

Corrosion Study of Hastelloy N with Electrochemical Impedance Spectroscopy in NaCl-MgCl₂-NiCl₂ systems

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1. Introduction

The molten salt reactor, one of the generation IV reactor types, has been studied in a number of national laboratories and startup companies due to its inherent safety and efficient fuel utilization. Among several types of molten salt reactors, molten salt fast reactors recently get noticed. The main advantage of fast-type molten salt reactors is the potential to reuse the transuranium elements in the spent nuclear fuel.

Chloride-based salts are a suitable option for molten salt fast reactors. However, the compatibility between chloride-based salts and structural materials has to be identified first. The difficulty in the selection of the proper structural materials exists due to the corrosive properties of high-temperature molten salts and several impurities contained in salts. To develop the molten salt fast reactors, further investigation related to the corrosion behaviors of candidate structural materials in various conditions has to be conducted.

Therefore, in this study, the corrosion behaviors of Hastelloy N, which is the candidate structural material, were investigated. Ni ions, one of the corrosion products that act as impurities, were added to NaCl-MgCl₂ eutectic to check their effects. Electrochemical impedance spectroscopy (EIS) methods were applied to the real-time corrosion analysis.

2. Experimental

All experiments were conducted in the glovebox filled with Ar (99.999%) and the oxygen as well as H₂O concentrations inside glovebox were controlled below 5ppm. The experimental temperature was set at 600±5°C with an electrical furnace. Glassy carbon cells were utilized as a sample container.

Samples of Hastelloy N with a dimension of 5.0mm×10.0mm×1.5mm were used. All specimens were ground up to 2000 grit SiC paper. Before and after corrosion experiments, samples were cleaned with ethanol and deionized water.

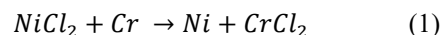
Anhydrous NaCl (99.999%, Sigma-Aldrich) and MgCl₂ (99.99%, Sigma-Aldrich) eutectic salt (NaCl = 44.9wt%) was utilized in this experiment. Anhydrous NiCl₂ (99.99%, Sigma-Aldrich) was added to the salt as a corrosion product. The salt was dried at 300°C for 10 hours to remove residual moisture before melting.

EIS measurements were conducted by the potentiostat (SP-240, BioLogic) with the three-electrode system. Sheet type of Hastelloy N, W rod, and Pt rod were utilized as a working electrode, counter electrode, and

reference electrode, respectively. The EIS data were measured in the frequency range from 10⁵ Hz to 10⁻² Hz with the AC signal (amplitude = 10mV) at the open circuit potential. EIS measurements were conducted for 100 hours with 10 hours of time intervals.

3. Result and Discussion

Table I shows the results of the analysis of the concentration of each element dissolved in the NaCl-MgCl₂-NiCl₂ system salt before and after corrosion experiments using inductively coupled plasma-mass spectroscopy (ICP-MS). The analysis revealed a decrease in Ni and an increase in Cr, indicating that Ni ions reacted with Cr in Hastelloy N, which has the most negative redox potential among the alloying elements. Thus, the following reaction expressed in equation 1 is expected to take place.



The presence of NiCl₂ resulted in a greater depletion of Cr compared to the NaCl-MgCl₂ system alone. As a result, it is expected that Hastelloy N underwent an accelerated corrosion. One of the alloying elements, Mo, does not exhibit a distinct variation due to the positive redox potential compared to Ni.

Table I: ICP-MS results before and after experiment conducted in the NaCl-MgCl₂-NiCl₂ system

	Before Exp.	After Exp.
Ni	14.2 mg/kg	0.30 mg/kg
Cr	1.78 mg/kg	12.7 mg/kg
Mo	< 1 mg/kg	<1 mg/kg

To compare the corrosion resistance of Hastelloy N in NaCl-MgCl₂ and NaCl-MgCl₂-NiCl₂ systems, EIS measurements were conducted. Fig. 1(a) displays the Nyquist plots obtained from the 100-hour immersion in both systems. The observed capacitance semicircle in the Nyquist plots indicates the presence of charge-transfer controlled reactions. Moreover, the Nyquist plots show that the corrosion resistance of Hastelloy N in NaCl-MgCl₂ is higher than in NaCl-MgCl₂-NiCl₂, as evidenced by the larger semicircle in the former. The Bode phase angle plots obtained from the 100-hour immersion in both systems are presented in Fig. 1(b). The presence of two valleys in the plots indicates the formation of films on the surface in both systems.

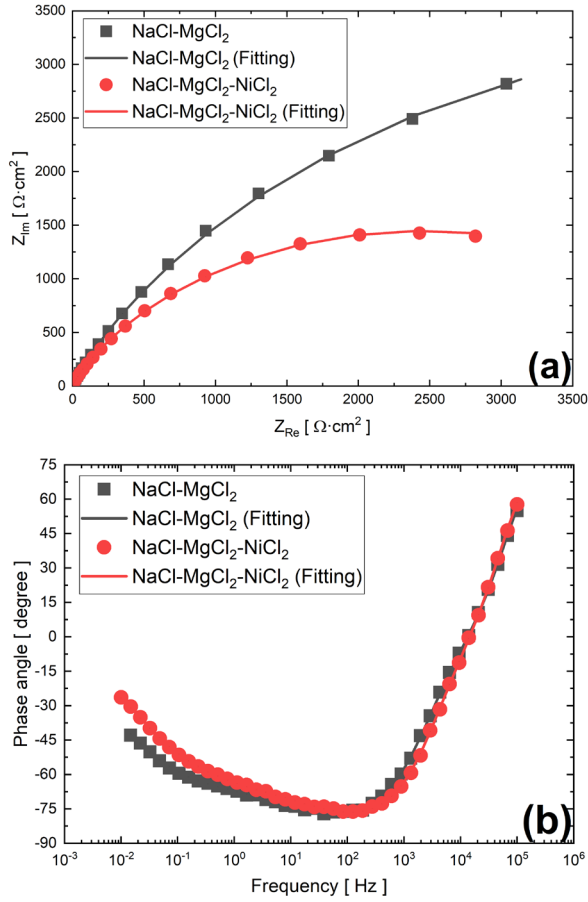


Fig. 1. EIS results of Hastelloy N for 100-hour reaction in NaCl-MgCl₂ and NaCl-MgCl₂-NiCl₂ systems at 600°C; Nyquist plot (a) and Bode phase angle plot (b)

To obtain quantitative results, the EIS results were fitted using the equivalent circuit shown in Fig. 2, which was utilized in the fitting. L represents the inductance formed by the connection of wires¹, R_s represents the solution resistance, Q_f represents the film constant phase element (CPE), R_f represents the film resistance, Q_{dl} represents the double layer CPE, and R_{ct} represents the charge transfer resistance.

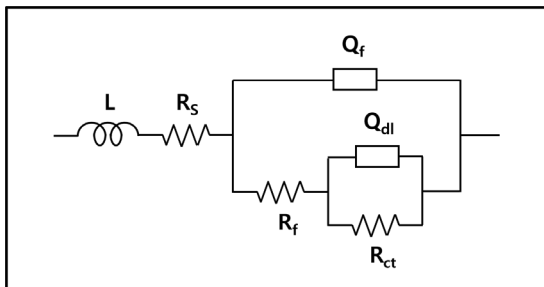


Fig. 2. Equivalent circuit used for fitting of EIS data

The results for the 100-hour reaction in NaCl-MgCl₂ and NaCl-MgCl₂-NiCl₂ systems are presented in Table II. As indicated by the χ^2 values on the order of 10^{-4} , the fitting appears to be reasonable². The circuits with two (QR) components suggest the presence of a film on the

surface in both systems³. However, the lower R_s values compared to the R_{ct} values indicate that the film does not serve a protective function. In addition, the higher R_{ct} values observed in the NaCl-MgCl₂ system compared to those in the NaCl-MgCl₂-NiCl₂ system indicate a higher corrosion rate.

Table II: Fitting results of EIS data for 100-hour reaction in NaCl-MgCl₂ and NaCl-MgCl₂-NiCl₂ systems at 600°C

After 100hrs	NaCl-MgCl ₂	NaCl-MgCl ₂ -NiCl ₂
L [H·cm ²]	8.41×10^{-7}	7.58×10^{-7}
R_s [Ω·cm ²]	0.35	0.28
$Y_{0,f}$ [Ω ⁻¹ ·s ^{nf} ·cm ⁻²]	4.69×10^{-4}	4.13×10^{-4}
n_f	0.90	0.92
R_f [Ω·cm ²]	1.71×10^2	7.13×10^1
$Y_{0,dl}$ [Ω ⁻¹ ·s ^{ndl} ·cm ⁻²]	6.10×10^{-4}	7.25×10^{-4}
n_{dl}	0.61	0.59
R_{ct} [Ω·cm ²]	1.10×10^4	5.08×10^3
χ^2	2.18×10^{-4}	2.49×10^{-4}

Figure 3 shows the time-dependent change in R_{ct} , which reflects the corrosion resistance of the systems. R_{ct} remained consistently higher throughout the entire period in the NaCl-MgCl₂ system, indicating that the addition of Ni ions accelerates the corrosion of Hastelloy N. Both NaCl-MgCl₂ and NaCl-MgCl₂-NiCl₂ systems exhibited an increase in R_{ct} values as time progressed. These findings suggest that the film formed on the surface acts as a passive film to a certain extent, despite its low resistance.

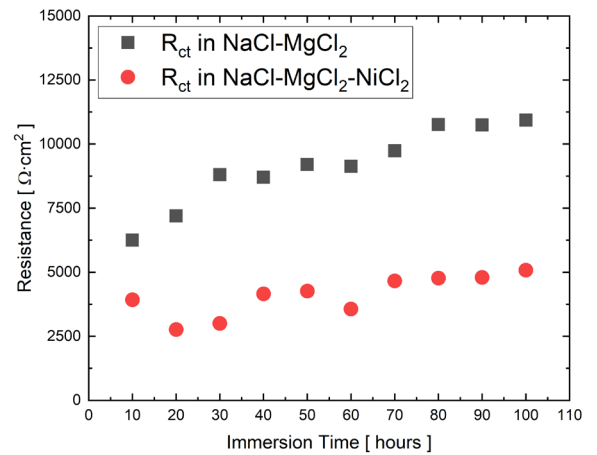


Fig. 3. Charge transfer resistance change with time in NaCl-MgCl₂ and NaCl-MgCl₂-NiCl₂ systems

4. Conclusion

Corrosion study of Hastelloy N in NaCl-MgCl₂-NiCl₂ systems at 600°C was conducted with EIS methods. Both qualitative and quantitative results obtained from EIS methods indicate that the presence of Ni ions accelerates the corrosion of Hastelloy N via the exchange reaction with Cr. Further work will include the addition of other elements such as Cr, Fe, and Sm.

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