Anodic dissolution behaviors of Inconel 600 in a molten salt system

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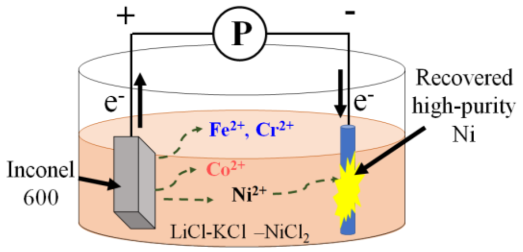
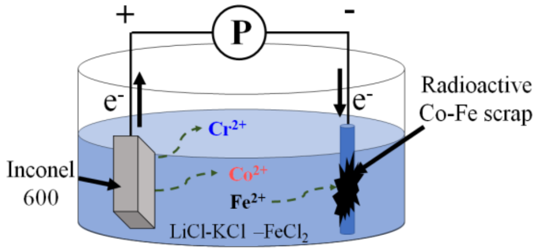
1. Introduction

A steam generator (SG) produces steam for the turbine operation by using the heat of primary water continuously radioactively contaminated during the operation. The major contaminants are ^{60}Co,^{134}Cs, ^{137}Cs, and actinides, and most of them are deposited on the primary side of the steam generator tubes [1]. A lot of micro-cracks whose thickness and depth are less than 2 μm and 20 μm are generated due to the stress corrosion cracking (SCC) and radioactive contaminants also deposited in these cracks [2]. Since the conventional decontamination process such as physical, chemical, or melting processes are not able to eliminate a sufficient number of contaminants in micro-cracks [3], designing a brand-new decontamination process that can remove the whole amount of contaminants in micro-cracks is needed.

By applying the molten salt system, the decontamination process and element separation can be done simultaneously. Inconel 600 which is the base material of the SG tubes is a Ni-based alloy with 14-17 wt% Cr and 6-10 wt% Fe. The additives such as Ni or Fe chlorides in a molten salt system can guarantee the high-purity cathode deposits and the expected decontamination process is described in Fig.1.



Decontamination process with $NiCl_2$ based salts



Decontamination process with $FeCl_2$ based salts

Fig. 1. Schematics of Inconel 600 decontamination processes with $NiCl_2$ or $FeCl_2$ additives

In this study, anodic dissolution behaviors in LiCl-KCl-5 wt% $NiCl_2$/$FeCl_2$ are analyzed. Anodic dissolution was conducted with potentiostatic and galvanostatic methods, microstructural change and dissolved elements were analyzed by SEM-EDS and ICP-OES.

2. Experimental Setup

2.1. Experimental equipment

All electrochemical experiments and specimen pretreatments were conducted in a glovebox filled with Ar (99.996%). As shown in Fig. 2, Inconel 600 was cut and used as the anode with an area of 3.48 cm^2. Two tungsten rods of 4 mm diameter were used as the cathode and 1 wt% Ag/AgCl reference electrode was used. The bottom of the Pyrex tube was divided into halves to avoid the mixing of cathode deposits and the detached particles from the anode.

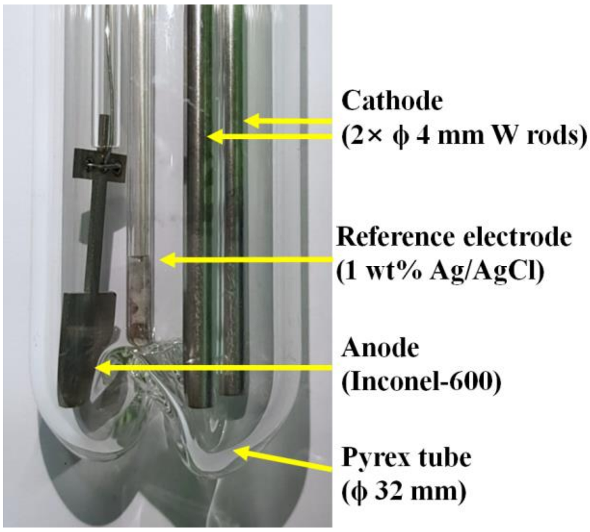


Fig. 2. Electrochemical cell image

During the anodic dissolution experiments, small particles whose size is less than 50 μm even less than 3 μm were detached from the anode. To recover those particles, a micro-particle recovery system was designed, and the schematic of this system is depicted in Fig. 3. The salt of the anode part which possesses the detached particles are positioned in the hopper and negative pressure of 1 kPa is applied to prevent the collapse of the detached particles.

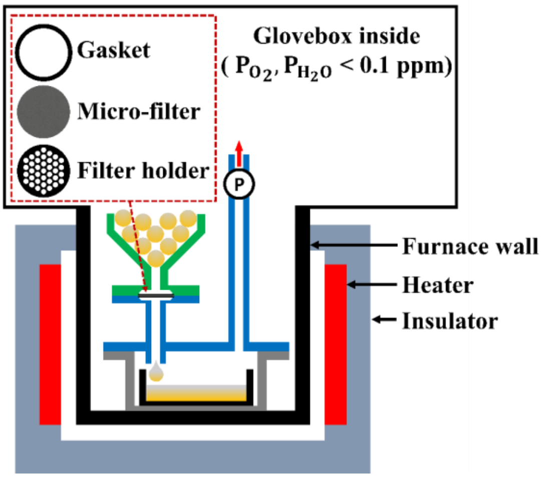


Fig. 3. Schematics of the detached particle recovery system

2.2. Experimental setup

The experiments aimed to figure out the microstructure change of Inconel 600 immersed in LiCl-KCl-5 wt% $NiCl_2$/$FeCl_2$ at 773 K (i) without any electrochemical application (Table 1- NI, FI) and (ii) with potentiostatic or galvanostatic electrochemical applications (Table 1- NP, NG, FP, FG). The NI and FI experiments were conducted to figure out the chemical reaction between Inconel 600 and additives ions when the specimen is immersed in LiCl-KCl-5 wt% $NiCl_2$/$FeCl_2$ molten salts. Applied potentials of the potentiostatic experiments were determined not to reduce additive Ni^{2+} or Fe^{2+} ions on the anode. Although anodic current density was observed when 0.10 V is applied to Inconel 600 in LiCl-KCl-5 wt% $NiCl_2$ salt at 773 K, reduction of Ni on the surface of Inconel 600 is observed during the preliminary experiments. To make an intuitive comparison between potentiostatic and galvanostatic experiments, the applied current density of the galvanostatic experiments were determined to be 6, 16, and 30 mA cm^{-2} which were average current density observed during potentiostatic experiments.

Table. 1. Corrosion and anodic dissolution experiment table

Test ID*	Applied potential (V vs. RE) / current density (mA cm^{-2})	Note
NI	-	3, 168 hours
NP 1-3	+0.15, +0.20, +0.25	287 C cm^{-2}
NG 1-3	+6, +16, +30	
FI	-	168 hours
FP 1-3	+0.05, +0.10, +0.15	80 C cm^{-2}
FG 1-3	+6, +16, +30	
FP 4	+0.05	1 C cm^{-2}
FG 4	+6	

* N; 5 wt% $NiCl_2$ additive salts, F; 5 wt% $FeCl_2$ additive salts, I; immersion test, P; anodic dissolution by the potentiostatic method, G; anodic dissolution by the galvanostatic method.

3. Results and Discussion

3.1. Anodic dissolution behaviors of Inconel 600 in $NiCl_2$ added salt

A ni-coated layer was formed on the Inconel 600 in molten LiCl-KCl-5 wt% $NiCl_2$ (NI experiment). A relatively dense Ni-coated layer was formed after 168 hours and coarsen Ni-coated layer was formed after 3 hours but their thicknesses were similar with 3 μm (Fig. 4). Cr contents in molten salt were increased whereas Fe contents were not changed and Cr contents along the surface of the base metal decreased.

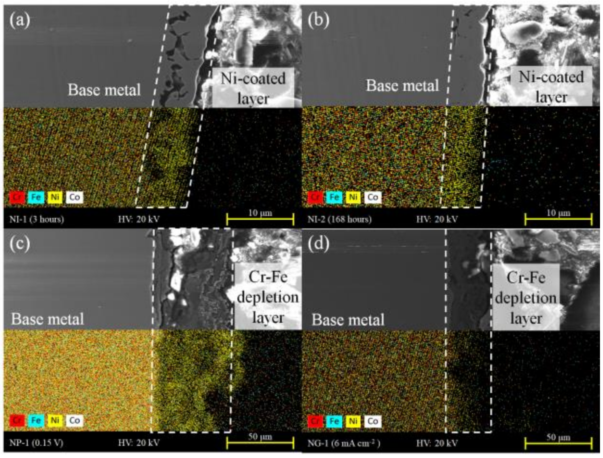


Fig. 4. Microstructure of Inconel 600 after NI-1 (a), NI-2 (b), NP-1 (c), and NG-1 (d) experiments

After the NP and NG experiments, the Cr-Fe depletion layer whose Ni content is higher than the base material whereas Cr and Fe are not, is formed on the anode surface. The thickness of the Cr-Fe depletion layer and its contents were investigated by SEM-EDS. The Cr-Fe depletion layer thickness decreases, and the remaining amount of Cr and Fe increases as the applied potential and current density increase. Compare to similar conditions but different anodic dissolution methods such as the NP-1 with the NG-1, the NP-2 with the NG-2, and the NP-3 with the NG-3, reduced specimen thickness, Cr-Fe depletion layer thickness, and Cr and Fe contents in Cr-Fe depletion layer of the NP experiment are larger than them of the NG.

The sheet-shaped detached particles from anodic dissolution experiments which were done in LiCl-KCl-5 wt% $NiCl_2$ molten salt system were observed with lots of smaller particles. The size of the particles and eliminated amount of Cr/Fe were decreased as the applied current density increased. The Cr and Fe contents in detached particles are lower than those of the Cr-Fe depletion layer.

3.2. Anodic dissolution behaviors of Inconel 600 in $FeCl_2$ added salt

As shown in Fig. 5 (a), Inconel 600 which was immersed in LiCl-KCl-5 wt% $FeCl_2$ for 168 h does not show any evident surface change. Reduced Fe layer like reduced Ni layer of the NI experiment exposed to $NiCl_2$ added salt (Fig. 4 (a, b)) does not occur. Major element contents in the salts before and after did not show significant changes.

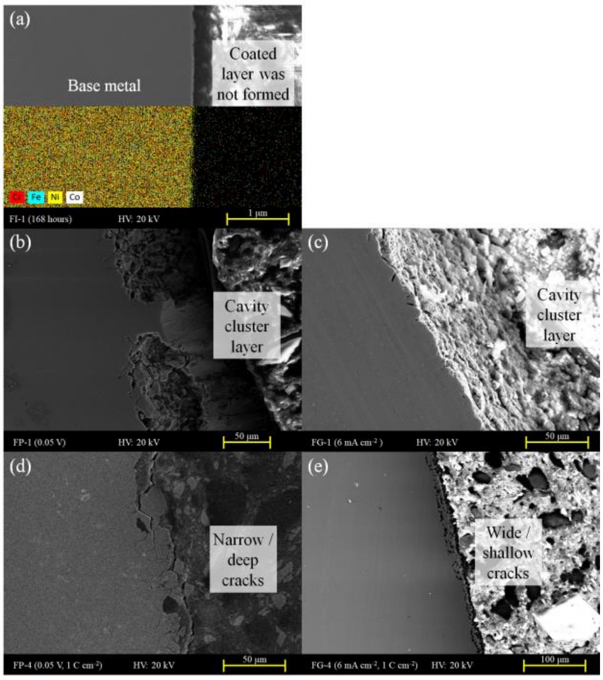


Fig. 5. Microstructure of Inconel 600 after FI (a), FP-1 (b), FG-1 (c), FP-4 (d), and FG-4 (e) experiments

As shown in Fig. 5 (b, c), the cavity cluster layer was generated along the surface of the anode after the FP and FG experiments. Contents of the cavity cluster layer were investigated by SEM-EDS and the tendency that decrement of Ni and increment of Fe and Cr contents with higher potential or current density was observed but was not much as the NP or NG experiments. The passed charge was 80 C cm^{-2}, the reduced thickness was 150 to 250 μm which is much higher than the NP and NG experiments although they passed 280 C cm^{-2}. At the boundary of the base material, cracks shorter than 15 μm were observed.

Detached particles from $FeCl_2$ added salts with very small sizes show the shape of stones. The size of the particles was decreased as the applied current density increased but did not show a huge difference. However, the contents of the detached particles show a large point of difference compared to the contents of the cavity cluster layer. From the molten salt composition analysis, a very little amount of Ni which is the noblest element in Inconel 600 was dissolved.

4. Conclusion

The anodic dissolution behaviors of Inconel 600 in LiCl-KCl-5 wt% $NiCl_2/FeCl_2$ at 773 K were investigated. Cr and Fe contents can be eliminated selectively from the Inconel 600 by forming the Cr-Fe depletion layer during the anodic dissolution process and most of them can be dissolved in molten salts by applying low current density. To explain the Cr-Fe dissolution layer generation mechanism, gluing ion effect concept was suggested and not only to Ni^{2+} but to any ions nobler than desiring ion to be dissolved can be used to extract ion selectively. When applying the anodic dissolution process to Inconel 600 within the LiCl-KCl-5 wt% $FeCl_2$ system, cavity cascade cause of Cr and Fe dissolution invade the cavity cluster layer on its surface with lots of detached particles. Also, the differences in dissolution mechanisms between potentiostatic and galvanostatic methods in the $FeCl_2$ additive system were analyzed.

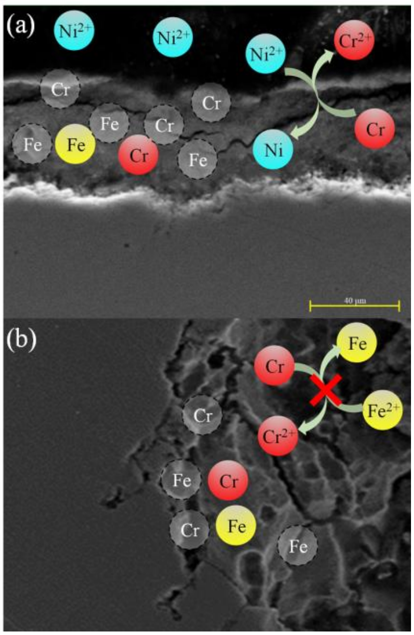


Fig. 6. Schematics of gluing Ni^{2+} ion effects which support the Cr-Fe depletion layer generation (a) and mechanism of the micro-particle detachment in $FeCl_2$ added salt.

5. Acknowledgement

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