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VI. 4. Electrochemical Properties of Austenitic Stainless Steel (R-SUS304ULC) in Nitric Acid Solution

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Introduction

Nuclear fuel reprocessing of PUREX (Plutonium and Uranium Recovery by Extraction) process uses nitric acid as the dissolution reaction medium. In this process, severe corrosive environment to the equipment material is caused by heating operation of the nitric acid solution. An austenitic stainless steel is one of important materials used in the reprocessing plant. R-SUS304ULC is the ultra-low-carbon austenitic stainless steel for the reprocessing plant developed in Japan (R: Reprocessing, ULC: Ultra Low Carbon) based on the corrosion problem in Tokai reprocessing plant¹⁻³). This stainless steel has high corrosion resistance because the carbon content is specified to be less than 0.020 wt% in order to avoid sensitization associated with chromium depletion along grain boundaries during the welding process, and it has been used in Rokkasho reprocessing plant⁴).

On the other hand, the corrosion of stainless steel in nitric acid solution is affected by the redox potential increases with concentrations in NO_3^- and H^+ , temperature increases and decreases with HNO_2 concentration⁵). Also, the gaseous species of NO and NO_2 affects the redox potential in nitric acid solution⁶). In addition, ions having high oxidizability such as Ru, Pu, Np and Cr accelerate the corrosion of stainless steel, and these show the complex redox behavior in nitric acid solution⁷⁻¹²). In the reprocessing plant, the nitric acid solution handled wide range nitric acid concentration and temperature. Therefore, to understand these changes in solution environment gives the useful information for grasping of the redox reaction of oxidation ions and corrosion behavior of the stainless steel.

In this study, we investigated relationship between the corrosion behavior of R-SUS304ULC steel and the environment change of nitric acid solution by temperature

increases using electrochemical measurements and thermodynamic calculations.

Experimental

Materials

Solutions used for electrochemical tests were 3 M ($M=\text{mol}\cdot\text{L}^{-1}$) and 8 M nitric acid. The concentration of 3 M nitric acid is equivalent of the nuclear spent fuel solution, and 8 M nitric acid is equivalent to use of the environment of HLLW (High Level Liquid Waste) evaporator and acid recovery evaporator in Rokkasho Reprocessing Plant⁴). The nitric acid concentration of the test solution was determined by potentiometric titration with 0.1 M NaOH solution. The test solution (100 mL) was introduced into a 300-mL Pyrex flask. Table 1 shows the chemical composition of R-SUS304ULC of the test specimen. The specimen is flag type (measurement part: $20\times 15\times 2^t$ mm, cross-section of lead part: 1×1 mm). This surface was wet polished with emery papers down to #800, and rinsed with pure water and acetone under sonication. The ratio of the test solution volume and surface area of the specimen were about $40\text{ mL}\cdot\text{cm}^{-2}$.

Electrochemical tests

Figure 1 shows the apparatus for electrochemical tests. The potentiostat was an ALS/CH Instruments Model 611DT electrochemical analyzer. A three electrode system was utilized, *i.e.*, R-SUS304ULC working electrode (surface area: 2.5 cm^2), a Hokuto Denko Corp. HX-C7 Pt counter electrode, and a BAS RE-1C reference electrode (SSE: Ag/AgCl, sat. KCl). The lead part of working electrode was coated with Teflon tube. The reference electrode connected by a salt bridge having a porous ceramic. The polarization measurement was performed after the rest potential was stable (about 1 hour after reaching the measurement temperature), and measured in order of cathode and anode in each temperature from the room temperature to the boiling point. The scan rate was performed by $0.01\text{ V}\cdot\text{s}^{-1}$.

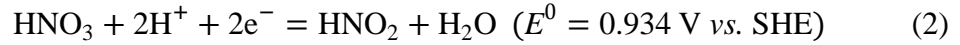
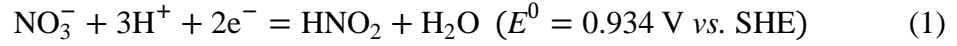
Thermodynamic calculations using the SOLGASMIX program

The thermodynamic calculation was performed by SOLGASMIX program. SOLGASMIX calculation code and thermodynamic constants were obtained from the HSC Chemistry version 7.1 software (Outokumpu Research, Finland). The calculation method was performed using the model calculation of boiling nitric acid devised by Kato *et al*⁵).

Results and discussion

Electrochemical tests

Figure 2 shows the results of polarization measurement. Corrosion potentials were shifted to the noble direction with temperature increases in either case. Also, we see from Figure 2 that the corrosion reaction of R-SUS304ULC is dominated by cathode reaction because the current density of cathode side was increased with temperature increases. Now, the equation of redox reaction of nitric acid is expressed as follows¹³⁾:



Nernst equation corresponding to equations (1) and (2) are as follows¹³⁾:

$$E = E^0 - \frac{2.303 \times 3 \times RT}{2F} \text{pH} + \frac{RT}{2F} \ln \frac{[\text{NO}_3^-]}{[\text{HNO}_2]} \quad (3)$$

$$E = E^0 - \frac{2.303 \times 2 \times RT}{2F} \text{pH} + \frac{RT}{2F} \ln \frac{[\text{HNO}_3]}{[\text{HNO}_2]} \quad (4)$$

where R is the gas constant ($=8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the temperature (K), F is the faraday constant ($=9.6485 \times 10^4 \text{ C mol}^{-1}$). We see from the equation (1) and (2) that the reduction reaction of nitric acid on the corrosion of stainless steel is reduction reaction of NO_3^- and HNO_3 , and the redox potential of nitric acid is dominated by concentration of NO_3^- , HNO_3 , and HNO_2 from the equation (3) and (4). Also, we consider that the reduction reaction on the surface of stainless steel is likely to proceed with increasing temperature in either case 3 M and 8 M nitric acid solution, because the cathode current density is increased with temperature increases. However, in the case of 8 M nitric acid, increases of current density with temperature increases were smaller than 3 M nitric acid. We consider that the factor is related to the composition change of nitric acid solution such as dissociated nitric acid, undissociated nitric acid, and nitrous acid. Figure 3 shows the change of degree of nitric acid dissociation (α), stoichiometric activity coefficient of nitric acid (y_s) (a product of a mean ionic activity coefficient, y_{\pm} , and a degree of dissociation, α , $y_s = y_{\pm}\alpha$), and activity coefficient of undissociated nitric acid (y_u) with nitric acid concentration change¹⁴⁾. The degree of dissociation is about 0.9 in the case of 3 M nitric acid. On the other hand, it decreases with increasing nitric acid concentration, and it is about 0.6 in the case of 8 M nitric acid. In addition, stoichiometric activity coefficient of nitric acid (y_s) and activity coefficient of undissociated nitric acid (y_u) are changed remarkably with more than 3 M nitric acid. Therefore, there is a possibility that the cathode reaction rate is changed by the shift of the equilibrium due to the composition change of the nitric acid solution.

Thermodynamic calculation using the SOLGASMIX program

In order to investigate the composition change of the nitric acid solution, we evaluated the equilibrium state of nitric acid solution at each conditions of 3 M and 8 M nitric acid using the SOLGASMIX calculation code. Table 2 shows the initial values used in the calculation. Nitrogen oxides for the calculation were used NO_3^- , HNO_3 , HNO_2 , NO_2 , and NO . These species are significant nitrogen oxides involved in the determination of the redox potential of nitric acid solution⁵⁾. The initial concentration of nitrous acid was 1 mM which is close to the measured redox potential⁵⁾. Figure 4 shows the calculation results of each condition. While the boiling point was deviated from the calculation results of the temperature at gas generation, it is considered that the calculation code does not accurately calculate the vapor-liquid equilibrium. Kato *et al.* also reported that a similar deviation occurs⁵⁾. In the case of 8 M nitric acid, the ratio of the undissociated nitric acid for the dissociated nitric acid is larger than the 3 M nitric acid. For example, in the case of 3 M nitric acid, the ratio of $\text{NO}_3^- / \text{HNO}_2$ changed to 1.8×10^3 from 2.5×10^3 (0.72 times) when the temperature increased to 373 K from 300 K, and the ratio of $\text{HNO}_3 / \text{HNO}_2$ changed to 1.3×10^3 from 4.9×10^2 (2.65 times). On the other hand, in the case of 8 M nitric acid, the ratio of $\text{NO}_3^- / \text{HNO}_2$ changed to 3.8×10^3 from 6.0×10^3 (0.63 times) when the temperature increased to 373 K from 300 K, and the ratio of $\text{HNO}_3 / \text{HNO}_2$ changed to 4.3×10^3 from 2.0×10^3 (2.15 times). We see from these calculation results that the decrease in $\text{NO}_3^- / \text{HNO}_2$ ratio and the increase in $\text{HNO}_3 / \text{HNO}_2$ ratio in the case of 8 M nitric acid are smaller than the 3 M nitric acid. Therefore, we consider that the redox potential of nitric acid solution is dominated by redox reaction of undissociated nitric acid with increasing of temperature and nitric acid concentration.

Conclusions

In polarization measurements, the corrosion potential of R-SUS304ULC was shifted to the noble direction with temperature increases, and it is dominated by the cathode reaction of nitric acid solution. In the thermodynamic calculation, the ratio of the undissociated nitric acid for the dissociated nitric acid in the case of 8 M nitric acid was larger than the 3 M nitric acid, and it is increased with temperature increases.

Therefore, the results suggested that the corrosion reaction of R-SUS304ULC is dominated by the concentration of undissociated nitric acid and nitrous acid with the increasing of temperature and nitric acid concentration.

References

- 1) Maki A., *JNC Technical review* **14** (2002) 39.
- 2) Hyakubu T., et al., *Proc. Int. Symp. on Plant Aging and Life Prediction of Corrodible Structures* Sapporo (Japan) (1995) 15.
- 3) Inazumi T., et al., *NKK Tech. Rev.* **144** (1993) 20.
- 4) Wada F., *Zairyo-to-Kankyo* **48** (1999) 771.
- 5) Kato C., et al., *Zairyo-to-Kankyo* **52** (2003) 44.
- 6) Armstrong R D., et al., *J. Appl. Chem.* **28** (1998) 1205.
- 7) Okubo M., et al., *Proc. RECOD 87*. Paris (France) (1987) 1181.
- 8) McIntosh A B., et al., *Proc. 2nd Int. Conf. on peaceful users of atomic energy*. Geneva (Switzerland) (1958) 206.
- 9) Hirose Y., et al., *Proc. RECOD 87* Paris (France) (1987) 501.
- 10) Arai Y., et al., *Zairyo-to-Kankyo* **48** (1999) 235.
- 11) Takeuchi M., et al., *Trans. At. Energy Soc. Jpn.* **5** (2005) 32.
- 12) Motooka T., et al., *J. Nucl. Sci. Technol. Suppl.* **3** (2002) 367.
- 13) Pourbaix M., *Atlas of electrochemical equilibria in aqueous solutions* 2nd ed. NACE, Texas (1974) 493.
- 14) Davis W Jr., et al., *J. Inorg. Nucl. Chem.* **26** (1964) 1069.

Table 1. Chemical composition of R-SUS304ULC (mass %).

C	Si	Mn	P	S	Cr	Ni	Fe
0.019	0.39	0.88	0.028	0.002	18.1	9.11	Bal.

Table 2. Initial conditions for thermodynamic calculations.

Total volume	Pressure	H ₂ O	H ⁺	NO ₃ ⁻	HNO ₃	HNO ₂	NO _x
L	MPa	mol/L					
1	0.101	41 51	8 3	8 3	0	1×10 ⁻³	0

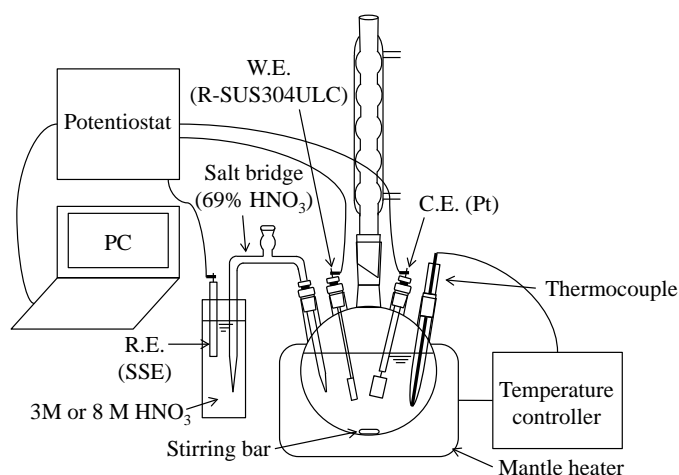


Figure 1. A schematic diagram of electrochemical tests.

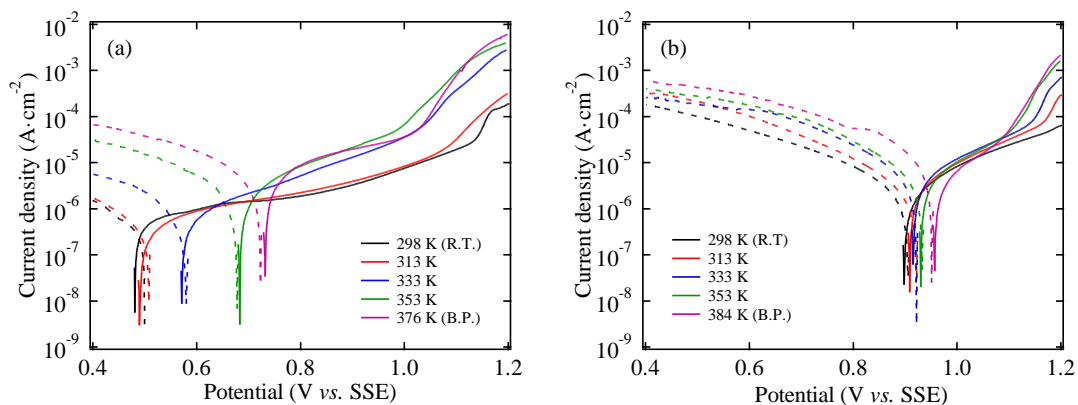


Figure 2. Polarization curves of R-SUS304ULC in nitric acid solution, broken line: cathodic, solid line: anodic, (a) 3 M HNO₃, (b) 8 M HNO₃.

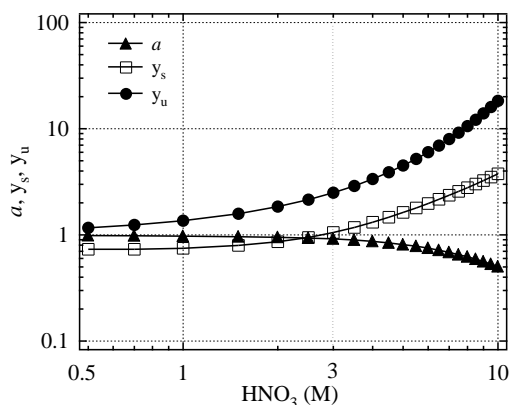


Figure 3. Degree of dissociation and activity coefficients in nitric acid solution at 298 K¹⁴.

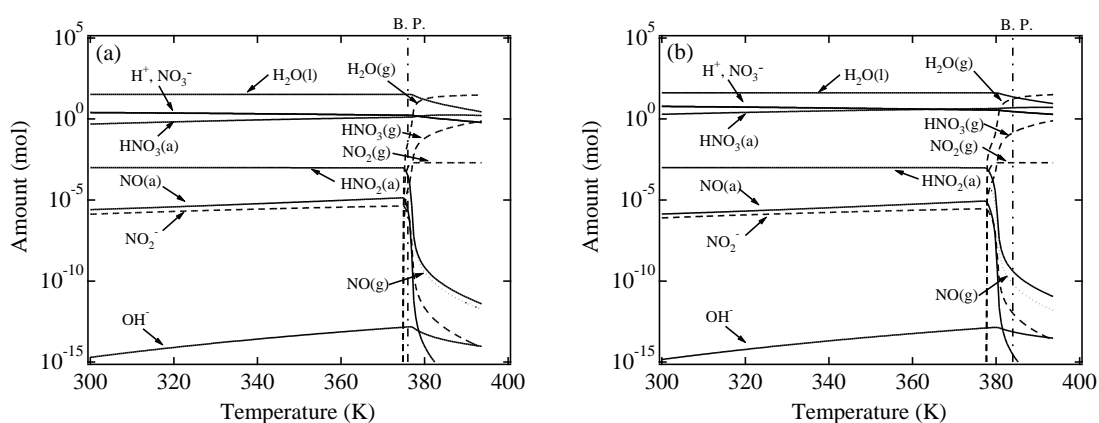


Figure 4. Relationship between temperature and amount of compounds in nitric acid solution calculated by SOLGASMIX program, state: g=gas, l=liquid, a=ion for aqueous species, (a) 3 M HNO₃, (b) 8 M HNO₃.