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Compatibility of structural materials with molten chloride mixture at high temperature

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Abstract

Ni-based superalloy Hastelloy-X and refractory metals were examined on compatibility with molten $NdCl_3$–NaCl–KCl mixture. Weight loss of the specimens caused by dipping was measured, and variation of compositions of Hastelloy-X also estimated by comparing RBS spectra obtained before and after the dipping. It was shown that moisture in these systems played an important role on the corrosion behavior. It was also shown that tantalum, tungsten and Hastelloy-X had sufficient corrosion-resistance against molten chlorides when moisture and oxygen were appropriately removed. © 1997 Elsevier Science B.V.

1. Introduction

A fast breeder reactor (FBR) fueled with molten chlorides can be considered as a candidate system realizing in situ plutonium recycling, which has large safety and enables us to lessen various difficulties on the fuel reprocessing using stable molten-salt mixtures under normal pressure [1,2]. A solution of trichlorides of uranium and plutonium dissolved in alkali and/or alkaline-earth chlorides will be adequate as an FBR fuel, and NaCl, KCl and $MgCl_2$ have been reported as promising components of the diluents.

On the other hand, molten chloride/cadmium system is thought to be useful for the application of pryometallurgy to the nuclear fuel recycle process [3,4]. In this system, noble metals as fission products in a spent fuel are extracted to liquid cadmium phase, and actinides which are distributed between chloride phase and molten cadmium cathodes.

The following subjects should be investigated for the design of those plants:

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

Regarding these two subjects, corrosion is one of the most important issue, for the compatibility of structural materials with molten chlorides strongly influences the durability of the system.

Corrosion by molten chlorides can be considered as a kind of electrochemical corrosion, and the followings could be cited as cathode reactions in molten salts:

(1) cations in molten salts, e.g.,

$$Cu^{2+} + 2e^- \rightarrow Cu, \tag{1}$$

(2) oxyanions in molten salts, e.g.,

$$SO_4^{2-} + 2e^- \rightarrow SO_3^{2-} + O^{2-}, \tag{2}$$

(3) oxygen in the atmosphere

$$O_2 + 4e^- \rightarrow 2O^{2-}, \tag{3}$$

(4) existence of water

$$2H^+ + 2e^- \rightarrow H_2, \tag{4}$$

$$2OH^- + 2e^- \rightarrow H_2 + 2O^{2-}. \tag{5}$$

Cases (1) and (2) need not be taken into account because the chlorides of structural materials elements are less stable than UCl_3 and $PuCl_3$ as well as NaCl, KCl and $MgCl_2$, and because no oxyanion exists in the molten salt for FBR or pyrochemical reprocessing plant of spent nuclear fuels. After all, the control of oxygen and water is

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very important in the concerning systems. Generally, it is so difficult to control the amount of impurities and to dehumidify the system that corrosion behavior data for structural materials are still very poorly provided and experimental data are strongly required.

In the present work, Ni-based superalloy Hastelloy-X and refractory metals Ta, W were examined on corrosion-resistance against molten chloride mixture, using $NdCl_3$ as an imitative substance in place of UCl_3 or $PuCl_3$.

2. Experimental

2.1. Dipping

Anhydrous neodymium chloride ($NdCl_3$) of 99.9% (3N) in purity, sodium chloride (NaCl) of 99.99%, and potassium chloride (KCl) of 99.8% were used to prepare the chloride mixtures. The neodymium chloride, received in a sealed glass ampule, was opened in a glove box under dry nitrogen and stored in sealed glass jars. Hastelloy-X provided from Mitsubishi Materials Corporation and refractory metals, Ta, W were used for specimens. The composition of Hastelloy-X is shown in Table 1.

As shown in Fig. 1, all dipping experiments were performed in a glove box with nitrogen ($O_2 < 2$ ppm, $H_2O < 10$ ppm); moisture was lessened with molecular sieve, but unspecified amount of water was brought into the experimental system by $NdCl_3$. Quartz crucibles were used as containers, in each of which a test specimen was put with chloride components which were weighed and sufficiently mixed in an alumina mortar. The chloride mixture had a composition of approximately $50NdCl_3$–$5NaCl$–$45KCl$, which could be considered to be near the ternary eutectic point. In the molten-salt FBR fuel, the fraction of $(U, Pu)Cl_3$ will be more than 30 mol%, and 50–60 mol% is considered to be more appropriate to achieve an efficiently compact core [1]. The chloride mixture was dried at 250°C for 2–3 h prior to evacuation and refilling up nitrogen gas. Slightly hydrated chloride was also used on trial for Hastelloy-X 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 500°C–800°C after the chloride mixture completely melted. Finally, the specimen was taken out of the frozen salt by flushing using an ultrasonic generator. Weight of specimen was measured before and after the dipping.

Table 1
Composition of Hastelloy-X [a]

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

[a] 1150°C×20 min/spray cooling.

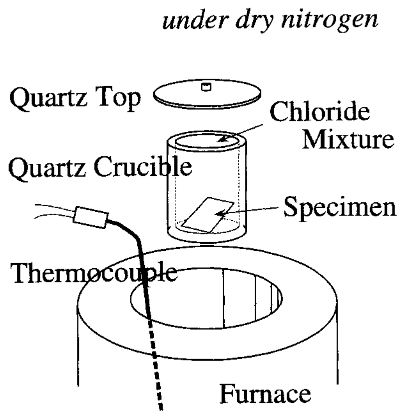

Fig. 1. Schematic drawing of the experimental system.

2.2. Measurement

X-ray diffractometry (XRD) was applied to confirm phases existing on the surface of specimens within the depth of μm scale.

Rutherford backscattering spectroscopy (RBS) were also used to determine the depth distribution of components of Hastelloy-X specimens. 3 MeV $^4He^{2+}$-ion beam of a Tandem accelerator in Research Center of Nuclear Science and Technology, the University of Tokyo was applied to RBS with the backscattering angle of 160°.

RBS is an appropriate method particularly to analyze the surface modification of a sample within the depth of submicron. Changes in the concentration profiles caused by corrosion can be determined very easily even if the changes are optically invisible. The variation of composition was estimated by comparing the results of RBS obtained before and after the dipping.

3. Results

3.1. Hastelloy-X

The test specimens became black after dipping. Yellow gas, not chlorine but probably Fe_2Cl_6, was observed to evaporate when slightly hydrated chlorides were used. It

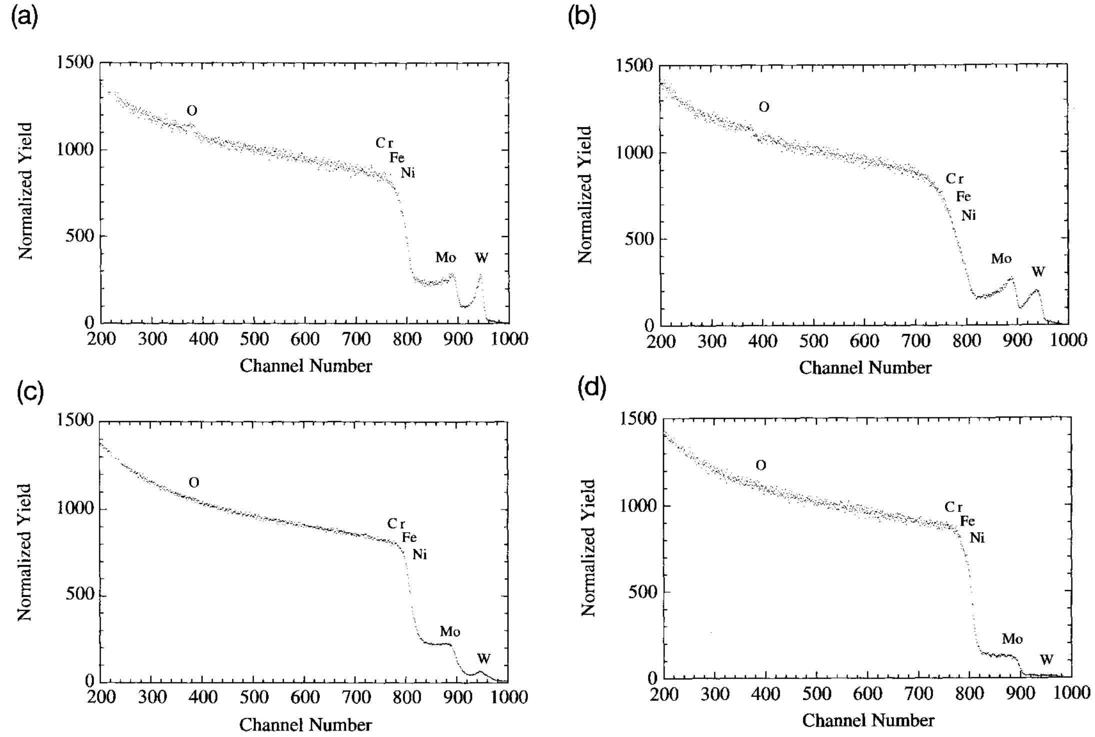

Fig. 2. RBS Spectra of Hastelloy-X: (a) specimen #1, (b) specimen #2, (c) specimen #3, (d) as received.

froze to be a yellow brown solid on the quartz top during cooling after dipping. Weight losses of three specimens (#1–#3) are shown in Table 2 with experimental conditions.

In the XRD patterns, the observed peaks were attributed only a Ni solution (shifted a little from the diffraction pattern of pure Ni) in spite of black 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. 2: for samples #1 (Fig. 2a), #2 (Fig. 2b), #3 (Fig. 2c) and as received (Fig. 2d). Fig. 3 was obtained by plotting the variation caused by dipping for Fig. 2a (obtained subtracting the spectrum of as-received sample, Fig. 2d). These spectra were normalized by gross counts and shown in ppm. The abscissas are the channel number of the α counter, which was calibrated using Au-deposited Si to be 2.8655 keV/channel. Change was found at higher channels of spectra for dipped specimens (Fig. 2a–c): increase of Mo and W in composition was observed. In contrast, some components were found to decrease (Fig. 3).

Table 2
Experimental conditions and loss in weight of Hastelloy-X

Condition	Weight (mg)	Loss in weight (mg)	Rate (mg cm^{-2} h^{-1})
#1 550°C×70 min/hydrated	356.5	8.2	5.0
#2 600°C×70 min/dried [a]	312.3	0.7	0.5
#3 800°C×600 min/dried [a]	547.9	5.5	0.25

[a] At 250°C for 3 h.

3.2. Refractory metals

Weight changes of the specimens are shown in Table 3. In the XRD patterns, the observed reflections were attributed to only pure metal phase. The specimens seemed

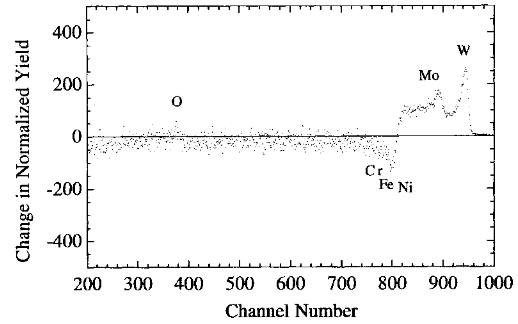

Fig. 3. Change in RBS spectra caused by dipping (specimen #1).

Table 3
Experimental conditions and change in weight of Ta and W

Condition	Weight (mg)	Change in weight (mg)	Rate (mg cm^{-2} h^{-1})
Ta 600°C × 60 min/dried [a]	265.5	+0.1	+0.08
W 600°C × 60 min/dried [a]	237.6	±0.0	±0.0

[a] At 250°C for 2 h.

to have no evidence to be attacked, and they still had glossy surfaces even after dipping.

4. Discussion

4.1. Process of corrosion

Ni-based superalloy Hastelloy-X is exceedingly resistive against oxidation owing to its adherent oxide scale. In case of this work, however, oxide phase containing Ni cannot exist as a protective scale because of the existing of $NdCl_3$, which tends to get oxygen to turn into fairly stable oxychloride, NdOCl,

$$NiO + NdCl_3 \rightarrow NiCl_2 + NdOCl, \qquad (6)$$

$$NiCr_2O_4 + NdCl_3 \rightarrow NiCl_2 + Cr_2O_3 + NdOCl, \qquad (7)$$

$$NiFe_2O_4 + NdCl_3 \rightarrow NiCl_2 + Fe_2O_3 + NdOCl. \qquad (8)$$

Consequently, oxide scale NiO and '$Ni(Cr,Fe)_2O_4$' which existed initially on the surface [5] was thought to be stripped off, and the alloy phase was exposed to molten salt mixture. According to the thermodynamic database system MALT2 [6,7], Gibbs free energy of each reaction described above was less than zero, and such a thermochemical characteristic and those discussed below are also true of UCl_3 and $PuCl_3$ as well as $NdCl_3$.

Neodymium chloride is very hygroscopic and deliquescent. Moreover, it reacts with water at higher temperature:

$$NdCl_3 + H_2O \rightarrow NdOCl + 2HCl. \qquad (9)$$

Therefore, hydrated chloride causes highly corrosive circumstance. In fact, as shown in Table 2, the corrosion rate of the specimen dipped in hydrated chloride (#1) was quite larger than those in dried chloride (#2 and #3).

After the oxide scale is removed, the components ready to be chlorinated begin to react with HCl. According to MALT2, the components of Mn, Cr, Fe and Cu are easier to be chlorinated than hydrogen. Those components would be chlorinated selectively:

$$M + xHCl \rightarrow MCl_x + \frac{x}{2}H_2. \qquad (10)$$

Especially, $FeCl_2$ would be chlorinated further because of evaporation of $FeCl_3$

$$2FeCl_2 + 2HCl \rightarrow Fe_2Cl_6 \uparrow + H_2. \qquad (11)$$

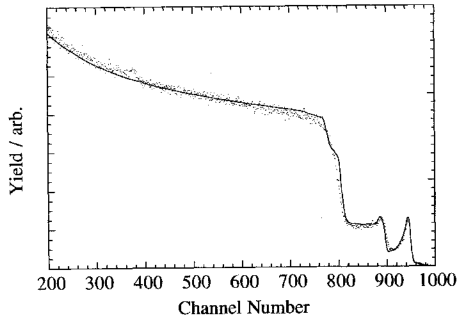

Fig. 4. RBS spectrum simulated by RUMP code (specimen #1).

The simulation of the RBS spectra obtained using a computer code RUMP [8,9] suggests decrease of these components in the near-surface layers. A result of simulation for Fig. 2a is shown in Fig. 4 (with solid line) with the experimental RBS spectrum (with scattered dots), and the depth profile applied to the simulation is shown in Fig. 5.

To the contrary, the most stable chlorides of Mo and W have higher Gibbs free energy of formation per equivalent-Cl_2 than that of HCl at temperatures approximately above 200°C, so it is not probable that Mo and W, which were found in RBS to be enriched in the near-surface region of the specimen, can be attacked by HCl according to formula (10).

Rense et al. [10] examined many kinds of materials which was expected to have the resistance against the molten salt of $90CaCl_2$–10CaO under an HCl atmosphere at 900°C, and reported that Ta and W have comparatively poor resistance. Though the system applied by Rense et al. resembles a hydrolyzate of a certain chloride component, it is very difficult to investigate the process of corrosion after all because CaO is ready to react with HCl and produce H_2O. In the present work, it was found that refractory metals showed applicable resistance against chloride mixtures when moisture and oxygen were appropriately removed.

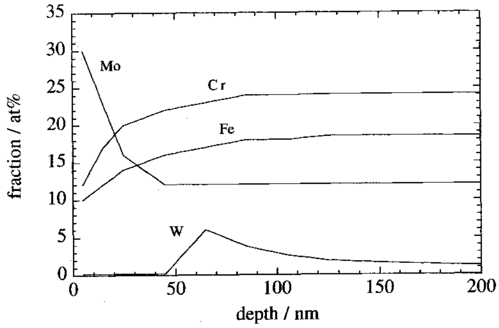

Fig. 5. Depth distribution of components for Fig. 4.

4.2. Manner and kinetics of corrosion

The loss in weight of the Hastelloy-X 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) in the base metal, Ni. 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.

The surface of specimen #1 was observed with an atomic force microscope (AFM), Shimadzu SPM-9500 System. Fig. 6a and b are 30 μm-square top views of specimen #1. Grooves were seen in Fig. 6a. Those grooves would be situated on grain boundaries and suggest the intergranular corrosion. As is seen in Fig. 6b, numerous pits were found when observed in detail at higher sensitivity of the undulation, and those suggest the pitting corrosion. The discrepancy between the measured and expected corrosion rate should be explained with these manners of the localized corrosion.

Fig. 7 schematically shows the progression of the corrosion. Grain boundaries were the paths of diffusing substance under the intergranular corrosion, and then noble components (Mo, W) were enriched relatively as remainders at the grain boundaries. The distribution of W would be peculiar due to its low diffusivity in Ni; the distribution would strongly affected by the arrangement of grain boundaries. The sharp peak in Fig. 2a around 950 channel attributed to the existence of W corresponds to the distinctive distribution in Fig. 7. As is seen in Fig. 2c, the peak got blunted at higher temperature which causes larger diffusion coefficient for W.

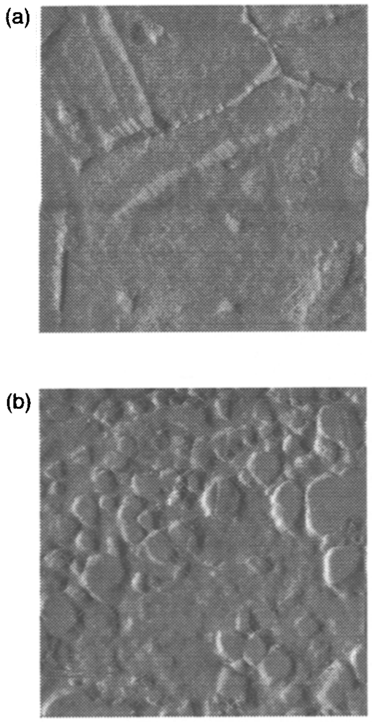

Fig. 6. AFM images of the specimen (see text).

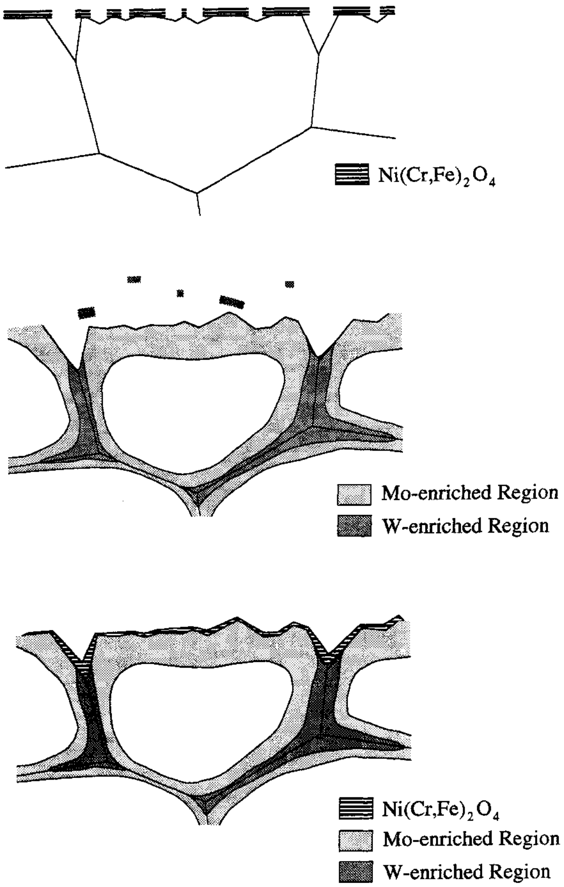

Fig. 7. Schematic drawing of near-surface region of corroded specimens: (a) the early stage of the corrosion, (b) the latter stage, (c) observed situation.

And yet, corrosion described above will terminate with the depletion of water in the system. As is seen in Table 2, in spite of higher dipping temperature, the corrosion rate of the specimen #3 dipped for longer time was smaller than that of specimen #2. This result shows that the reactions practically ended in comparatively early stage, for the corrosion itself is probable to follow the linear law when the reactions progress; there is no protective scale and reaction products are immediately removed from the interface. Under the dried environment, Hastelloy-X would show the sufficient corrosion-resistance against molten chlorides.

5. Conclusion

Ni-based superalloy Hastelloy-X and refractory metals were examined on the corrosion-resistance against molten

$NdCl_3$–NaCl–KCl mixture. In these systems, the existence of moisture affects the corrosion behavior. The process of corrosion was thermochemically discussed and the form of the corrosion was illustrated. It was shown that Hastelloy-X as well as refractory metals tantalum and tungsten had corrosion-resistance against molten chlorides under an inert atmosphere when moisture and oxygen were appropriately removed although they were reported to have poor resistance in molten $CaCl_2$–CaO under an HCl atmosphere.

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