CORROSION BEHAVIOUR OF FeCrAl-ODS STEELS IN NITRIC ACID SOLUTIONS WITH SEVERAL TEMPERATURES

Y. TAKAHATAKE, H. AMBAI, Y. SANO, M. TAKEUCHI, K. KOIZUMI
Japan Atomic Energy Agency
4-33 Muramatsu, Tokai-mura, Naka-gun, Ibaraki-ken 319-1194, Japan

K. SAKAMOTO
Nippon Nuclear Fuel Development, Co., Ltd.
2163 Narita-cho, Oarai-machi, Ibaraki-ken, 311-1313, Japan

S. YAMASHITA
Japan Atomic Energy Agency
2-4 Shirakata Shirane, Tokai-mura, Naka-gun, Ibaraki-ken 319-1195, Japan

ABSTRACT

The corrosion behaviour of FeCrAl-ODS steels for the accident tolerant fuel cladding of LWRs were investigated in nitric acid solutions for the reprocessing process of spent fuels. The corrosion tests were carried out at 60°C, 80°C and the boiling point of the solutions, and the specimens were then analysed by XPS. The corrosion remarkably progressed at the boiling point, and the highest corrosion rate was 0.22 mm/y. In the oxide film, the atomic concentration of Fe was lower, than that in the base material, and those of Cr and Al were higher. The results show that the corrosion of FeCrAl-ODS steels in hot nitric acid solution is not severe because of the high corrosion resistance of the oxide film formed on the material; hence, it was estimated that the corrosion resistance of the new cladding materials in the dissolution process of spent fuel is acceptable for reprocessing operations.

1. Introduction

A FeCrAl-oxide dispersion strengthened (ODS) steel has been developed for the accident tolerant fuel cladding of light water reactors (LWRs) in Japanese projects. Spent fuels are reprocessed in Japan, namely spent fuel pins are chopped and immersed in hot nitric acid solutions to leach out the fuel components. The components of claddings dissolved in the nitric acid solution may affect the separation process, which is contiguous with the dissolution process, part of them is then treated as high-level radioactive liquid waste [1], and the insoluble constituents are treated as low-level radioactive solid waste. The behaviour of a FeCrAl-ODS steel in the dissolution process should be evaluated to investigate the influence of the fuel cladding corrosion on the reprocessing process.

The corrosion behaviour of ODS steel with chromium in nitric acid solutions has been evaluated [2], but that of ODS steel with chromium and aluminium is almost unknown [3, 4]. The reaction of a FeCrAl-ODS cladding in a dissolver is unclear, so its corrosion behaviour has been investigated at the Rokkasho Reprocessing Plant (RRP, Japan Nuclear Fuel Ltd.). The dissolver was designed to be mainly used with 3 mol/dm^3 nitric acid solutions and at the boiling point (approximately 110°C) [1], and the residence time of chopped spent fuel pins was about 2.7 h [5]. In this paper, the corrosion rates of the FeCrAl-ODS steel in nitric acid solutions were evaluated at several temperatures considering the dissolution condition of the RRP.

2. Experimental

2.1 Material

The FeCrAl-ODS steel utilized for experiments was ferrite steel before recrystalisation, with the chemical composition shown in Tab 1, as obtained by electron-induced X-ray fluorescence (EDX) analysis. Fig 1 shows the typical microstructure of the FeCrAl-ODS steels obtained by electron backscattering diffraction (EBSD) mapping with a field emission scanning electron microscope (FE-SEM, DigiviewIV, TSL solutions, Inc.). The grain size varied from <1 to 20 µm, and a strong anisotropy was observed.

Fe	Cr	Al	Ti	Zr
76	12	11	<1	<1

Tab 1: Chemical composition of the FeCrAl-ODS steel (at %).

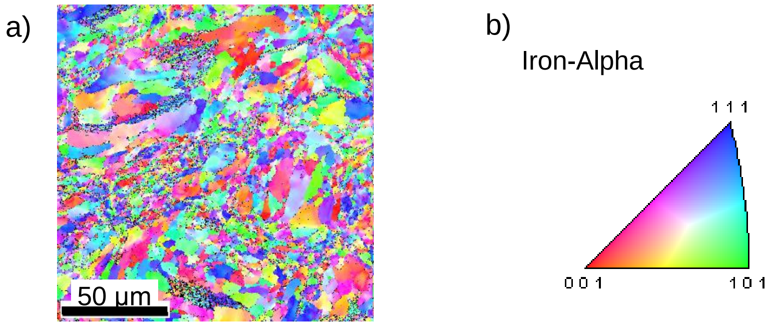


Fig 1. EBSD image of the microstructure of the FeCrAl-ODS steel for the α-Fe phase; a) inverse pole figure (IPF) map and b) colour legend for the grain orientation of α-Fe phase in a).

2.2 Method

The immersion tests were carried out for 48 and 96 h in 3.0 mol/dm^3 nitric acid solution at 60°C, 80°C and the boiling point for estimating the steady corrosion rate and investigating the temperature dependence. Specimens with a total surface area of about 2.8 cm^2 were cut from the base material and mechanically polished with 600 grit silicon carbide paper for these tests. Three specimens were immersed in 500 cm^3 of solution, as shown in Fig 2 a). Before and after immersion tests, specimens were ultrasonically cleaned by distilled water. And then they were dried in air after cleaning by ethyl alcohol. Their mass loss were measured, and the corrosion rate were calculated, as follows:

Corrosion rate (mm/y) = $\Delta M / (t \times S \times d)$, Eq 1.

where ΔM, t, S and d are the mass loss (g), immersion time (y), surface area of a specimen (mm^2) and density of FeCrAl-ODS steels (g/mm^3), respectively. The density of the base material was 7.1 g/cm^3. The mass loss of each specimen was measured after 3, 6, 9, 24, 48, 72 and 96 h of immersion, and their surfaces were observed at the laser microscope (LEXT OLS4000-SAF, Olympus Co.). The immersion test at the boiling point was carried out for a longer time because of considering the corrosion form. After the immersion tests, some specimens were analysed by X-ray photoelectron spectroscopy (XPS) with an ESCA5600Ci (ULVAC-PHI, Inc.) to measure the thickness and chemical composition of the oxide film. The XPS spectra were recorded with Mg-Kα radiation ($h\nu$ = 1253.6 eV) at a pressure under 2 × 10^{-8} Pa. XPS depth profiles were measured using an argon gun. Electrochemical tests consisting of the linear voltammetry test were conducted on Fig 2 b) to obtain the polarisation curves for the discussion of the corrosion mechanism. The counter and reference electrodes were Pt plate and Ag/AgCl electrode, respectively. Initially, the specimen with a surface area of approximately 7.0 cm^2 was immersed in 400 cm^3 of 3.0 mol/dm^3 nitric acid solution at the same temperatures as those for the immersion tests, and the measurement of the immersion potential was started. After 30 min, the potential was swept from the value that was 600 mV lower than the immersion potential, with a potential sweep rate of 20 mV/min.

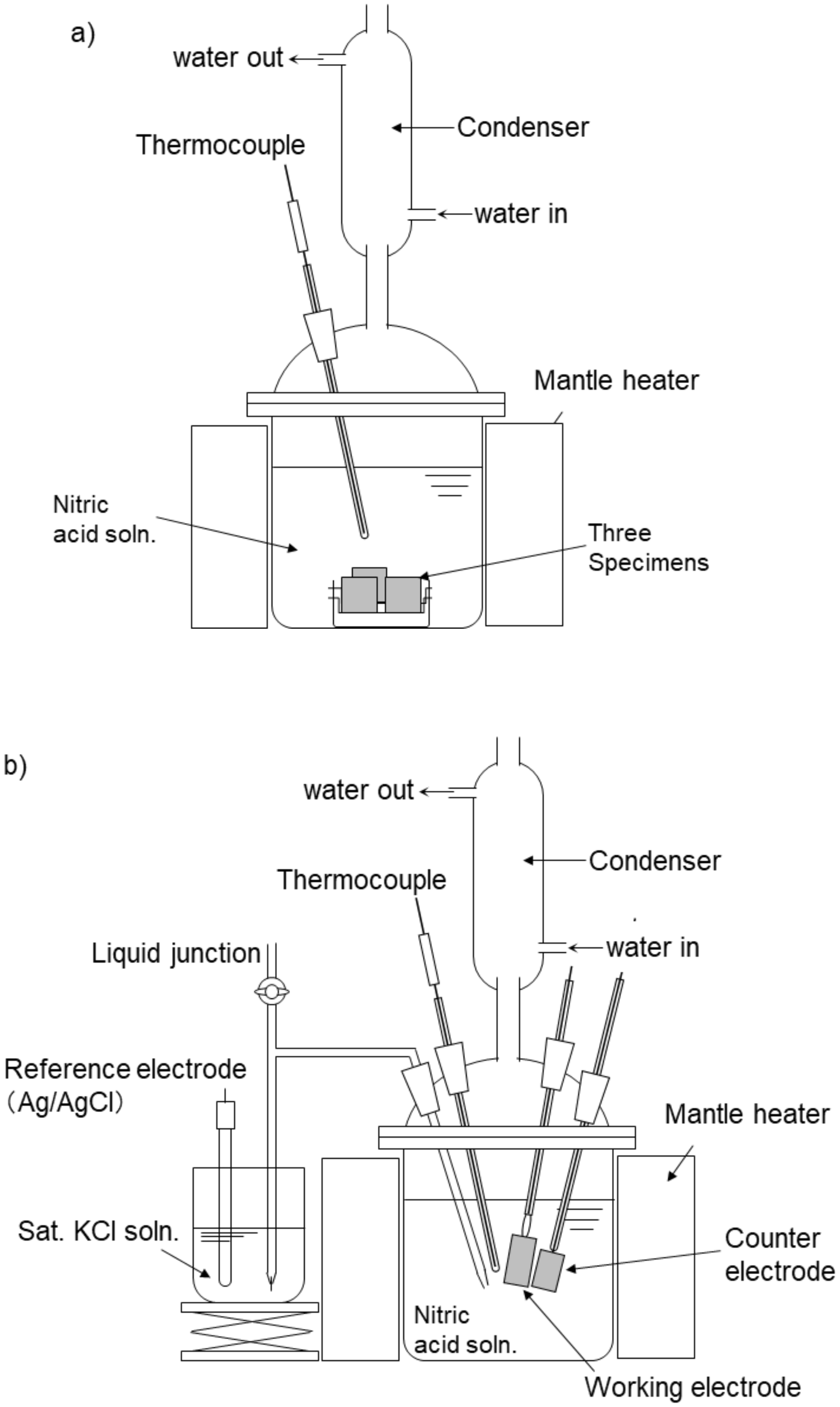


Fig 2. Schematic tests apparatus; a) the immersion tests and b) electrochemical tests.

3. Results and Discussion

3.1 Temperature dependence of corrosion behaviour

Fig 3 shows the corrosion rates in the nitric acid solution at different temperatures. At 60°C, after 3 h of immersion, the corrosion rate was higher than that for any other immersion time because the mass loss of the specimens was not confirmed after 9 – 48 h. Hence, the main reaction of the FeCrAl-ODS steel with nitric acid is initial dissolution at 60°C. The corrosion rates at the boiling point were higher than those at 60°C and 80°C, and it decreased down about 0.22 mm/y with the immersion time. The corrosion rate of 12Cr-ODS steel in 3.5 mol/dm^3 nitric acid solution at 95°C is over 10 mm/y after 30 min of immersion[2]; hence, a better corrosion resistance to nitric acid by FeCrAl-ODS steels was already expected. The larger error bar for the corrosion rate after 3 h of immersion shows that the oxide film is still forming at that time. The changes in the specimen surfaces are shown by laser micrographs in Fig 4. The surface roughness was evaluated by arithmetical mean height of the surface (S_a) obtained by scanning data with the laser microscope. S_a values on Fig 4 were calculated the average of 9 and 3 specimens on as received and each immersing condition. After 3 h of immersion, no clear sign of corrosion is observed at any temperatures. Changes in the surface colour are more remarkable at 80°C than at 60°C after 24 h of immersion; therefore, the increase in temperature affects the surface reaction on the FeCrAl-ODS steel. Intergranular corrosion can be argued by the micrographs for the immersion test at the boiling point. The grain size of the base material was <20 μm, but that in the intergranular corrosion was >100 μm. The specimen in which the corrosion progressed should be carefully observed to understand this disagreement.

Fig 5 shows the polarisation curves of the FeCrAl-ODS steel at different temperatures. The corrosion potentials were 0.54, 0.44 and 0.43 V at 60°C, 80°C and the boiling point, respectively. The corrosion potential remained in the passive region under every condition; hence, the FeCrAl-ODS steel has good corrosion resistance in 3 mol/dm^3 nitric acid solution at the tested temperatures. The increase in temperature increased the cathodic potential and slightly enhanced the passive current.

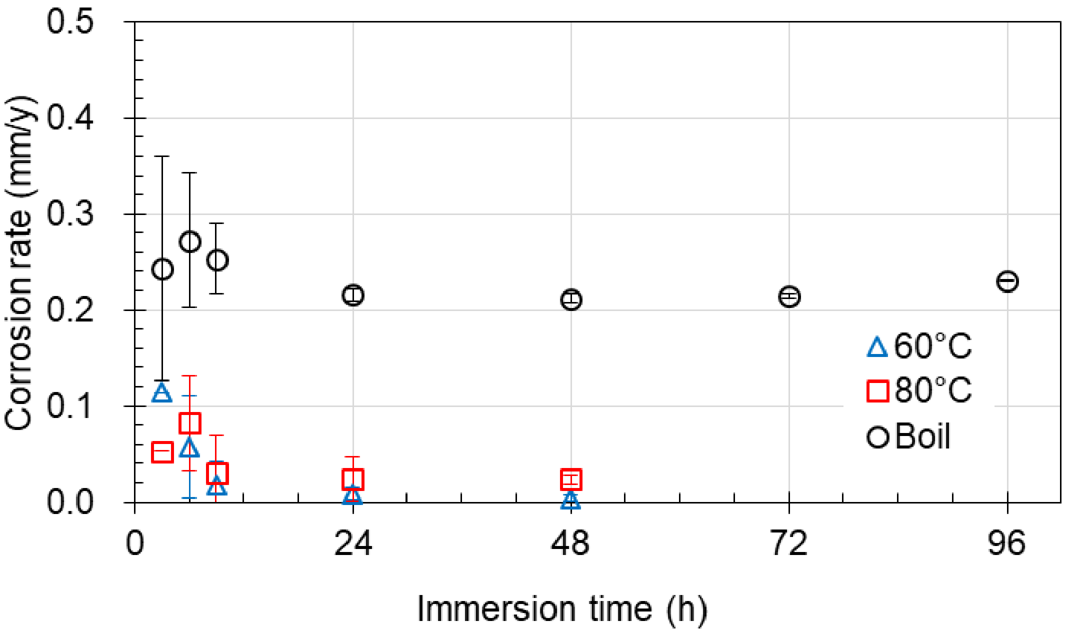


Fig 3. Corrosion rates of the FeCrAl-ODS steel in 3 mol/dm^3 nitric acid solution at different temperatures.

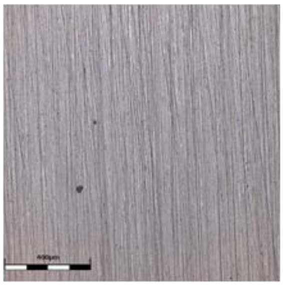
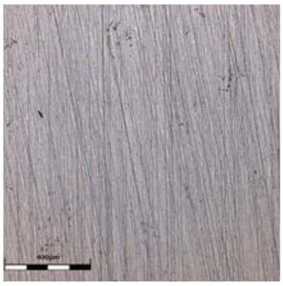
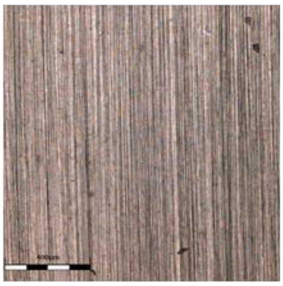
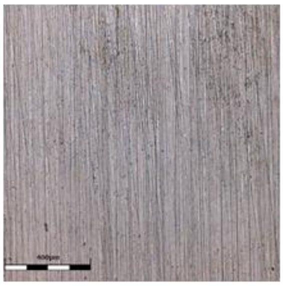
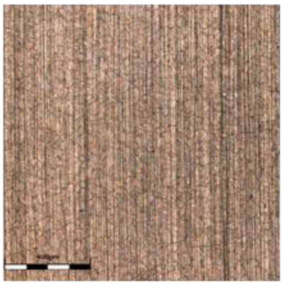
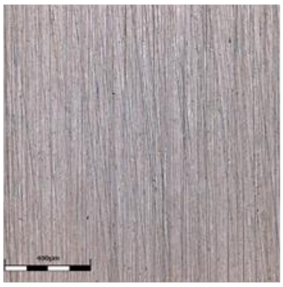
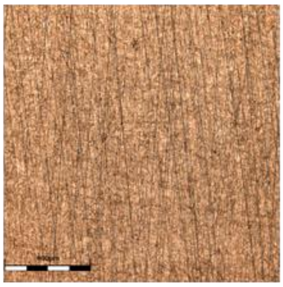
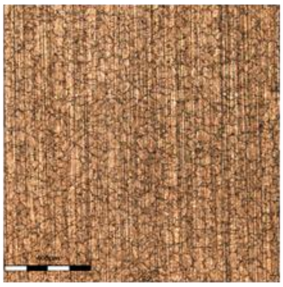
Immersion time (h)	Immersion temperature		
	60° C	80° C	Boiling point
0 -As received	 $S_a=96 \pm 16$ nm		
3	 $S_a=110 \pm 31$ nm	 $S_a=74 \pm 15$ nm	 $S_a=99 \pm 23$ nm
24	 $S_a=120 \pm 31$ nm	 $S_a=150 \pm 29$ nm	 $S_a=130 \pm 16$ nm
48	 $S_a=110 \pm 31$ nm	 $S_a=120 \pm 15$ nm	 $S_a=150 \pm 18$ nm
96			 $S_a=250 \pm 20$ nm

Fig 4. Laser micrographs of the specimen surfaces before and after immersion in 3 mol/dm^3 nitric acid solution.

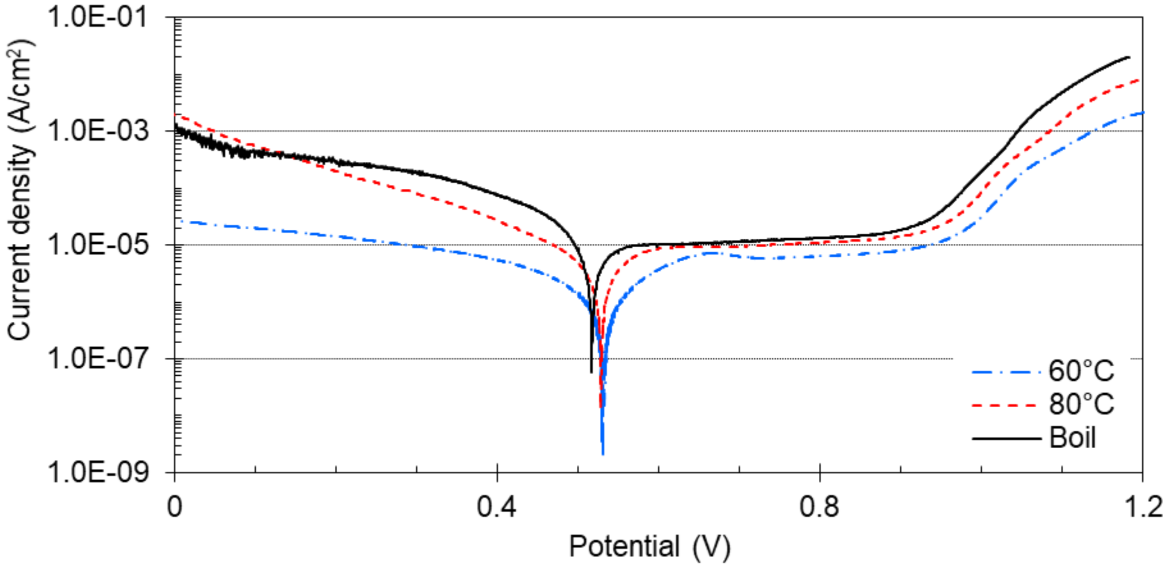


Fig 5. Polarisation curves of the FeCrAl-ODS steel in 3 mol/dm^3 nitric acid solution at different temperatures.

3.2 Oxide film composition

Fig 6 shows the thickness of the oxide film on the specimen before and after the immersion tests. The thickness was derived by the atomic concentration of oxygen measured by XPS depth profiling; the interface between the oxide film and the substrate was identified as the depth at which the atomic concentration of O was half of that at the top surface. After 48 h of immersion at 60°C, the thickness of the oxide film remained almost unchanged. The oxide film on the specimen became thicker in the immersion tests at other temperatures; specifically, the thickness became higher at 80°C than at the boiling point. Because the corrosion rates were steady at the end of the immersion tests, the thickness of the oxide film was also in a steady state.

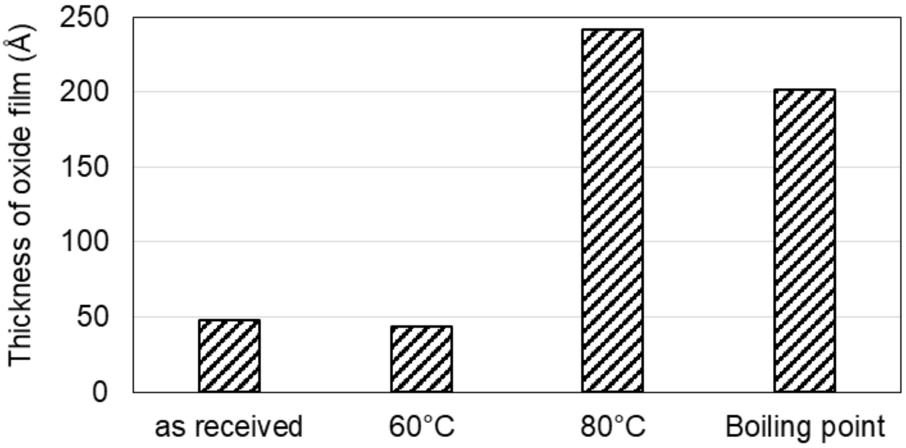


Fig 6. Thickness of the oxide film before and after the immersion tests in 3 mol/dm^3 nitric acid solution at different temperatures.

The chemical compositions of the oxide films before and after the immersion tests are shown in Fig 7, where 100% (atomic concentration) = Fe + Cr + Al. The atomic concentration was computed by integration of the peaks of Fe, Cr and Al, which corresponded to 700– 740 eV, 567– 607 eV and 68– 88 eV, respectively. The atomic concentration of Fe in the oxide film decreased after 48 h of immersion at 60°C, and that of Cr increased. The influence of nitric acid was very small within 48 h according to the variation of the corrosion rate and laser micrograph of the specimen surfaces, but its reaction with the FeCrAl-ODS steel was confirmed by XPS depth profiling. At 80°C and the boiling point, the atomic concentration of Fe decreased from bulk to surface, and those of Cr and Al increased, especially near the surface. This indicates that the Fe contained in the oxide film dissolves more than Cr and Al in 3 mol/dm^3 nitric acid solution.

The dissolution process in the 3 mol/dm^3 nitric acid solution on the reprocessing process at RRP for FeCrAl-ODS steels will be secure until 80°C, because of the low corrosion rate and the thick oxide film.

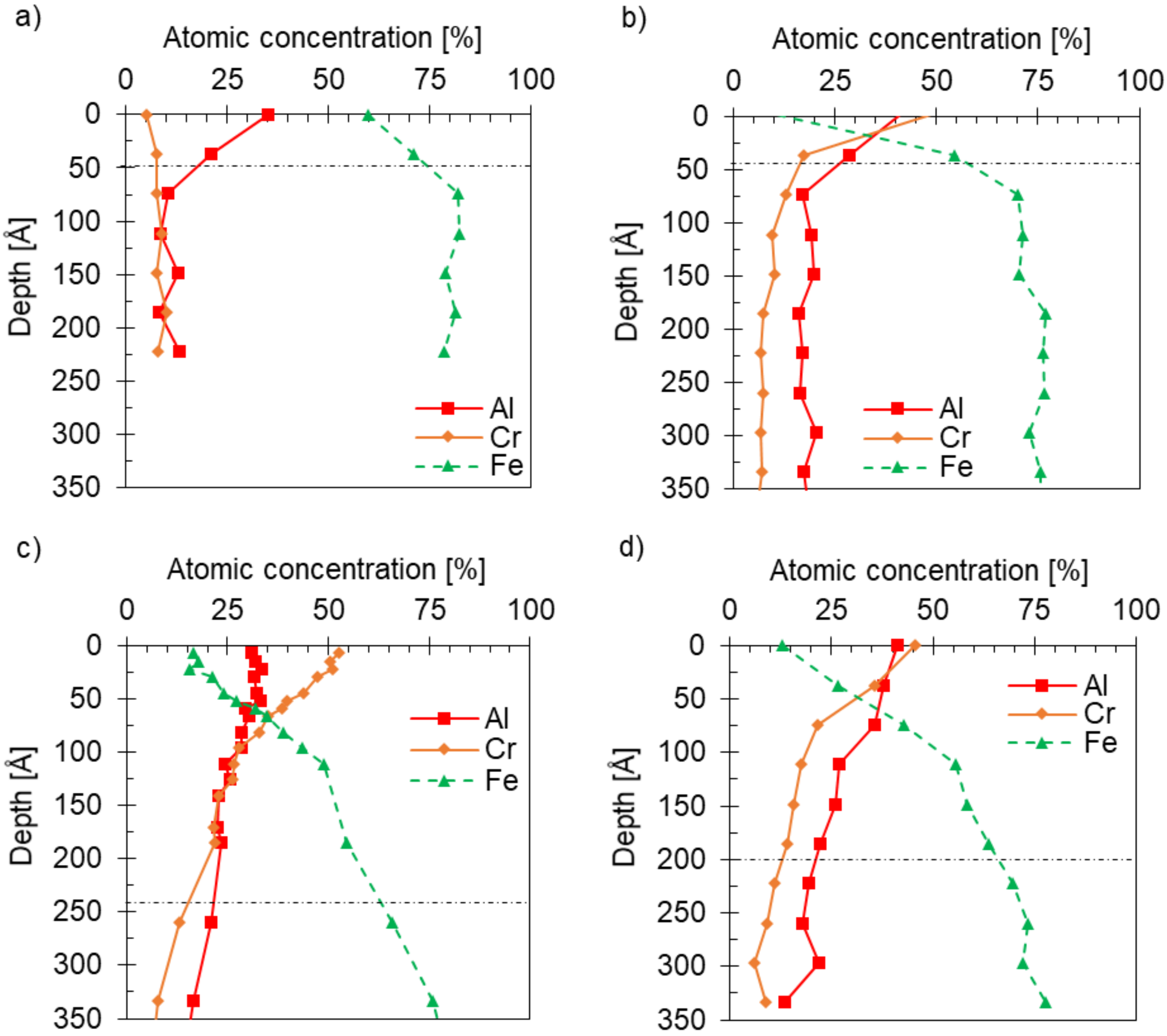


Fig 7. Depth profile of the atomic concentrations of Fe, Cr and Al in the specimen before and after immersion tests; a) as received, b) after 48 h at 60°C, c) after 48 h at 80°C and d) after 96 h at the boiling point.

* The depth of the oxide layer is represented by the dashed lines.

** The 100% atomic concentration is the sum of Fe, Cr and Al ratios.

Fig 8 shows the XPS depth profile of Fe2p$_{3/2}$, Cr2p$_{3/2}$ and Al2p in the specimen immersed at the boiling point for 96 h. In the Fe2p$_{3/2}$ spectra, the intensity of the identifying peak at 707.0 eV [6] decreases from bulk to surface, and no peaks corresponding to iron oxides are observed. Hence, Fe dissolves in 3 mol/dm^3 nitric acid solution without passing through oxide. The peak at 577.4 eV at the top surface of the specimen is identified as chromium hydroxide, and that at 574.3 eV in the bulk represents chromium metal [6]. The peaks of Cr2p$_{3/2}$ shifts from hydroxide to metal according to the increase of sputter depth. In the Al2p spectra, the peak corresponding to the metal (72.6 eV) is not visible, but that of oxide is observed at 74.6eV [6]. The intensity of the peak of aluminium oxide decreases from the surface to the bulk. Chromium oxide is present within 111Å from the surface of the specimen, and aluminium oxide arrives until the deepest layer. Hence, the chemical binding condition of Al is more strongly affected by the 3 mol/dm^3 nitric acid solution than that of Cr. The binding energy between Al and O is higher than that between Cr and O at 25°C [7]; thus, Al forms bonds with O more deeply in the specimen than Cr when the FeCrAl-ODS steel is immersed at the boiling point.

The results show that the corrosion of FeCrAl-ODS steels in hot nitric acid solution is not severe because of the high corrosion resistance of the oxide film formed on the material; hence, the corrosion resistance of the new cladding materials in the dissolution process of spent fuel would be acceptable for reprocessing operations.

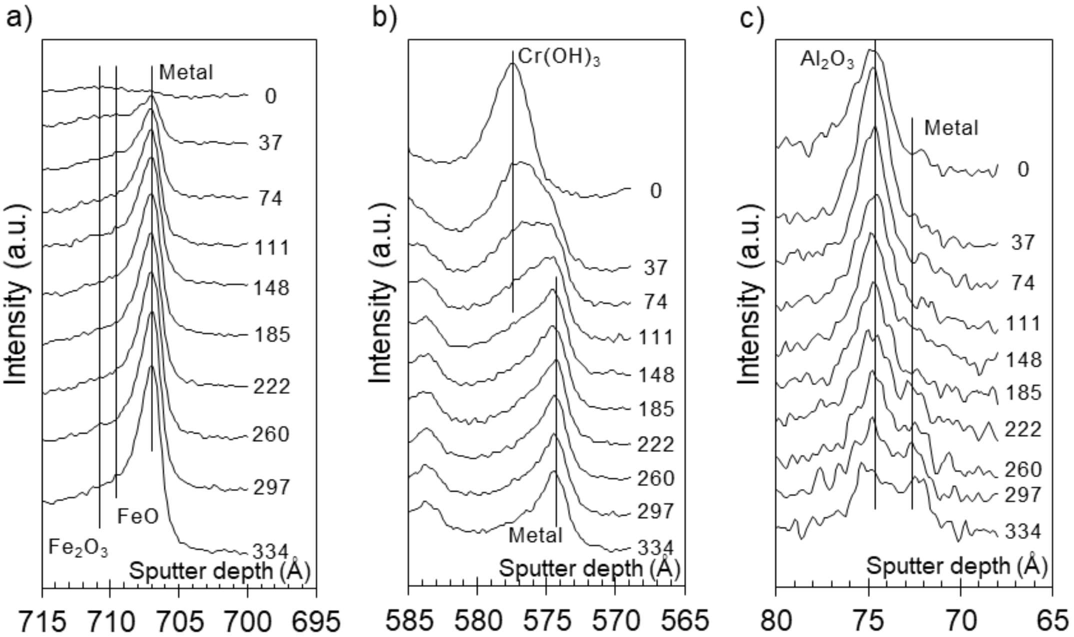


Fig 8. XPS depth profiles of the specimen after 96 h of immersion in 3 mol/dm^3 nitric acid solution at the boiling temperature for the bond energies corresponding to a) Fe2p$_{3/2}$, b) Cr2p$_{3/2}$ and c) Al2p.

4. Conclusion

The corrosion mechanism of the FeCrAl-ODS steel was evaluated in nitric acid solution to investigate the influence of the corrosion behaviour of fuel cladding in a dissolver for the reprocessing process of spent fuels. The corrosion tests were carried out in 3 mol/dm^3 nitric acid solution at 60°C, 80°C and the boiling point. The corrosion rate of the FeCrAl-ODS steel increased with temperature up to 0.22 mm/y at the boiling point. Thickness of oxide film was in order of 60°C < the boiling point < 80°C. And chemical composition of the oxide film was different from the bulk one. Fe was selectively dissolved in the nitric acid solution, and Cr and Al remained in the oxide film as oxides. The dissolution process in the 3 mol/dm^3 nitric acid solution on the dissolver at RRP will be secure until 80°C, because of the low corrosion rate and the thick oxide film. The results indicated that the FeCrAl-ODS steel corrosion in hot nitric acid solution was not severe because of the formation of an oxide film with high corrosion resistance; hence, the corrosion resistance of new cladding materials in the dissolution process of spent fuel is acceptable for reprocessing operations. The effects of some factors, such as concentration of nitric acid, coexisting ions and irradiation, on corrosion the behavior of FeCrAl-ODS steel will be suspected, therefore these effects are being evaluated.

Acknowledgement

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5. References

[1] F. Wada, "Improvement of Reliability in Nuclear Fuel Reprocessing Plant" Zairyo-to-Kankyo, 48, 12, 771-775 (In Japanese) (1999). https://doi.org/10.3323/jcorr1991.48.771

[2] T. Tanno, M. Takeuchi, S. Ohtsuka, T. Kaito, "Corrosion behavior of ODS steels with several chromium contents in hot nitric acid solutions ", Journal of Nuclear Materials, 494, 219-226 (2017). https://doi.org/10.1016/j.jnucmat.2017.07.008

[3] J. Isselin, R. Kasada, A. Kimura, “Effect of Aluminum on the Corrosion Behavior of 16%Cr ODS Ferritic Steels in a Nitric Acid Solution”, Journal of Nuclear Science and Technology, 48, 2, 169-171 (2011). https://doi.org/10.1080/18811248.2011.9711691

[4] S. Ningshen, M. Sakairi, K. Suzuki, S. Ukai, “The corrosion resistance and passive film compositions of 12% Cr and 15% Cr oxide dispersion strengthened steels in nitric acid media”, Corrosion Science, 78, 322-334 (2014). http://dx.doi.org/10.1016/j.corsci.2013.10.015

[5] Japan Nuclear Fuel Lit., "Rokkasyo Jigyousyo Saisyorijigyousiteisinnseisyo", (In Japanese) (1989).

[6] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, “Handbook of X-ray Photoelectron Spectroscopy”, Perkin-Elmer (1992), ISBN0-9627026-2-5.

[7] M. Tanino, S. Suzuki, "Tekkouzairyou no Kagaku", Uchida Rokakuho, 65, (In Japanese) (2001), ISBN978-4-7536-5615-8.