

Effects of Oxidation States of Np on Polarization Curve of Stainless Steel in boiling 3M-HNO₃.

Chiaki Kato*, Fumiyoshi Ueno*, Masahiro Yamamoto*, Yasutoshi Ban*, Gunzo Uchiyama*, Yasuo Nojima**, Sachio Fujine**

* Japan Atomic Energy Agency

2-4, Shirane, Shirakata, Tokai-mura, Naka-gun, Ibaraki-ken, 319-1195 Japan

** Japan Nuclear Energy Safety Organization,

Kamiya-cho MT Building, 4-3-20, Tora-no-mon, Minato-ku, Tokyo-to, 105-0001 Japan

Corrosion of stainless steel in reprocessing plants is quite severe due to presence of some kinds of cations which promote corrosion in boiling concentrated nitric acid solution [1]. Among the cations included in the reprocessing solutions, Np ion reported to accelerate corrosion of stainless steel [2]. However a role of Np ions related valence states in boiling nitric acid solution is not clear in corrosion reactions of stainless steel.

In this study, valence states of Np ion and polarization curves of stainless steel in nitric acid solutions containing Np are concomitantly evaluated by using specially designed small electrochemical test cell integrated with spectroscopic analysis.

Figure 1 shows polarization curves of Pt electrode and type 310Nb stainless steel in boiling 3 M-HNO₃ at 376K. Pt electrode potential was nobler than corrosion potential in stainless steel. Pt electrode potential indicates redox potential of HNO₃/HNO₂ equilibrium in nitric acid solution [3]. Meanwhile, corrosion potential of stainless steel indicates relation between cathodic reactions related with NO_x/HNO₂ equilibrium and anodic reaction on stainless steel [4]. Therefore it is considered that redox reactions of nitric acid are difference between in nitric acid solution and on stainless steel.

Figure 2 shows polarization curves of type 310Nb stainless steel in boiling 3 M-HNO₃ with/without Np ions. Initial Np(V) was controlled by electrolytic reduction. Corrosion potential on stainless steel in nitric acid solution with Np ion is nobler than one without Np ion. While anodic polarization curves are approximately same with or without Np ion, cathodic polarization curves are dramatically changed. This cathodic reaction changing related Np ion causes nobler corrosion potential and accelerates corrosion of stainless steel. In contrast, cathodic polarization curves in boiling 3 M-HNO₃ with initial Np(V) or Np(VI) were almost same. It is estimated that initial Np(V) is oxidized in boiling 3 M-HNO₃ and change to Np(VI). Np ion is known to have valence states of Np(IV), Np(V), and Np(VI) in nitric acid solution [5]. Therefore it is important to evaluate oxidation states of Np in boiling nitric acid in understanding the role of Np ions.

Figure 3 shows existence ratio of Np(VI) and Np(V) in 3 M-HNO₃ with initial Np(V) ions at various temperatures. Absorption spectrum was measured after 1 hour heating to evaluate the valence state of Np ions. Np(IV) absorption spectrum was not appeared in 3 M-HNO₃. After measuring absorption spectrum, electrochemical tests were continuously performed. While Np(V) was oxidized to nearly 80% Np(VI) in boiling 3 M-HNO₃ at 376K, Np(V) was hardly oxidized to Np(VI) at 303K. This result shows that Np(V) ion is easily oxidized to Np(VI) in boiling 3 M-HNO₃. Absorption peak related to Np(IV) was not observed in

the spectrum.

This easy oxidation of Np ion in the solution promotes re-oxidation cycle of Np ions from Np(V) to Np(VI) in boiling 3 M-HNO₃. This cycle is thought to accelerate corrosion of stainless steel due to activation of cathodic reaction. Namely nobler redox potential in nitric acid solution promotes oxidation of Np ion and less noble corrosion potential on stainless steel promotes reduction of oxidized Np ion and it accelerate corrosion of stainless steel.

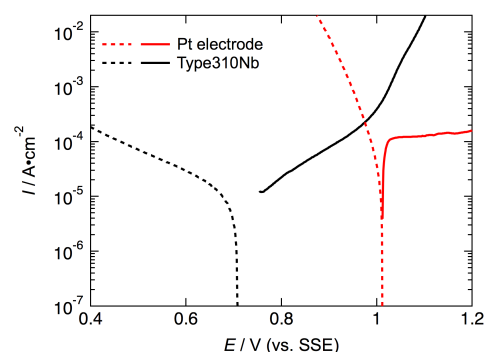


Fig. 1 Polarization curves of Pt electrode and type 310Nb stainless steel in boiling 3 mol/dm³ nitric acid solutions at 376K; solid lines are anode, dotted lines are cathode.

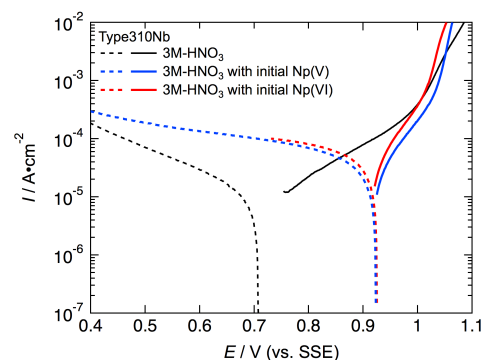


Fig. 2. Polarization curves of type 310Nb stainless steel in boiling 3 mol/dm³ nitric acid solutions with/without Np ion containing 5.3 mmol/dm³ initial Np(V) or Np(VI) at 376K; solid lines are anode, dotted lines are cathode.

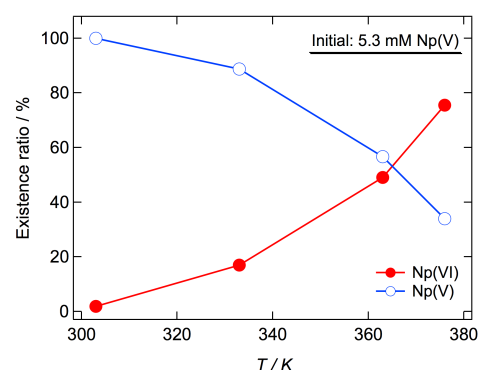


Fig. 3 Existence ratio of Np(VI) and Np(V) in 3 mol/dm³ nitric acid solutions containing 5.3 mmol/dm³ initial Np(V) ions at various temperatures.

References

- 1) P. Fauvet et al., *J. Nuclear Materials*, **375**, 52 (2008).
- 2) T. Motooka et al., *Zairyo to Kankyo (JSCE Corrosion Engineering)*, **57**, 536 (2008).
- 3) C. Kato et al., *Zairyo to Kankyo (JSCE Corrosion Engineering)*, **52**, 35 (2003).
- 4) F. Balbaud et al., *Eur. J. Inorg. Chem.*, **2000**, 665 (2000).
- 5) R. Gauthier et al., *Radiochimica Acta*, **33**, 35 (1983).