system to enable the use of a nitric acid solution containing uranium and alpha

nuclides.
- The simulation of high-dose radioactive reprocessing solutions such as high-level radioactive liquid waste using a gamma ray source.

An electrochemical measurement system to obtain polarization curves for understanding corrosion mechanisms.
As shown in Fig. 1, we installed the corrosion testing apparatus inside an airtight concrete cell which has containment capability to avoid internal exposure. A pressure inside the concrete cell is kept negative at all time. A few people can work inside the cell using a frogman airline suit.

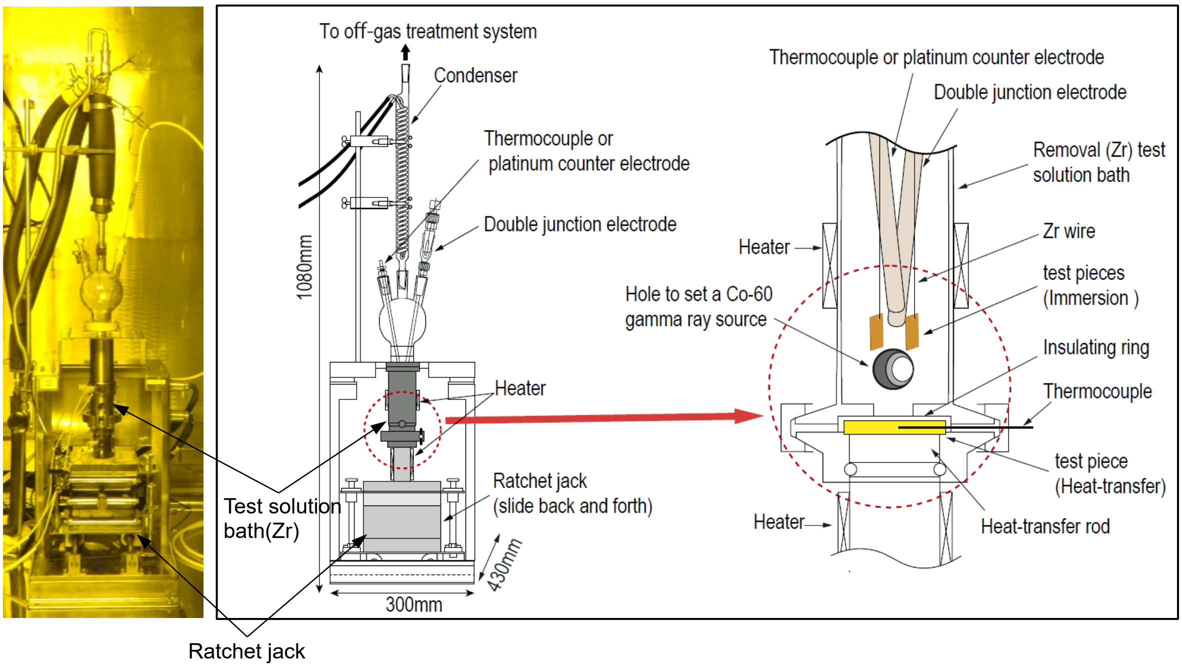

Fig.1 Schematic figure of corrosion test apparatus

The size of the corrosion test apparatus is 30 cm wide, 50 cm deep, and 1 m high. It comprises a removal test solution bath, a ratchet jack to move the test bath up and down, glass-condensing parts, and a gas pump. The ratchet jack is made of stainless steel and set on a frame which can move back and forward. The test solution bath is made of zirconium, which has high corrosion resistance to nitric acid solution. In addition, it has a hole to set a Co-60 gamma ray source as shown in Fig.1. Maximum value of solution filled in the test bath is 150mL, which is as less as possible to reduce the amount of Np treating inside a concrete cell. The test solution bath and solution are heated by a band heater around the test solution bath.
Two types of corrosion test can be performed; one is an immersion test and the other is a heat-transfer surface test. In case of the immersion test, small test pieces are immersed directly into the solution inside the bath. On the other hand, in case of the heat-transfer surface test, a disk test piece is connected with the bottom of the solution bath. One side of disk test piece is in contact with the solution, the other side is heated by the rod and band heater. All heaters are controlled using the heat controller located outside the concrete cell. Conducting wires for K-type thermocouples are connected between the inside and outside the cell through current introduction terminals to monitor the temperature and power supply to the heaters.
The connection between the heat-transfer test piece and the test bath is sealed using a Teflon packing (or a polyether ether ketone packing under gamma ray exposure) and a fluororubber-based coating. The glass-condensing parts are connected with the solution bath at the top, a dimroth condenser is used. For the connection between glasses, a SIBATA PRECISE CLEAR (SPC) type glass joint is used. Cooling water for the condenser circulates through a closed

system comprising a stainless steel tube and a cooling chiller located outside the cell. The gas pump is connected to the end of a dimroth condenser to control the pressure inside the test bath. The corrosion test in the boiling nitric acid solution under reduced pressure can be performed.
Using this corrosion test apparatus, the electrochemical measurements can be performed. All electrodes (a working electrode, a platinum counter electrode and a liquid junction which is connected with an Ag/AgCl electrode) are placed into the solution from a glass part. And, a potential and a current can be controlled and measured using a potentiostat located outside the cell through cables connected with current introduction terminals on the wall of the cell.

2.2 Corrosion test procedures

Test pieces

Test pieces were made from a type 304 austenitic stainless steel (SUS304ULC), which is the same type used in real reprocessing plants. The chemical composition of R-SUS304ULC is listed in Table 1. The size of the immersion test piece was 10x6x5 mm^3. The size of heat-transfer test piece is 30 mm in diameter and 6 mm in thickness. All samples were washed with acetone before the corrosion test.

Table 1 Chemical composition of SUS304ULC (wt%)

C	Si	Mn	P	S	Cr	Ni	Fe
0.009	0.38	1.11	0.012	0.002	18.43	10.63	Bal.

Preparation of Np-237 solutions

A nitric acid solution containing Np for the corrosion test was prepared inside a glove box. 1 mol/L of nitric acid solution containing NpO_2 powder was heated on a hot stirrer in an Erlenmeyer flask that was connected to a Liebig condenser cooled via circulating water, the solution until NpO_2 melted. During the heating process, 0.2mL of 30%H_2O_2 solution was injected into the solution every three or four hours during the day. the corrosion test solution was prepared using this Np solution and concerned Np solution. After preparation, the concentration of Np-237 in the test solution was confirmed via a germanium semiconductor detector method.

Corrosion test procedure

After all parts of the corrosion test apparatus were set up, the immersion test pieces and test solution were injected into the test solution bath. Then after the pressure of inside the test bath solution was kept at arbitrary value using the gas pump, heating up of all heaters was started. The temperature of solution was controlled at arbitrary value within the range from 303K up to boiling point of normal pressure for corrosion duration. The corrosion duration was maximum 500 h per one batch. In case of corrosion test under gamma ray irradiation, the Co-60 gamma ray source was set in the hole of the test solution bath before heating.

Weight and dimension measurement of the test pieces

Before and after corrosion tests, the test pieces were washed with acetone. The size and weight of test pieces were measured in a fume hood. The corrosion rate was calculated by the weight loss of the test piece. And, surface of samples was observed via scanning electron microscopy (SEM).

3. Results of corrosion tests

Figure 2 presents the Scanning Electron Microscope (SEM) images of the sample surfaces after about 500 h of corrosion tests at 353 K. Figure 2 (a) and (b) show the results of 8 mol/L of nitric acid solution and that of 8 mol/L of nitric acid solution containing Np-237, respectively. In the results of the nitric acid solution containing Np as shown in Fig.2(b), it can be observed that the grain boundaries of the stainless steel were depleted. This depletion of the grain boundary by corrosion is called as an intergranular corrosion. However, the intergranular corrosion cannot be observed in the results of the nitric acid solution without Np as shown in Fig.2(a). From these observations, we can see that the presence of Np in the nitric acid solution accelerates the corrosion of stainless steel.

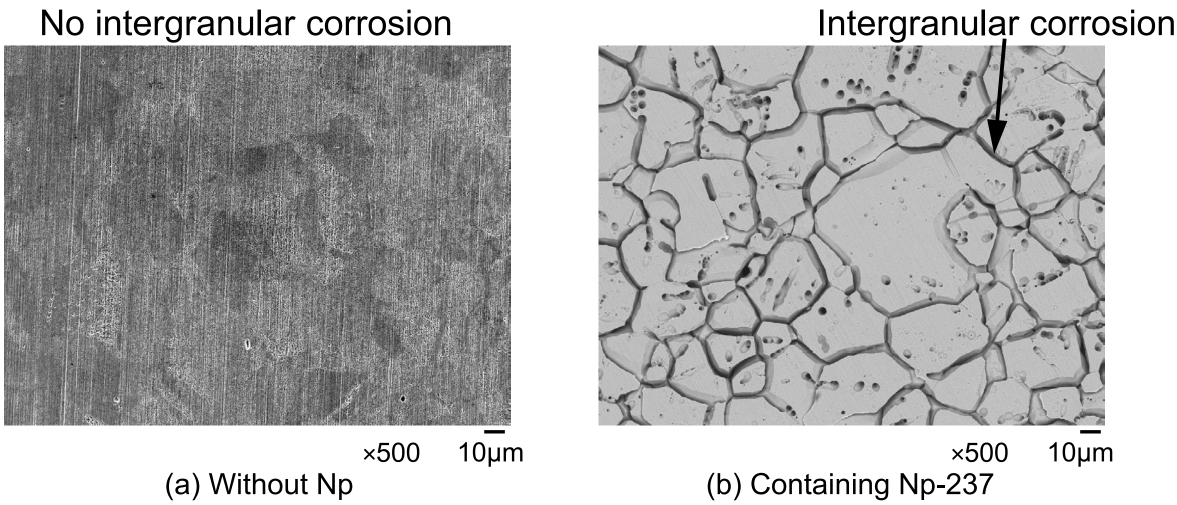

Fig.2 SEM images of sample surface after corrosion tests in the solution containing and not containing Np-237

4. Conclusions

A Corrosion testing apparatus was integrated into the WASTEF hot laboratory to study the corrosion behavior of metal devices used in reprocessing plants. To simulate a real environment, many functionalities were included in the apparatus that allowed for the corrosion behavior of stainless steel to be investigated under a variety of conditions. The results of a corrosion test using nitric acid solution containing Np-237 showed that the presence of Np in the nitric solution accelerates the corrosion of stainless steel.

References

1. E. Irisawa, F. Ueno, C. Kato, H. Abe, “Effect of Boiling under Reduced Pressure on Corrosion of Stainless Steels in Nitric Acid Solution Simulating High-level Radioactive Liquid Waste”, Zairyo-to-Kankyo, 65, 134-137 (2016)