Corrosion Behavior of Superalloys in 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 lithium oxide (Li$_2$O), which builds up in the salt bath. This process requires a high purity inert gas atmosphere inside remote hot cell nuclear facility to prevent unwanted Li oxidation and fires during the handling of 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 process safety and economic viability. The electrolytic reduction of spent oxide fuel involves the liberation of 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 metals in LiCl-Li$_2$O molten salt under oxidation condition are not clear. In the present work, the corrosion behavior and corrosion mechanism of superalloys have been studied in the molten salt of LiCl-Li$_2$O under oxidation condition.

2. Experimental Procedure

Corrosion tests were conducted in a molten LiCl-Li$_2$O using an oxidizing atmosphere at 675°C for 72~216hrs with an Ar-10%O$_2$ sparge gas. The materials evaluated are included Table 1. The corroded specimens were analyzed by X-Ray Diffraction(XRD), Electron Probe Microanalysis (EPMA) and Scanning Electron Microscopy(SEM) coupled with Energy Dispersive X-ray Microanalysis (EDX).

Table 1. Chemical Compositions of Tested Alloys

Alloy	Ni	Cr	Fe	Co	Al	Ti	Nb	Mo
Inconel 713LC	74.00	11.57	0.10	0.08	6.05	0.76	1.95	4.15
Nimonic 80A	74.90	19.24	1.14	-	1.68	2.40	-	-
Nimonic 90	59.88	19.38	0.57	16.05	1.38	2.40	-	-

3. Results and Discussion

3.1 Corrosion rate

The weight loss of the samples after the corrosion test at 675°C for 72 ～ 216 hrs are presented in Fig. 1. Every tested sample showed a weight loss with time and the corrosion rate was as such: Inconel 713LC < Nimonic 80A < Nimonic 90. Among the tested superalloys, Inconel 713Lc showed the best corrosion resistance.
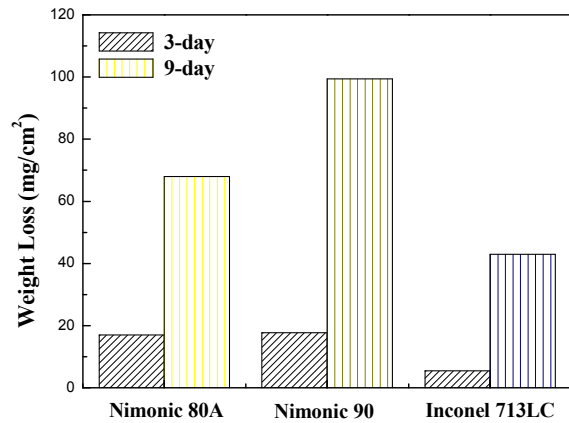

Figure 1. Weight loss of the alloys corroded at 675°C, as a function of time.

3.2 Corrosion products

The corrosion products left from ultrasonic cleaning of tested alloys were analyzed by XRD and the results of Inconel 713LC, Nimonic 80A and Nimonic 90 are given in Table 2.

Table 2. Corrosion products of the alloys

Alloy/Time	3-day	9-day
Inconel 713LC	NiCr$_2$O$_4$, Cr$_2$O$_3$, NiO	NiCr$_2$O$_4$, Cr$_2$O$_3$, NiO
Nimonic 80A	Cr$_2$O$_3$, LiFeO$_2$	Cr$_2$O$_3$, Li$_2$Ni$_8$O$_{10}$
Nimonic 90	Cr$_2$O$_3$, NiO	Cr$_2$O$_3$, CoCr$_2$O$_4$,

A mixture of several complex oxides shows different types of oxide with the corrosion time. Also the species and structures of the corrosion products are affected by the amount and diffusivity of alloying constituent elements.

3.3 Corrosion behavior

Fig. 2 presents the SEM images of Inconel 713LC corroded for 72 hrs. The corrosion layer of Inconel 713LC mostly consists of oxygen active elements such as Al, Ti and Cr. The oxygen active elements might be preferentially oxidized and participate in the formation of the corrosion layer[1]. The corrosion layer was relatively dense and adherent. Fig. 3 shows the SEM images of Inconel 713LC corroded for 216 hrs. Compared to the 72 hrs tests, the growth of a corrosion layer and the internal corrosion underneath a corrosion layer were observed. The corrosion layer mostly consists of the oxides of Al, Ti, and Cr similar to the 72 hrs tests.
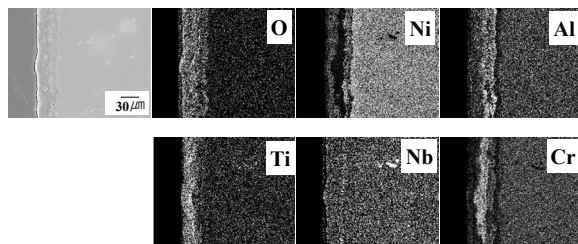

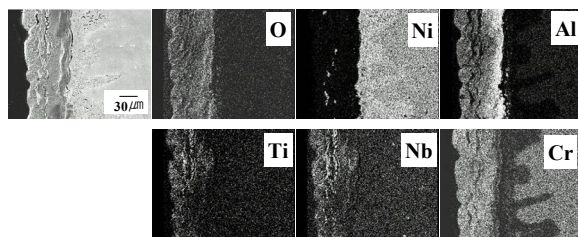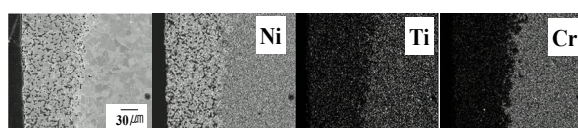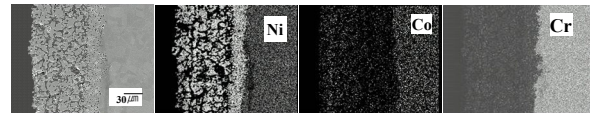Figure 2. Cross-sectional SEM image and the elemental distribution of Inconel 713LC corroded at 675℃ for 72 hrs.

Figure 3. Cross-sectional SEM image and the elemental distribution of Inconel 713LC corroded at 675℃ for 216 hrs.

Fig. 4 presents the SEM images of Nimonic 80A and Nimonic 90 corroded for 216 hrs. Compared to the corrosion of Inconel 713LC in the same condition shown in Fig. 3, an outer corrosion layer was not observed in Nimonic 80A and Nimonic 90. Nimonic 80A and Nimonic 90 are similar in their chemical compositions except that a part of Ni in Nimonic 80A is substituted for Co in Nimonic 90. Nimonic 90 showed the depletion of a large amount of Co in the corrosion layer. Co can easily form oxides or chlorides when compared to Ni. Therefore, an increase of Ni rather than Co is beneficial for the corrosion resistance in a oxidative molten salt[2,3].

(a)

(b)

Figure 4. Cross-sectional SEM image and the elemental distribution of Nimonic 80A(a) and Nimonic 90(b) corroded at 675℃ for 216 hrs.

4. Conclusion

Inconel 713LC showed the best corrosion resistance among the tested alloys and Nimonic 90 showed the highest weight loss. Compared to Co, Ni was much more beneficial for a corrosion resistance. Al increased the adherence of an oxide layer in the nickel base alloys and inhibited the internal intrusion of the oxygen ion. Therefore it is a useful element for a corrosion resistance.

In this corrosion environment, the overall oxidation rate depends on the diffusion rate of each ion and the thermodynamic stability of the corresponding oxides.

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