

ARTICLE

Electrochemical properties of zirconium in highly concentrated plutonium nitrate solution

Masaumi Nakahara^{a*}, Yuichi Sano^a and Hitoshi Abe^b

^aNuclear Fuel Cycle Engineering Laboratories, Japan Atomic Energy Agency, 4-33 Muramatsu, Tokai-mura, Naka-gun, Ibaraki-ken, 319-1194, Japan; ^bNuclear Safety Research Center, Japan Atomic Energy Agency, 2-4 Shirakata, Tokai-mura, Naka-gun, Ibaraki-ken, 319-1195, Japan

To evaluate the corrosion resistance of a Pu evaporator made of Zr in the Rokkasho Reprocessing Plant (RRP), the electrochemical properties of Zr were evaluated in highly concentrated aqueous Pu nitrate solutions. The open circuit potential of Zr in the Pu nitrate solution increased with increasing temperature, and with increasing HNO₃ and Pu concentrations. At the boiling point, Pu⁴⁺ and PuO₂²⁺ co-existed in the Pu nitrate solution. To evaluate the influence of PuO₂²⁺ on the corrosion potential of Zr, the polarization curve of the Pu nitrate solution containing a high concentration of PuO₂²⁺ with 5 mol dm⁻³ HNO₃ and 250 g dm⁻³ Pu was measured. The corrosion potential of Zr stayed in the passive region. The influence of PuO₂²⁺ was not significant in highly concentrated Pu nitrate solution. These results suggest that Zr shows high corrosion resistance, even in highly concentrated Pu nitrate solution.

Keywords: Rokkasho Reprocessing Plant; evaporator; corrosion resistance; electrochemistry; open circuit potential; polarization curve; zirconium; plutonium

1. Introduction

The Rokkasho Reprocessing Plant (RRP) in Aomori, Japan was built for reprocessing irradiated light water reactor fuel, and it is operated with an irradiated nuclear fuel to check the reprocessing equipment. An aqueous separation technique with HNO₃ and tri-*n*-butyl phosphate (TBP)/*n*-dodecane system, called the Plutonium Uranium Redox Extraction (PUREX), has been adopted in RRP. In this process, U and Pu are separated from each other as products. Before denitration and conversion, the Pu nitrate solution is condensed in a Pu evaporator under the conditions of 50–250 g dm⁻³ of Pu and 3–7 mol dm⁻³ of HNO₃ at the boiling point [1]. The evaporator is made of Zr because Zr has high corrosion resistance to HNO₃ solution [2]. The corrosion behavior and electrochemical properties of Zr have been investigated in HNO₃ solution, Pu nitrate solution, and a dissolver solution of irradiated fast reactor fuels [3,4]. It was reported that the corrosion potential of Zr increased with increasing Pu concentration in the low Pu concentration range [4]. Ishijima et al. [5] reported that stress corrosion cracking (SCC) of Zr, with the formation of a black oxide film, occurred when the potentials were nobler than the passivity breakdown potential (around 1.40 V vs. Ag/AgCl in saturated KCl) in 9 mol dm⁻³ HNO₃ at the boiling point in constant load tensile tests. Although Takeda et al. [4] reported the corrosion potential of Zr in

3 mol dm⁻³ HNO₃ and approximately 100 g dm⁻³ of Pu in Pu nitrate solution at the boiling point, there is little experimental data on the electrochemical properties of Zr in Pu nitrate solution containing high concentrations of HNO₃ and Pu. In addition, it is important to examine the influence of PuO₂²⁺ on the electrochemical properties of Zr in the Pu nitrate solution because PuO₂²⁺/Pu⁴⁺ has high oxidation-reduction potential [6,7] and is very corrosive.

In this study, the electrochemical properties of Zr in highly concentrated Pu nitrate solution were investigated to evaluate the corrosion resistance of Zr. These experiments were carried out in a glove box at the Chemical Processing Facility (CPF) in the Japan Atomic Energy Agency (JAEA).

2. Experimental

2.1. Materials

As the working electrode, an ASTM B551-04 R60702 grade Zr rolled-plate was used in the experiments. The chemical composition of the Zr rolled-plate was H: <0.0003 mass%, C: 0.01 mass%, N: 0.005 mass%, O: 0.13 mass%, Fe + Cr: 0.07 mass%, Hf: 1.1 mass%, and Zr + Hf: ≥99.2 mass%. The Zr rolled-plate was cut to 2 mm diameter Zr rods and covered with polyether ether ketone (PEEK). The tip of the Zr electrode with PEEK was cut to 45° and polished with an abrasive-coated paper.

*Corresponding author. Email: nakahara.masaumi@jaea.go.jp

Special grade HNO_3 , TBP, *n*-dodecane, and hydrazine were purchased from Wako Pure Chemical Industries, Ltd. The extraction solvent for U and Pu purification, TBP/*n*-dodecane, was used after a further purification step, but HNO_3 and hydrazine were used without further purification.

A Pu nitrate solution was prepared from mixed oxide (MOX) fuel powder derived from irradiated fast reactor fuels. The MOX fuel powder was dissolved in 8 mol dm^{-3} HNO_3 solution. The MOX fuel dissolver solution was purified with TBP/*n*-dodecane, and Pu was separated from U using hydroxylamine nitrate (HAN) purchased from Mitsuwaka Pure Chemicals Research Institute Limited and hydrazine. A small amount of U was detected, but Pu was essentially separated from U. The valence of Pu in the Pu nitrate solution was changed to Pu^{4+} by bubbling through with NO_x gas.

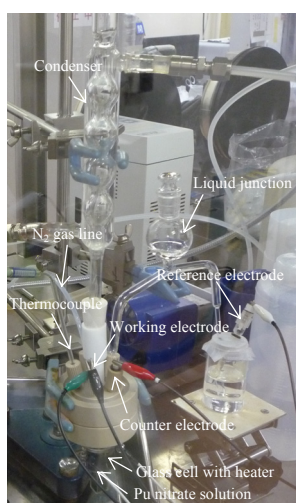


Figure 1. Apparatus setup for electrochemical measurements taken in the glove box.

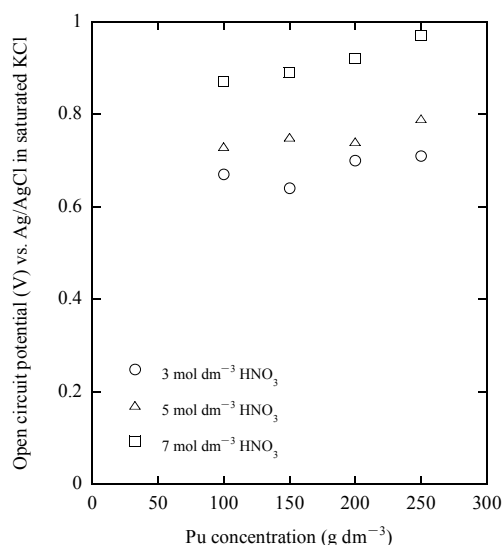


Figure 2. Influence of HNO_3 and Pu concentrations on the open circuit potential of Zr in Pu nitrate solution at the boiling point.

2.2. Procedure

Figure 1 shows the apparatus setup for the electrochemical measurements taken in the glove box. The apparatus consists of a glass cell with a heater, condenser, working electrode, counter electrode, reference electrode, liquid junction, thermocouple, and thermostat. The Pu nitrate solution was placed in a glass cell with a heater. The solution temperature was controlled using the thermostat. The PEEK-covered Zr rod, the working electrode, was immersed in the Pu nitrate solution. The Pt electrode was placed in the Pu nitrate solution and used as the counter electrode. As the liquid junction, a glass tube with a glass filter containing approximately 13.1 mol dm^{-3} HNO_3 solution was placed in the glass cell and the intermediate cell. The reference electrode, Ag/AgCl in saturated KCl, was placed in the intermediate cell.

The Pu nitrate solution was bubbled with N_2 gas for 10 min. The solution was heated to the target temperature in the glass cell. After the target temperature was reached, the open circuit potential was measured 30 min thereafter. Subsequently, the polarization curve was measured from 0 to 2 V at a scan rate of 0.003 V s^{-1} . The electrochemical measurements of Zr in the Pu nitrate solution were controlled using a potentiostat.

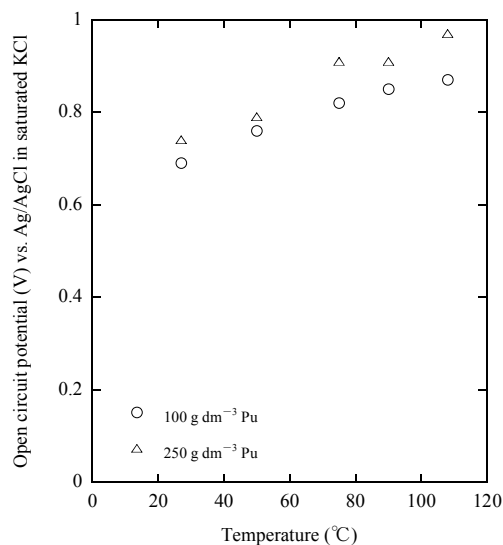


Figure 3. Influence of temperature on the open circuit potential of Zr in Pu nitrate solution containing 7 mol dm^{-3} HNO_3 .

2.3. Analysis

The acidity of the Pu nitrate solution was analyzed using titration (COM-1700S, Hiranuma Sangyo Co., Ltd.). The concentrations of U and Pu were measured by colorimetry (V-670, JASCO Corporation). An aliquot of the Pu nitrate solution was diluted with HNO_3 before and after the electrochemical measurements, and the valence of Pu was confirmed using spectroscopy.

3. Results and discussion

3.1. Influence of temperature, nitric acid, and plutonium concentrations on electrochemical properties of zirconium

Figure 2 shows the influence of HNO_3 and Pu concentrations on the open circuit potential of Zr in the Pu nitrate solution at the boiling point. The open circuit potential of Zr increased with increasing HNO_3 and Pu concentrations at the boiling point. The open circuit potential of Zr in relation to Pu concentration was trended similarly to the results reported by Takeda et al. [4].

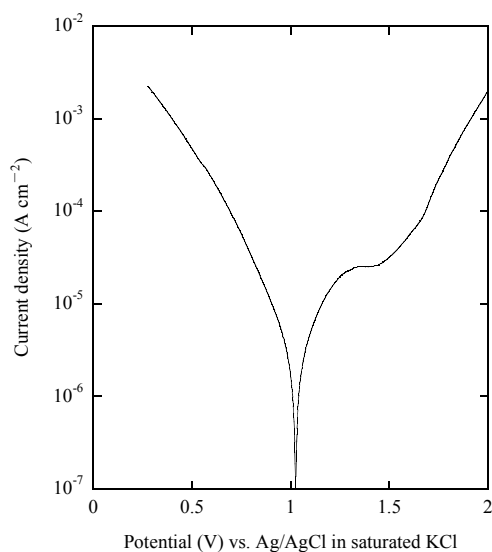


Figure 4. Polarization curve of Zr in Pu nitrate solution containing $7 \text{ mol dm}^{-3} \text{ HNO}_3$ and $250 \text{ g dm}^{-3} \text{ Pu}$ at the boiling point.

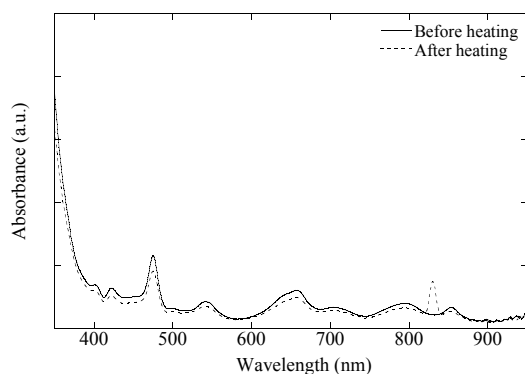


Figure 5. Spectrum of Pu nitrate solution containing $3 \text{ mol dm}^{-3} \text{ HNO}_3$ and $100 \text{ g dm}^{-3} \text{ Pu}$ before heating and after heating.

The influence of temperature on the open circuit potential of Zr in the Pu nitrate solution containing $7 \text{ mol dm}^{-3} \text{ HNO}_3$ is plotted in **Figure 3**. The open circuit potential of Zr increased with increasing temperature in the Pu nitrate solution. The open circuit potential of Zr in the Pu nitrate solution containing $250 \text{ g dm}^{-3} \text{ Pu}$ was slightly larger than that in the Pu nitrate solution

containing $100 \text{ g dm}^{-3} \text{ Pu}$.

Figure 4 shows the polarization curve of Zr in the Pu nitrate solution containing $7 \text{ mol dm}^{-3} \text{ HNO}_3$ and $250 \text{ g dm}^{-3} \text{ Pu}$ at the boiling point. The experimental results show that the corrosion potential of Zr stayed in the passive region.

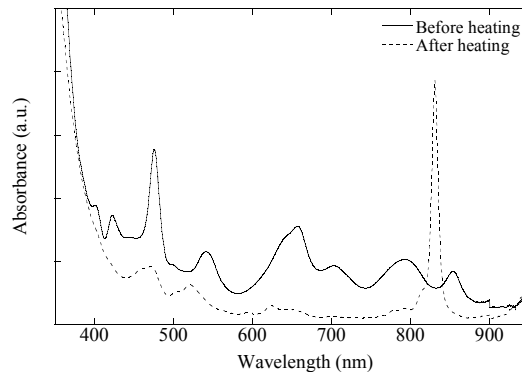


Figure 6. Spectrum of Pu nitrate solution containing $5 \text{ mol dm}^{-3} \text{ HNO}_3$ and $250 \text{ g dm}^{-3} \text{ Pu}$ before heating and after heating for 75 h.

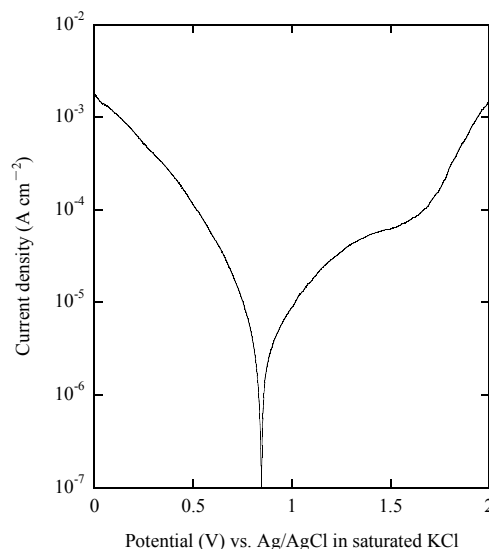


Figure 7. Polarization curve of Zr in Pu nitrate solution containing $5 \text{ mol dm}^{-3} \text{ HNO}_3$ and $250 \text{ g dm}^{-3} \text{ Pu}$ after heating for 75 h at the boiling point.

It is known that Pu^{4+} is oxidized to PuO_2^{2+} by heating aqueous Pu nitrate as follows [4].



The ratio of PuO_2^{2+} increases with decreasing initial Pu^{4+} and HNO_3 concentrations upon heating the solution [8]. In addition, the PuO_2^{2+} ratio increases with increasing solution temperature [8]. **Figure 5** shows the spectrum of the Pu nitrate solution containing $3 \text{ mol dm}^{-3} \text{ HNO}_3$ and $100 \text{ g dm}^{-3} \text{ Pu}$ before and after heating to the boiling point. Although the Pu^{4+} peak was only observed in the Pu nitrate solution before heating, a PuO_2^{2+} peak was

observed at 831 nm after heating. However, the amount of PuO_2^{2+} was small (some dozen g dm^{-3}) in the experimental sample.

It is assumed that the two reduction reactions of NO_3^- and PuO_2^{2+} occur as the main cathode reaction [4] and that the reduction of NO_3^- proceeds under conditions of high HNO_3 concentration. High Pu concentration and temperature would promote the Pu^{4+} oxidation reaction, as shown in Eq. (1), and cause an active PuO_2^{2+} reduction reaction on the surface of the electrode. Then, Pu^{4+} would be oxidized to PuO_2^{2+} with HNO_3 again in the bulk. Therefore, activation of cathode reaction can be considered to make the open circuit potential of Zr high in the Pu nitrate solution, as shown in Figures 2 and 3.

3.2. Influence of plutonyl ion on electrochemical properties of zirconium

To investigate the effect of Pu valence on the corrosion potential of Zr in Pu nitrate solution, the polarization curves of Zr were measured using a Pu nitrate solution with high concentrations of PuO_2^{2+} . The Pu nitrate solution was adjusted by heating it at the boiling point for 75 h. **Figure 6** shows the spectrum of the Pu nitrate solution containing 5 mol dm^{-3} HNO_3 and 250 g dm^{-3} Pu before and after heating for 75 h at the boiling point. After heating, a PuO_2^{2+} peak was observed at 831 nm, and a large amount of Pu^{4+} was oxidized to PuO_2^{2+} (some hundred g dm^{-3}). **Figure 7** shows the polarization curve of Zr in the Pu nitrate solution containing 5 mol dm^{-3} HNO_3 and 250 g dm^{-3} Pu after heating for 75 h at the boiling point. The corrosion potential of Zr stayed in the passive region under our experimental conditions, and it was considerably lower than the passivity breakdown potential.

4. Conclusion

The open circuit potentials and polarization curves of Zr in aqueous Pu nitrate solution were obtained using electrochemical techniques. The open circuit potential of Zr in Pu nitrate solution increased with increasing temperature, HNO_3 concentration, and Pu concentration. According to the polarization curve, our research revealed that the corrosion potential of Zr in a Pu nitrate solution containing high concentrations of PuO_2^{2+} stayed

in the passive region. Therefore, the experimental results indicate that Zr is corrosion resistant in highly concentrated Pu nitrate solution.

Acknowledgements

This work includes experimental results under the auspices of the Nuclear Regulation Authority.

References

- [1] K. Kiuchi, Corrosion problems and countermeasures to corrosion of reprocessing materials used in boiling nitric acid, *Nihon-Genshiryoku-Gakkai Shi (J. At. Energy Soc. Jpn.)* 31 (1989), pp. 229-238. [in Japanese]
- [2] F. Wada, Improvement of reliability in nuclear fuel reprocessing plant, *Zairyo-to-Kankyo* 48 (1999), pp. 771-775. [in Japanese]
- [3] S. Takeda, T. Nagai and T. Koizumi, Corrosion behavior of materials in FBR spent fuel reprocessing solutions, *Nihon-Genshiryoku-Gakkai Shi (J. At. Energy Soc. Jpn.)* 36 (1994), pp. 146-157. [in Japanese]
- [4] S. Takeda, T. Nagai, S. Yasu and T. Koizumi, Corrosion performance of several metals in plutonium nitrate solution, *Zairyo-to-Kankyo* 44 (1995), pp. 24-29. [in Japanese]
- [5] Y. Ishijima, C. Kato, T. Motooka, M. Yamamoto, Y. Kano and T. Ebina, Stress corrosion cracking behavior of zirconium in boiling nitric acid solutions at oxide formation potentials, *Mater. Trans.* 54 (2013), pp. 1001-1005.
- [6] J.D. Moore, R.L. Walser and J.J. Fritch, *Purex Technical Manual*, RHO-MA-116, Rockwell Hanford Operations, (1980).
- [7] R.J. Lemire, J. Fuger, H. Nitsche, P. Potter, M.H. Rand, J. Rydberg, K. Spahiu, J.C. Sullivan, W.J. Ullman, P. Vitorge and H. Wanner, *Chemical Thermodynamics of Neptunium and Plutonium*, OECD Nuclear Energy Agency, Elsevier, North Holland, (2001), pp. 301-316, ISBN 0-444-50379-X.
- [8] S.A. Glazyrin, P.Yu. Rodchenko and L.P. Sokhina, Oxidation of plutonium(IV) on heat treatment of concentrated nitrate solutions, *Radiokhimiya* 31 (1989), pp. 48-52.