

Characterization of near-surface region of Ni-based superalloy examined on corrosion resistance against molten chloride mixture

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Abstract

Rutherford backscattering spectroscopy was successfully applied to determine the elemental distribution profile of Ni-based superalloy specimens tested on the compatibility with molten chloride mixture at elevated temperature. Hastelloy-X (Ni/Cr21/Fe18/Mo9/W) was examined as a structural material for molten chloride baths. Dipping experiments were performed under dry nitrogen. Neodymium chloride, sodium chloride and potassium chloride were used for the components of chloride mixture, which was dried at 250°C for 3 hours. Slightly hydrated chloride was also used for a severely corrosive condition.

Rutherford backscattering spectroscopy (RBS) using He-ions as projectiles and X-ray diffractometry (XRD) were applied to the measurements of tested specimens. Variation of near-surface composition was observed by comparing the results of RBS obtained before and after the dipping, while any change in phase was not found in XRD patterns.

Loss in weight of tested specimens was quite larger than its estimation considering uniform corrosion by ordinary outward bulk diffusion of components ready to be chlorinated. The depth profiles of components were estimated by the simulation of the RBS spectrum obtained using the RUMP code. Taking the profiles and the surface morphology observed by an atomic force microscope (AFM) into consideration, the excess loss in weight would be due to intergranular corrosion.

1. Introduction

A fast breeder reactor (FBR) fueled with molten chlorides can be considered as a candidate system realizing "in-situ" plutonium recycling[1,2]. A solution of trichlorides of uranium and plutonium dissolving in alkali and/or alkaline-earth chlorides will be adequate as a FBR fuel; NaCl, KCl, and MgCl₂ have been reported as promising components of the diluents. Furthermore, molten chloride/cadmium system is thought to be useful for the application of pyrometallurgy to the nuclear fuel reprocessing[3,4].

Followings would be cited as subjects to be investigated for the design of those plants:

- study on physico-chemical properties of molten chloride mixture
- research on the materials to be utilized for the container or internals.

Accordingly, corrosion is one of the most important issues; the compatibility of structural materials with molten chlorides strongly influences the durability of the system.

In the present work, Ni-based superalloy Hastelloy-X was examined on corrosion-resistance against molten chloride mixture, using NdCl₃ as an imitative substance in place

of UCl₃ or PuCl₃.

2. Experimental

2.1 Dipping

Anhydrous neodymium chloride (NdCl₃) of 99.9% in purity, sodium chloride (NaCl), and potassium chloride (KCl) were used to prepare the chloride mixtures. Hastelloy-X samples supplied by Mitsubishi Materials Corporation were used for examination specimens, which were heat-treated at 1150°C for 20min followed by spray cooling. Chemical composition of Hastelloy-X is shown in Table 1.

All dipping experiments were performed in a glove box with dry nitrogen as shown in Fig.1. Quartz crucibles were used as containers, in each of which a test specimen was put with chloride components weighed and sufficiently mixed in an alumina mortar. The chloride mixture was dried at ca. 250°C for about 3 hours prior to evacuation and refilling up nitrogen gas. Slightly hydrated chloride was also used on trial as a severely corrosive condition. A quartz top was put on the crucible to restrain the evaporation of chloride components prior to raising temperature again, and the crucibles were kept at prescribed

Table 1 Composition of Hastelloy-X

element	wt.%	at.%
Ni	Balance	Balance
Cr	21.41	24.10
Fe	17.64	18.49
Mo	8.95	5.46
Co	0.74	0.74
Mn	0.57	0.61
W	0.55	0.18
Cu	0.07	0.06
Si	0.37	0.77
C	0.01	0.05
S	<0.005	<0.009
B	0.001	0.005

under dry nitrogen

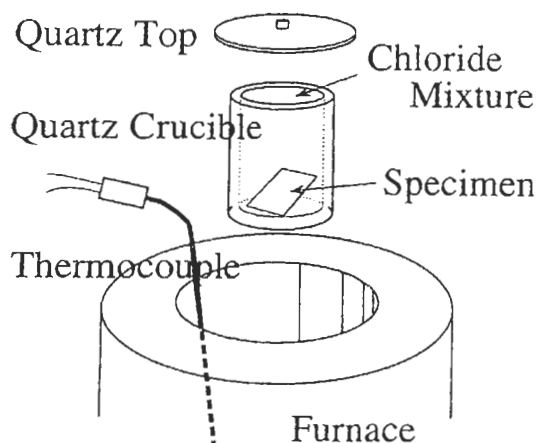


Fig.1 Schematic Drawing of the Experimental System

temperature after the chloride mixture completely melted. Finally, the specimen was taken out of the cooled-down and frozen salt by flushing using an ultrasonic generator. The specimen was weighed before and after the dipping.

2.2 Characterization

The surface of tested specimens was observed with an atomic force microscope (AFM) of a Shimadzu SPM-9500 System.

The depth distribution of components of tested specimens was determined by Rutherford backscattering spectroscopy (RBS) using 3MeV $^4\text{He}^{2+}$ -ions (θ_{lab} : 160°) at a tandem accelerator in Research Center of Nuclear Science and Technology, the University of Tokyo. X-ray diffractometry (XRD) was also

applied to confirm the μm -scale phase.

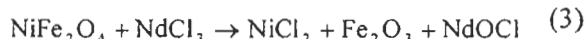
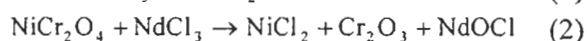
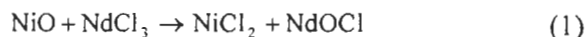
The RBS technique is based on the following principle: a mono-energetic beam of ions impinges on a sample, and the backscattered ions are detected and energy-selected. Projectiles lose their energy along the inward path and again along the outward path after the simple elastic collision with atoms of the sample. Consequently, mass numbers and their depth profiles of the atoms collided with projectiles are informed by the RBS spectrum. In other words, information regarding the kind and the relative concentration of atoms in the sample can be obtained from the results.

This technique is particularly satisfactory when it is used to analyze the surface modification of a sample within the depth of sub-micron; changes in the concentration profiles caused by corrosion and/or diffusion can be determined very easily even if the changes are optically invisible.

3. Results and Discussion

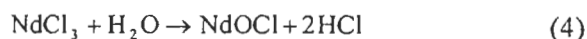
3.1 Process of Corrosion

All of the test specimens lost their gloss of surface after dipping. In case of this work, oxide phase containing Ni cannot exist as a protective scale (Fig.2a) owing to the existence of NdCl_3 :



Consequently, oxide scale which existed initially on the surface was thought to be stripped off, and the alloy phase was exposed to molten salt mixture.

Neodymium chloride is very hygroscopic and deliquescent. Moreover, it reacts with water at higher temperature, approximately above $300^\circ\text{C} \sim 400^\circ\text{C}$:



Therefore, hydrated chloride causes highly corrosive circumstance. In fact, the specimen which was dipped in hydrated chloride was quite different in weight loss from the one dipped in dried chloride. The weight losses of two specimens (#1, #2) are shown in Table 2 with experimental conditions.

Table 2 Experimental Conditions and Loss in Weight of Hastelloy-X

	#1 (severe)	#2 (moderate)
Chloride Composition	53NdCl ₃ -4NaCl-43KCl	54NdCl ₃ -5NaCl-41KCl
Moisture	exist	removed at 250°C for 3 hours
Dipping temperature	550°C	500°C / 550°C / 600°C
Exposure time	70min	20min / 10min / 70min
Dimensions of sample	14mm×5mm×0.65mmt	9mm×7mm×0.65mmt
Loss in weight	8.2mg (356.5mg → 348.2mg)	0.7mg (312.3mg → 311.6mg)

After the oxide scale was removed, the components ready to be chlorinated reacted with HCl. According to the thermodynamic database system MALT2, the components of Mn, Cr, Fe and Cu are easier to be chlorinated than the base metal, Ni, in case of Hastelloy-X. Those components would be chlorinated selectively. Actually, yellow gas, probably Fe₂Cl₆, was observed to evaporate when slightly hydrated chlorides were used, and pale green sediment, probably Cr₂O₃, was seen in the water after flushing; Fe and Cr were severely leached. To the contrary, chlorides of noble components, Mo and W, are less stable than HCl, so these components and Ni as well would remain in the alloy as they were initially (Fig.2b).

Gibbs free energy of each reaction described above was less than zero according to MALT2, and those thermochemical characteristics of NdCl₃ are also true of actinide trichlorides, UCl₃ and PuCl₃.

The loss in weight of the tested specimens was estimated from the solution of the diffusion equation assuming uniform corrosion via outward bulk diffusion of components ready to be chlorinated (Mn, Cr, Fe and Cu). However, the experimental results were quite larger than the estimation. The localized corrosion should be taken into account to explain this excess loss in weight.

3.2 Morphology of Surface

Figures 3a and 3b are 30μm-square top views of AFM images for the severely corroded specimen (#1). Grooves were seen in Fig.3a. Those grooves would be situated on grain boundaries and suggest the intergranular corrosion. As seen in Fig.3b, numerous pits were found evenly on the grains when observed in detail at higher sensitivity of the undulation, and those pits suggest the pitting corrosion. Those forms of the localized corrosion enable us to explain the discrepancy between the measured and expected corrosion rate.

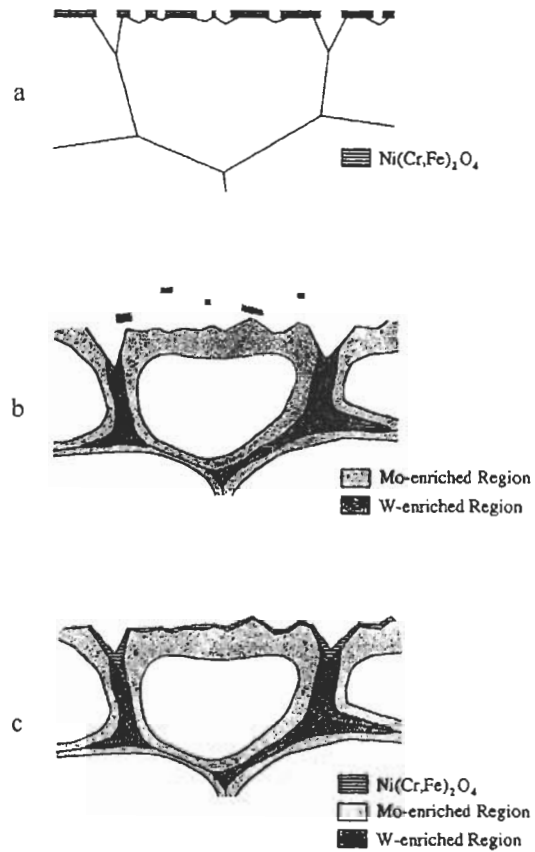


Fig.2 Schematic Drawing of the Near-surface Region of Corroded Specimens; (a) the early stage of the corrosion (b) the latter stage (c) measured condition

Grain boundaries were the paths of diffusing substance under the intergranular corrosion, and, as a consequent, noble components (Mo, W) were enriched relatively at the grain boundaries. Figure 2 schematically shows the progression of such a process of the corrosion. The distribution of W would be peculiar due to its low diffusivity in Ni; the distribution would strongly be affected by the arrangement of grain boundaries. This is also discussed below.

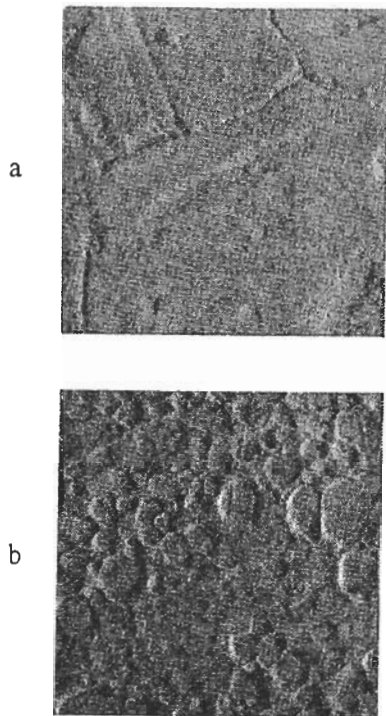


Fig.3 AFM Images of the Tested Specimen

3.3 Characterization of Near-surface Region of Tested Specimens

In the XRD patterns, the observed reflections were attributed to only a Ni solution (shifted a little from the diffraction pattern of pure Ni) in spite of the changed appearance of the specimens. Tested specimens did not change those μm -scale phase, as expected for superalloy.

RBS spectra of Hastelloy-X are shown in Fig.4; for two places of sample #1 (Fig.4a, Fig.4b) and one place of sample #2 (Fig.4c) and as received (Fig.4d). Figure 5 was obtained by plotting the variation caused by dipping for Fig.4a (obtained subtracting the spectrum of as-received sample). These spectra were normalized by gross counts and shown in ppm. The abscissas are the channel number of the counter, which was calibrated using Au-deposited Si to be 2.8655keV/channel. Changes in the near-surface region of the specimens were observed successfully by means of RBS. Remarkable change was found at higher channels of spectra for dipped specimens (Fig.4a-4c): increase of Mo and W in composition was observed. In contrast, some components were found to decrease (Fig.5); chlorides of Mn, Cr, Fe and Cu are more stable than HCl at the temperatures considered in this work, and the simulation of the RBS spectra

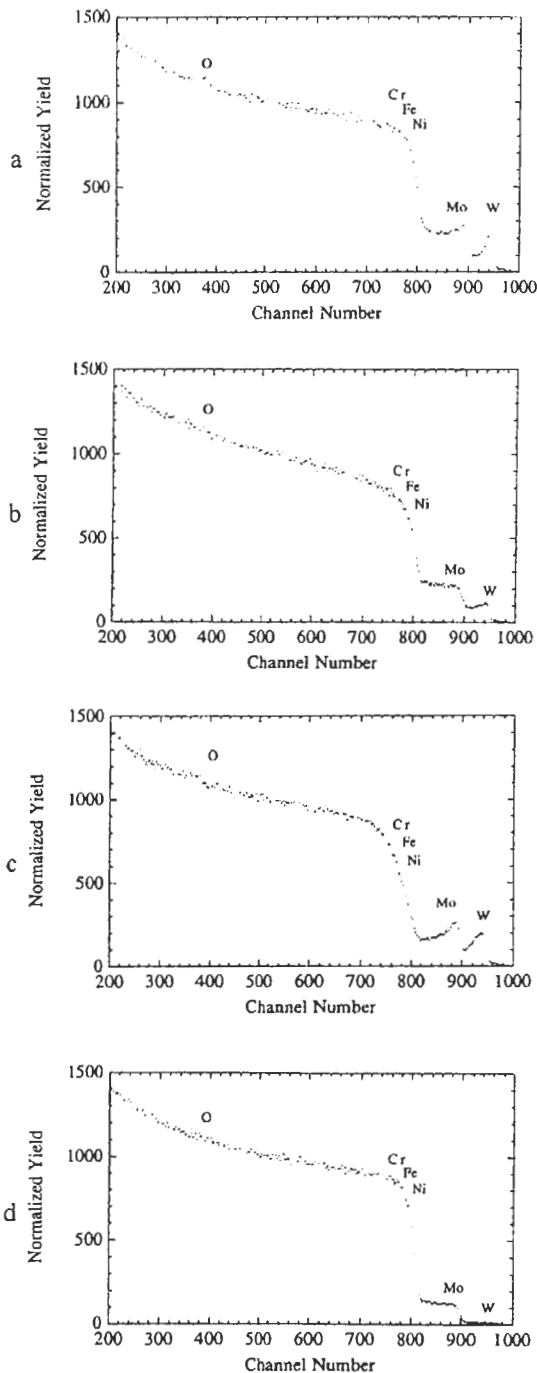


Fig.4 RBS Spectra of Hastelloy-X; (a) specimen #1a (b) specimen #1b (c) specimen #2 (d) as received

obtained using a computer code RUMP[5,6] suggests decrease of these components in the near-surface layers. A result of simulation for Fig.4a is shown in Fig.6 (with solid line) with the experimental RBS spectrum (with scattered dots), and the depth profile applied to the simulation is shown Fig.7. The sharp peak in Fig.4a around 950ch attributed to the existence of W-enriched region

may mean that grain boundaries lie in the trajectory of He-ion beam, and flat profile of W seen in Fig.4b mean not, conversely. The difference in the spectra is considered to come from the localized nature of the corrosion taken place; the grain size of Hastelloy-X is approximately sub-millimeter and comparatively large to the diameter of the magnetically focused beam, *ca.* 1mm, and then a certain RBS spectrum contains information of very small number of grains. In other words, composition of near-surface region was locally assayed with a sectional resolution of millimeters in case of this work. The difference in the profile of W corresponds to the distinctive distribution depicted in Fig.2. RBS and its simulation are very powerful to discuss with near-surface region in the scale of nanometer and its local characteristics in the sectional resolution of the beam diameter.

4. Conclusion

Ni-based superalloy Hastelloy-X was examined in compatibility with a NdCl₃-NaCl-KCl mixture. RBS was successfully applied to characterize the near-surface region of tested specimens, and the near-surface composition was locally analyzed.

Acknowledgment

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References

1. P.A.Nelson, D.K.Butler, M.G.Chasanov and D.Meneghetti, *Nucl. Appl.* **3** (1967) 540
2. M.Taube, EIR-249 (1974)
3. T.Koyama, T.R.Johnson and D.F.Fischer, *J.Alloys and Compounds* **189** (1992) 37
4. J.P.Ackerman and J.L.Settle, *J.Alloys and Compounds* **199** (1993) 77

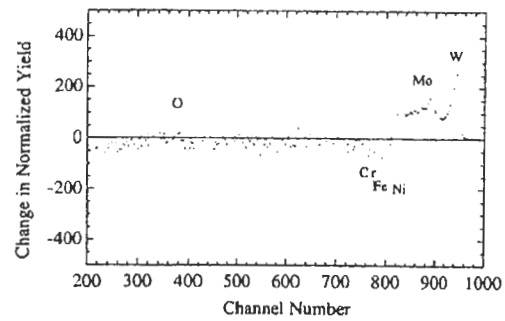


Fig.5 Change in RBS Spectrum Caused by Dipping (specimen #1a)

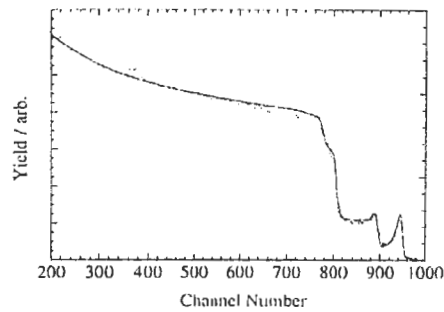


Fig.6 RBS Spectrum Simulated by RUMP code (specimen #1a)

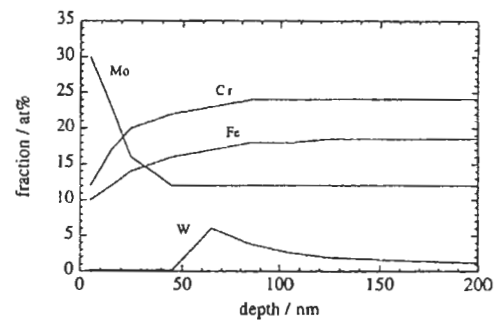


Fig.7 Depth Distribution of Components for Fig.6

5. L.R.Doolittle, *Nucl. Instr. and Meth. in Phys. Res.* **B9** (1985) 344
6. L.R.Doolittle, *Nucl. Instr. and Meth. in Phys. Res.* **B15** (1986) 227