

Electrochemical Impedance Spectroscopy and Polarization Resistance for In-Situ Corrosion Monitoring of SS316H and Hastelloy N in Molten NaCl-KCl

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1. Introduction

Molten salt reactors (MSRs) operating with chloride salts offer high thermal efficiency at elevated temperature, but the corrosivity of the melt toward structural materials remains the principal barrier to deployment [1]. Two alloy families dominate the candidate list: Fe-Cr-Ni austenitic stainless steels such as SS316H, attractive for their availability and code qualification but subject to intergranular penetration in NaCl-KCl at 700 °C [2,3], and Ni-Mo-Cr alloys such as Hastelloy N, developed for the Molten Salt Reactor Experiment [1]. Selecting between them requires knowing not only the extent of corrosion, but also how the attack develops with time.

Electrochemical techniques make that development observable while the exposure is still running. Linear polarization resistance (LPR) applies a small potential perturbation about the corrosion potential and returns a resistance inversely related to the corrosion activity of the interface; a single sweep takes about a minute, so it can be repeated every few hours and yields a continuous record [4]. Electrochemical impedance spectroscopy (EIS) applies a small alternating signal over a wide frequency range and separates the contributions of the melt, the interface and any surface layer that forms on it, and both techniques have been applied to monitoring in molten salt systems [5].

In this study, SS316H and Hastelloy N were exposed to molten NaCl-KCl at 700 °C for 100 h and monitored throughout by LPR and EIS. The salts were then analyzed by ICP-OES, and cross-sections of the specimens were examined by SEM-EDS.

2. Experimental Methods and Results

2.1 Experimental setup

The measured elemental compositions of the two alloys are given in Table 1. Both alloys were machined into 2 mm × 2 mm square bars, ground to 4000 grit SiC, rinsed with deionized water and dried at 60 °C for 24 h.

Table 1: Elemental composition of the alloys (wt%).

	Fe	Ni	Cr	Mo	C	Si	Mn	P	S
SS316H	Bal.	10.18	16.8	2.002	0.04	0.596	0.872	0.035	0.016
Hastelloy N	4.008	Bal.	8.26	15.115	0.071	0.613	0.942	0.004	0.004

Sodium chloride (NaCl, >99% purity) and potassium chloride (KCl, >99% purity) were purchased from Sigma-Aldrich. These salts were weighed according to the eutectic ratio of 50.6 mol% NaCl and 49.4 mol% KCl and dried in the solid state at 150 °C for 17.5 h, 300 °C for 25 h and 600 °C for 5 h.

Corrosion tests were conducted in a quartz cell inside a glovebox under Ar (O₂, H₂O < 1 ppm) at 700 °C, with the specimen itself as the working electrode, a W counter electrode and an Ag/AgCl reference electrode (NaCl-KCl + 1 wt% AgCl, mullite membrane), using a PMC-1000 potentiostat (Fig. 1). A single automated sequence alternated open-circuit holds, LPR (−20 to +20 mV vs. OCP, 0.5 mV/s) and EIS (10 kHz to 10 mHz, 10 mV RMS) on the same specimen, yielding 29 LPR and 8 EIS records over 100 h.

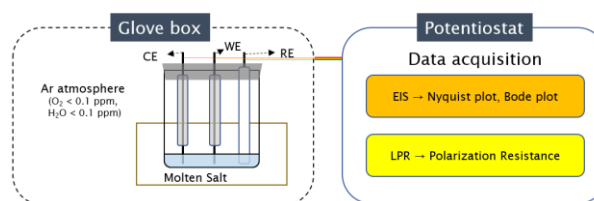


Fig. 1. Schematic of corrosion experiment used for in-situ electrochemical monitoring in molten NaCl-KCl at 700 °C.

2.2 In-situ electrochemical monitoring

Fig. 2(A) shows the area-normalized polarization resistance, R_p , obtained by LPR during the 100 h exposure. The LPR-derived R_p was obtained from the slope of the linear potential-current response around the OCP and normalized by the initially exposed electrode area. The resistance was corrected for the electrolyte resistance, R_s , estimated from the high-frequency real-axis intercept of the EIS spectra. R_s remained below 1 Ω throughout the exposure, and the resulting iR correction was less than 1% of R_p .

Fig. 2(B) shows the area-normalized R_p obtained from equivalent-circuit fitting of the EIS spectra, while the corresponding area-normalized Nyquist plots are presented in Fig. 2(C) and (D). The EIS-derived R_p was determined as the total fitted interfacial resistance excluding R_s and was normalized by the initially exposed electrode area. The Nyquist arc of SS316H contracted with immersion time (Fig. 2(C)), whereas that of Hastelloy N progressively expanded (Fig. 2(D)). Consistent with these changes, the EIS-derived R_p of SS316H decreased from approximately $167 \Omega \cdot \text{cm}^2$ at 5 h to $88 \Omega \cdot \text{cm}^2$ at 98 h, whereas that of Hastelloy N increased from approximately 64 to $119 \Omega \cdot \text{cm}^2$ over the same period. Thus, the EIS fitting supported the opposite temporal evolution of polarization resistance observed by LPR for the two alloys.

Although the temporal trends obtained by the two techniques were consistent, their absolute R_p values were not identical. For SS316H, the EIS-derived R_p was generally within about 20% of the corresponding LPR value, whereas a larger discrepancy was observed for Hastelloy N. The Hastelloy N EIS measurements showed greater uncertainty in the low-frequency region, which likely affected the fitted polarization resistance. Accordingly, the EIS-derived R_p of Hastelloy N should be interpreted with greater caution, and the comparison between LPR and EIS was based mainly on the temporal evolution rather than the absolute magnitude of R_p .

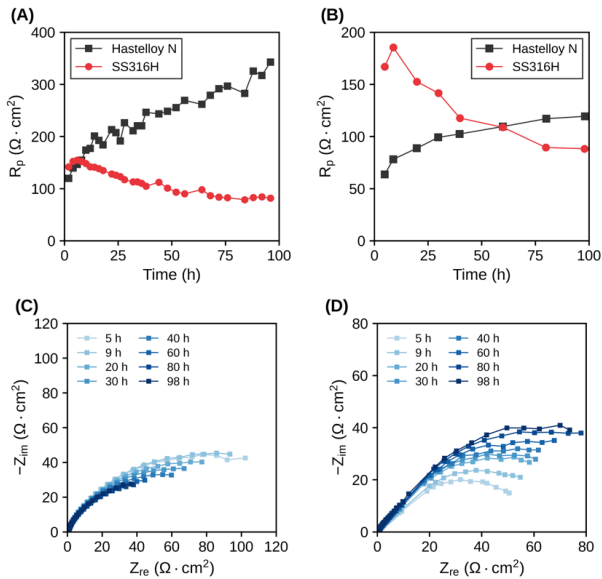


Fig. 2. In-situ electrochemical monitoring during 100 h immersion in molten NaCl-KCl at 700 °C: (A) iR-corrected area-normalized polarization resistance obtained by LPR, (B) area-normalized polarization resistance obtained from EIS fitting, and Nyquist plots of (C) SS316H and (D) Hastelloy N.

2.3 Dissolved elements in the salt

Iron accounted for most of the dissolved metal for both alloys (Table 2). Nickel underwent limited dissolution: it was below the detection limit in the salt exposed to SS316H, which contains 10.2 wt% Ni, and

reached only 46.6 ppm for Hastelloy N although nickel is the base metal of that alloy. Chromium remained below 10 ppm in both melts.

Table 2: Concentration of dissolved elements in the NaCl-KCl salt after the 100 h corrosion test (ppm).

	Fe	Ni	Cr	Mn
SS316H	199.7	< LOD	8.2	4.2
Hastelloy N	86.5	46.6	5.9	9.8

2.4 Microstructural changes

In SS316H (Fig. 3(A)) the attack was confined to the grain boundaries. Each boundary was opened into a void decorated with a bright discontinuous phase. The Cr and Fe maps trace the matrix and reproduce the boundary network as dark lines, and no continuous surface layer was present.

No such network was observed in Hastelloy N (Fig. 3(B)). The grain boundaries were unaffected at every depth, and the attack was instead confined to a thin zone following the surface contour, indicating uniform rather than localized corrosion.

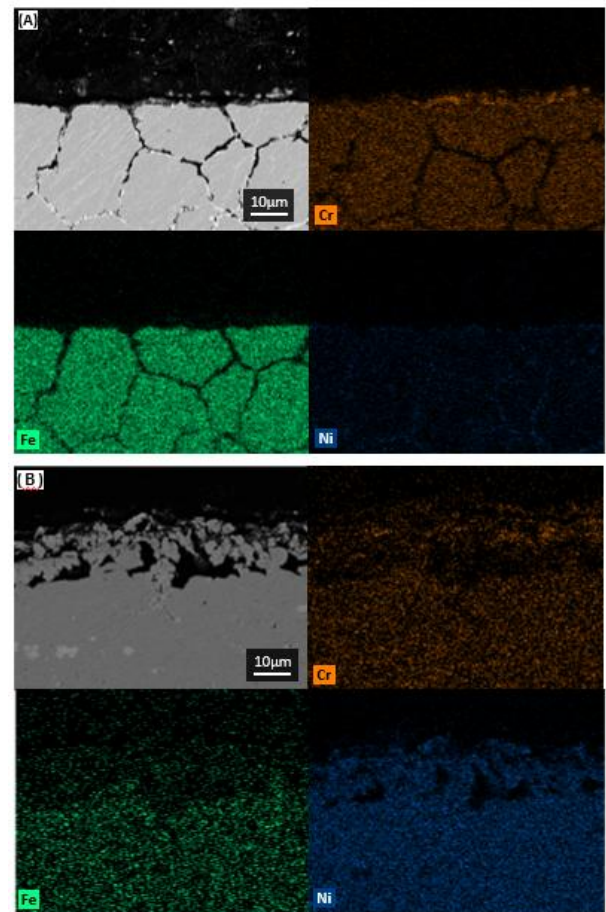


Fig. 3. Cross-sectional BSE images and EDS elemental maps (Cr, Fe, Ni) after 100 h immersion in molten NaCl-KCl at 700 °C: (A) SS316H and (B) Hastelloy N.

3. Conclusion

SS316H and Hastelloy N were exposed to molten NaCl-KCl at 700 °C for 100 h and monitored in situ by LPR and EIS, with the salt and the specimens examined afterwards by ICP-OES and SEM-EDS.

The two alloys showed opposite electrochemical trends in the same melt. The polarization resistance of SS316H decreased with immersion time, whereas that of Hastelloy N increased progressively, and the corresponding EIS responses changed in the same direction. According to the Stern–Geary relation, $i_{\text{corr}} = B/R_p$ [4], polarization resistance is inversely related to corrosion current density when the Stern–Geary constant, B , is known. In this study, however, B could not be reliably determined because Tafel polarization prior to exposure was avoided to prevent perturbation of the subsequent long-term corrosion test, while post-exposure polarization curves exhibited multiple peaks without well-defined Tafel regions. Therefore, the electrochemical results were interpreted in terms of the relative evolution of corrosion activity rather than converted to absolute corrosion current densities. The decreasing R_p of SS316H is consistent with progressively increasing corrosion activity during exposure, whereas the increasing R_p of Hastelloy N is consistent with the opposite trend.

The chemical and microstructural results help explain this difference. Iron dominated the dissolved metal for both alloys while nickel did not: no nickel was detected in the salt exposed to SS316H although that alloy contains 10.2 wt% Ni, and for Hastelloy N iron, present at only 4.0 wt%, contributed more dissolved metal (86.5 ppm) than nickel, which makes up the balance of the alloy (46.6 ppm) — a release of iron over nickel of about thirty times relative to the alloy composition. This ordering is the one expected from the relative stabilities of the chlorides, FeCl_2 being more stable than NiCl_2 at 700 °C, so that nickel is comparatively noble in the melt [1]. The two alloys differ in the structural role of the element that is removed. In SS316H iron is the matrix, and the attack advanced along the grain boundaries to form the network of Fig. 3(A). Each boundary that was opened added internal surface, so the electrochemically active area increased throughout the exposure and the area-averaged resistance could not stabilize. In Hastelloy N iron accounts for only 4.0 wt% of the alloy, and its removal from a thin surface zone left the nickel-rich residue of Fig. 3(B). This zone thickened over an area that did not grow, and progressively shielded the metal beneath. Nickel-based alloys are therefore generally more resistant than iron-based alloys in unpurified chloride melts [2].

Monitoring corrosion by LPR and EIS is therefore feasible in molten chloride salt, and the temporal evolution of polarization resistance can serve as an in-situ indicator of differences between localized and more uniform corrosion behavior.

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