Corrosion Behavior of Superalloys in a LiCl-Li₂O Molten Salt

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A study on the corrosion behavior of Inconel alloys and Incoloy 800H in a molten salt of LiCl-Li₂O was investigated at 650°C for 24–312 hours in an oxidation atmosphere. The order of the corrosion rate was Inconel 600 < Inconel 601 < Incoloy800H < Inconel 690. Inconel 600 showed the best performance suggesting that the content of Fe, Cr and Ni are the important factor for corrosion resistance in hot molten salt under an oxidation conditions. The corrosion products of Inconel 600 and Inconel 601 were Cr₂O₃ and NiFe₂O₄. In case of Inconel 690, a single layer of Cr₂O₃ was formed in the early stage of corrosion and an outer layer of NiFe₂O₄ and inner layer of Cr₂O₃ were formed with an increase of corrosion time. In case of Incoloy 800H, Cr₂O₃ and FeCr₂O₄ were observed. Most of the outer scale of the alloys was observed to be spalled from the results of the SEM analysis and the unspalled scale which adhered to the substrate was composed of three layers. The outer layer, the middle one, and the inner one were Fe, Cr, and Ni-rich, respectively. Inconel 600 showed localized corrosion behavior and Inconel 601, 690 and Incoloy 800H showed uniform corrosion behavior. Ni improves the corrosion resistance and too much Cr and/or Fe content deteriorates the corrosion resistance. [doi:10.2320/matertrans.M2013262]

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1. Introduction

Molten salt technology has been widely applied in the industrial world because of its physical and chemical characteristics, because of its high electrical conductivity, high processing rate, fluid features, etc. Molten salts can cause corrosion on the container materials and other accessories used in the construction of various equipments. Reactions between alloys and molten salt are technologically important considering the long term stability and compatibility of materials. A few studies have been carried on the corrosion behavior of metals in a molten salt such as sulphates¹⁾ and nitrates.²⁾ Also there are many reports on an accelerated oxidation in chloride molten salts.^{3,4)} Liu *et al.* studied the corrosion behavior of pure nickel in a molten LiCl-Li₂O at 750°C.⁵⁾ However, they are mainly short time electrochemical experiments and few reports are found on long term experiments for the corrosion of commercial alloys in a chloride molten salt considering the corrosion products, rate and behaviors. The electrochemical reduction process for spent oxide nuclear fuel is carried out in a LiCl-Li₂O molten salt at 650°C.^{6,7)} The liberation of oxygen on an anode and the high temperature molten salts of the process cause a chemically aggressive environment that is too corrosive for ordinary structural materials. Therefore, for an implementation of the electrochemical reduction technology, corrosion resistance materials should be developed. In this study, it is aimed to study the corrosion behavior of four types of superalloys in a LiCl-Li₂O molten mixture under oxidizing atmosphere; Inconel 600, Inconel 601, Incoloy 800H, Inconel 690.

2. Experimental Procedure

Superalloys of Inconel 600, Inconel 601, Inconel 690 and Incoloy 800H are tested and the chemical compositions are shown in Table 1. The 70 × 15 × 2 (mm) plates were cut

Table 1 Chemical composition of tested alloys.

Sample	Fe	Cr	Ni	C	Si	Mn	P	S	Al	Cu	Ti
Incoloy 800H	43.70	21.00	34.00	0.03	0.40	0.50	0.002	0.002	—	—	—
Inconel 600	8.15	16.30	73.66	0.07	0.21	0.32	0.002	0.002	—	0.05	—
Inconel 601	13.00	22.5	60.53	0.03	0.30	0.30	0.002	0.002	1.30	0.03	—
Inconel 690	10.00	29.82	56.30	0.08	0.53	0.28	0.001	0.002	0.32	0.01	0.32

from a cold-rolled sheet. They were polished with #2000 SiC paper on all sides, ultrasonically cleaned in acetone, rinsed with distilled water, dehydrated by ethanol and then dried. The experimental apparatus used is shown in Fig. 1. High purity reagent of LiCl and Li₂O were used. Before testing, the LiCl-3%Li₂O mixture contained in MgO crucible was melted in a glove box. And samples were located at the uniform temperature zone of a vertical resistance furnace. The temperature was raised to 300°C under Ar atmosphere and at this temperature for about three hours constantly Ar flowing to remove moisture pick-up. The temperature was then raised to 650°C and the samples were lowered into salt to start the test. At this time Ar-10%O₂ gas mixture was blown into and bubbled in the molten salt through gas lance made by Al₂O₃. The flow rate of gas mixture was 20 ml/min and accurately controlled using a mass flow controller. After the corrosion test, the sample was withdrawn from molten salt and kept under Ar gas while the furnace cooled to room temperature. The samples were cleaned with distilled water in an ultrasonic cleaner and then dried. The weight loss of the specimens after the cleansing would be the total amount of corrosion in a given time. The corroded samples were investigated by X-ray diffraction (X-ray Diffractometer, Rigaku, DMAX/1200XRD), scanning electron microscopy (Scanning Electron Microscope, Hitachi, SU-6600) and Energy Dispersive Spectroscopy (EDS).

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① Heating furnace	⑨ Sample hanger & elevator
② Container	⑩ Baffle plate
③ Thermo-Couple	⑪ Cooling jacket
④ Protection crucible	⑫ Ar gas inlet
⑤ Gas nozzle	⑬ Mixed gas supply system
⑥ Test crucible	⑭ Flow meter
⑦ Molten salt	⑮ Gas outlet
⑧ Sample	

Fig. 1 Schematic Diagram of Apparatus for Corrosion Test.

Fig. 2 Weight losses of tested alloys at 650°C in LiCl-3%Li₂O melt as a function of reaction time.

3. Results and Discussions

The weight losses of Inconel 600, Inconel 601, Inconel 690 and Incoloy 800H after the corrosion tests in a LiCl-3%Li₂O molten salt at 650°C as a function of the time are presented in Fig. 2. Inconel 600 showed the lowest corrosion rate while Inconel 690 showed the highest corrosion rate. It was thought that the weight loss of the specimens under a high temperature oxidative molten salt environment was caused by anodic dissolution ($M \rightarrow M^{n+} + ne^-$, M: metal, M^{n+} : metal ion) of metals. Presumably the protective oxide film is not expected in this melt.

Therefore, it was thought that the weight variations of the specimen would be affected by the adhesive strength between

Fig. 3 XRD patterns of corrosion products of Incoloy 800H corroded at 650°C for 24–312 h.

Fig. 4 XRD patterns of corrosion products of Inconel 600 corroded at 650°C for 24–312 h.

the corrosion layer and the base metal considering the formation and spallation of the corrosion layer as well as the stability of the growth of the corrosion layer. At high temperature, to keep corrosion resistance, alloys should have protective films on the surface which has adhesion strength on the matrix and low growth rate. So, the corrosion resistance is directly related to the structure and species of corrosion layer on the surface of alloys. To find out the types of outer corrosion layer, the corrosion products left from ultrasonic cleaning of tested alloys were analyzed by XRD. As shown in Fig. 3, the corrosion products of Incoloy 800H were Cr₂O₃ and FeCr₂O₄ regardless of corrosion time. Inconel 600 (Fig. 4) and Inconel 601 (Fig. 5) showed similar XRD patterns including Cr₂O₃ and NiFe₂O₄. In the thermodynamic view, Cr₂O₃ is the most stable oxide in the Ni-Cr-Fe based alloys so, the oxidation will start with the formation of Cr₂O₃.⁸⁾ Since the diffusion rate of a metal ion in a Cr-oxide is $Fe^{3+} > Fe^{2+} > Ni^{2+} > Cr^{3+}$,⁹⁾ the Fe and Ni ion diffuse through the initially formed Cr oxide layer to form the oxide. Bittel *et al.*¹⁰⁾ revealed, by X-ray diffraction study, that the oxides of 304L stainless steel formed at 1200–1300°C in steam were predominately Fe₂O₃. In their study the oxides consisted of a first layer formed of dense coarse-grained oxide and second, porous fine-grained structure of spinel with a high Cr content next to the metal. It is because

Fig. 5 XRD patterns of corrosion products of Inconel 601 corroded at 650°C for 24–312 h.

Fig. 6 XRD patterns of corrosion products of Inconel 690 corroded at 650°C for 24–312 h.

Spot	O	Cr	Fe	Ni
Standard	-	16.30	8.15	73.66
1	31.18	1.32	60.26	7.24
2	25.32	54.92	10.27	9.49
3	8.00	42.08	1.26	48.67
4	3.35	4.93	0.61	91.12
5	12.46	5.79	1.06	80.69
6	1.58	2.88	1.43	94.11
7	6.45	2.46	1.13	89.95
8	0.58	15.37	7.43	76.62

Fig. 7 SEM cross sectional image and spot chemical analysis results of unspalled outer scale of Inconel 600 corroded at 650°C for 168 h.

the outer diffusion of Fe through the Cr-oxide. For oxidation, oxygen has to diffuse through the melt to metal surface. It may be provided either by dissolution from the gas phase or by dissolution of oxygen bearing molecules in molten salts. In the LiCl-Li₂O melt, the strong basic Li₂O resulted in basic dissolution in the corrosion process. During immersion in LiCl-Li₂O melt, initially, Cr₂O₃ was formed by reaction with oxygen dissolved from the gas in the melt, and might be accompanied by succeeding dissolution of Cr₂O₃ and acted as a medium through which corrodents diffused.

In case of Inconel 690 (Fig. 6), a single layer of Cr₂O₃ was formed in the early stage of corrosion and NiFe₂O₄ with Cr₂O₃ were observed with increasing of corrosion time.

In the multi-component alloy, to keep oxide single phase, a solute should be provided sufficiently to the interface of metal and oxide layer. In case of Inconel 690, the content of Cr is about 30%, relatively high level, so it forms single layer of Cr₂O₃ in the early stage of corrosion.¹¹⁾ With increase of

corrosion time, Cr in matrix is depleted to form corrosion layer. And with the diffusion of Fe and Ni ion, NiFe₂O₄ is formed on the top of the Cr₂O₃ which is formed at first. The morphology and EDS results of the unspalled corrosion scale which is adherent on substrate of Inconel 600 after corrosion test is shown in Fig. 7. Cracking was observed in the oxide/metal interface. The corroded zone is composed of three layers. The outer layer, the middle one, and the inner one (close to the oxide/metal interface) were Fe, Cr, and Ni-rich, respectively. Cr-oxide is located underneath the outer layer. As a result, the Ni-rich phase was observed in the interface of the oxide and metal. Figure 8 showed the morphology and elemental distribution of O, Cr, Fe and Ni obtained by mapping using an EDS of unspalled outer scale of Incoloy 800H. The corrosion depth shows about 200 μm and uniform corrosion behavior. The outer part consists of Cr or Fe oxide which is consistent with the results of Fig. 3 showing the results of corrosion products analysis. In the inner part, Cr depletion was observed and the reason was attributed to the consumption of Cr for the formation of the oxide film. Cracking which was observed in the interface might be caused by the increase of the thermal stress and growth stress in the oxide layer during its formation. When the scale is spalled from the base metal, the depletion of the constituent

Fig. 8 SEM cross sectional image and spot chemical analysis results of unspalled outer scale of Incoloy 800H corroded at 650°C for 168 h.

Fig. 9 SEM cross-sectional images and elemental distribution of Cr, Fe and Ni of tested Inconel alloys at 650°C for 312 h.

element of the oxide film will deteriorate the corrosion resistance of the alloys. A Ni-rich phase was observed underneath the oxide layer and thermodynamically, the oxygen affinity of Ni is relatively weaker than Cr and Fe.^{8,12)} From this, it can be deduced that an enrichment of the

Ni underneath oxide layer can prevent internal oxidation and corrosion. From the results of weight loss analysis shown in Fig. 2, the higher Ni content in alloy, the better corrosion resistance is. Therefore, Ni content should be higher than a certain critical amount for a corrosion resistance. Figure 9

showed the cross-sectional SEM images and elemental distribution of Inconel 600, Inconel 601 and Inconel 690.

From the results of from Fig. 7 to Fig. 9, larger amounts of Cr and Fe are expected to dissolve into the molten salts. Because the oxide film ($\sim 10\ \mu\text{m}$) is much thinner than the depletion zone ($\sim \text{mm}$). It is thought that the selective dissolution of Cr and Fe causes formation of the thick depletion zone of Cr and Fe.

In comparing of the depths of corrosion attack, Inconel 600 had the weakest, followed by Inconel 601 and then Inconel 690. The depth of corrosion attack is proportional to weight loss. While Inconel 600 showed localized corrosion behavior, Inconel 601 and 690 showed uniform corrosion behavior. In the corrosion layer of tested alloys, Cr and Fe are depleted and Ni is concentrated. In the study of hot corrosion of Ni-Cr alloys, Ling *et al.*¹³⁾ reported that, there exists Cr-depleted zone beneath the Cr_2O_3 because Cr is consumed to form oxide on the surface. With oxidation, Cr-depleted zone expands into the matrix to compensate for Cr exhausted. Spallation and Cracks could occur including stress relaxation process if the strain energy within the oxide scale or oxide/metal interface, resulting from growth and thermal stresses, exceeded the interfacial fracture energy. Cr which forms oxide scale is depleted in the process of spallation and reproduction of corrosion layer. In this approach, Cr content in alloy is related to the corrosion resistance. And too much Cr deteriorates the corrosion resistance from the lowest corrosion resistance of high Cr-containing Inconel 690.

4. Conclusion

- (1) The order of corrosion rate was Inconel 600 < Inconel

601 < Incoloy 800H < Inconel 690.

- (2) The corrosion products of Inconel 600 and 601 which high Ni containing alloys were Cr_2O_3 and NiFe_2O_4 . Cr_2O_3 and FeCr_2O_4 were formed on Incoloy 800H which has high Fe content.
- (3) Inconel 600, 601, Incoloy 800H showed uniform corrosion behavior and Inconel 600 showed localized corrosion behavior.
- (4) Too much Cr and Fe content in a matrix can be deleterious on the corrosion resistance.
- (5) Ni-enrichment underneath the oxide improves corrosion resistance with preventing the oxygen penetration into matrix.

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