

# Corrosion Behavior of a Surface Modified Superalloy in a Hot Lithium Molten Salt

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## 1. Introduction

The Li-reduction process involves the chemical reduction of spent fuel oxides by liquid lithium metal in a molten LiCl salt bath at 650°C followed by a separate electrochemical reduction of the lithium oxide (Li<sub>2</sub>O), which builds up in the salt bath. This process requires a high purity inert gas atmosphere inside a remote hot cell nuclear facility to prevent an unwanted Li oxidation and fires during the handling of the chemically active Li metal. In light of the limitations of the Li-reduction process, a direct electrolytic reduction technology is being developed by KAERI to enhance the process safety and economic viability. The electrolytic reduction of spent oxide fuel involves the liberation of the oxygen in a molten LiCl electrolyte, which results in a chemically aggressive environment that is too corrosive for typical structural materials. Even so, the electrochemical process vessel must be resilient at 650°C in the presence of oxygen to enable high processing rates and an extended service life. But, the mechanism and the rate of the corrosion of the metals in a LiCl-Li<sub>2</sub>O molten salt under an oxidation condition are not clear. In the present work, the corrosion behavior and corrosion mechanism of a surface modified superalloy have been studied in the molten salt of LiCl-Li<sub>2</sub>O under an oxidation condition.

## 2. Experimental Procedure

Corrosion tests were conducted in a molten LiCl-Li<sub>2</sub>O using an oxidizing atmosphere at 650°C for 72~168 hrs with an Ar-10%O<sub>2</sub> sparge gas. Haynes 263 was employed for these investigations. The chemical compositions are given in Table 1. 10μm thickness of Al on the alloy was coated onto it by a magnetron sputtering process[1] and 0.3μm of Y was coated onto the Al-layer using a single process of EB-PVD[2]. These coating processes and the thickness were applied through preliminary experiments that showed a good adhesion with a base metal. The corroded specimens were analyzed by X-Ray Diffraction (XRD), Electron Probe Microanalysis (EPMA) and Scanning Electron Microscopy(SEM) coupled with an Energy Dispersive X-ray Spectroscopy(EDS).

Table. 1. Chemical Compositions of Haynes 263.

	Ni	Cr	Fe	Co	Al	Ti	Mo
Haynes 263	51.35	20.0	0.50	19.20	0.45	2.39	5.80

## 3. Results and Discussion

### 3.1 Corrosion Rate

Fig. 1 presents the weight variation of the noncoated and Y+Al coated Haynes 263 during the test in LiCl-3%Li<sub>2</sub>O and LiCl-8%Li<sub>2</sub>O molten salt. Y+Al coating decreased the corrosion rate but the

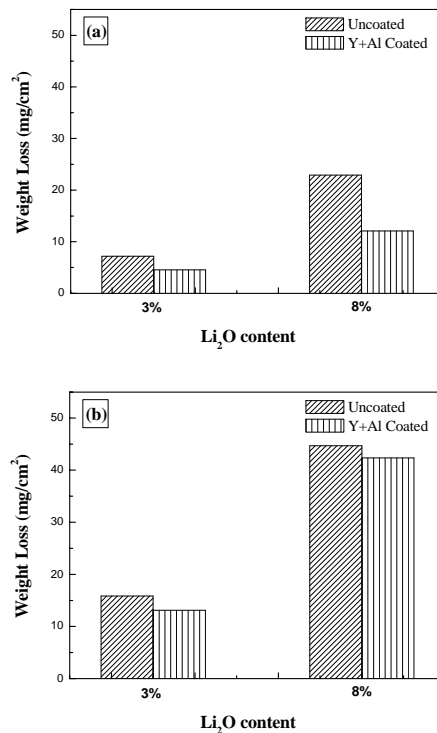


Figure 1. Weight loss of the non-coated and Y+Al coated Haynes 263 corroded at 650 °C for (a) 72 hrs and (b) 168 hrs.

effects lessened with an increase of the Li<sub>2</sub>O concentration in the molten salt or the corrosion time.

### 3.2 Corrosion Behavior

The morphology and elemental distribution of the Y+Al coated Haynes corroded at 650°C for 72h in molten salt of LiCl-3%Li<sub>2</sub>O is shown in Fig. 2. Y is known to facilitate the oxidation of Al and consequently densify the oxide film[3,4]. However the effect of Y was not observed and the reason was attributed to the spallation of Y during the oxide formation. On the contrary, Al oxide acted as a protective film and contributed to the prevention of

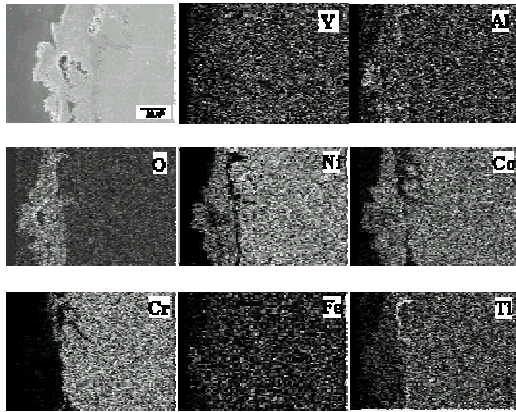


Figure 2. Cross-sectional SEM image and EDS results of Al-Y coated Haynes 263 corroded at 650°C for 72h in molten salt of LiCl-3%Li<sub>2</sub>O.

an internal corrosion. The erosion on the surface of the Al oxide layer was due to its acidic nature in a molten salt containing Li<sub>2</sub>O as a strong base[5]. Fe showed the highest diffusion rate through the Al oxide, and when the corrosion condition became severe, it was spalled, creating Ni and Co oxides in the outer layer. Ti diffused externally and was concentrated in the interface of the oxide layer/base metal, and then eventually spalled in the severe condition.

### 3.3 Corrosion Products

XRD analysis was carried out to characterize the corrosion product of the Y+Al coated Haynes 263 after the corrosion test in a LiCl-3% Li<sub>2</sub>O molten salt (Fig. 3). In the initial phase of a corrosion, Al was oxidized by a reaction with oxygen to form a solid solution, LiAlO<sub>2</sub>. Li originated from the molten salt. The formation of Li<sub>5</sub>Fe<sub>5</sub>O<sub>8</sub> means a high diffusion rate of the Fe ion through the Al oxide. When the corrosion test was continued to 168 hrs, Li(Ni,Co)O<sub>2</sub> and LiTiO<sub>2</sub> were also detected suggesting an external diffusion of Ni and Co with the progress of the corrosion. In the most severe corrosion condition (8% Li<sub>2</sub>O and 168 hrs), Co and Ni oxides were detected. However an Al based oxide was not found because of its erosion and leaching by a reaction with the molten salt.

### 3. Conclusion

The corrosion rate of Y+Al coated Haynes 263 was low while that of bare Haynes 263 was high in a molten salt of LiCl-Li<sub>2</sub>O. An Al oxide layer acted as a protective film which prohibited the penetration of the oxygen ion into the matrix. Corrosion products formed were Li(Ni,Co)O<sub>2</sub> and LiTiO<sub>2</sub> on bare Haynes 263, but LiAlO<sub>2</sub>, Li<sub>5</sub>Fe<sub>5</sub>O<sub>8</sub>, Li(Ni,Co)O<sub>2</sub> and LiTiO<sub>2</sub> with Y+Al coated Haynes 263.

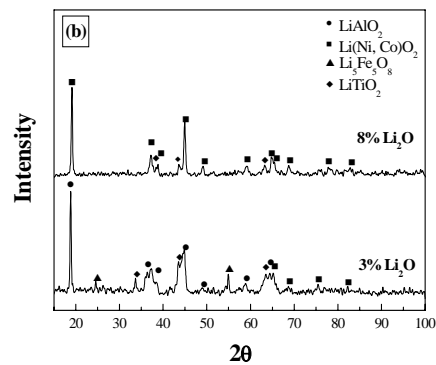
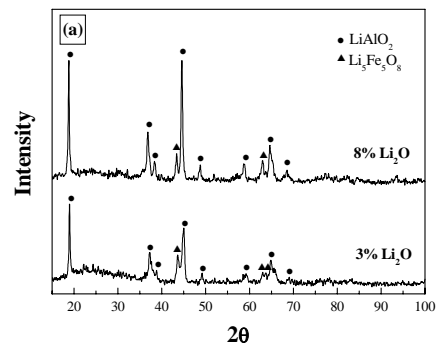


Figure 3. Corrosion products of the Y+Al coated Haynes 263 corroded at 650 °C for (a) 72 hrs and (b) 168 hrs.

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